Molecules, Crystals, and Quantum Statistics

By

Enrico Fermi

Translated by

M. Ferro-Luzzi

CERN

Edited by

Lloyd Motz

Columbia University

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Foreword

In the early 1930's the Italian National Research Council (Consiglio Nazionale delle Ricerche) initiated the writing of what was hoped would become a comprehensive treatise of physics. The main reason for this effort was to facilitate the mastering of modern physics by the younger generation of Italian students. Three volumes of this projected treatise were published: E. Persico, *Quantum Mechanics;* F. Rasetti, *The Atomic Nucleus;* E. Fermi, *Molecules and Crystals*. A fourth by E. Segrè on atomic spectroscopy was in manuscript, but a legislation, better left unmentioned, prevented its publication.

Fermi's book was translated into German, but the German edition was allegedly destroyed during the war, and the relatively small Italian edition was soon out of print. The book has thus become a rarity. The publication now of an English translation has the purpose of making it accessible to a larger public.

Clearly a physics book written in 1934 cannot be expected to be up to date. However there is very little in it that is obsolete. Much more is required of a modern student of the subjects treated in it, but what is there is still of fundamental importance. Furthermore, it is well written and presented with the characteristic Fermi touch. It is thus still very valuable as an introduction to the subject.

The choice of topics strongly reflects Fermi's research interests at the time the book was written. In the part dealing with molecules and crystals, the original investigations of Fermi and Rasetti on the Raman effect are given prominence. The last part of the book is not really described by the original title; it is an elaboration of Fermi's thoughts on statistical mechanics.

This translation was made by Dr. M. Ferro-Luzzi of CERN and edited by Dr. L. Motz of Columbia University, who many years ago took down and published a course of lectures on thermodynamics which Fermi gave at Columbia. Although the original text of *Molecule e Cristalli* has not been altered, Dr. Motz has added appendices at the end of Chapters 1, 5, and 6 to outline more recent developments. Also he has added references at the end of the book and included reference numbers throughout the text to assist the reader. The original book included no reference citations.

It is hoped that this translation will be useful to upper-division students. They can acquire from it valid and important, albeit incomplete, information on interesting chapters of physics, and, more important, they will be put into contact with Fermi's style in physics.

THE PUBLISHER

Preface

The death of Enrico Fermi in 1953 deprived the world not only of a great human being and physicist, but also of a great teacher, for very few of Fermi's contemporaries could present a subject, either orally or in writing, as forcefully and as simply as he did. To those of us who studied or worked with Fermi, his analysis of any particular phase of physics was always in the nature of a revelation. However subtle and difficult the material appeared, no obscurities remained after Fermi had finished his presentation, and one generally walked away wondering why it had seemed difficult in the first place.

Fermi's success as a teacher and expositor lay in his ability to separate the basic physical elements from the mathematical formalism of a subject and to reveal these to the listener in an extremely striking manner. Although he was at his best as a lecturer, his books and articles are almost as exciting and as delightful to read as he was to listen to. One need only recall his magnificent article on "Quantum Electrodynamics" in *Reviews of Modern Physics*, and his books, in English: *Thermodynamics*, *Nuclear Physics*, *Elementary Particles*, and *Quantum Mechanics*, to appreciate his ability to communicate his ideas and feelings for a subject. However, some of his finest treatises were written in Italian and thus, unfortunately, are not available to most English-speaking students.

This book is a translation of the 1934 Italian edition of Fermi's *Molecole e Cristalli*, which is one of the finest introductions to the physics of molecules and crystals, and statistical mechanics, now in print. Aside from its usefulness as a textbook in a first-year graduate course, and as a reference book for physicists in general, it is of historical importance as part of Fermi's published works and as one of the earliest treatises on the application of quantum mechanics to various phases of the many-body problem.

The book is divided into three broad sections: the physics of molecules, the physics of crystals, and quantum statistics. The first part of the section on molecules is devoted to the quantum mechanics of the chemical bond as developed in the theories of Heitler and London and of Wang. The second part treats diatomic molecular spectra, with special emphasis on selection rules, spin-orbit coupling, nuclear spin, and molecular statistics. The Raman effect is also treated in some detail. A third part of this first section gives a brief discussion of the specific heats of diatomic molecules and the evaluation of the entropy of mixtures of gases using the entropy constant which is derived later in the book on the basis of Nernst's heat theorem. The fourth part of the section on molecules is devoted to polyatomic molecules with particular attention paid to the derivation of molecular structure from the symmetry properties of molecules and from rotational and vibrational analysis. The infrared and Raman spectra of polyatomic molecules are also treated.

In the second part of the book the theory of crystals is developed from the atomic point of view. After a brief discussion of the symmetry properties of crystal lattices and their structural analysis via X rays, their physical properties are discussed and are shown to be consequences of the ordered arrangement of the atoms in the lattice. The Debye theory of the specific heat of crystals, the theory of fundamental vibrations as revealed in infrared and residual-ray spectroscopy, the Raman effect in crystals, and the thermal, electromagnetic, and optical properties of crystals are also analyzed in this section.

The last section of the book deals with statistical mechanics. After generalizing the Boltzmann law to apply to quantized systems, Fermi points out the deficiencies of classical statistics and shows why the quantum theory requires a different kind of statistics. The Bose-Einstein and the Fermi-Dirac statistics are then introduced, analyzed, and applied to various systems. The book ends with a discussion of degenerate matter and the Fermi-Thomas atom.

Although a great deal of work has been done in the fields covered by the book since it was written, it was felt that the student and general reader could best be served by hewing closely to the original edition and not spoiling the continuity of Fermi's presentation with interpolated material. The translation by M. Ferro-Luzzi from the Italian was edited in such a way as to keep the text as close to Fermi's style as possible.

New developments in the various fields have been outlined by the editor in appendices at the end of chapters. No attempt at a complete presentation is made in this appended material; only broad outlines of recent progress are given with the hope that the reader can be guided along the proper paths and will go on to study the current literature or, wherever possible, to fill in the missing steps himself. Finally, a list of references has been added and reference numbers included throughout the text to provide more modern and more extensive references to the available literature than are offered by Fermi's bioliography.

As it now stands, this volume ranks with Fermi's other books in English. To the student just beginning his work in modern physics, it is a masterful introduction to some of the most subtle phases of quantum mechanics; to the practicing physicist and physics teacher, it is a fascinating example of how the basic physical concepts of a subject can be derived without a welter of formalism; to the historian, it is another source of information about the thinking processes of one of the greatest physicists of the twentieth century.

LLOYD MOTZ

Rutherford Observatory
Columbia University
October 1965

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PART I

Molecules

1

The Chemical Bond

1-1 POLAR AND HOMOPOLAR MOLECULES

Two or more atoms separated by small distances attract or repel one another with forces that decrease quite rapidly when the separations are increased even slightly. In the case of attractive forces, the atoms can be bound together to form a molecule.

The source of these forces is primarily electrical; gravitational attractions are completely negligible in these phenomena. Nevertheless, there is no way of explaining the formation of a molecule by invoking only the electrostatic actions between the nuclei and the electrons of two atoms, without using quantum theory. Moreover, without this theory one could not explain why all the electrons of an atom do not fall into the nucleus.

For simplicity, we first consider a diatomic molecule. We obtain a very important classification of the chemical bonds between the two atoms by studying the systems into which the molecule breaks up when the two nuclei are separated adiabatically, that is, so slowly that at each instant the motion of the electrons around the nuclei is the same as it would be if the nuclei were resting at the distance considered.

When the two nuclei are separated by a distance large with respect to the atomic dimensions, we find the electrons of the molecule divided into two groups, each around one of the nuclei. We have, indeed, two separate atoms. Now, the following may happen:

1. The two separate atoms are not in a neutral state; one of them contains one or more extra electrons as compared to the neutral atom corresponding to its nucleus and is thus a negative ion; the other lacks the corresponding number of electrons, and is therefore a positive ion. In this case the chemical bond of the molecule is called *polar* (or etheropolar); it is then classified as mono-, bi-, or trivalent, if the number of electrons of the two ions in excess of or defect with respect to the number in the neutral atom is one, two, or three.
2. At the end of the process, the molecule splits into two neutral atoms. In this case the chemical bond between the two atoms is called *homopolar*.

1-2 (THE POLAR BOND)

Salt molecules are typical examples of polar bonds. A molecule of $NaCl$, for instance, does not dissociate into two neutral atoms of sodium and chlorine, but into two ions: a positive sodium ion (Na^+), with one electron missing with respect to the normal number, and a negative chlorine ion (Cl^-), that is, a chlorine atom with the missing electron of the Na^+ added.

Compounds made of a metallic and a metalloid atom (or radical) show a tendency to form polar salt molecules. In fact the metal atoms are characterized by a low ionization potential; that is, a small amount of energy is sufficient to remove one of their electrons. Instead, the metalloids are characterized by a considerable electron affinity (energy is released when an electron is added).

The formation process of a salt molecule, for example, $NaCl$, can therefore be analyzed schematically as follows: At first an electron is lost by Na and absorbed by Cl, thus producing the two ions Na^+ and Cl^-. The ions, owing to their opposite electric charges, attract each other according to Coulomb's law until they approach within a certain minimum distance. At this point, repulsive forces come into action, inhibiting any further approach. The two ions remain separated at the correct distance for the attractive and repulsive forces to balance, thus creating the $NaCl$ molecule.

As we have already mentioned, this description of the formation of a salt molecule is somewhat fictitious. In reality, the electron affinity of the metalloid is often slightly less than the ionization potential of the metal. The formation of the two opposite ions, involving the subtraction of an electron from the metal and its addition to the metalloid, requires a small amount of energy; consequently, it cannot happen spontaneously. The missing energy is provided by the electrostatic energy of the two opposite ions when they are near each other. Therefore, the formation of the ions and their approach caused by the electrostatic attraction cannot occur in sequence but must be simultaneous. That is, the metal electron passes over to the metalloid only when the two atoms are sufficiently near for the process to be exothermic.

Thus, in the usual example of sodium chloride, we have the following values: ionization potential of Na = 5.1 volts; electronic affinity of Cl = 3.8 volts. The formation process of Na^+ and Cl^- from the neutral atoms requires an amount of energy equal to the difference between the ionization energy of Na and the electronic affinity of Cl; that is, $5.1 - 3.8 = 1.3$ volts. On the other hand, with the two ions separated by a distance r, the electrostatic energy is $-e^2/r = -300e^2/r$ volts. Recalling that the elementary charge e is 4.803×10^{-10} esu, we see immediately that the electrostatic energy compensates for the difference between the ionization potential and the electronic affinity at a distance $r = 11 \times 10^{-8}$ cm. The transfer of the electron from Na to Cl is an exothermic process only when the two ions are at a distance shorter than this. The equilibrium distance between the two atoms in the NaCl molecule is in fact much smaller than this limit. Its value is not precisely known, but is not far from 1.4×10^{-8} cm. Assuming this value for the separation, one finds an electrostatic energy of 10.2 volts, which exceeds by 8.9 volts the difference between the ionization potential and the electronic affinity.

The formation energy of one mole of sodium chloride from its constituents (starting from monatomic gases) would then be equal to 8.9 volts times Avogadro's number, that is, 205 kcal. This value, in practice, must be reduced somewhat to take into account the potential energy of the repulsive forces also.

In the monovalent metals, the alkali metals, for instance, the energy necessary to separate one electron from the atom is small, whereas a considerably greater amount of energy is required to separate a second one. This is because the alkali metals have an electronic configuration analogous to that of the noble gases plus an additional electron; this electron is easily removed, but the next one, belonging to the very stable noble-gas configuration, requires an appreciable amount of energy. In contrast to this, the alkali earth metals, with two electrons in addition to the noble-gas configuration, are easily deprived of two electrons, and this tends to produce bivalent ions. In other cases, for instance, the metals belonging to the copper group, sometimes a monovalent, and at other times a bivalent ion can be found, since the difference between the first and second ionization potentials is neither as great as in the alkali metals, nor as small as in the alkali earth metals. Correspondingly, two different series of salts (cuprous and cupric) can be formed by these elements.

Since the two ions in a polar molecule are essentially bound by an electrostatic force, this force is greatly reduced when the molecule is in aqueous solution (dielectric constant of water ≈ 80). As a consequence, the salt molecules in aqueous solution dissociate into the constituent ions. The same dissociation takes place in other solvents with a high dielectric constant, for instance, in alcoholic solutions.

1-3 THE HOMOPOLAR BOND; THE HYDROGEN MOLECULE

We shall now try to understand the homopolar bond. Typical examples of this bond are found in molecules consisting of two identical atoms, such as H_2, N_2, O_2. We shall also discuss, at the same time, the origin of the repulsive force that separates the two atoms of a polar molecule.

The binding forces of a homopolar molecule are mainly due to the electrostatic interaction between the nuclei and the electrons of the two atoms. An essential role in this binding mechanism is played by the resonance between the electrons of the two atoms. We use the Heitler-London theory[98] of the hydrogen molecule to explain what happens.

We want to compute the forces between the two hydrogen atoms as a function of the distance. Our system consists of two protons and two electrons. The suffixes *a* and *b* designate the two protons, 1 and 2 the two electrons. An exchange degeneracy is present, because we obtain identical states when we associate electron 1 with nucleus *a* and electron 2 with nucleus *b*, or vice versa.

Because of their relatively large masses, we assume, as a first approximation, that the two nuclei are at rest, separated by a distance r. We call r_{a1}, r_{a2}, r_{b1}, r_{b2} the distances of electrons 1, 2 from nuclei *a*, *b*, respectively. If the distance between the atoms is not too small we may—as a first approximation—neglect the mutual perturbation; the two atoms may be treated as if they were completely independent. With electron 1 belonging to proton *a* and electron 2 to proton *b*, the eigenfunction of the system is given by the product

$$\psi_1 = \varphi(r_{a1})\varphi(r_{b2}), \tag{1}$$

where φ is the eigenfunction of the ground state of the hydrogen atom; φ is a function only of the radial coordinate when—as in this treatment—the spin of the electron is neglected.

A different state of the system with the same energy can be obtained by assuming that electron 2 belongs to proton *a* and electron 1 to proton *b*. The eigenfunction for this state is, in analogy with (1),

$$\psi_2 = \varphi(r_{a2})\varphi(r_{b1}). \tag{2}$$

The eigenfunctions ψ_1 and ψ_2 represent actual quantum states of the system only when the distance between the two atoms is very large with respect to the atomic dimensions; if this is the case, any linear combination of ψ_1 and ψ_2 also represents a quantum state, since ψ_1 and ψ_2 have the same energy. We now determine which linear combinations of ψ_1 and ψ_2 are appropriate when the perturbation between the two atoms is taken into account. For this, we use the perturbation method, up to the zero-order approximation. In this way we can compute the mutual energy of the two atoms approximately and estimate its dependence on the distance between them. We take this as the potential energy from which the forces between the two atoms originate.

The potential energy of our system is

$$U = e^2\left(\frac{1}{r} + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}}\right); \tag{3}$$

therefore the total energy is

$$H = e_2\left(\frac{1}{r} + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}}\right) + \frac{p_1^2 + p_2^2}{2m}. \tag{4}$$

Here p_1 and p_2 are the momenta of the two electrons, corresponding to the Schrödinger equation operators $-(h^2/4\pi^2)\ \Delta_1$ and $(h^2/4\pi^2)\ \Delta_2$ (Δ_1 and Δ_2 are the laplacians for coordinates of the first and second electron, respectively).

Since $\varphi(r_{a1})$ obeys the Schrödinger equation for the hydrogen atom with proton a as nucleus, we have

$$\left(-\frac{e^2}{r_{a1}} - \frac{h^2}{8\pi^2 m}\Delta_1\right)\varphi(r_{a1}) = W\varphi(r_{a1}); \tag{5}$$

where W is the energy of the ground state of the hydrogen atom. Analogous equations are valid for $\varphi(r_{b1})$, $\varphi(r_{a2})$, $\varphi(r_{b2})$.

Using these relations and interpreting the hamiltonian H of Eq. (4) as an operator, we immediately find

$$\begin{aligned} H\psi_1 &= \left\{2W + e^2\left(\frac{1}{r} + \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}}\right)\right\}\psi_1, \\ H\psi_2 &= \left\{2W + e^2\left(\frac{1}{r} + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{b2}}\right)\right\}\psi_2. \end{aligned} \tag{6}$$

The unperturbed zero-order eigenfunctions are given, as we shall verify, by the sum and difference of the two eigenfunctions ψ_1 and ψ_2. Indeed, the sum $\psi_1 + \psi_2$ is a symmetric function of the positions of the electrons, that is, it does not change sign under the interchange of the two electron coordinates; but the difference $\psi_1 - \psi_2$ is antisymmetric, which means it changes sign under the same operation. As a consequence, the two functions $\psi_1 + \psi_2$ and $\psi_1 - \psi_2$ are orthogonal to each other; furthermore, since the operator (4) is symmetric with respect to the electron coordinates, one also has

$$\int\int(\psi_1 + \psi_2)H(\psi_1 - \psi_2)\, d\tau_1\, d\tau_2 = 0.$$

This demonstrates that $\psi_1 + \psi_2$ and $\psi_1 - \psi_2$ are the linear combinations to be taken in the zero-order approximation.* Our new eigenfunctions,

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* It should be noticed that all the eigenfunctions considered are real, and therefore the question of their complex conjugates does not arise.

after normalization, are given by

$$\psi_{\text{sym}} = \frac{\varphi(r_{a1})\varphi(r_{b2}) + \varphi(r_{a2})\varphi(r_{b1})}{[2(1+\beta^2)]^{1/2}},$$
$$\psi_{\text{ant}} = \frac{\varphi(r_{a1})\varphi(r_{b2}) - \varphi(r_{a2})\varphi(r_{b1})}{[2(1-\beta^2)]^{1/2}}. \tag{7}$$

The square root in each denominator represents the normalization factor; here,

$$\beta = \int \varphi(r_{a1})\varphi(r_{b1})\,d\tau_1 = \int \varphi(r_{a2})\varphi(r_{b2})\,d\tau_2. \tag{8}$$

The hydrogen eigenfunction is considered already normalized.

By means of the zero-order eigenfunctions given by Eq. (7), we can calculate the first approximation to the energy. Corresponding to the two unperturbed eigenfunctions, we find two values for the energy:

$$U_{\text{sym}} = \int\int \psi_{\text{sym}} H \psi_{\text{sym}}\,d\tau_1\,d\tau_2,$$
$$U_{\text{ant}} = \int\int \psi_{\text{ant}} H \psi_{\text{ant}}\,d\tau_1\,d\tau_2. \tag{9}$$

These values are easily computed with the aid of Eq. (6). Neglecting the term $2W$, which represents the unperturbed energy (equal to the sum of the energies of the two separate atoms), we find

$$U_{\text{sym}} = \frac{A+B}{(1+\beta^2)^{1/2}}; \qquad U_{\text{ant}} = \frac{A-B}{(1-\beta^2)^{1/2}}, \tag{10}$$

where

$$A = \int e^2\left(\frac{1}{r} + \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}}\right)\varphi^2(r_{a1})\varphi^2(r_{b2})\,d\tau_1\,d\tau_2,$$
$$B = \int e^2\left(\frac{1}{r} + \frac{1}{r_{12}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}}\right)\varphi(r_{a1})\varphi(r_{b1})\varphi(r_{a2})\varphi(r_{b2})\,d\tau_1\,d\tau_2. \tag{11}$$

The physical meaning of the integral A is obviously the following: Let us assume that the two atoms consist of two nuclei and two negative charge distributions; the charge distributions are further assumed to be rigidly coupled to each nucleus, with charge densities $e\varphi^2(r_a)$ and $e\varphi^2(r_b)$, respectively (r_a and r_b represent the distances from the two nuclei). Then A is the electrostatic energy of the system of the two atoms.

The interpretation of the integral B, which we call the *exchange integral* is less simple. It arises from a typical quantum effect with no analog in classical mechanics; because the two electrons are identical, we are allowed to exchange their positions with respect to the atoms. We may interpret B/h as the frequency with which the two electrons exchange their places. If we neglect the departure from unity of the denominators in the Eq. (10), we can consider A the average value of the two energy values into which the interaction energy of the two atoms has been split by the exchange degeneracy.

The values of the energies U_{sym} and U_{ant} corresponding to the symmetric and antisymmetric states are shown graphically in Fig. 1 as a function of the distance r between the two atoms. For comparison, the curve representing the electrostatic energy A has also been plotted on the same graph. The curve representing U_{sym} lies below that for U_{ant} because the integral B is negative.

Until now we have completely neglected both the effect of the electron spin and the Pauli principle.

We recall that in quantum mechanics the Pauli principle has the following form: In a system with more than two electrons the probability amplitude which is a function of all the coordinates (including

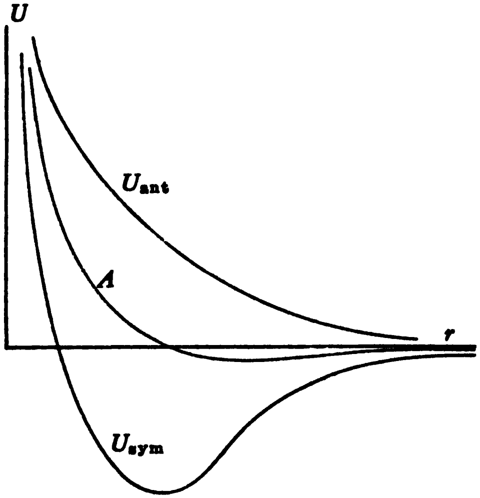


Figure 1

the spin coordinate) must be antisymmetric with respect to the interchange of all the coordinates of any two electrons.

We may not conclude, however, on the basis of this argument that ψ_{ant} is the only physically realizable eigenfunction of the two given in Eq. (7). The reason is that we have not introduced in Eq. (7) the part of the eigenfunction which depends on the spin coordinates, and the application of the Pauli principle demands, of course, the presence of a complete eigenfunction.

It is very simple to take the spin into account when the system contains only two electrons and the interaction between spins and orbital momenta can be neglected. In this case the eigenfunction can be split into two factors; one depending only on the position coordinates of the electrons, and the other only on their spin coordinates. The latter is symmetric or antisymmetric according to whether the electron spins are parallel or antiparallel. To have an over-all antisymmetric eigenfunction, as required by the Pauli principle, the factor depending on the space coordinates must be antisymmetric when the electrons spins are parallel and symmetric when they are antiparallel.

Therefore, in our case, both functions (7) represent physically possible states for the hydrogen molecule. The eigenfunction ψ_{sym} corresponds to a state in which the two spins are antiparallel and the eigenfunction ψ_{ant} to a state with parallel spins.

From the curves in Fig. 1, we notice that the state with the energy U_{sym} (i.e., the state with antiparallel spins) does indeed correspond to a molecule; the curve representing the interaction energy between the two atoms has a well-defined minimum which corresponds to the equilibrium distance of the two atoms. However, in the state with energy U_{ant} (parallel spins) the atoms cannot be held together to form a molecule. From the U_{ant} curve in Fig. 1 we see that no minimum exists for the interaction energy of the two atoms; therefore they repel each other no matter what the distance between them is.

Finally, notice in Fig. 1 that all three energies, U_{sym}, U_{ant}, and A, become infinite when r goes to zero. This shows that in all cases there is a strong repulsion preventing the two nuclei from getting nearer than a certain minimum distance. The origin of this repulsion can be found mainly in the Coulomb repulsion between the two nuclei; this effect prevails over all others when the nuclei are very close.

Heitler and London [98] and Suguira [188] have carried out quantitative calculations for the hydrogen molecule. They find a value for the equilibrium distance between the two atoms very near the experimental one. However, this agreement must be considered partly fortuitous. Indeed, the zero approximation chosen by Heitler and London as the starting point in their perturbation method is sufficiently good only when the two atoms are quite far apart; it is very far from being correct when the two atoms are very close.

The method of Heitler and London is appropriate for a qualitative result but is not particularly good when quantitative results are needed.

A better approximation for the eigenfunctions of the hydrogen molecule has been obtained by Wang.[137] He considers eigenfunctions of the following form

$$\psi = \exp\left[-\frac{z}{a}(r_{a1} + r_{b2})\right] + \exp\left[-\frac{z}{a}(r_{a2} + r_{b1})\right];$$

where a is the radius of the first Bohr orbit for the hydrogen atom, z is a numerical parameter (function of the distance r between the two nuclei) which Wang determines by the Ritz variational method.[128] For each fixed value of r, Wang finds the value of z which minimizes the energy (4) averaged over the eigenfunction ψ.

Corresponding to the equilibrium distance, Wang finds $z = 1.66$, whereas the Heitler-London approximation gives $z = 1$ for any value of r.

The comparison of Wang's results with the experiments gives the values in Table 1 for the equilibrium position of the two nuclei.

Table 1

	Wang	Experiment
Energy of the molecule, rydberg	-2.278	-2.326
Moment of inertia	0.459×10^{-40}	0.467×10^{-40}
Frequency of oscillation of the nuclei, cm^{-1}	4900	4360

1-4 APPLICATION TO OTHER MOLECULES

Without leaving the qualitative approach, we briefly mention the results of the method of Heitler and London for the case of more complicated homopolar bonds. The homopolar bond between the two atoms is always mainly determined by the interaction between pairs of electrons (one pair for each valence) belonging to the two atoms. If the spins of the two electrons are parallel, their interaction produces a repulsion between the two atoms; the curve representing this interaction as a function of the distance is similar to the curve U_{ant} of Fig. 1. There is an attraction, instead, if the spins of the two electrons are antiparallel; the curve representing the interaction energy in this case is similar to U_{sym} of Fig. 1. There is a clear minimum in the interaction energy, corresponding to an equilibrium position of the two atoms.

In general, every atom has some electrons bound in closed shells (*K* shell, *L* shell, etc.) with no resultant angular momentum. It may also have pairs of electrons with zero total angular momentum, as, for instance, two *s* electrons with the same principal quantum number. These closed configurations generate a repulsion between two atoms; an attraction of the homopolar type can only be produced by the interaction of electrons which are not in a total zero angular momentum configuration. For example, molecules are formed, even if not very stable, between two alkali metals, owing to the interactions of the two valence electrons. There is a repulsion, instead, between two atoms of a noble gas, since these have only closed electronic shells. A possible exception to this rule seems to be the formation of the extremely unstable molecule, He_2. It has been demonstrated, however, that these molecules are not produced by the coupling of two helium atoms in their normal state; to produce a molecule of He_2, helium must be excited, for example, by an electric discharge. In this way the *K* shell is broken, and the two electrons belonging to it are then free to enter into a chemical bond with other atoms.

A similar mechanism is also present in the polar molecule, and it determines the repulsion between the two ions of the molecule when they approach each other. Thus, for instance, in the sodium chloride molecule, both Na^+ and Cl^- ions have an external configuration resembling that of the noble gases. Consequently, a repulsion of the homopolar kind arises when the two ions are very near; eventually, this repulsion prevails over the Coulomb attraction.

The above analysis of the homopolar forces is, of course, only qualitative. It is meant to show the principal factors that are responsible for the forces between the atoms of a molecule. From a quantitative point of view, we cannot apply it, even for approximate calculations. It is also worth mentioning that in many cases it is impossible even to determine if the bond is of the polar type (where each electron may be considered belonging to one of the two nuclei) or of the homopolar type (where one or more pairs of electrons belong simultaneously to both atoms).

1-5 THE VAN DER WAALS ATTRACTION

The mechanism proposed by Heitler and London to explain the attraction or the repulsion between two atoms assumes that these forces originate in the exchange energy between pairs of electrons belonging to different atoms. Since the eigenfunctions of the two atoms decrease exponentially starting from their centers, the exchange integrals also depend on the distance between the two atoms, according to an approximately exponential law. The attractive or repulsive forces of the Heitler-London theory, therefore, have a very small range and in practice vanish when the distance between the two atoms exceeds a few Ångstroms.

However, besides these there are other forces between the two atoms which decrease more slowly with distance and therefore prevail over the exchange forces at large distances. These are due to the electrical polarizability of the two atoms and are attractive. Since they are the largest part of the cohesion term in the van der Waals law, we call them the *van der Waals attractive forces.*

The quantum theory of the van der Waals forces has been developed by London and Eisenschitz [112] and can be summarized as follows. Let A and B be two atoms; we assume that their separation is so large that their eigenfunctions do not overlap. Under these conditions, the effect of the electron exchange between the atoms is practically negligible. Thus we can take, as unperturbed eigenfunctions of the system, the simple product $\psi_n\varphi_m$ of an eigenfunction ψ_n of the first atom and an eigenfunction φ_m of the second. The corresponding eigenvalue of the unperturbed problem (when the interaction between the two atoms is neglected) is

$$E_{nm} = A_n + B_m.$$

Here A_n and B_m are the energies of the state n of the first atom and of the state m of the second. We take the two atoms as fixed and separated by the distance r. As coordinates, we take a system x, y, z, where z is parallel to the direction AB. Call X, Y, Z and ξ, η, ζ the components of the electric moments of the atoms. The mutual energy of these two electric moments can be calculated in an elementary way and is

$$H = \frac{2Z\zeta - X\xi - Y\eta}{r^3}.$$

This coupling energy between the two atoms, which we treat as a perturbation in our problem, is the source of the van der Waals attraction.

We must calculate the perturbation introduced in the ground state of our system by the coupling energy H. One can immediately see that, in a first approximation, this perturbation is zero. We have to average H over the unperturbed eigenfunction $\psi_0\varphi_0$; calling $d\tau_1$ and $d\tau_2$ the elements of the configuration space of the two atoms, we have

$$H_{00.00} = \iint H\psi_0^2\varphi_0^2\, d\tau_1\, d\tau_2 = \frac{2Z_{00}\zeta_{00} - X_{00}\xi_{00} - Y_{00}\eta_{00}}{r^3},$$

where

$$X_{00} = \int X\psi_0^2\, d\tau_1$$

and analogous expressions are valid for the other quantities. Now, all these quantities are equal to zero because the average electric moment of the unperturbed atom is zero. Therefore the first-order perturbation of the eigenvalue is equal to zero, as mentioned before.

The first-order perturbation being zero, we must calculate the second approximation. Following perturbation theory, we obtain (for the case where no first-order effect is present)

$$\Delta W = -\sum \frac{|H_{00.mn}|^2}{E_{mn} - E_{00}},$$

where $H_{00,mn}$ is the element of the perturbation matrix,

$$H_{00,mn} = \iint H\psi_0\psi_n\varphi_0\varphi_m \, d\tau_1 \, d_2 = \frac{2Z_{0m}\zeta_{0n} - X_{0m}\xi_{0n} - Y_{0m}\eta_{0n}}{r^3}.$$

Here X_{0m}, and the analogous quantities, are the matrix elements of the electric moment between the two atoms; they are the same quantities that determine the optical transition probabilities. Substituting and recalling the expressions for E_{mn} and E_{00}, we obtain

$$\Delta W = -\frac{K}{r^6},$$

where

$$K = \sum_{m,n} \frac{|2Z_{0m}\zeta_{0n} - X_{0m}\xi_{0n} - Y_{0m}\eta_{0n}|^2}{A_m - A_0 + B_n - B_0}.$$

Notice that the constant K is positive: Each term in the numerator of the above expression is necessarily positive and the denominator is also positive, because A_0 and B_0 are the energy levels of the ground states of the two atoms.

We thus see that the van der Waals forces are indeed attractive and that their potential energy decreases as the sixth power of the distance between the two atoms.

The order of magnitude of the coefficient K can be evaluated easily. For instance, we can calculate the van der Waals attraction between two atoms of an alkali metal by making the following assumptions: (1) the effect of the spin can be neglected, (2) the only contributing transition is the one corresponding to the resonance line, and (3) a single dispersion electron is involved in this transition. In this case we obtain

$$K = \frac{3he^4}{32\pi^3 m^2 c^3} \lambda_0^3,$$

where λ_0 is the resonant wavelength. For sodium, this gives

$$K = 1.5 \times 10^{-57}.$$

For other atoms, which are usually much less polarizable than those of the alkali metals, one finds values which of course are considerably smaller than this. Thus, for instance, Eisenschitz and London [112] find $K = 6 \times 10^{-60}$ for atomic hydrogen.

APPENDIX. CORRECTIONS TO THE HEITLER-LONDON THEORY

Since the Heitler-London theory is not very satisfactory quantitatively, various attempts have been made to improve it.[51] Thus Wang,[137, 138] keeping the same form for the electronic wave functions, multiplied the individual hydrogenic orbital function for each electron by an adjustable scale factor. This scale factor behaves as an "effective nuclear charge" or a "screened nuclear charge." Using these adjustable orbital wave functions, Wang then determined the value of the scale factor that minimized the expectation or average value of the hamiltonian. This gave a considerable improvement over the Heitler-London theory.

A more general approach to the problem is an extension of the Hartree [95] self-consistent wave-function method first applied by Hartree to the helium atom. Here, individual orbital functions for each electron are used, but they are molecular-orbital functions in the sense that they are obtained not from wave equations of form (5) but from equations of the form (for the orbital of electron 1)

$$\left[-\frac{1}{2}\Delta_1 - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} + \int \frac{1}{r_{12}} |\psi(r_2)|^2 \, d\tau_2\right] \psi(r_1) = \mathcal{E}\psi(r_1),$$

where $\psi(r_1)$ is the molecular orbital of electron 1, and $\psi(r_2)$ the molecular orbital of electron 2. The integral on the left side of this equation takes account of the potential energy of electron 1 in the field of electron 2.

One now minimizes the average value of the hamiltonian (4) for arbitrary variations of the orbital wave functions, subject to the normalization

$$\int |\psi(r)|^2 \, d\tau = 1.$$

Thus one seeks the minimum value of the average value of the hamiltonian

$$\int\int \psi^*(r_1)\psi^*(r_2)H(r_1,r_2)\psi(r_1)\psi(r_2) \, d\tau_1 \, d\tau_2 - \lambda \int |\psi(r)|^2 \, d\tau,$$

for arbitrary variations of $\psi(r_1)$, $\psi(r_2)$, and $\psi(r)$.

In the treatment of this problem by James and Coolidge,[102, 103] the exact number of degrees of freedom available to the two electrons is taken into account as first suggested by Nagamiya.[118] The exact wave function of the electrons should depend on five coordinates, since one of the six degrees of freedom is eliminated by the symmetry properties of the molecule. A correct treatment of the problem therefore demands the use of wave functions that depend on five coordinates. For this reason, James and Coolidge constructed wave functions for the hydrogen molecule without introducing individual orbital functions and without reference to the individual hydrogen atoms. They took for their total molecular wave function a product of an exponential and a polynomial in five appropriately chosen coordinates with undetermined coefficients. These coefficients were then determined by applying a variational principle to minimize the energy of the system.

For a complete discussion of these methods and their application to molecular systems with more than two electrons, see the article by Kotani et al.[36] In this treatise the methods of Slater,[58] Hartree, and Hartree-Fock as applied to many-electron systems, are discussed. These are special cases of the more general procedure of LCAO (linear combination of atomic orbitals), which is described in detail in this article.

2

Spectra of Diatomic Molecules

2-1 GENERAL SCHEME OF THE MOLECULE TERMS

The spectra of molecules are different, even at first sight, from those of the atoms, because of their great line multiplicity. These lines, grouped into characteristic bands, have their origin in the different vibrations and rotations which are possible for the nuclei in the molecule. Since the masses of the nuclei are much larger than those of the electrons, the energy differences between the molecular levels are much smaller when they are produced by variations in the vibration or the rotation of the nuclei than when they are produced by changes in the electronic motion. This generates the characteristic line grouping observed in the molecular spectra.

Although the spectra of diatomic molecules are now largely understood, at least in simple cases, very little is known yet about polyatomic molecules. First we consider diatomic molecules.

The study of molecular term structure can be simplified considerably by the following approximate criterion. The energy differences between terms differing only in the rotational motion of the molecule are small compared to those between terms differing in vibrational motion; the latter are, in turn, smaller than the energy differences between terms with different electronic motions.

Consequently, we may, as a first approximation, take the rotation, the vibration, and the electronic motion as three separate and distinct motions. In a second stage we take into account the perturbations that these three motions have on each other. We first develop the most elementary theory, assuming complete independence of these motions.

To study the electron motion, we assume that the nuclei are fixed. This hypothesis is justified because of the very small frequency of the nuclear motions compared to that of the electron motions. With the nuclei separated at a fixed distance r, the electrons can be in different quantum states; the corresponding energy can have different values, which we indicate by U_q, where q distinguishes the different quantum states. It is convenient to include in U_q the electrostatic energy $ZZ'(e^2/r)$ (Z, Z' = atomic numbers of the two nuclei) between the two nuclei; this energy behaves as an additive constant to the energy of the electronic motion, once the distance between the nuclei is fixed. Thus U_q is the actual total energy of the molecule if the two nuclei are fixed. The value of U_q depends of course on the distance r between the two nuclei.

In Fig. 2 we have represented graphically the dependence of $U_q(r)$ on the distance r for the case of four electronic quantum states (a,b,c,d). The common characteristic of the four curves is that they all approach $+\infty$ as $r \rightarrow 0$, because, if the two nuclei get too close together, the repulsive force, arising mainly from the electrostatic effects, prevails over all other forces, its energy going to infinity for $r = 0$. The four curves in Fig. 2 also have the common feature of an asymptote parallel to the r axis. This means that, for a definite electronic quantum state, the energy of the system approaches a well-determined limit when the distance between the two nuclei becomes infinite. The limit is different, in general, for the different electronic quantum states. We can understand this by noticing that, when the two nuclei are very far apart, the electrons of the molecule divide into two separate groups, one for each nucleus. If the molecule is homopolar, the two groups produce two neutral atoms; if it is polar, they produce two ions of opposite signs. At the limit $r = \infty$, the energy of the system consists of the sum of the energies of these two atoms (or ions) and has a well-determined value. The two separate atoms (or ions) produced are not necessarily in their ground states, but may be found in various excited states according to the quantum state of the initial molecule. Therefore, the limiting values of the energy when $r = \infty$ are different for the different states. Each of these values is given by the sum of two energy levels of the separate atoms (or ions).

Notice in Fig. 2 that curves *b* and *c* decrease continuously for all values of the distance *r*. Curves *a* and *d*, instead, have a minimum. This different behavior is of great importance for molecular formation. Thus, for case *a* or *d*, the two nuclei can be in an equilibrium configuration when their separation corresponds to the energy minimum $U_q(r)$, or they may oscillate around it. For case *b* or *c*, they repel each other at any separation: The molecule cannot exist because it would immediately dissociate.

Notice finally that in the theory of the hydrogen molecule we have already met curves of the type discussed above (cf. Fig. 1). In the case of the hydrogen molecule, only the symmetric quantum state produces a molecule; the antisymmetric state generates a repulsion between the two atoms at all distances. In the hydrogen molecule we considered only the states that dissociate into two hydrogen atoms in

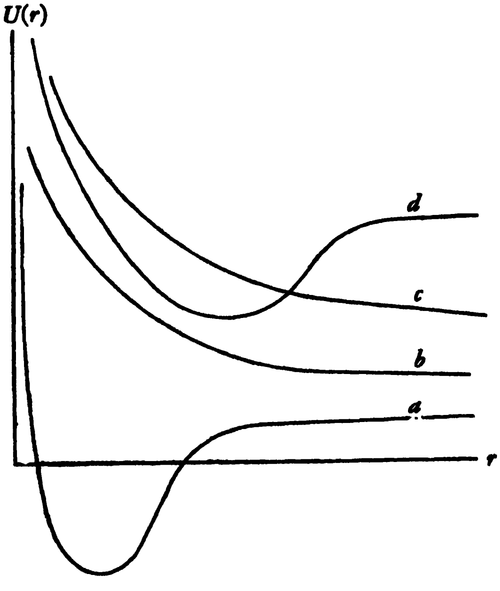


Figure 2

their ground states. Consequently, the two curves U_{sym} and U_{ant} of Fig. 1 have the same asymptotic limit for $r = \infty$. Apart from these, however, many other states exist for the hydrogen molecule; when these states are dissociated, they correspond to excited atoms. We shall deal with these states later.

Consider now an electronic state of the molecule such that the energy $U_q(r)$ as a function of the separation is a minimum for a certain value r_e of r (e.g., states a and d of Fig. 2). At a distance r_e, then, there is an equilibium configuration for the molecule. We can expand $U(r)$ in powers of $x = r - r_e$. In this expansion the first-order term is missing, obviously, because r_e corresponds to a minimum. We have

$$U(r) = a + bx^2 + cx^3 + \cdots, \tag{1}$$

where a, b, c, are constants depending on the electronic quantum state. This state will be designated, when necessary, by the suffix q.

We neglect, as a first approximation, all terms beyond the second in (1). The energy, then, apart from a constant term, is proportional to the square of the displacement x from its equilibrium position. This means that there is an elastic type of force between the two nuclei, tending to restore them to the equilibrium position. The two nuclei are thereby forced to vibrate around the equilibrium position, alternately approaching and receding from each other. Let $c\nu$ be the vibration frequency, so that ν expresses the frequency in wave numbers (which will be convenient later on). The energies of the various vibrational states are then given, as is well-known, by the formula

$$E_v = hc\nu(v + \tfrac{1}{2}) \equiv \hbar c\omega(v + \tfrac{1}{2}), \tag{2}$$

where v, the vibrational quantum number can have the values 0, 1, 2, . . . , and where $\hbar = h/2\pi$, $\omega = 2\pi\nu$.

Expression (2) is, of course, only approximate and is valid only for small values of v. For large values of v the vibration amplitude becomes large, and terms of an order higher than the second must be taken into account in (1). Because of these terms, the vibrations are not purely harmonic; this case will be considered later.

We still have to discuss the rotational motion of the molecule. As a first approximation, we disregard the variations in distance between the two nuclei; these variations are generally rather small, so that the two nuclei can be thought of as being rigidly connected to each other.

However, we cannot ignore the motions of the electrons, even though their mass is negligible with respect to that of the nuclei. To see how the rotation of the molecule can be affected by the motions of the electrons we use the following semiclassical analysis.

As long as we neglect the rotation of the line joining the two nuclei (the molecular axis), the moment, with respect to this line, of forces acting on the electron system is obviously zero. The angular momentum of the electrons, with respect to the molecular axis is then a constant. The value of this constant, according to quantum theory, can be only a multiple (integer or half-integer) of $\hbar$. Let $\Omega\hbar$ be its value; Ω is an integer or a half-integer. We now consider the two nuclei rotating around the center of mass of the molecule. Let R be their angular momentum (measured in units of $\hbar$). R is evidently perpendicular to the molecular axis. The total angular momentum J of the molecule is then given by the vector sum of Ω and R (Fig. 3); this angular momentum is, of course, a constant both in magnitude and direction. The two vectors R and Ω precess uniformly around the constant direction of J. The phenomenon is analogous to the motion of a gyroscope supported at its center of mass, with the gyroscope axis corresponding to the molecular axis. The motion of the molecule reduces to a simple rotation around an axis perpendicular to the line joining the two nuclei only if the angular momentum Ω is zero.

If I is the moment of inertia of the molecule, the classical rotational

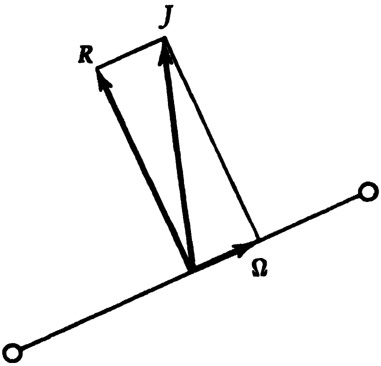


Figure 3

energy of the two nuclei is given by

$$E_r = \frac{1}{2I}(R\hbar)^2 = \frac{\hbar^2}{2I}R^2 = \hbar cBR^2, \tag{3}$$

where

$$B = \hbar/2Ic. \tag{4}$$

From Fig. 3 we also have

$$R^2 = J^2 - \Omega^2,$$

and hence (3) becomes

$$E_r = \hbar cB(J^2 - \Omega^2).$$

The above analysis is confirmed and partly modified by a rigorous quantum-mechanical derivation. In particular, the expression for the rotational energy becomes

$$E_r = \hbar cB\{J(J+1) - \Omega^2\} \qquad (J \geq \Omega). \tag{5}$$

In this formula both Ω and J can assume integer values (or half-integers if the molecule contains an odd number of electrons).

Notice further that B has different values for different electronic states; indeed, expression (4) depends on the moment of inertia, hence on the equilibrium distance between the two nuclei, and the latter is different for different electronic states. When necessary, we shall indicate by the suffix q the dependence of B on the electronic quantum states. Less important is the dependence of B on the vibrational and rotational motions, which have a small influence on the average distance between the two nuclei.

The total energy of the molecule can finally be written as the sum of the electronic energy [i.e., the value $U(r_e) = E_e$, corresponding to the equilibrium configuration of the two nuclei], plus the vibration energy, plus the rotation energy:

$$E = E_e + \hbar c\omega(v + \tfrac{1}{2}) + \hbar cB\{J(J+1) - \Omega^2\}. \tag{6}$$

This expression for the energy, together with a few simple selection rules which will be discussed shortly, yields the general structure of the band spectrum.

2-2 SELECTION RULES FOR J AND v

A fundamental selection rule, valid both for atoms and molecules, is the one that restricts the changes in total angular momentum J to 0 or ± 1. The only allowed transitions are:

$$J \begin{array}{l} \nearrow J+1, \\ \rightarrow J, \\ \searrow J-1, \end{array} \tag{7}$$

with the additional exclusion of the transition

$$J = 0 \rightarrow J = 0.$$

This selection rule is completely independent of the particular structure of the system to which it is applied (atom, diatomic molecule, polyatomic molecule).

Selection rule (7) immediately gives a preliminary idea of the structure of the band spectra. We shall discuss later, after classifying the electronic levels, the other more complex selection rules which mainly affect the transitions between different electronic levels.

At first sight, it may seem that the vibrational selection rule $v \rightarrow v \pm 1$ should be valid for the vibrational quantum number v. This rule, however, does not apply to band spectra, principally for the following two reasons:

1. There are transitions in a molecule for which, in general, the electronic state is also changed, in addition to the variations in the vibrational and rotational states. But, a change in the electronic state is related to a change of the vibration frequency and the equilibrium separation of the two nuclei. Hence, we cannot apply to such transitions a selection rule that is valid only for an oscillator with a fixed frequency and in a fixed position.
2. Even when the electronic states are unmodified by the transition, the selection rule $v \rightarrow v \pm 1$ is only valid as a first approximation. This is because the vibration is generally somewhat anharmonic, and the above rule is exactly valid only for a harmonic oscillator; furthermore, the electric moment of the molecule is not exactly proportional to the displacements of the nuclei from their equilibrium positions.

2-3 VIBRATION AND ROTATION BANDS

To find the frequencies that can be emitted by the molecule, we must, as usual, compute the difference between two energy levels of type (6) and divide this difference by h (by hc if we want the frequencies in wave numbers).

It is convenient, at this point, to distinguish between the transitions that include a change in the electronic state and those that do not. In the first case the energy difference between the two states, and consequently the emitted frequency, is much higher than in the second case; we have already mentioned that the energy differences between the various electronic states are normally larger than those arising from vibrational or rotational changes. In general, the bands corresponding to electronic transitions lie in the visible or in the ultraviolet region; those corresponding only to a variation of the vibrational and rotational states lie in the infrared. This is why the bands of these two types are called visible and infrared bands, respectively. These expressions, of course, are not always to be taken literally. It is more appropriate to designate these as electronic bands, as distinguished from vibration and rotation bands.

The infrared bands consist, almost exclusively, of transitions between different vibrational and rotational states corresponding to the lowest electronic state. This is because they are usually absorption bands observed in cold gases or vapors, where the low temperature prevents the excitation of higher electronic states.

No infrared bands are observed in the spectra of diatomic molecules consisting of two identical atoms ($H_2, N_2, O_2, \ldots$). This can be understood in the following way: The emission of the infrared bands can be attributed, via the correspondence principle, to the existence, for a diatomic molecule, of a permanent electric moment parallel to its axis. Molecules consisting of two identical atoms are an exception, their moments obviously being zero because of symmetry. When the molecule rotates, its electric moment changes (only in direction, not in magnitude), and this change generates the emission of the rotation bands. Similarly, if the two nuclei vibrate relative to each other, there is a corresponding vibration in the magnitude of the electric moment and consequently an emission of radiation with the same frequency as the vibration. In conclusion, we see that, for the existence of vibration or rotation bands, the molecule must have a permanent electric moment and therefore must not consist of two identical atoms.

To analyze the structure of a vibration and rotation band, we can use expression (6), for the energy of a molecular term. If the electronic state remains constant, all values E_e, ω, B which depend on this state are also the same for both initial and final terms. We may also assume $\Omega = 0$, a condition almost always valid for the ground states of the molecules whose vibration and rotation bands have been analyzed. A selection rule more restrictive than (7) is valid in this case: All transitions for which J does not vary are forbidden. This is because, when $\Omega = 0$, then R and J coincide (see Fig. 3); since the electric moment of the molecule in these transitions is parallel to the molecular axis, the projection of this moment on J is zero.

Assuming that $\Omega = 0$, that the vibrational quantum numbers for the initial and final terms are equal to v' and v'', and that the values of the quantum number J (which in the case of $\Omega = 0$ may be called the *rotational quantum number*) are equal to J' and J'', respectively, we finally obtain, for the energy of the two terms, the expressions

$$\begin{aligned} E' &= E_e + \hbar c\omega(v' + \tfrac{1}{2}) + \hbar cBJ'(J' + 1), \\ E'' &= E_e + \hbar c\omega(v'' + \tfrac{1}{2}) + \hbar cBJ''(J'' + 1). \end{aligned} \tag{8}$$

The frequency emitted in the transition between these two terms is given, in wave numbers, by

$$w = \frac{E' - E''}{\hbar c} = \omega(v' - v'') + B[J'(J' + 1) - J''(J'' + 1)]. \tag{9}$$

The selection rule mentioned earlier requires that $J'' = J' \pm 1$. We obtain the first series of frequencies when $J'' = J' + 1$:

$$w = \omega(v' - v'') - B(2J' + 2) \qquad (J' = 0, 1, 2, 3, \ldots). \tag{10}$$

If, instead, $J'' = J' - 1$, we have

$$w = \omega(v' - v'') + 2BJ' \qquad (J' = 1, 2, 3, \ldots). \tag{11}$$

(In this second series we cannot have $J' = 0$, for then J'' would be negative.)

If we fix v' and v'', and vary J' over its allowed values, Eqs. (10) and (11) give us a system of lines representing the infrared band. This band consists of two branches: one (the P branch) is represented by Eq. (10) and extends toward frequencies lower than $\omega(v' - v'')$; the other (R branch) is represented by Eq. (11) and extends toward frequencies higher than $\omega(v' - v'')$. As can be seen from Eqs. (10) and (11), both branches display a succession of lines whose frequency spacing is given by

$$\Delta\omega = 2B = \hbar/Ic \quad \mathrm{cm}^{-1}. \tag{12}$$

The smallest separation between the two branches is $4B$; this gives the band the appearance of Fig. 4. We have a simple sequence of lines with spacings given by (12) and with one line missing (the *zero line*), where the two branches P and R join each other. The absence of this zero line marks the beginning of the two branches. We shall see later, when discussing the intensities of the lines, that they are low at the beginning of the branch, then increase to a maximum after which they decrease again. Figure 5 illustrates this behavior: the absorption curve shown belongs to an infrared band of the hydrochloric acid molecule.

Equation (12) indicates that the frequency interval between the successive lines of a band is inversely proportional to the moment of inertia of the molecule. This interval, then, is relatively large for diatomic molecules containing a hydrogen atom characterized by a small moment of inertia. The lines are more crowded together, however, for molecules containing heavier atoms. Because of the low resolving power in the infrared region, the various rotational lines, in practice, are not always separable.

The measurement of the frequency interval between the lines, in the few cases where the various lines of an infrared band are well-resolved, is quite important; through its value and Eq. (12), we obtain the moment of inertia of the molecule. If the moment of inertia is known,

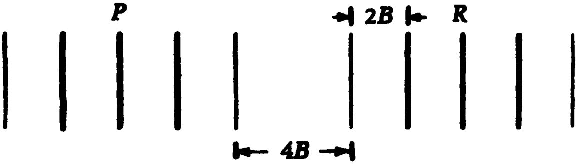


Figure 4

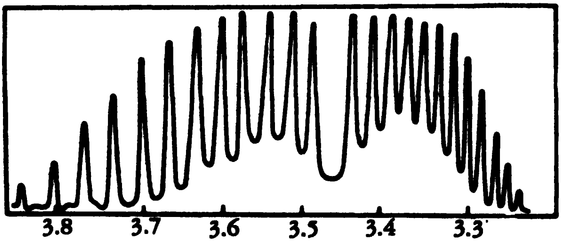


Figure 5

then the distance between the two nuclei can also be determined. Thus, for example, the frequency difference in the bands of the hydrochloric acid molecule has been measured and found to be 20.9 cm^{-1}. By means of (12), we then find

$$I = \frac{\hbar}{\Delta\omega c} = 2.6 \times 10^{-40}.$$

If r is the distance between Cl and H in the HCl molecule, the moment of inertia of the molecule with respect to its center of mass is given from elementary mechanics by

$$I = \frac{m_{\mathrm{H}} m_{\mathrm{Cl}}}{m_{\mathrm{H}} + m_{\mathrm{Cl}}} r^2,$$

where m_{H} and m_{Cl} are the masses of the two atoms. The latter are found by multiplying the corresponding atomic weights (that is, 1 and 35.5) by 1.66×10^{-24}. The result is then

$$I = 1.61 \times 10^{-24} r^2.$$

From this and the preceding value of I, we obtain the distance between the two nuclei

$$r = 1.27 \times 10^{-8} \text{ cm}.$$

Since the infrared bands are usually observed in absorption, only those lines whose lowest term is nearest to the ground state appear.

Figure 6 shows the scheme of the vibrational and rotational terms of the molecule. The two numbers near each line represent the quantum numbers v and J (vibrational and rotational). At absolute zero, all molecules would be in the state 00. At ordinary temperatures, however, they are distributed among several different rotational states, the energy difference between these states being small with respect to kT. In many cases the energy difference between the vibrational quantum states is somewhat larger than kT, so that the great majority of the molecules are in the lowest vibrational state. In this case only those lines whose lowest term has a vibrational quantum number equal to zero are observed in absorption. That is, $v'' = 0$ in Eqs. (10) and (11). The band with the highest intensity corresponds to the vibrational quantum transition 1 → 0; this is the fundamental frequency. Much weaker however, are the transitions 2 → 0, 3 → 0. The pure rotation band appears beyond these, at the limit of the infrared, with $v' = v'' = 0$.

2-4 ELECTRONIC BANDS

We now describe, schematically, the structure of an electronic (or "visible") band. This is a band in which, in addition to a change in the vibrational and rotational states, there is also a change in electronic state. Here again, to calculate the frequency of the various lines,

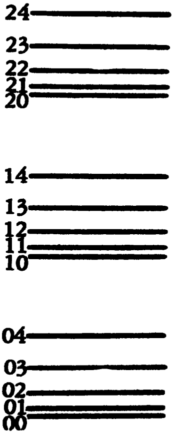


Figure 6

expressed in wave numbers, we must write the difference between two energy levels and divide it by $\hbar c$. We designate with one or two primes the various quantities referring to the highest or the lowest term, respectively.

According to (6), the energies of the two terms are

$$\begin{aligned} E' &= E'_e + \hbar c\omega'(v' + \tfrac{1}{2}) + \hbar cB'[J'(J' + 1) - \Omega'^2], \\ E'' &= E''_e + \hbar c\omega''(v'' + \tfrac{1}{2}) + \hbar cB''[J''(J'' + 1) - \Omega''^2]. \end{aligned} \tag{13}$$

Notice that, the electronic state having changed, the values v' and B' are different here from v'' and B''. The frequency of a line is then equal to the difference between the two preceding energy levels divided by $\hbar c$:

$$w = A + \omega'v' - \omega''v'' + B'J'(J' + 1) - B''J''(J'' + 1), \tag{14}$$

where

$$A = \frac{1}{\hbar c}(E'_e - E''_e) + \tfrac{1}{2}(\omega' - \omega'') + B''\Omega''^2 - B'\Omega'^2. \tag{15}$$

Since the value of A does not depend on the vibrational and rotational quantum numbers, it remains constant for all the lines corresponding to the same electronic-state transition.

The system of lines corresponding to a definite electronic-state transition and to all possible variations of the vibrational and rotational states is what we call a *band system*. The name "band," on the other hand, is given to the combination of lines belonging to a certain band system that corresponds to a definite transition of the vibrational states. The frequency of the lines of a band are then given by (14), with v' and v'' having two definite numerical values.

According to selection rule (7), we see that J'' may assume only the values $J' + 1, J', J' - 1$; correspondingly, the typical band consists of three branches P, Q, and R. Equation (14) gives the frequencies of the lines belonging to these branches:

$$\begin{aligned} &P\colon w = A + \omega'v' - \omega''v'' + (B' - B'')J'^2 - (3B'' - B')J' - 2B'', \\ &Q\colon w = A + \omega'v' - \omega''v'' + (B' - B'')J'(J' + 1), \\ &R\colon w = A + \omega'v' - \omega''v'' + (B' - B'')J'^2 + J'(B' + B''). \end{aligned} \tag{16}$$

The smallest values for J' and J'' are Ω' and Ω'', respectively; this means, for example, that if $\Omega' = \Omega'' = \Omega$ for branches P and Q, then J' can only be Ω, $\Omega + 1$, $\Omega + 2$, . . . , whereas J' has only the values $\Omega + 1$, $\Omega + 2$, $\Omega + 3$, . . . , for branch R (otherwise the first term would have $J'' = \Omega - 1$).

Figure 7 illustrates graphically the dependence of the various lines of a band on the rotational quantum number; the frequencies are the abscissas of the points with an integer ordinate (equal to J'). The curves drawn are three parabolas as required by Eq. (16); the figure applies to the case for which $\Omega' = \Omega'' = 0$ and $B' > B''$. In this case, as shown by the figure, the band terminates abruptly toward the low frequencies with a high line density; both the density and the intensity of the lines decrease toward the violet. The opposite would have happened with $B' < B''$: the band would slowly disappear toward the red and terminate suddenly toward the violet.

In several cases, however, the band structure is somewhat different from the typical one described above. It may often happen, for example, that the Q branches are missing. This is due to certain symmetries of the electronic terms, which we shall describe later. This occurs, for example, in the infrared bands. Very frequently

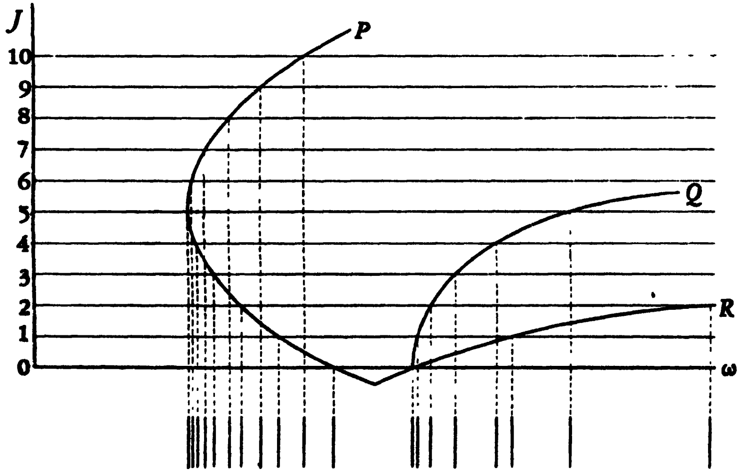


Figure 7

bands occur with more than three branches; this happens every time the electronic terms are multiple or degenerate.

There are not many cases of bands in which the electronic terms are both simple and nondegenerate. An example is given by a band system belonging to AlH, where $A = 44{,}597\ \mathrm{cm}^{-1}$:

$$\omega' = 2\pi(1326), \qquad \omega'' = 2\pi(1625),$$
$$B' = 2\pi(6.37), \qquad B'' = 2\pi(6.30).$$

With (4), we can calculate the moments of inertia of the initial and final states; the results are $I' = 4.33 \times 10^{-40}$ and $I'' = 4.38 \times 10^{-40}$. From these data and knowing the masses of the atoms, we can finally obtain the equilibrium distance of the nuclei for the two quantum states; they are $r'_e = 1.65 \times 10^{-8}$ and $r''_e = 1.66 \times 10^{-8}$.

We have already mentioned that the harmonic oscillator selection rule is not valid for the electronic bands. We now briefly discuss a rule, due to Franck and Condon, which allows a qualitative determination of the vibrational quantum transitions occurring with the highest intensity in an electronic band. In Fig. 8 we have represented $U_q(r)$,

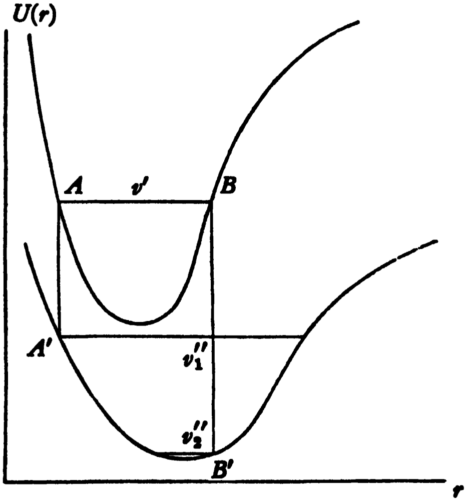


Figure 8

the mutual energy between the two atoms, as a function of the distance, for the upper and lower electronic state. We assume that the initial state of the molecule is in the upper electronic level AB, corresponding to the vibrational quantum number v'. Classically, this means that, when the two atoms vibrate, their separation varies between two limits given by the abscissae of the points A and B. Even classically, the probability of finding a definite separation at a certain moment is by no means uniform over the interval between the two limits. The probability of a separation near the maximum or the minimum value is obviously much higher than that for an intermediate value; the velocity being zero at these extremes, the two nuclei remain there relatively longer than at an intermediate distance.

When the quantum transition takes place, both the configuration and the motion of the electrons change; the mutual energy of the two atoms also changes, and is now represented by the lower curve of Fig. 8. If the transition occurs while the nuclei are at a separation given by the abscissa of A, the nuclei oscillate along the energy level marked v_1''. If, instead, the transition occurs while the separation is given by the abscissa of B, the final oscillation is along v_2''. Now, we have just seen that the transition probability is higher when the distance between the two nuclei is near its maximum or minimum value; hence the most probable final levels are v_1'' and v_2''. Thus we expect two vibrational states in the final term to occur with a high probability. Indeed, we can also determine these states from the above considerations.

An illustrative example is the following, reported by Kronig.[37, 108] In Fig. 9 the values v' and v'' of the vibrational quantum numbers are plotted along the abscissa and the ordinate of the graph, respectively. The curve gives, for each value of v', the two values of v'' corresponding to the maximum transition probability. The shape of the curve is approximately parabolic (*Condon parabola*). The numbers inside the circles give the intensity of the transitions experimentally observed in the case of a band of the molecule Na_2.

2-5 ANHARMONIC VIBRATIONS; DISSOCIATION

We have already mentioned that the force responsible for restoring the two atoms of a molecule to their equilibrium position is propor-

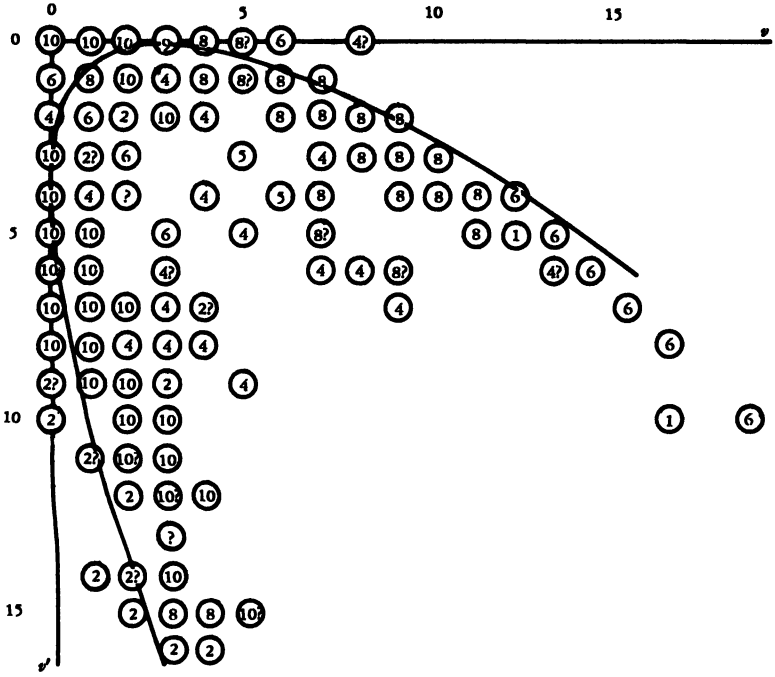


Figure 9

tional to the displacement only to a first approximation. In view of this, the vibration of a molecule is only approximately harmonic. In particular, Eq. (2), giving the vibrational energy, is valid only for small values of the vibrational quantum number v. For large values, a quadratic formula can be written which gives a better approximation:

$$E_v = hc(av - bv^2). \tag{17}$$

Here we have omitted, for simplicity, the term $\frac{1}{2}\omega$, representing the oscillator energy for $v = 0$.

There is an important correlation between the anharmonicity of the molecular vibration and its dissociation energy. Notice that, for a

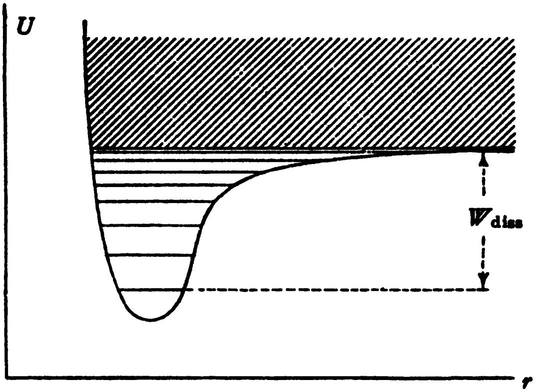


Figure 10

pure harmonic oscillation, the distance between the successive levels is always the same. In reality however, the vibrational levels have an increasing density, as shown in Fig. 10. The curve in the figure represents the energy $U(r)$ of the molecule as a function of the distance; the horizontal lines are the vibrational energy levels.

The dissociation energy W_{diss} is given by the difference between the energy of the two atoms at infinite separation and the energy of the lowest vibrational state.

Above the dissociation energy there are no more discrete energy levels: The eigenvalue spectrum is continuous (cross-hatched area in Fig. 10). Immediately below, the levels are very crowded, becoming gradually more sparse when their distance from the lower limit of the continuous spectrum increases. The dissociation energy of the molecule can therefore be determined, as suggested by Franck, from a knowledge of the distribution of the vibrational levels in the lowest electronic term.

We assume, for example, that the vibrational energy for the lowest electronic term of a molecule is accurately represented by Eq. (17), even for large values of v. Then the derivative of E_v with respect to v gives approximately the energy difference between two consecutive levels:

$$\Delta E_v = hc(a - 2bv).$$

The dissociation corresponds to the point where all lines converge, that is, $\Delta E_v = 0$; this gives

$$v = \frac{a}{2b}.$$

Substituting into (17), we get the dissociation energy

$$W_{\text{diss}} = \hbar c \frac{a^2}{4b}. \tag{18}$$

This result, of course, is only a rough approximation because (17) is not well-justified for high-vibrational terms. A much better result is given by the direct knowledge of the higher vibrational levels; these allow a more precise determination of the energy toward which the consecutive energy levels converge.

We find, for example, that the dissociation energy for the hydrogen molecule as given by the convergence of the vibrational levels is 4.34 eV. Equation (18) with $a = 2\pi(4247)$ and $b = 2\pi\ (114.4)$ gives, instead, a dissociation energy of 4.86 eV; the difference is due to the inaccuracy of Eq. (17).

In several cases the dissociation energy cannot be obtained directly from the study of the vibrational levels of the fundamental electronic term, because too few of these are known. One can then use some excited electronic state for which more vibrational terms are known. Thus, for example, in the case of the hydrogen molecule, we know where the vibrational levels of two excited electronic terms observed in absorption converge. This corresponds to about 118,000 cm^{-1}, equivalent to 14.6 volts above the ground state. The dissociation energy, of course, is not simply given by 14.6 volts; the two atoms produced in the dissociation of the two electronic terms are not both in their ground states. One of them is in the ground state, the other in the first excited state with an energy of $\frac{3}{4}$ rydberg = 10.2 volts. The energy necessary to dissociate the hydrogen molecule into two atoms, both nonexcited, is then given by the difference 14.6 − 10.2 = 4.4 volts, in very good agreement with the preceding result.

A second example is given by the molecule Cl_2. This molecule has a very well-known absorption spectrum which converges at 4785 Å, equivalent to 2.58 volts. There are arguments by which one can demonstrate that this molecule dissociates into an atom in its ground state plus another atom in the ${}^2P_{\frac{1}{2}}$ level, 0.11 volt above the ground state. The energy for the dissociation into two nonexcited atoms is then given by the difference 2.58 − 0.11 = 2.47 volts, in agreement with the chemical result of 57 cal.

Because of the slow increase in the vibrational energy of its atoms, a molecule may dissociate as a result of a collision with another molecule during thermal motion. Another cause of dissociation can be the absorption of a quantum of radiation which brings the molecule directly to an electronic level higher than that for which the dissociation occurs. The dissociation mechanism is different for each of these cases. It may happen that the radiation brings the molecule directly to an electronic state whose energy as a function of the distance is of the type *b* and *c* of Fig. 2. Then the dissociation takes place immediately because the two atoms in their new electronic state repel each other. Another possibility is that the radiation may bring the molecule to a higher electronic state; from this it then decays, emitting light and ending in an electronic state of the type *b* or *c* of Fig. 2 or perhaps of the type *a* of Fig. 2, but with vibrational energy higher than that needed for the dissociation.

2-6 PREDISSOCIATION

In line with the same argument, we mention now the phenomenon of predissociation. First observed in the S_2 bands by Henri [99], it has been interpreted by Bonhöffer and Farkas.[69] Figure 11 shows the various vibrational levels corresponding to two electronic states *a* and *b*. The cross-hatched area indicates, as usual, that the continuous part of the spectrum thus corresponds to dissociation and extends above the discrete levels.

Suppose the molecule is in electronic state *b*. Then, if the vibrational state is one of those indicated as 0, 1, 2 in the figure, below the dotted line, the situation is very different from what it would be if the vibrational level were 3, 4, or 5, . . . , above the line. This line marks the limit of the dissociation spectrum of the state *a*. In the first case there is not generally a corresponding level of the state *a* at the same energy as one of the levels 0, 1, 2. Even if, by chance, two discrete levels of *a* and *b* were approximately coincident so that they perturbed each other considerably, the result would still be two well-separated energy levels.

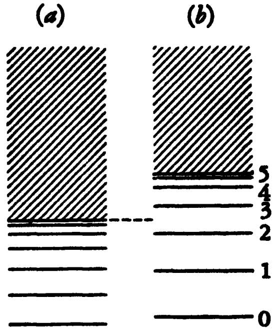


Figure 11

The situation is different in the case of the levels 3, 4, 5, . . . belonging to state *b* and lying in the continuous part of the spectrum of state *a*. A spontaneous transition can now take place in these levels; without emission of radiation, the vibrational level changes from the discrete domain of electronic state *b* to that level in the dissociation spectrum of electronic state *a* which has the same energy. Consequently, the molecule dissociates. This phenomenon is completely analogous to the Auger effect observed in atoms. As a result, the mean life of states 3, 4, 5, . . . of electronic term *b* is very much shortened; apart from the normal radiative transitions, the above processes contribute to the decay of these states. Owing to their very short lives, these states do not appear as distinct lines; broad and diffuse lines are observed at the end of the spectrum with these states as extremes. Kronig[87, 108] has discussed this phenomenon quantitatively and has demonstrated that the observed line diffusion has the same order of magnitude as predicted by the theory.

2-7 DEVIATIONS FROM THE RIGID-ROTATOR FORMULAS

Just as the vibrational energy of a molecule is not given, except to a first approximation, by the harmonic oscillator formulas, so, too, the rotational energy is not always accurately represented by the rigid-rotator formulas. Indeed, it is easily seen, even classically, that rapid rotation produces a centrifugal force that eventually increases the distance between the nuclei, thereby increasing the moment of inertia of the molecule. Accordingly, there is a perturbation between vibration and rotation, particularly for large values of the vibrational quantum numbers. Because of the asymmetry of the forces restoring the two nuclei to the equilibrium position, the average distance between the two atoms of the molecule deviates considerably from the equilibrium distance. As a consequence, the moment of inertia of the molecule depends on its vibrational state; this, in turn, affects the spacing of the rotational levels.

These deviations from the laws of the rigid rotator, which depend in a regular and continuous way on the vibrational and rotational quantum numbers, are often superimposed on the so-called perturbations of the rotational terms. Sometimes a line is found in a band at a place not given by an interpolation of the neighboring lines. This occurs by chance, if there is an almost exact coincidence of two rotational levels, each belonging to a different electronic term. The two levels, then, according to ordinary perturbation theory, affect each other very strongly, displacing each other relative to the unperturbed lines. Owing to the very large number of energy levels in the molecules, this phenomenon is by no means exceptional.

Perturbations are sometimes useful when analyzing band spectra; lines with a common perturbed term can be easily identified by the similarity of their perturbations.

2-8 ELECTRONIC STATES

Until now, we have not discussed the structure of the electronic states. We have assumed that the energy difference between the various electronic states is almost always large with respect to the rotational energy of the molecule. However, there are several instances in which this hypothesis is very far from correct. This is particularly so when the electronic levels are multiple or degenerate. We now consider the classification and properties of the electronic terms.

The classification of the electronic terms of a molecule is somewhat analogous to that for atoms. First, the multiplicity of the various terms can be obtained in the same way as for atoms. Consider all the electrons of the molecule or, possibly, just the valence electrons, which are less tightly bound; a strong coupling energy exists among their spins. Only a negligible part of this energy, both in molecules and atoms, is due to the magnetic interaction between the electronic magnetic moments, the main contribution being produced by the resonance phenomenon; that is, the coupling is mainly electric and not magnetic. Owing to this coupling, the spins of the electrons in a molecule are aligned either parallel or antiparallel to each other, giving a total spin S. Just as in the case of atoms, the value of S in units of $\hbar$ is either an integer or a half-integer, depending on whether the total number of electrons is even or odd (each electron has an angular momentum equal to $\frac{1}{2}$). In analogy with atomic spectra, the maximum multiplicity of a term is determined by the total spin S and is equal to $2S + 1$, that is, to the number of different orientations that S can assume with respect to a fixed direction.

In addition to the total spin, the value L of the total orbital angular momentum is used in the classification of the atomic spectra. This is not the case, however, for molecules. Here the total orbital angular momentum is very far from being an integral of the motion; the forces acting on the electrons are not even approximately central. In diatomic molecules, however, as long as rotation can be neglected, the moment of the forces acting on the electrons with respect to the axis of the molecule is zero. Consequently, in this case, the orbital angular momentum with respect to this axis is an integral of the motion; this is valid, of course, only to the approximation in which the molecule's rotation can be neglected.

The total orbital angular momentum of the electrons with respect to the molecular axis can assume integer values only (in units of $\hbar$) and will be indicated by Λ. The electronic terms of the molecule are specified by the letters Σ, Π, Δ, . . . , corresponding to the values 0, 1, 2, . . . of Λ. Just as for atoms, an upper left index gives the multiplicity. Thus, for example, the symbol $^3\Pi$ represents a triplet (i.e., a total spin $S = 1$) with $\Lambda = 1$.

Apart from the multiplicity, which differs with the various possible orientations of S, there is a fundamental distinction between the Σ terms (i.e., terms with $\Lambda = 0$) and the Π, Δ, . . . terms (i.e., those with $\Lambda > 0$). Whereas the first are simple, all the others are degenerate. This can be seen immediately by reversing the direction of rotation of the electrons around the axis, which corresponds to a change in sign of the angular momentum; in the case of a Σ term one obtains the same state (because $\Lambda = 0$). However, when $\Lambda > 0$, we obtain a new state which is clearly degenerate with respect to the preceding one.

2-9 QUANTUM-MECHANICAL DISCUSSION OF ELECTRONIC TERMS

We begin by studying the case of a single electron, and assume that the others are either absent (for instance, in the H^+ ion) or, if present, that they have an over-all action that can be reduced to an axially symmetric potential that modifies the potential of the two nuclei. This procedure is the same as that followed, for example, in the study of the atoms of the alkali metals; here the over-all action of the remaining electrons on the valence electron is usually represented as a screening effect on the nuclear charge, resulting in a field that is still central but no longer newtonian. Since our interest is in the electronic terms, we disregard the vibrations and rotations of the nuclei and consider them fixed.

We take the line joining the two nuclei as our z axis. Together with the cartesian coordinates x, y, z of a point, we shall also use a cylindrical coordinate system: z, ρ (distance of the point from the z axis) and φ (angle between the xz plane and the plane determined by the point and the z axis).

Neglecting for the moment the spin, we can write the Schrödinger equation for our electron in the classical form:

$$W\psi = -\frac{\hbar^2}{2m}\Delta\psi + V\psi, \tag{19}$$

where Δ is the Laplace operator which, in cylindrical coordinates, is equal to

$$\Delta = \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial}{\partial \rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial \varphi^2}, \tag{20}$$

and V is the electrostatic potential. According to what we said above, V has axial symmetry; therefore it does not depend on φ: $V = V(z,\rho)$.

We can then write

$$W\psi = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial z^2} + \frac{\partial^2\psi}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial\psi}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2\psi}{\partial\varphi^2}\right) + V(z,\rho)\psi \qquad (21)$$

The variables z and ρ can easily be separated from φ by writing

$$\psi = \chi(z,\rho)\Phi(\varphi). \qquad (22)$$

Substituting into (21), we find the following equations for χ and Φ:

$$\frac{d^2\Phi}{d\varphi^2} + \Lambda^2\Phi = 0, \qquad (23)$$

$$W\chi = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\chi}{\partial z^2} + \frac{\partial^2\chi}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial\chi}{\partial\rho} - \frac{\Lambda^2}{\rho^2}\chi\right) + V\chi, \qquad (24)$$

where Λ is a constant.

Equation (23) can be immediately integrated; the fundamental integrals are

$$e^{i\Lambda\varphi} \quad \text{and} \quad e^{-i\Lambda\varphi}. \qquad (25)$$

Obviously, we must impose the condition that these be periodic functions of φ with the period 2π; it follows that Λ must be real and that it must take on integer values

$$\Lambda = 0, 1, 2,$$

We see immediately that Λ measures (in units of $\hbar$) the orbital angular momentum of the electron with respect to the z axis. The eigenfunction (22) can now be written

$$\psi = \chi e^{\pm i\Lambda\varphi} \qquad (26)$$

where χ is an integral of (24). Notice that both χ and the eigenvalue W of (24) depend on Λ. What we stated at the end of the preceding section follows immediately from Eq. (26). When $\Lambda \neq 0$ (terms Π, Δ, etc.), there are two degenerate eigenfunctions for each eigenvalue, corresponding to the two signs in (26). When, instead, $\Lambda = 0$ (Σ terms), there is only one eigenfunction $\psi = \chi$.

2-10 SPIN EFFECTS

Thus far, we have neglected the spin. We now study its effect. We limit our analysis to qualitative considerations only, making use of the Pauli theory instead of the Dirac theory.

Owing to the two possible spin orientations, the degeneracy of each function is twice as large as without spin. Consequently, the Σ terms that are single without spin are now doubly degenerate; the Π, Δ, . . . terms then change from a twofold to a fourfold degeneracy.

We investigate, to a first approximation, the perturbation introduced by the spin-orbit interaction. This arises because the electron's own magnetic moment is affected by the virtual magnetic field associated with the motion of the electron in an electric field. The interaction term, taking into account the Thomas correction factor of $\frac{1}{2}$, can as in the case of atoms, be written as

$$H = \frac{e\hbar}{4m^2c^2} (\mathbf{E} \times \mathbf{p}) \cdot \boldsymbol{\sigma}, \tag{27}$$

where $\mathbf{E}$ is the electric field, $\mathbf{p}$ the momentum of the electron corresponding to the operator

$$\mathbf{p} = \frac{\hbar}{i} \operatorname{grad}, \tag{28}$$

and $\boldsymbol{\sigma}$ is the Pauli spin vector having as components the following operators:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{29}$$

In the Pauli theory each eigenfunction is represented by a system of two functions of the position coordinates alone; the operators of (29) operate on these two functions as linear substitutions.

One can demonstrate that the only term of the scalar product in (27) that introduces a first-approximation perturbation of the energy is the one given by the product of the z components. We can therefore take, as the perturbing hamiltonian,

$$H = \frac{e\hbar}{4m^2c^2} (E_x p_y - E_y p_x)\sigma_z. \tag{30}$$

The other two terms do not have nonzero matrix elements corresponding to pairs of degenerate states.

Owing to the axial symmetry of the electric field, the vector **E** lies in the horizontal plane; thus we can write

$$E_x p_y - E_y p_x = E_\rho p_\varphi = \frac{\hbar}{i}\frac{1}{\rho} E_\rho \frac{\partial}{\partial\varphi}, \tag{31}$$

where $E_\rho = -(\partial V/\partial\rho)$ is the electric field component in the ρ direction; $p_\varphi = (\hbar/i)\,(1/\rho)\,(\partial/\partial\varphi)$ is the operator representing the momentum component along the direction perpendicular to z and ρ. As unperturbed eigenfunctions, we may take the pairs of functions

$$\begin{pmatrix} \chi e^{i\Lambda\varphi} \\ 0 \end{pmatrix} \begin{pmatrix} 0 \\ \chi e^{i\Lambda\varphi} \end{pmatrix} \begin{pmatrix} \chi e^{-i\Lambda\varphi} \\ 0 \end{pmatrix} \begin{pmatrix} 0 \\ \chi e^{-i\Lambda\varphi} \end{pmatrix} \tag{32}$$

For $\Lambda = 0$, these four functions reduce, of course, to only two.

Using (29) and (31), we find that the operator (30) applied to the four unperturbed eigenfunctions (32) transforms them into

$$\frac{e\hbar^2\Lambda E_\rho}{4m^2c^2\rho}\begin{pmatrix} \chi e^{i\Lambda\varphi} \\ 0 \end{pmatrix}; \quad -\frac{e\hbar^2\Lambda E_\rho}{4m^2c^2\rho}\begin{pmatrix} 0 \\ \chi e^{i\Lambda\varphi} \end{pmatrix};$$

$$-\frac{e\hbar^2\Lambda E_\rho}{4m^2c^2\rho}\begin{pmatrix} \chi e^{-i\Lambda\varphi} \\ 0 \end{pmatrix}; \quad \frac{e\hbar^2\Lambda E_\rho}{4m^2c^2\rho}\begin{pmatrix} 0 \\ \chi e^{-i\Lambda\varphi} \end{pmatrix}. \tag{33}$$

We can now easily obtain that portion of the perturbation matrix corresponding to the four degenerate eigenfunctions (32). This matrix is identically zero for $\Lambda = 0$ [notice that the expressions (33) all have Λ as a factor]; that is, the spin perturbation on the electronic term is zero, in the first approximation, for the Σ terms.

When $\Lambda > 0$, we obtain the following perturbation matrix:

$$\frac{e\hbar^2}{4m^2c^2}\int \frac{E_\rho}{\rho}|\chi|^2\,d\tau \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

This matrix is diagonal; therefore the four perturbations of the eigenvalue for the four eigenfunctions (32) are given directly by the diagonal values. They are

$$\Delta W = \pm \frac{e\hbar^2\Lambda}{4m^2c^2} \int \frac{E_p}{p} |\chi|^2 \, d\tau. \tag{34}$$

Here the sign is positive for the first and fourth of the eigenfunctions (32) and negative for the second and third.

We conclude that, in the case of a single-valence electron, each one of the Π, Δ, . . . terms breaks up into two terms whose separation equals twice the value given by (34). Each of the two terms still remains doubly degenerate.

The above results on the effects of the spin on those electronic terms that depend on a single electron can be easily understood from the following intuitive considerations. The interaction between the electron spin and the orbital motion can always be attributed, in molecules as well as in atoms, to a coupling between spin and orbital angular momentum. The average angular momentum in a diatomic molecule reduces to only the axial component Λ; therefore the spin is aligned along this direction, having one or the other of the two possible orientations. There are two distinct terms corresponding to the parallel or antiparallel orientation with respect to Λ. If we indicate by Ω the total angular momentum with respect to the molecular axis, we have for the two cases:

$$\Omega = \Lambda \pm \tfrac{1}{2}.$$

Obviously, each term is still doubly degenerate because reversal of the rotation (i.e., reversal of both Λ and the spin) produces a state equivalent to the preceding one. A special situation occurs for the Σ terms, with $\Lambda = 0$; here the angular momentum Λ with respect to the axis is zero; hence the spin cannot be aligned, and so it is not coupled to the orbital motion. Thus these electronic terms are not split by the spin.

The customary notations for distinguishing the various terms described above are the following. The symbols ${}^2\Sigma$, ${}^2\Pi$, ${}^2\Delta$, . . . designate the values of Λ and indicate that the terms are doublets. In addition, a new subscript is used to indicate the value of Ω. Thus we have the terms

$${}^2\Sigma_{1/2}, \qquad {}^2\Pi_{1/2}, \qquad {}^2\Pi_{3/2}, \qquad {}^2\Delta_{3/2}, \qquad {}^2\Delta_{5/2}.$$

All these terms are doubly degenerate, since Ω can be reversed.

2-11 THE CASE OF SEVERAL VALENCE ELECTRONS

The preceding considerations can easily be extended to several valence electrons. Here we limit the discussion to a few qualitative considerations, assuming for simplicity that there are only two electrons. Neglecting the spin at first, we find, in analogy to the results of Section 2-9 that the orbital angular momentum with respect to the axis can only assume the values 0, 1, 2, . . . corresponding to the terms Σ, Π, Δ, ... Furthermore, in agreement with the general properties of all systems containing two electrons, the terms can be subdivided into symmetric and antisymmetric ones with respect to the exchange of the position coordinates only. (For the moment we are not concerned with spin effects.)

If the Pauli principle is to apply, the over-all eigenfunctions, including the spin coordinates, must be antisymmetric with respect to the interchange of the two electrons. Hence, in analogy to the helium atom, we find that a symmetric eigenfunction of the position coordinates must be associated with an antisymmetric eigenfunction of the spin coordinates (antiparallel spins) and vice versa (parallel spins).

The terms then separate into singlets (antiparallel spins; total spin = 0; symmetric eigenfunctions of the position coordinates) and triplets (parallel spins; total spin = 1; antisymmetric eigenfunctions of the position coordinates).

For a singlet, the orientation of the total spin with respect to the orbit is meaningless, since this spin is zero. For the triplets, however, we must distinguish the Σ terms from the Π, Δ, . . . terms since the total spin is 1. For a Σ term there is no spin-orbit coupling (in the first approximation), since there is no orbital angular momentum. For the other terms, however, the spin is oriented in one of three possible directions with respect to the angular momentum, that is, with respect to the axis of the molecule. These three orientations of the spin correspond to the three possible components $(1, 0, -1)$ of the spin along Λ. These orientations correspond to three distinct terms, for which the total angular momentum Ω with respect to the molecular axis has the values $\Lambda + 1$, Λ, $\Lambda - 1$.

The symbols used to indicate the various singlet terms are

$$^1\Sigma_0,\ ^1\Pi_1,\ ^1\Delta_2,\ \ldots .$$

The subscript gives the total angular momentum Ω along the axis (equal to Λ for singlets).

$$^3\Sigma_1,\ ^3\Sigma_0,\ ^3\Pi_2,\ ^3\Pi_1,\ ^3\Pi_0,\ ^3\Delta_3,\ ^3\Delta_2,\ ^3\Delta_1,\ \ldots$$

are the analogous symbols for the triplet terms.

The case of a molecule with any number of valence electrons is very similar to the case considered above. Again the total spin S is oriented with respect to Λ, yielding a total angular momentum Ω whose values range from $\Lambda + S$ to $\Lambda - S$. No coupling exists between total spin and the angular momentum about the molecular axis, in the first approximation, for the Σ terms.

From a quantitative point of view, one notes that the separation between the various terms of an electronic multiplet, that is, between the various terms corresponding to the possible orientations of S with respect to Λ, can assume very different values. As in the case of atoms, the separation increases rapidly with the atomic weights of the constituents of the molecule; its order of magnitude is comparable to the separation of the multiplets in the atoms composing the molecule.

2-12 HUND'S COUPLINGS *a* AND *b*

Up to this point, we have analyzed the electronic terms of a molecule assuming the molecular axis to be fixed; we have completely neglected, in other words, the rotation of the molecule. This rotation can be very important, in some cases, in determining the spin-orbit coupling of the electrons. As an example, we study the two extreme cases of coupling, which Hund[30] called cases *a* and *b*.

Case a: The coupling energy of the spin to the molecular axis is large compared to the energy differences between successive rotational levels.

Case b: The coupling energy of the spin to the molecular axis is small compared to the energy differences between successive rotational levels.

Case *b* is usually valid for the lighter molecules because here the spin-axis coupling (as measured by the separation of the electronic multiplets) is small, whereas, at the same time, the separation of the rotational levels is large because of the small moment of inertia. Case *a*, on the other hand, occurs for heavier molecules. The Σ terms follow case *b* even for heavy molecules, because of the absence of coupling, in the first approximation, between spin and orbit.

In several cases we may also have a continuous transition, for the same electronic term, from case *a* to *b*; this occurs because the separation between the successive rotational levels increases with the rotational quantum number. Thus, for small rotational quantum numbers, the separation between the rotational states may be small compared to the spin-orbit coupling (case *a*), whereas for high rotational quantum numbers the opposite may be true (case *b*).

In case *a*, the electronic spin is oriented along the molecular axis; it then adds on to the axial component Λ of the orbital angular momentum to give the total electronic angular momentum Ω parallel to the axis. According to the scheme of Fig. 3, the angular momentum Ω adds on to the angular momentum R of the rotating nuclei giving rise to the total angular momentum J of the whole molecule.

In case *b*, on the other hand, we may neglect, to a first approximation, the coupling of the spin to the molecular axis; the angular momentum R then adds on to the orbital angular momentum Λ to give a resultant angular momentum vector K (see Fig. 12). In the second approxima-

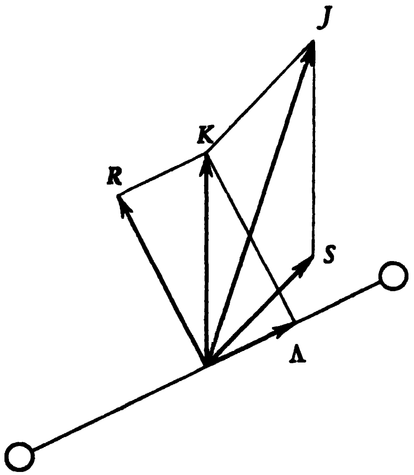


Figure 12

tion, the spin S and the angular momentum K are then oriented with respect to each other, combining to give the total angular momentum J of the entire molecule.

One can easily see, using a semiclassical argument, what the arrangement of the rotational levels in case b is. The rotational energy is given by

$$E_r = \hbar cBR^2.$$

On the other hand, Fig. 12 gives

$$R^2 = K^2 - \Lambda^2,$$

and therefore

$$E_r = \hbar cBK^2 - \hbar cB\Lambda^2.$$

Quantum-mechanical corrections replace this formula by

$$E_r = \hbar cBK(K+1) - \hbar cB\Lambda^2, \tag{35}$$

where K, according to the figure, must be greater than or equal to Λ and therefore assumes the values Λ, $\Lambda + 1$, $\Lambda + 2$, ... Thus, to a first approximation, the positions of the rotational levels are determined by the quantum number K (and not by J). For each value of K, depending on the different relative orientations between this vector and S, the total angular momentum J can take on values in the interval from $K + S$ to $|K - S|$. If the spin-axis coupling were exactly zero, these values of J would all correspond to identical energy terms. But a weak coupling does exist, and this generates a small separation between terms with the same value of K and different values of J. More precisely, for each J the average value of the projection of S along the molecular axis is different; this introduces a change in the average value of the coupling energy between Λ and S.

The arrangement of the levels in case b is shown schematically in Fig. 13 for the values $\Lambda = 2$ and $S = \frac{1}{2}$. Here K has the values 2, 3, 4, . . . , and for each value of K there is a rotational level (levels at the left in Fig. 13). For each value of K, two values of J exist if $S = \frac{1}{2}$: $J = K \pm \frac{1}{2}$. Two very nearly equal energy levels correspond to these values of J, as shown on the right side of Fig. 13.

Figure 14 shows, the level scheme for case a, again with $\Lambda = 2$ and $S = \frac{1}{2}$. Owing to the strong spin-axis coupling, the spin is coupled

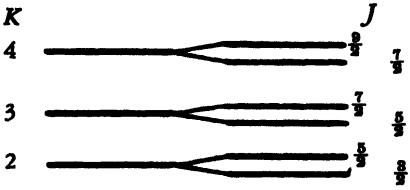


Figure 13

to the axis. The result is a total angular momentum Ω parallel to the axis and equal to the sum of Λ and the component of S along the axis. In our case Ω assumes either of the two values $2 \pm \frac{1}{2}$. Each of these values then generates a different succession of rotational terms corresponding to the different values of $J \geq \Omega$.

In addition to the two couplings just mentioned, there are a few others whose main characteristics we shall only indicate.

Case c: A strong coupling exists between the orbital angular momentum L and the spin S, resulting, in a first approximation, in a total angular momentum J^a with values between $S + L$ and $|S - L|$. Then J^a or L is moderately coupled to the molecular axis, and J^a orients itself with respect to this axis. The projection Ω of J^a, equal to the

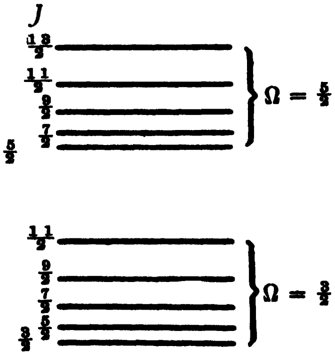


Figure 14

average value of this vector, finally combines with the rotation to give the total angular momentum of the molecule.

Case d: A strong coupling exists between the rotation of the nuclei and the angular momentum L or the spin S of the electrons: intermediate coupling between L and the molecular axis, weak coupling between L and S.

Case e: This is like the previous case, with the difference that the coupling between L and the axis is weaker than that between L and S.

2-13 Λ-SPLITTING

We have often noted that an electronic term with $\Lambda \neq 0$ is always doubly degenerate, even when we consider a system of singlets. Indeed, if we reverse the rotations of the electrons around the molecular axis, the new electronic state obviously has the same energy as the original one.

As long as we completely neglect the molecular rotation and assume the axis to be fixed in place, these two electronic states are completely degenerate. If, instead, we take the rotation into account, the two degenerate states are distinct. This phenomenon is called Λ-splitting.

In systems of singlets or, in the case of b coupling, where the spin S can be considered not coupled to the molecular axis, the Λ-splitting increases rather quickly with J. For Π terms, it is proportional to $J(J+1)$ [or to $K(K+1)$ when the spin has a b coupling]; the proportionality factor is of the order of B^2/ω, where ω is a frequency of the order of the electronic frequencies and B is given by (4). The effect is therefore particularly important in the bands of molecules with small moments of inertia, where B is large. This effect has been carefully studied in the bands of the hydrides. For Δ terms, the Λ-splitting is much smaller but its increase with J is faster; for these terms, the effect is much too small to be observed.

The situation for terms with $S \neq 0$ and a coupling is more complicated. Formulas for the Λ–splitting have also been obtained for these cases by perturbation methods; the results have been confirmed in experiments by Mulliken.[45, 117]

The Σ states also have a fine structure when $S \neq 0$; here only b coupling is present, and the structure is determined by the various coupling possibilities between S and the molecular rotation. According to the calculations of Van Vleck,[186] for example, the terms with $S = \frac{1}{2}$ have a fine structure consistent with a separation proportional to $K + \frac{1}{2}$.

2-14 CONNECTION BETWEEN MOLECULAR AND ATOMIC TERMS

In classifying the electronic terms of a diatomic molecule it is very helpful to compare them with the atomic terms. From this comparison, we can sometimes even predict, generally with some uncertainty, the positions of the electronic terms. The following considerations are mostly due to Hund.[80]

The comparison can be made as follows: We assume that the distance between the nuclei of the two atoms can be altered (adiabatically) at will; in particular, the two nuclei may be brought almost together or separated an infinite distance. If Z and Z' are the atomic numbers of the two nuclei, the system obtained when they are together is a neutral atom with atomic number $Z + Z'$. If, instead, the two nuclei are separated by an infinite distance, the molecule splits into two atoms (or ions) with atomic numbers Z and Z'. Consider now a given electronic term of the molecule: In the first case, it must transform continuously into a term of the atom $Z + Z'$; in the second case, into the sum of a term of the atom Z and a term of the atom Z'. Therefore, we expect a continuous correlation between the terms of the atom $Z + Z'$ and the sum of the terms of the two atoms Z and Z'. Once this correlation is known, it can be used to find the electronic terms of the molecule in an intermediate position between these two.

These considerations, apart from practical difficulties, allow quantum numbers to be assigned to the orbits of the individual electrons of the molecule in analogy to what is done for the atoms when the presence of the residual electrons is schematically represented by an over-all screening effect on the particular electron considered.

Let us then consider one electron of the molecule, with spin effects neglected for the moment. The presence of the remaining electrons is represented by a screening action on the charges of the two nuclei. The resulting field on our electron is then axially symmetric. Consequently, as we have already mentioned, the orbital angular momentum with respect to the molecular axis is constant and equal to $\lambda\hbar$. Here

λ is an integer representing one of the quantum numbers characterizing the electron orbit; using the same convention as for the atoms, we indicate with lower case letters (l, λ, m, . . .) the angular momentum of a single electron, with capital letters (L, Λ, M, . . .) the angular momenta of all the electrons of the atom or the molecule.

If we move the two nuclei toward each other adiabatically until they form a single nucleus $Z + Z'$, the orbit of the electron becomes an orbit of the atom $Z + Z'$, whereas the angular momentum λ remains constant throughout the operation. If we let n and l be the total and azimuthal quantum numbers of the atomic orbit, so that λ may be considered the projection of l on the molecular axis, the orbit of our electron can be characterized by three numbers n, l, λ. In place of l and λ, the letters s, p, d, . . . (for l) and σ, π, ∂, . . . (for λ) are frequently used, according to the usual conventions. Thus for example, the symbol $3d\pi$ represents the orbit of an electron of the molecule having angular momentum $\lambda = 1$ with respect to the axis and going over into the orbit $3d$ ($n = 3$, $l = 2$)of the atom $Z + Z'$ when the two nuclei are adiabatically superposed.

Even if we do not consider the spin, the orbit ($nl\lambda$) is doubly degenerate for the reasons mentioned before, except when $\lambda = 0$. Taking into account the spin, which doubles the number of all states, we then have two orbits ($nl\lambda$) for $\lambda = 0$ and four orbits in all other cases.

We now take the spin into account and discuss the transition of the terms from their values when the two nuclei are near one another to their values when the nuclei are far apart. For simplicity, we consider a single electron; the presence of the others is represented by a simple screening action. Consider first the two nuclei joined together to form a single nucleus $Z + Z'$; the quantum states of our electron can be characterized by the quantum numbers n (principal), l (azimuthal), j (internal $= l \pm \frac{1}{2}$), m (magnetic). The position of a term, in the absence of perturbations, does not depend on m; in other words, the term is $2j + 1$ times degenerate, corresponding to the $2j + 1$ values $m(= j, j - 1, \ldots, -j)$, that is, to the $2j + 1$ possible orientations of the total angular momentum j with respect to some axis which we may take, for instance, to be the z axis.

We now separate the two nuclei by a very small distance along the axis (z direction). The degeneracy mentioned above is then partially removed; the $2j + 1$ degenerate levels break up into $j + \frac{1}{2}$ separate terms (not $2j + 1$, because the terms with equal and opposite values of m are obviously coincident). As the distance between the two nuclei increases, the separation between the levels increases, because of the effect mentioned above; eventually this separation becomes larger than that between the two terms of the atomic multiplet.

In the limiting case in which the atomic multiplet separation is negligible compared to the separation arising from the distance between the nuclei, the positions of the various terms may be conveniently described in the following way: As a first approximation, we neglect the spin-orbit coupling. Then a term of the atom $Z + Z'$ remains characterized by the value l of the azimuthal quantum number.

When the two nuclei are separated, this term splits into $l + 1$ levels corresponding to the following values of the projection m_l of l on the z axis: $m_l = \pm l, \pm (l - 1), \ldots, \pm 1, 0$. From the molecular viewpoint, m_l corresponds to Λ (angular momentum with respect to the axis). As for the spin, we can now see that it will orient itself with respect to m_l. There are two terms corresponding to the two possible orientations. The term with $m_l = 0$, that is, $\Lambda = 0$, is, of course, an exception and remains single.

These relations are illustrated in Fig. 15 for the case $l = 2$. As long as the separation effect remains very small (left side of the figure), the two levels $j = \frac{5}{2}$ and $j = \frac{3}{2}$ split into three and two levels, respectively. The values of m are indicated in the figure. The case for which the spin effect is small compared to the separation, owing to the distance between the nuclei, is shown on the right side of the figure. If the spin is neglected, a term with $l = 2$ splits, when the nuclei are separated,

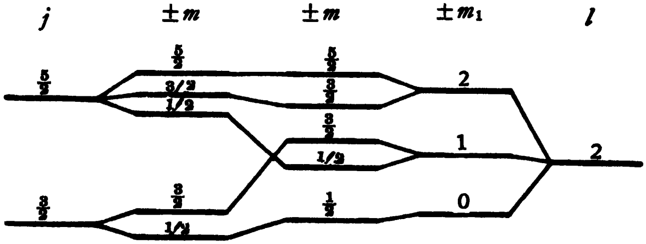


Figure 15

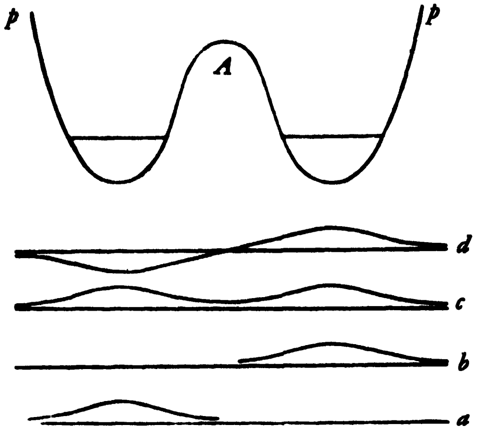


Figure 16

into three terms with $m_l = 0, \pm 1, \pm 2$ (according to molecular terminology, they are designated by Σ, Π, Δ). The Π and Δ levels, then, because of the spin, split further into two levels each; the Σ level remains single. The lines in the center indicate the connection between the levels of the two limiting cases.

The diatomic mononuclear molecules, that is, molecules having two identical nuclei, are particularly interesting. Several of the most important cases belong to this category. Furthermore, these molecules exhibit some important features which we shall consider later and which are particularly interesting for the study of nuclei.

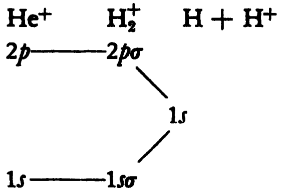
The structure of the electronic terms in this case can be easily understood by means of a very rough schematization of the problem. We consider the motion of a point along a line under the action of a force derived from a potential of the form *pp*, shown in Fig. 16 as a function of the abscissa. Here two "potential wells" are separated by a higher potential barrier, the two wells corresponding to the two atoms, and the point to the electron. We first assume that the potential barrier between the two wells is very high and wide; this implies that the probability for the point to go across it is negligible. The two wells can then be considered completely separated from each other; the point remains in one of the two wells. If, for instance, the point is found in the well at the left, its energy has one of the various values w_1, w_2, . . . There are known eigenfunctions corresponding to each of these values. In particular, let w_1 be the energy and let curve *a* in Fig. 16 represent the eigenfunction. Of course, since the two wells are identical, the same situation could be realized with the point in the well at the right; in this case the eigenfunction corresponding to w_1 would be represented by curve *b*.

Hence, as long as the two wells are separated by an impenetrable potential barrier, there is degeneracy; indeed, for the same energy level w_1 we have two eigenfunctions *a* and *b*. If, however, the potential barrier is not infinitely high, this degeneracy disappears; the level w_1 splits into two different levels. The lower and narrower the potential barrier, the larger is the separation between the two levels. It is easily seen that these two eigenvalues correspond to eigenfunctions of the type *c* and *d* in Fig. 16; these curves approximate the sum and the difference of the eigenfunctions *a* and *b*, respectively. Eigenfunction *c*, which corresponds to the lower eigenvalue (because it has no nodal points) is symmetric with respect to the central point between the two wells. The eigenfunction *d*, instead, is antisymmetric with respect to the same point.

The situation is very similar to that occurring when two identical atoms are brought together. As an example, we consider the system of two hydrogen nuclei plus an electron (H_2^+); the spin is neglected. As long as the nuclei are far apart, the electron can be placed in a 1*s* orbit around one or the other of the two protons. The two eigenfunctions that are thus obtained will, of course, be degenerate as long as the two protons are so far away that they do not significantly perturb each other. When the two protons are brought near each other, the degeneracy disappears and there are then two different energy levels: one lower, with a symmetric eigenfunction, the other higher, with an eigenfunction antisymmetric with respect to the axial plane of the line joining the two protons.

The first eigenfunction obviously has no nodal surfaces; therefore, when the two nuclei are together, it becomes the 1*s* eigenfunction of the ion He$^+$, since this is the only eigenfunction of the ion without nodal points. We designate this eigenfunction with the symbol 1*sσ*. The antisymmetric eigenfunction, on the other hand, has only one nodal surface, namely, the axial plane. When the two protons are together, this plane becomes a plane through the resulting nucleus (with $Z = 2$). The eigenfunction thus becomes an eigenfunction of the ion He^+ with its only nodal surface a plane across the nucleus. It is, therefore, a $2p$ eigenfunction with $m = 0$. The symbol for the corresponding molecular term is then $2p\sigma$.

The previous considerations can be summarized by the following diagram:



Both states $1s\sigma$ and $2p\sigma$ are double, because of the spin which has two possible orientations; $1s\sigma$ is the lower state.

We now keep the two protons close together and construct a hydrogen molecule by successively adding two electrons. Both of them can be placed into the $1s\sigma$ state; their spins must be antiparallel because otherwise the Pauli principle would forbid their belonging to the same orbit. Thus we obtain the ground state of the hydrogen molecule. Since the two spins are antiparallel, the resulting spin S is zero; the term belongs to the singlet system, in agreement with the Heitler-London theory. The complete symbol for this term is

$$(1s\sigma)^2\ {}^1\Sigma,$$

indicating that the term is a Σ singlet with two electrons bound in a $1s\sigma$ orbit.

The excited electronic terms of the hydrogen molecule can be described if we assume that one of the two electrons remains in the $1s\sigma$ orbit, while the other occupies a higher orbit from which it may emit light.

Therefore the terms can be characterized by specifying the orbit of the radiating electron. Except for the ground term, which belongs only to the singlet system, we have, for each orbit occupied by the radiating electron, singlet or triplet terms according to whether the spins of the two electrons are parallel or antiparallel. Table 2 gives

Table 2 Singlet Electronic Terms for H_2

$1s\sigma = 128525$	$2p\sigma = 37371$	$2p\pi = 29503$
$2s\sigma = 29340$	$3p\sigma = 13742$	$3p\pi = 12719$
		$4p\pi = 7067$
		$5p\pi = 4493$
$3d\sigma = 15771$	$3d\pi = 15541$	$6p\pi = 3107$

the values of the electronic terms of the singlet system of H_2, given by Weizel.[61]

The five $p\pi$ terms are particularly worth noticing because, as observed by Richardson,[127] they can be arranged in a rydberg series, so that the absolute values of the terms can be determined.

2-15 EVEN AND ODD LEVELS

The eigenfunction of a molecular term depends on the coordinates of the nuclei and the electrons. We can take, for instance, a cartesian coordinate system with the origin at the molecular center of mass. Let ψ be an eigenfunction which at first is taken as not degenerate; if we neglect spin effects, ψ is a function of the coordinates of the electrons and nuclei. We operate on ψ with what we call a reflection through the origin; this operation consists of changing the signs of all coordinates of the electrons and nuclei which appear in ψ. Thus we obtain a new function ψ_R. Obviously, this new function also satisfies the Schrödinger equation and with the same eigenvalue that belongs to ψ. We assumed at the beginning that ψ is not degenerate; therefore the two eigenfunctions ψ and ψ_R cannot differ by more than a constant multiplicative factor, $\psi_R = K\psi$.

We see that, necessarily $K = \pm 1$. Indeed, under a double reflection through the origin, we must return to the initial state. On the other hand, under two reflections, ψ is multiplied by K^2; thus $\psi = K^2\psi$, which gives $K = \pm 1$. This means that, under a reflection through the origin, our eigenfunction ψ either remains unchanged or changes sign. In the first case we call the eigenfunction even, in the second odd. The respective states are referred to as being of even and odd *parity*, respectively.

These ideas can easily be extended to the case in which we have degeneracy and in which spin effects are taken into account. If we refer the spin coordinates to the x, y, z axes, we see that they must not change under a reflection through the origin. Indeed, the spin must transform like an angular momentum, i.e., apart from constant coefficients, like the expressions $y(\partial/\partial x) - x(\partial/\partial y) \cdots$, which are obviously invariant with respect to a change of sign of the coordinates x, y, z.

The identification of the terms of a molecule as even or odd is particularly important, because of the following selection rule: Only radiative transitions between opposite parity levels are allowed. This means that the possible transitions take place from even to odd levels and vice versa, but never from even to even or from odd to odd levels.

To demonstrate this rule, we recall that, to mix (that is, to have radiative transitions between) two levels, the matrix element of the electric moment between these two states must be different from zero; that is, the matrix element of the following vector quantity must not be zero:

$$\Sigma e_i r_i = \mathfrak{M}, \tag{36}$$

where e_i represents the charge of the ith particle and r_i its vector position. The sum must extend to all particles of the molecule. All this is true, of course, only if the quadrupole radiation can be neglected; this is usually valid, since its intensity relative to the dipole radiation is of the order of about one millionth.

It is apparent from (36) that the electric moment $\mathfrak{M}$ behaves as an odd quantity, since it changes its sign under a reflection around the origin.

We now take two terms (a and b) of our molecule and designate their respective eigenfunctions by ψ_a and ψ_b. The condition for the two terms a and b to combine is that the matrix element

$$\mathfrak{M}_{ab} = \int \psi_a \mathfrak{M} \psi_b \, d\tau \tag{37}$$

be different from zero. The integral must extend over the whole configuration space.

We can change the sign of all the cartesian coordinates belonging to the different particles in (37); this is equivalent to a reflection through the origin. Now, if ψ_a and ψ_b are both even or both odd, the reflection does not alter their product; $\mathfrak{M}$ however, being odd, changes sign so

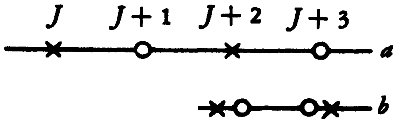


Figure 17

that $\mathcal{M}_{ab}$ also changes sign. Hence $\mathcal{M}_{ab}$ is zero because it equals $-\mathcal{M}_{ab}$. There are thus no radiative transitions between states of the same parity, as stated by the selection rule given above.

It is interesting to study the distribution of the even and odd levels among the various rotational states of a given electronic term.

We first consider the same kind of coupling as in Hund's case *a*. If $\Omega = 0$, the successive rotational levels are simple; they are, then, alternately even and odd, as shown in Fig. 17*a*. Here the levels are indicated by × if even, by o if odd. If, however $\Omega \neq 0$, the successive rotational levels are double because of the Λ-splitting. In this case the distribution of even and odd levels is the one shown in Fig. 17*b*; one of the two components of the Λ doublet, which lie very near each other, is even, the other odd. In the successive rotational terms the even one lies alternately below and above the odd one.

Hund's case *b* is practically the same as the previous one, if we substitute K for J and Λ for Ω; furthermore, each level has the multiplicity $2S + 1$.

Thus, for example, the distribution of even and odd levels for $S = \frac{1}{2}$ is the one shown in Fig. 18. This distribution can be obtained from the analogous distribution of Fig. 17 by a doubling of all levels ($S = \frac{1}{2}$; $2S + 1 = 2$).

A division into even and odd, analogous to the one introduced above, also exists for the case of the mononuclear molecules in the classification of the various electronic terms. We now assume that the two

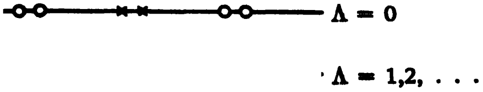


Figure 18

nuclei are fixed, and we consider the eigenfunction ψ, which depends on the electronic coordinates only, corresponding to a certain electronic term. By arguments similar to the previous ones, we can show that when the nuclei are identical, the reflection of all the electron's coordinates with respect to the center of the line joining the nuclei has the following effect: ψ either remains unchanged or becomes $-\psi$. According to which case applies, the term considered is then called electronically *even* or *odd.*

If the two nuclei were fixed, we would have a selection rule for the electronic parity completely analogous to the one given above, according to which only terms with opposite parity may combine. Owing to the rotation of the nuclei, however, this selection rule is only approximately valid, which means that the transitions between electronic terms with the same parity are, indeed, possible but occur with only a very reduced intensity.

To distinguish between even and odd electronic terms, the index g or u is attached to the term symbol (g, from *gerade* stands for even; u from *ungerade*, stands for odd). Thus, for example, $^3\Pi_g$ is a triplet term with $\Lambda = 1$, and it is electronically even.

In a molecule with a single electron, the various terms are electronically even or odd according to whether the quantum number l of the electron is even or odd. We can see this immediately by noticing that, if the two nuclei are joined together into a $2Z$ nucleus, an eigenfunction with l as its azimuthal quantum number can always be represented by the product of a function of the radius vector alone and a spherical harmonic of order l. This function, therefore, under a reflection with respect to the center, either remains invariant or changes sign corresponding to l even or odd. If we then separate the two nuclei adiabatically, the parity of the eigenfunctions obviously remains invariant, because of continuity. Thus in any case the parity is determined by l. If more than one electron is present in the molecule and if the azimuthal quantum numbers of the various electrons are l_1, l_2, l_3, . . . , the term is electronically even or odd, respectively, if the algebraic sum of all the l's,

$$l_1 + l_2 + l_3 + \cdots ,$$

is even or odd. (Notice that this is not the vectorial sum L.) This follows at once because the eigenfunction is a product of eigenfunctions with azimuthal quantum numbers l_1, l_2, l_3, ... A reflection with respect to the center multiplies the individual eigenfunctions by $(-1)^{l_1}$, $(-1)^{l_2}$, $(-1)^{l_3}$, . . . ; therefore, the over-all eigenfunction is multiplied by $(-1)^{l_1+l_2+l_3+\cdots}$.

Notice, in particular, that for a molecule whose electrons are subdivided into pairs with identical quantum numbers n, l, λ, the parity of the term is certainly even.

We apply the above considerations to the case, analyzed by Mulliken,[45, 117] of atmospheric bands of oxygen. We know that most of the Fraunhofer lines in the solar spectrum are caused by the absorption, in the sun's atmosphere, of the light emitted by the solar photosphere. Other lines, however, have a terrestrial origin arising from the absorption of the sunlight in the atmosphere of the earth. Among the latter, an important band system of oxygen is found in the red. The oxygen absorption is very weak; the sunlight, even after traversing the whole thickness of the atmosphere, is only very weakly absorbed. By using large layers of compressed oxygen, one can also observe this phenomenon in the laboratory.

The lowest terms of the O_2 molecule are due to the action of 2 electrons bound in equivalent π orbits, the other 14 electrons being grouped into closed shells.

It is easy to see that two electrons in equivalent π orbits can produce three electronic terms: $^1\Delta$, $^1\Sigma$, and $^3\Sigma$. Indeed, if the two electrons revolve in the same direction around the molecular axis, the total orbital angular momentum with respect to this axis is $\Lambda = 1 + 1 = 2$, so that the term is a Δ term. However, the two electrons are in the same quantum state if one considers the orbital motion alone. The Pauli principle, then, requires antiparallel spins; the total spin is therefore $S = 0$, and the term belongs to the singlet system, so that it is designated $^1\Delta$. If, however, the two electrons revolve in opposite directions, the total angular momentum with respect to the molecular axis is $\Lambda = 1 - 1 = 0$, so that the term is a Σ term. But the two electrons, even with respect to the orbital motion alone, are in two different quantum states because of the opposite directions of motion; therefore their spins can be either parallel or antiparallel. In the first case, $S = 0$—the term is a singlet $^1\Sigma$; in the second, $S = 1$—the term is a triplet $^3\Sigma$.

The lowest electronic terms of O_2 are thus $^1\Sigma$, $^3\Sigma$, and $^1\Delta$. The lowest among these, the ground state, is $^3\Sigma$. This is in agreement with our knowledge that oxygen is a paramagnetic gas; the paramagnetism, analyzed in detail by Van Vleck,[60] arises from the total spin $S = 1$ of the two electrons.

The O_2-absorption bands are due to transitions from the ground state $^3\Sigma$ to higher states. To explain the absorption in the red observed in the atmospheric bands, we must consider transitions from the $^3\Sigma$ term to a term not much higher. Mullikén,[45, 117] showed that the observations can be adequately explained by the transition $^1\Sigma \rightarrow {}^3\Sigma$.

To explain the very low intensity of this absorption band, note first that there are two factors that independently contribute to this effect. First, we are dealing with a singlet-triplet transition. In molecules, as in atoms, the transitions between terms having a different multiplicity always have a very low intensity, particularly in the case of light elements. Second, the two terms $^1\Sigma$ and $^3\Sigma$, which are responsible for the atmospheric bands, are both electronically even. Both are due to pairs of electrons occupying equivalent orbits (electrons in closed shells plus two electrons in equivalent π orbits).

We do not have the space here to describe the structure of the oxygen ground state $^3\Sigma$. The spin-orbit coupling of this state exhibits some interesting properties, which have been studied by Kramers and by Einaudi; the latter has analyzed the special behavior of oxygen as observed by Schurmann in the Stern-Gerlach experiment.

2-16 SYMMETRIC AND ANTISYMMETRIC LEVELS

The distinction between symmetric and antisymmetric levels with respect to the interchange of the two nuclei of a molecule is of fundamental importance for the homonuclear molecules.

Because of the identity of the two nuclei, the interchange of their coordinates in any eigenfunction ψ obviously produces another eigenfunction belonging to the same eigenvalue. If the eigenfunction ψ is not degenerate, the new eigenfunction obtained by interchanging the coordinates cannot differ from the original one by more than a constant factor. By an analysis similar to that made at the beginning of Section 2-15, one can demonstrate that the proportionality factor has only the values ± 1. This can also be proved in the case of degeneracy. We therefore conclude that the eigenfunctions of homonuclear molecules can be divided into two classes: symmetric eigenfunctions, which remain unaltered under the interchange of the coordinates of the two nuclei, and antisymmetric eigenfunctions, which change sign under the same operation.

The following property is particularly important: No transitions can take place between states with different symmetry. This is valid not only for radiative transitions, but for all kinds of transitions, such as those caused by collisions or other perturbations. The reason for this is the same as that for the analogous property of eigenfunctions symmetric or antisymmetric with respect to the interchange of two electrons. Let P be the operator representing whatever perturbation may act on the system. Owing to the identity of the two nuclei, P necessarily contains the coordinates of the two nuclei in a symmetric way. To demonstrate that P cannot induce transitions between two states with different symmetry, we consider two eigenfunctions, ψ_s and ψ_a, the first symmetric and the second antisymmetric with respect to the interchange of the nuclei. The transition probability between the two states depends on the matrix element

$$P_{as} = \int \psi_a P \psi_s \, d\tau.$$

Let us interchange the coordinates in this integral; since P and ψ_s are symmetric and ψ_a is antisymmetric, the integral changes sign. Consequently P_{as}, which must be equal to $-P_{as}$, is necessarily zero; that is, there is no possibility of a transition between symmetric and antisymmetric states.

For electrons, the wave interpretation of the Pauli principle shows that only antisymmetric eigenfunctions are possible in nature; this corresponds to the validity of the Fermi statistics for electrons. The possible states of particles obeying the Bose-Einstein statistics can be described only by symmetric eigenfunctions.

For a system of two electrons with a negligible spin-orbit interaction, we may disregard the spin, as a first approximation, and deal only with the ordinary position coordinates of the electrons. The over-all eigenfunction is then the product of a factor depending on the position coordinates alone and a factor depending on the spin coordinates alone. Schematically, we can write

$$\Psi = \Phi(x)u(\sigma), \tag{38}$$

where Φ and u are the two factors and x and σ represent the position and spin coordinates.

According to the Pauli principle the eigenfunction Ψ must be antisymmetric with respect to the interchange of the two electrons. This means that Φ may be symmetric or antisymmetric as long as the other factor is antisymmetric or symmetric, respectively. We may say that, neglecting the spin for two electrons, the eigenfunction $\Phi(x)$ may equally well be symmetric or antisymmetric. In the first case we must have an antisymmetric $u(\sigma)$, which means, as we know, antiparallel spins for the two electrons and therefore a total spin $S = 0$. If, instead, $\Phi(x)$ is antisymmetric, $u(\sigma)$ must be symmetric, and this requires parallel spins, that is, a total spin $S = 1$. We may thus talk about symmetric or antisymmetric states of the two electrons, as long as we mean symmetry or antisymmetry with respect to the interchange of the position coordinates alone, not of the spin coordinates. The symmetric levels $S = 0$ have weight 1, because S does not have different possible orientations. The antisymmetric ones, $S = 1$, have weight 3, because of the three possible orientations of the total spin S. The contrary would be true if the Bose-Einstein statistics were valid for the electrons instead of the Fermi statistics: $S = 1$ would then correspond to symmetric eigenfunctions, and therefore their weight would be 3; antisymmetric eigenfunctions would have $S = 0$, weight 1.

2-17 NUCLEAR SPIN

What has been said about the two electrons applies also to two identical nuclei. Nuclei, like electrons, have or may have an intrinsic angular momentum—a spin; it must equal some integer multiple of $\hbar/2$ (in particular, zero). Examples of nuclei with zero spin are He and O; H has spin equal to $\hbar/2$; N has spin $\hbar$; Bi has $\frac{1}{2}\hbar$; and so on. In terms of the usual unit, $\hbar$, the nuclear spin I can assume the values $0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$. We shall discuss in a moment how one can measure the nuclear spin; various methods exist, based on the study of the hyperfine structure of the atomic spectra. A magnetic moment is also associated with the nuclear spin; its magnitude, however, is much smaller than that of the intrinsic magnetic moment of the electron. The order of magnitude of the nuclear magnetic moment, as calculated from the hyperfine structures of spectral lines, is one-thousandth of the Bohr magneton.

The existence of an intrinsic mechanical and magnetic moment of the nucleus is not surprising, if one believes that the nucleus is a more or less complicated system of neutrons and protons, that is, of particles having intrinsic moments. However, we must keep in mind that the interpretation of the nuclear moment as a sum of the intrinsic and orbital moments of the constituent particles is perhaps too simple.

A natural interpretation for the phenomena observed in the spectra of the homonuclear molecules can be found by dividing the nuclei into two categories: the nuclei that obey the Bose-Einstein statistics and those that obey the Pauli principle (those subject to Fermi statistics). The eigenfunctions are then symmetric or antisymmetric with respect to the exchange of coordinates, depending on the category to which the nuclei belong.

Of course, for nuclei also we can neglect the effect of the nuclear spin to a first approximation. Indeed, it is much easier to do this with nuclei, whose magnetic moments associated with the nuclear spin are very small, than with electrons. With this approximation, the eigenfunction depends only on the position coordinates of the nuclei. The over-all eigenfunction is then the product, analogous to (38), of a function Φ which depends on the position coordinates alone, and a function u in which only nuclear spin coordinates appear.

If the Bose-Einstein statistics is valid for the two nuclei, then Φ and u must both be either symmetric or antisymmetric; their product (the over-all eigenfunction) is then symmetric with respect to the interchange of the two nuclei. If, instead, the two nuclei obey the Pauli principle, then to a symmetric Φ there must correspond an antisymmetric u and vice versa, if the over-all eigenfunction is to be antisymmetric.

In general, when one discusses symmetry or antisymmetry of a molecular term, one has in mind the position coordinates alone (and not the spin coordinates); we shall also follow this convention. In other words, the symmetry properties refer to the factor Φ alone, and not to the factor u, which depends on the spin coordinates.

What we said at the beginning of Section 2-16 regarding the nonmixing of terms with different symmetries can be repeated here, the symmetries being defined with respect to the interchange of position coordinates alone (not the spin coordinates). The statement is not exactly valid, but its degree of approximation is very high. Indeed, because of the smallness of the magnetic moment associated with the nuclear spin, the effect of any perturbation is always extremely small. In other words, the operator P introduced in the previous section affects only by a negligible amount the portion of the eigenfunction that depends on the spin coordinates.

As for the factor u of the eigenfunction, which depends only on the spin coordinates, one can easily demonstrate the following properties: Let I be the spin of each nucleus (in units of $\hbar$). There are then $(2I+1)^2$ linearly independent functions of the spin coordinates of the two nuclei. Of these, $I(2I+1)$ are antisymmetric and $(I+1)(2I+1)$ are symmetric with respect to the interchange of the nuclei. We are interested specifically in the ratio of the number of symmetric to the number of antisymmetric functions, which is

$$\rho = \frac{(I+1)}{I}. \tag{39}$$

We now assume that our nuclei obey Bose-Einstein statistics. In this case a symmetric eigenfunction of the position coordinates is associated with a symmetric spin function; this occurs in $(I+1)(2I+1)$ ways. If the function of the position coordinates is antisymmetric instead, the spin function is also antisymmetric; this can be arranged in $I(2I+1)$ ways. We see that the weight of a symmetric state (we still refer to symmetry with respect to the position coordinates) is equal to $(I+1)(2I+1)$; the weight of an antisymmetric state is equal to $I(2I+1)$.

The opposite is true if the nuclei under discussion obey the Pauli principle. The weight of the antisymmetric states is then $(I+1)(2I+1)$, and the weight of the symmetric ones is $I(2I+1)$.

The ratio ρ of the weights of the symmetric to antisymmetric states in the case of Bose-Einstein statistics, or the weights of the antisymmetric to symmetric states in the case of the Pauli principle, is given by (39).

In particular, if $I = 0$, that is, if the nuclei have no intrinsic angular momentum, the weights of the symmetric and antisymmetric states are 1 and 0, respectively, in the case of Bose-Einstein statistics and 0 and 1 in the Pauli case. Thus, when $I = 0$, all antisymmetric (symmetric) levels are absent in the case of the Bose-Einstein (Fermi) statistics. So, for example, one finds only symmetric states in O_2 and He_2 molecules, whose nuclei have $I = 0$ and obey Bose-Einstein statistics.

In the case of $I = \frac{1}{2}$ nuclei, the weights of the symmetric and antisymmetric states are 3 and 1, or 1 and 3, depending on the statistics. The ratio ρ is equal to 3. Thus, for example, the antisymmetric states of the H_2 molecule (whose nuclei obey the Pauli principle) have three times the weight of the symmetric ones.

In the case of nuclei with $I = 1$, the weights of the symmetric and antisymmetric states are, respectively, 6 and 3 or 3 and 6. The ratio ρ is equal to 2.

2-18 ALTERNATE INTENSITIES

The theories just mentioned are confirmed by interesting experimental results. The bands of several homonuclear molecules (e.g., H_2, N_2, Li_2) show an intensity variation from one line to the next which, instead of being continuous, exhibits a characteristic alternation of intense and weak lines. This phenomenon is clearly visible in one of the bands of N_2, shown in Fig. 19. This important phenomenon has been explained by Heisenberg in the following way: According to what we said, only transitions between states with the same symmetry (with respect to position coordinates) are allowed for a homonuclear

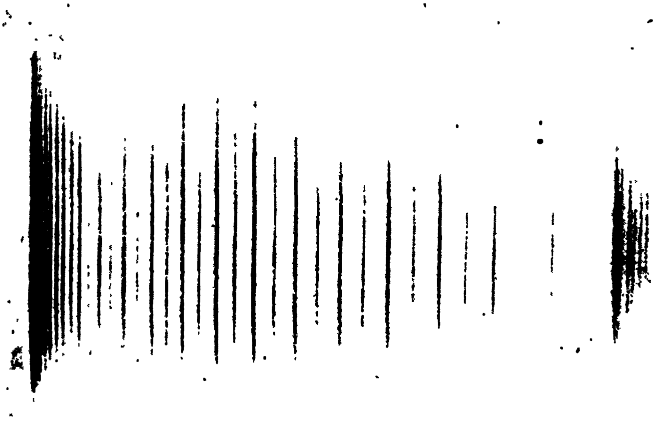


Figure 19

molecule. We must distinguish two cases, depending on whether the nuclear spin is zero or nonzero.

If $I = 0$, only symmetric or only antisymmetric terms are present in the molecule, depending on the type of statistics that govern the nuclei. Therefore, all the lines of the molecular spectrum arise from transitions between symmetric states, if Bose-Einstein statistics is valid and between antisymmetric states if the Pauli principle is valid. In this case (that is, for zero nuclear spin), there are no alternating intensities.

If, on the other hand, the nuclear spin differs from zero, the molecule has symmetric and antisymmetric states. Consequently, the lines of the spectrum can be divided into those arising from transitions between symmetric states (which we shall call *symmetric lines*) and those arising from transitions between antisymmetric states (*antisymmetric lines*).

According to the type of statistics valid for the two nuclei, the symmetric states have a greater or smaller weight than the antisymmetric states. Therefore, the symmetric lines in the Bose-Einstein case, all other conditions being the same, are more intense than the antisymmetric lines, and vice versa for the Pauli case. Since the symmetric and antisymmetric lines are in alternate positions, the line intensity alternates from one line to the next.

To discuss this in more detail, we first assume that the effect of the electrons is negligible; we picture the molecule as consisting of the nuclei alone, separated by a fixed distance. In this case, without taking into account the nuclear spin, the position of the molecule (that is, its center of mass) can be characterized by the direction of the line which joins the two nuclei; for instance, one can use the two angles θ and φ (colatitude and longitude). The eigenfunctions, as is known, are simply the spherical harmonics $P_J^m(\theta,\varphi)$. Interchanging the two nuclei corresponds to the inversion of the line joining them (i.e., the change of θ to $\pi - \theta$ and φ to $\varphi + \pi$). We easily see from the properties of spherical harmonics that this operation leaves unaltered the even spherical harmonics, and changes the sign of the odd ones.

In this simple case we see that the symmetric states are those with J even and the antisymmetric ones are those with J odd.

Even if the contribution of the electrons to the molecule is taken into account, the result is not very different. One can demonstrate, for a given electronic level, that either the states with J even are symmetric, and those with J odd are antisymmetric (in this case the electronic level is referred to as electronically symmetric), or the states with J even are antisymmetric and those with J odd are symmetric. If we consider multiple or degenerate electronic states, the symmetric and antisymmetric states are generally intermixed in a manner analogous to that of the even and odd states (cf. Figs. 17 and 18).

From the measurement of the intensity ratio of successive lines of an alternating intensity band, we can obtain the nuclear moment I. The intensity ratio is, indeed, equal to the ratio between the weights of the symmetric and the antisymmetric states, or vice versa, and is given by (39). Thus, a measurement ratio 3 means that $I = \frac{1}{2}$ (e.g., hydrogen); if the ratio is 2, then $I = 1$; etc.

If we can analyze the electronic terms in a band spectrum and observe the alternate intensities, we can then determine which of the two statistics the nuclei of the molecule obey. If, for example, we find that an electronically symmetric term has intense lines with J even, we conclude that the nuclei obey Bose-Einstein statistics, and if the lines with J even are the weaker lines, the nuclei obey the Fermi statistics.

Thus, from the intensity of the H_2 lines, we have found that the protons, like the electrons, obey the Pauli principle. The nitrogen nuclei, on the other hand, obey Bose-Einstein statistics. This fact, discovered from the measurements made by Rasetti [125, 126] on the Raman effect in nitrogen, which we shall discuss later, has considerable importance in the study of nuclear structure.

Alternate intensities are not present in the spectra of homonuclear molecules with zero spin, like O_2 and He_2, because these molecules have either exclusively symmetric or exclusively antisymmetric lines. Since O_2 and He_2 possess only symmetric lines, we deduce that both oxygen and helium nuclei obey Bose-Einstein statistics.

2-19 PARA- AND ORTHOHYDROGEN

A very interesting confirmation of the above interpretation of the alternate intensities is found in the following experiment. The electronic ground term H_2 is a $^1\Sigma$ electronically symmetric term. Hence, its symmetric rotational levels are those with J even, and the antisymmetric ones are those with J odd (cf. Fig. 20).

In the hydrogen molecule the rotational levels are quite far apart

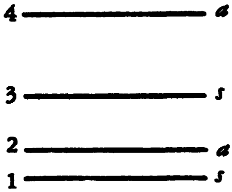


Figure 20

because of the small moment of inertia of the molecule. Consequently, at liquid hydrogen temperatures, the thermal equilibrium between the different rotational states is such that almost all the molecules are in the lowest rotational level (with $J = 0$). However, we should not assume that thermal equilibrium can be reached at once. Indeed, we have seen that transitions between symmetric and antisymmetric states are extremely unlikely, and this is true not only for spontaneous radiation but also for transitions induced by any kind of perturbation. Consequently, when the hydrogen is cooled, the molecules that were in symmetric states concentrate into the rotational level with $J = 0$ (the lowest symmetric level); the molecules that, before the cooling, were in antisymmetric states are quickly brought into the lowest antisymmetric state (the rotational level with $J = 1$). However, the transition probability between symmetric and antisymmetric states, even if extremely small, is not exactly zero. Therefore, if the hydrogen is kept at a very low temperature for a long time, there is a slow migration, lasting for a few days, from the antisymmetric state with $J = 1$ to the symmetric state with $J = 0$ until thermal equilibrium is reached.

Therefore, if we liquefy some hydrogen and keep it at a very low temperature for about a week, all its molecules end up in the symmetric state with $J = 0$. If we then heat the hydrogen again, its molecules, although going to higher states, still remain in symmetric states for a certain time because of the extreme slowness of the transitions between states of different symmetry. If we then introduce the hydrogen treated in this way into a Plücker tube, we observe that its spectrum contains only half the lines that appear in the normal hydrogen spectrum. Only the symmetric lines are present, which in the normal hydrogen spectrum are weaker than the antisymmetric ones (because the Pauli principle is valid for the hydrogen nucleus). Only after some time do a few molecules begin to appear in the antisymmetric states to produce the antisymmetric lines missing initially.

The symmetric levels of the H_2 molecule are usually called the parahydrogen levels; the antisymmetric ones the orthohydrogen levels. This designation is analogous to the para- and orthohelium designation of the singlet and triplet lines in the spectrum of the helium atom. Note, however, that whereas the distinction between para- and orthohelium depends on the symmetry or antisymmetry with respect to the interchange of the position coordinates of the two electrons, in the case of H_2 this distinction depends on the symmetry of the eigenfunction with respect to the interchange of the position coordinates of the two nuclei.

Consequently, transitions from para to ortho terms or from ortho to para for H_2 are much less probable than they are for He. One can also group the terms of H_2 in a manner analogous to that used for He; besides grouping the terms according to symmetry with respect to the position interchange of the nuclei, one can use the symmetry with respect to the position interchange of the electrons (see Section 1-3 for a particular case). Thus the electronic terms of hydrogen separate into singlets and triplets, and transitions between these two categories occur only very infrequently. The probability for such transition, however, is not so low as for the transitions from the para- to the orthohydrogen levels.

Finally, it is interesting to note that the parahydrogen, prepared, as we described, by means of long cooling, differs from normal hydrogen not only in its spectrum (where only half the lines appear) but also in its other properties (for example, specific heat). We shall return to this point later.

2-20 ISOTOPIC EFFECTS IN THE BANDS

For atoms, the difference between the spectra of two isotopes is always very small and difficult to observe. On the contrary, the spectrum of a molecule in which one of the two nuclei is the isotopic nucleus is remarkably different from the spectrum of the normal molecule (both nuclei identical). The reason for this difference is that the nucleus in an atom remains practically at rest, so that a change in its mass has a negligible effect. In a molecule, however, the nuclei both vibrate and rotate, so that the frequencies of these motions are altered if their masses change.

We consider two molecules AB and AB′, which differ only in that B and B′ are different isotopes of the same nucleus. To fix our ideas, we take B′ heavier than B. First, it is easy to see that the electronic terms of the two molecules are practically identical; these terms, indeed, are calculated assuming that the nuclei are fixed; they are therefore independent of any difference in the nuclear masses. For the same reasons the equilibrium distance between the two nuclei for a given electronic term remains practically identical for the two molecules. The quasi-elastic force that restores the two nuclei to the equilibrium distance after they have been separated also remains the same for the two cases.

The vibrational frequency of the molecule will, on the other hand, be considerably altered; indeed, elementary considerations show that this frequency is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K(M_A + M_B)}{M_A M_B}},$$

where K is the coefficient of the elastic force which, as we said, is the same for both molecules, and M_A, M_B are the masses of the two constituents. If we replace B by B′, the frequency is obviously different; in particular, the ratio between the two frequencies is given by

$$\frac{\nu}{\nu'} = \left(\frac{M_{B'}}{M_B}\,\frac{M_A + M_B}{M_A + M_{B'}}\right)^{1/2}.$$

As an example, we take two isotopes of Li with atomic weights 6 and 7. Three types of molecules can be made with them: Li^6Li^6, Li^6Li^7, Li^7Li^7. The vibrational frequencies of these three molecules are in the ratios 1:0.96:0.93. The differences in this case are as high as 7 per cent. For molecules with heavier constituents, the relative differences in the masses of the different isotopes are smaller, and therefore the relative differences in the vibrational frequency are also smaller. This variation in the vibrational frequency displaces the bands; in particular, for bands that correspond to a large variation of the vibrational quantum number, the displacement can be as large as a few hundred wave numbers. An effect of the same kind, although quantitatively much smaller, is also present in the rotation of the molecules. We said before that the equilibrium distance for the two molecules AB and AB′ is the same. If B′ has a larger mass than B, the moment of inertia of AB′ is larger than that of AB; consequently, the rotational levels of AB′ are denser than those belonging to AB.

That the bands of molecules consisting of different isotopes of the same element have different positions has been applied to the discovery of isotopes that are extremely rare in nature. Thus, for example, two different oxygen isotopes with weights of 17 and 18 were revealed by the presence of very faint bands in the spectra of the molecules $O^{16}O^{17}$ and $O^{16}O^{18}$.

Finally, we note another characteristic associated with the presence of different isotopes in homonuclear molecules. We consider an element A and its isotope A′. Three types of molecules can be formed with these: AA, AA′, A′A′. The first and last are homonuclear and therefore either exhibit alternate line intensities (if the nuclei have a spin) or contain only half the lines (if the nuclear spin is zero). The molecule AA′ on the other hand, does not have identical nuclei and therefore contains all the lines and does not show alternate intensities. Thus, for example, the spectrum of the oxygen molecule $O^{16}O^{16}$, which is by far the most common, has only the symmetric lines, because the O^{16} nucleus has no spin and obeys Bose-Einstein statistics. But the spectra of the molecules $O^{16}O^{17}$ and $O^{16}O^{18}$ also contain the antisymmetric lines with equal intensity; thus the bands of these molecules have twice as many lines as the corresponding bands of the $O^{16}O^{16}$ molecule.

2-21 THE ZEEMAN AND STARK EFFECTS

The spectra of molecules, like those of atoms, are influenced by the electric or magnetic field in which the radiating molecules are placed. We first treat the electric effect. As is well known, in the case of atoms, the terms are altered by an amount which, for hydrogen, to a first approximation, depends linearly on the electric field only (*linear Stark effect*); for all the other atoms the effect is quadratic. This is because hydrogen has quantum states with an average electric moment $\mathfrak{M}$ different from zero (according to a semiclassical model, the states with eccentric elliptical orbits have an average electric moment along the major axis), whereas the average electric moment of the other atoms is always zero. As a result, when we place a hydrogen atom in an electric field E, the electrostatic energy $-\mathfrak{M}E$, averaged over the unperturbed orbit, has a value different from zero and therefore produces a perturbation of the first order, proportional to E. In the other atoms the first-order perturbation vanishes, since the average value of the electric moment $\mathfrak{M}$ is zero, and only a second-order effect, proportional to E^2, remains.

The situation in molecules is rather similar to the above description. Here, too, the condition for a linear Stark effect is that there be an average electric moment different from zero. If the two nuclei are fixed, it is obvious from symmetry considerations that the direction of the average electric moment can only be parallel to the axis. Furthermore, for a homonuclear molecule it is zero. We thus conclude that the linear Stark effect is present only in heteronuclear molecules.

Limiting our discussion to the latter case, we let $\overline{\mathfrak{M}}$ be the average value of the electric moment parallel to the axis. We first assume that the coupling is of type *a*; the following semiclassical argument illustrates the situation. When the molecule rotates, its axis (see Fig. 3) precesses around the fixed direction J of the total angular momentum, at an angle whose cosine equals Ω/J. The moment $\mathfrak{M}$, of course, also participates in this precession; its average (vector) value is therefore given by its projection along the fixed direction J:

$$\overline{\mathfrak{M}} = \mathfrak{M}\frac{\Omega}{J}.$$

If we now place the molecule in an electric field E, the orientation of J is such that its projection M along the field direction has integer or half-integer values according to whether J is integer or half-integer. The cosine of the angle between J and E therefore equals M/J; thus the average electric moment along the field direction becomes

$$\overline{\mathfrak{M}}_E = \overline{\mathfrak{M}}\frac{M}{J} = \mathfrak{M}\frac{\Omega M}{J^2}.$$

The average electrostatic energy then equals

$$-\overline{\mathfrak{M}}_E E = -E\mathfrak{M}\frac{\Omega M}{J^2}.$$

This formula can also be confirmed by quantum-mechanical arguments, except that in this case J^2 must be replaced, as usual, by $J(J+1)$. We finally obtain the electric perturbation of the energy levels

$$\Delta W = -E\mathfrak{M}\frac{\Omega M}{J(J+1)}. \tag{40}$$

Coupling of type *b* can be treated in a similar manner. Here the spin S is not coupled to the molecule and, moreover, no electric moment is connected with it. We can thus neglect it altogether and again apply (40), if we substitute K for J, M_K for M, and Λ for Ω. We thus find

$$\Delta W = -E\mathfrak{M}\frac{\Lambda M_K}{K(K+1)}. \tag{41}$$

Notice, in particular, that the linear effect for the Σ terms must always be zero; for these terms, $\Lambda = 0$, and since they are always present in *b*-type coupling, the formula to apply is (41).

Experimentally very little is known about the Stark effect in band spectra.

The theory of the Zeeman effect in molecules is quite analogous to the theory of the Stark effect. For type-*a* coupling, the magnetic moment along the molecular axis is $(\Lambda + 2\Sigma)$ Bohr magnetons, where Σ is the projection of the total spin S along the axis of the molecule. (The factor 2 occurs because each electron with angular momentum $\frac{1}{2}\hbar$ has a magnetic moment of 1 Bohr magneton.) Using (40), we can easily compute the perturbation of the levels in a magnetic field H; one has only to replace E by H, and M by $(\Lambda + 2\Sigma)(e\hbar/2mc)$. The result is

$$\Delta W = -\frac{e\hbar H}{2mc}(\Lambda + 2\Sigma)\frac{\Omega M}{J(J+1)}. \tag{42}$$

For type-*b* coupling, there is a magnetic moment equal to Λ Bohr magnetons along the molecular axis, and a magnetic moment equal to $2S$ Bohr magnetons associated with the total spin S; the latter, in type-*b* coupling, is not coupled to the molecular axis. The contribution of the Λ magnetons along the axis can be computed by a formula obtained from (41) after substituting H for E and $\Lambda(e\hbar/2mc)$ for $\mathfrak{M}$. The contribution of the $2S$ magnetons associated with the spin can be computed by noting that, since the spin S is not coupled to the molecule, it orients itself independently along the external field H in such a way that the values of its possible projections M_S along the field differ by integers and lie between $+S$ and $-S$ inclusive. The magnitude of the component of the magnetic moment along H is therefore $2M_S$ Bohr magnetons and the energy is $-2M_S(e\hbar/2mc)H$. Finally, the magnetic perturbation of the energy levels is

$$\Delta W = -H\frac{e\hbar}{2mc}\left[\frac{\Lambda^2 M_K}{K(K+1)} + 2M_S\right]. \tag{43}$$

It must be understood that these formulas are valid for the extreme coupling cases. Furthermore, in case *a*, the electric or magnetic separation must be small with respect to the separation of the rotational levels. In case *b*, instead, the separation must be small with respect to the separation of the rotational levels and large with respect to the spin-molecule coupling energy; the spin can then truly be considered not coupled to the molecule. If these conditions are not satisfied, more complicated phenomena arise in analogy to the transition states between the normal Zeeman effect and the Paschen-Back effect, which can be observed in atoms.

The theory of the Zeeman effect has been verified for the bands $^1\Sigma \longrightarrow {}^1\Pi$ of CO; the experimental results are in good agreement with predictions.

2-22 FLUORESCENCE OF DIATOMIC MOLECULES

The spectra of molecules are usually excited by passing an electric current through a discharge tube. However, just like atomic spectra, they can also be excited by fluorescence. When the molecule is illuminated by light with a frequency equal to that of an absorption line, the molecule jumps to a higher energy level from which it then returns in one or more quantum steps until all the absorbed radiation is eventually re-emitted.

The fluorescence of diatomic molecules, which, in particular, has been carefully studied in iodine vapor, exhibits some feature worth noticing. The difference between excitation by fluorescence and normal excitation, like that produced, for example, in a discharge tube, is that in the latter the various molecules of the gas are excited to all their energy levels; when returning to the ground state they emit, with different intensities, all the spectral lines of the molecule. In fluorescence excitation, on the other hand, the molecules absorb photons of one definite frequency and therefore are brought to a definite energy level from which they can re-emit only those lines that start from that level. Consequently, in the fluorescence of molecules one does not usually observe complete bands, but only a few lines of each band. Let us assume, for instance, that the molecule absorbs light of such a frequency that it is excited to the second rotational level of the β state (Fig. 21). From here it can fall to the α state; but since the quantum number J can vary only by $+1$, 0, -1, the complete band $\beta \rightarrow \alpha$ will not be emitted. Only three lines will be emitted, corresponding to the transitions $J = 2 \rightarrow 3$, $2 \rightarrow 2$, $2 \rightarrow 1$. In many cases the transition $J \rightarrow J$ is also forbidden, so that one often sees only two lines per band instead of three. Accordingly, the typical fluorescence spectrum consists of a series of small groups each with two or three lines. Each group corresponds to a different transition of the vibrational quantum state or of the electronic state.

The typical appearance of the fluorescence spectrum as described

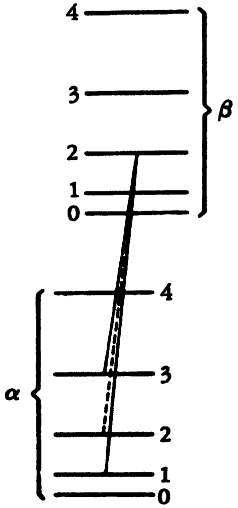


Figure 21

above is somewhat altered when the fluorescence is observed in a gas at high pressure, particularly when other extraneous gases are added to the fluorescent gas. In this case the absorption of the primary radiation excites the molecule to some rotational level of a higher electronic state. However, before the excited molecule has time to re-emit the radiation, it undergoes a certain number of collisions, so that its rotational energy is altered in one direction or another. Hence, the fluorescence spectrum at high pressure exhibits more rotational lines than at a lower pressure.

2-23 RAMAN EFFECT IN DIATOMIC MOLECULES

The Raman effect in diatomic molecules is important because it reveals the molecular ground state, the structure of which is not easily analyzed in other ways.

To understand the structure of the Raman spectrum of a diatomic molecule, one should keep in mind the following fundamental selection rule: The frequency (or energy) difference between two terms in any system appears in the Raman effect only if a third term exists which combines with both. We consider, for example, the rotational terms of the electronic ground state of a molecule. We want to know which differences between these rotational levels can appear in the Raman effect. For this we must examine the rotational levels of a higher electronic state of the molecule (Fig. 22). For the two rotational levels of the electronic ground state with rotational quantum numbers J and J' to combine in the Raman effect, it is necessary that both should be able to combine with a rotational level of this higher electronic state. One can immediately see, recalling the selection rule for $J(\Delta J = \pm 1, 0)$ that it is necessary for this that J and J' (note that J and J' refer to the rotational levels in the electronic ground state) differ by not more than 2. In the particular case where the transitions $J \rightarrow J$ are forbidden, the Raman effect will involve only those energy differences of the rotational levels in the ground state for which J differs as follows:

$$\begin{tikzcd} & J+2, \\ J \arrow[ur] \arrow[r] \arrow[dr] & J, \\ & J-2. \end{tikzcd} \qquad (44)$$

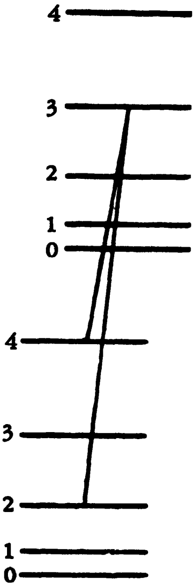


Figure 22

In the first case a transition occurs from the electronic ground state with the given J to the higher electronic state with $J \rightarrow J+1$. Then there is a transition back to the electronic ground state with $J+1 \rightarrow J+2$. Since in the transition back to the ground state we can also have $J+1 \rightarrow J$ again, we have the second case. In the third case the transition from the ground state to the higher state occurs with $J \rightarrow J-1$. The transition back to the ground state now occurs with $J-1 \rightarrow J-2$. If a transition from the ground state to the higher state with $J \rightarrow J$ were allowed, additional Raman differences such as $J' = J+1$ would appear. Assume that for the ground state $\Omega = 0$, the energy of a rotational level is then given by $chBJ(J+1)$.

The following frequencies then appear in the Raman effect:

$$\begin{aligned} B[J(J+1)-(J+2)(J+3)] &= -B(4J+6), \\ B[J(J+1)-(J-2)(J-1)] &= B(4J-2), \qquad (45) \\ B[J(J+1)-J(J+1)] &= 0. \end{aligned}$$

The last expression gives, of course, zero change in the frequency, corresponding to the normal diffused light with unmodified frequency. The other two expressions give, respectively, the anti-Stokes and Stokes branch of the Raman effect. The first expression can be taken with $J = 0, 1, 2, \ldots$; the second with $J = 2, 3, 4, \ldots$ (because $J' = J - 2$ is negative when $J = 0, 1$).

The Raman lines we have considered have the same order as the lines of a rotational band. The only difference is that the frequencies of any two neighboring lines differ by $4B$ instead of $2B$, as in the case of the rotational bands; this is because J changes by ±2 in the Raman effect instead of by ±1 as in ordinary emission or absorption. Figure 23 shows the rotational Raman effect of nitrogen as obtained for the first time by Rasetti.[124–126]

One can see in the figure the characteristic alternate intensities that arise because N_2 is a homonuclear molecule. From the arrangement of the weak and strong lines observed in this Raman spectrum, we deduce that the nitrogen nucleus obeys Bose-Einstein statistics; this, as we shall discuss later, is of considerable interest in problems of nuclear structure.

Besides the rotational Raman spectra, which we have just discussed, there are also lines in the Raman spectrum of diatomic molecules with the vibrational frequencies of the molecule. For reasons we shall discuss in connection with polyatomic molecules, one can usually observe only the ground frequency in the Raman effect corresponding to the transition from the ground level to the first excited vibrational level; transitions for which the vibrational quantum number changes by more than 1 are very weak and have never been observed in diatomic molecules. The diatomic molecules usually show only a single Raman

Figure 23

frequency corresponding to a change of the vibrational state. Only in H_2 has Rasetti observed several lines of a Raman band which correspond to a change in both the rotational and vibrational states. These lines reproduce, with a much lower intensity, the rotational Raman spectrum described above and observed around the exciting or primary line. In the other molecules the rotation-vibration Raman effect has a very low intensity, and such lines have never been observed.

Finally, we note that only in one case did Rasetti find a line in the Raman effect corresponding to a change in the electronic state, because the frequency differences between the ground term and the other electronic terms are usually so large that they fall outside the range that is easily observable in the Raman effect. Only for NO, whose electronic ground term is double ($^2\Pi_{1/2}$, $^2\Pi_{3/2}$) can one observe the frequency in the Raman effect corresponding to the transition between these two electronic terms.

3

Thermal Properties of Diatomic Molecules*

3-1 SPECIFIC HEAT

Thermal equilibrium can always be reached, at any given temperature, by a gas of diatomic molecules. This equilibrium determines the percentage of molecules in each energy level. Besides the distribution of the molecules among the various energy levels, there is also, of course, a distribution of their translation velocities which, we may assume, is always determined by the Maxwell law. The deviations from this law arising from Bose-Einstein or the Fermi statistics are extremely small for ordinary gases, and particularly small for the polyatomic ones.

To calculate the thermal energy of the molecules, we must take into account, therefore, the energy of the translational motion and the internal energy of the molecules. The energy of the translational motion can be immediately calculated because, as we said, the Maxwell law may be assumed to be valid for this motion. The average kinetic

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* In this chapter we use concepts and results that will be established in Part III of this book.

energy is then equal to $kT/2$ for each degree of freedom, for each molecule, where k is the Boltzmann constant and T the absolute temperature. For the three degrees of freedom of translation, the average kinetic energy is then $\frac{3}{2}kT$. When we have N molecules, the total kinetic energy of their translational motion is given, as for a monoatomic gas, by

$$W_{\text{trans}} = \tfrac{3}{2}NkT. \tag{1}$$

We now compute the average internal energy of the molecule. The distribution of the molecules among the various energy levels (rotational, vibrational, and electronic) is governed by the Boltzmann law (cf. Part III). In thermal equilibrium, the probability that a molecule is in a quantum state with energy w_i is proportional to

$$e^{-w_i/kt}. \tag{2}$$

This is true, of course, for each single state. If the multiplicity of the state is p_i, the preceding probability has to be multiplied by p_i. In particular, (2) shows that the probability for excited states with energies much larger than that of the ground state to be in thermal equilibrium is very small; in practice, the molecules are in states with energies, measured from the lowest level, not much larger than kT. Now, in a large number of cases, at least for temperatures which are not too high, all the electronic levels with the exception of the ground level are too high to be thermally excited. In addition, for many molecules, and especially for those that are not very heavy, the vibrational quantum energy levels are also too high to be excited thermally; almost all the molecules at ordinary temperatures are then in the electronic ground state with the vibrational quantum number equal to zero. If these conditions prevail, the molecule may be considered, with respect to thermal behavior, to have only those degrees of freedom that are available to a system of two points connected by a rigid rod; all other degrees of freedom are frozen.

If we neglect for the moment the structure of the rotational levels and apply classical statistics to this rudimentary model of the molecule, we may consider the molecule to have two rotational degrees of freedom around its center of mass. To each of these we can assign an average kinetic energy $kT/2$, so that the average rotational kinetic energy is equal to kT; when we add to this the average energy of the translational motion, $3kT/2$, we obtain $5kT/2$ for the total thermal energy of the molecule. For N molecules, the thermal energy is then $\frac{5}{2}NkT$. The thermal capacity of the N molecules (at constant volume) is then equal to

$$C_v = \frac{d}{dT}(\tfrac{5}{2}NkT) = \tfrac{5}{2}Nk.$$

If we refer to one gram molecular weight (one mole), N is Avogadro's number and $Nk = R$ is the gas constant. The specific heat at constant volume (referred to a gram molecular weight) is equal to

$$C_v = \tfrac{5}{2}R. \tag{3}$$

This expression for the specific heat is actually valid for many molecules only when the temperature is in an intermediate range: not high enough to excite the higher electronic and vibrational levels, and yet high enough that kT is large compared to the energy differences between successive rotational levels, so that we may neglect the quantization of the rotational motion.

At low temperatures the specific heat drops below the value given by (3); the portion due to the rotation goes to zero when kT becomes small relative to the energy difference between the two lowest rotational terms. This behavior is particularly noticeable in H_2, because the rotational levels of this molecule are quite far apart, owing to its small moment of inertia.

At high temperatures, on the other hand, the specific heat rises above the value (3). Here the vibrational levels and possibly also some of the electronic levels are excited.

To discuss low-temperature phenomena in more detail, we assume that the lowest electronic term of our molecule is a $^1\Sigma$ term; its rotational energy is then given by

$$w_J = c\hbar BJ(J+1).$$

We first neglect the nuclear spin which, as we shall see in a moment, has considerable importance, at least for homonuclear molecules. Then the weight of the state J is $2J+1$, corresponding to the $2J+1$ possible orientations of the molecule. The probability of the state J is then given by

$$(2J+1)\exp\left[-\frac{c\hbar B}{kT}J(J+1)\right]. \tag{4}$$

Thus the average value of the rotational energy is equal to

$$\overline{W}_{\text{rot}} = \frac{\sum\limits_{0}^{\infty} c\hbar BJ(J+1)(2J+1)\exp\left[-(c\hbar B/kT)J(J+1)\right]}{\sum\limits_{0}^{\infty}(2J+1)\exp\left[-(c\hbar B/kT)J(J+1)\right]}$$

$$= -\frac{\partial}{\partial(1/kT)}\log\sum_{0}^{\infty}(2J+1)\exp\left[-\frac{c\hbar B}{kT}J(J+1)\right]. \quad (5)$$

One easily sees that in the limit of high temperatures (one replaces the sums by integrals) this formula becomes $W_{\text{rot}} = kT$; at low temperatures, however, one finds that not only W_{rot}, but also its derivative with respect to T, is zero, so that the rotation does not contribute to the specific heat. By evaluating Eq. (5) numerically at intermediate temperatures, we can find the decrease of the specific heat with temperature. However, if we compare these calculated values with the measurements, we find that there are considerable differences for the hydrogen molecule. Equation (5) gives the qualitative behavior of the H_2 specific heat, but it is quite unsatisfactory from a quantitative point of view.

As a possible explanation of the differences, we may invoke the following analysis: The electronic ground term of hydrogen is, as we have already said, a $^1\Sigma$ term with even electronic symmetry; as a consequence, the even J levels are symmetric and those with odd J are antisymmetric. Further, the hydrogen nuclei have spin $\frac{1}{2}$ and obey the Pauli principle; so the symmetric levels (parahydrogen levels) have a total nuclear spin zero and therefore a statistical weight $2J+1$. The odd J levels, instead, are antisymmetric (orthohydrogen levels), and therefore have a total nuclear spin one, with three possible orientations. Hence, the weight of the states with odd J is equal to $3(2J+1)$. Consequently, the probability of the state J is

$$(2J+1)\exp\left[-\frac{c\hbar B}{kT}J(J+1)\right]$$

or

$$3(2J+1)\exp\left[-\frac{c\hbar B}{kT}J(J+1)\right]$$

for J even or odd, respectively. Corresponding to these different statistical weights, one must also modify Eq. (5), which gives the average rotational energy.

However, one finds that even this correction is not sufficient to make the experimental and theoretical values of the specific heat of hydrogen agree. The reason for this, which was discovered by Dennison,[11, 80] is the following: When the gas temperature changes, thermal equilibrium of the molecules in their different quantum states does not occur immediately. However, since transitions among the states having the same symmetry are very fast, thermal equilibrium occurs immediately for the molecules in each of the two different states of symmetry. A much longer time, however (of the order of a few days), is necessary for equilibrium between the molecules of para- and those of orthohydrogen (between different symmetry states).

Now, the measurements are usually made so quickly at different temperatures that there is no time for equilibrium to be reached between para- and orthohydrogen. A theoretical model that represents the conditions in hydrogen quite well when its specific heat is being measured can be constructed on the assumption that the para- and orthohydrogen are two different gases mixed in the ratio 1: 3. One can then calculate the specific heat of the parahydrogen by taking into account only the symmetric levels of H_2, and that of the orthohydrogen by taking into account only the antisymmetric ones. In this way perfect agreement is obtained between the calculated and measured values of the specific heat at low temperatures.

3-2 INTENSITY VARIATION IN THE LINES OF A BAND

The statistical distribution of the molecules among the different rotational energy levels when thermal equilibrium is reached is one of the factors that determine the law of variation of the intensity of the different rotational lines of the bands.

First, we note that the distribution law (4) gives the probability that the rotational level J of the electronic and vibrational ground state is occupied. But if the gas is excited, as, for example, in an electric discharge, some of its molecules are brought into higher electronic states; returning to the ground state, after one or more quantum steps, they emit a band spectrum. Under these conditions the distribution of the molecules among the various states is quite different from that predicted by the Boltzmann law.

One finds, however, that the molecules in a certain excited electronic and vibrational state are again distributed among the various rotational levels of that state according to a law approximately the same as (4). The reason for this is that the molecules of a gas subject to an electric discharge are excited by collisions with ions that traverse the gas at high speed because of the electric field. Now, the probability that a collision will change the quantum number by several units is very low. This means that the distribution of the molecules among the different values of J is really not modified very much because of the collisions, even though very high electronic and vibrational levels may be excited by these collisions.

The intensity of a line in a band depends on the product of the number of molecules in the initial quantum state and the transition probability associated with that particular line. If, for simplicity, we limit our considerations to the case of transitions between the two $^1\Sigma$ states and also assume that the transition frequencies are large compared to the frequencies of the rotational terms, we find that the intensity of a line produced in a transition for which the quantum number J changes from J to $J + 1$ (the P branch of the band spectrum) is proportional to

$$(J + 1) \exp\left[-\frac{hcB}{kT} J(J + 1)\right],$$

whereas for a transition $J \rightarrow J - 1$ (the R branch of the band spectrum), it is proportional to

$$J \exp\left[-\frac{hcB}{kT} J(J + 1)\right].$$

Note that the Boltzmann factors in these two expressions arise only from the initial state J, since the probability of a transition depends on the population of the initial state. The weight factor in each case is obtained by averaging the multiplicities of the initial and final states. Thus, for $J \rightarrow J + 1$, we have $\frac{1}{2}[2J + 1 + 2(J + 1) + 1] = 2(J + 1)$, and for $J \rightarrow J - 1$, we have $\frac{1}{2}[2J + 1 + 2(J - 1) + 1] = 2J$.

It appears from these formulas that the intensities of the lines belonging to the different branches (one branch refers to $J \rightarrow J + 1$, the other to $J \rightarrow J-1$) of the band are small in the vicinity of the zero line. (They are very small for the transition to $J \rightarrow J-1$). They then increase up to a maximum beyond which they start decreasing again for larger values of J. One can easily see that the maximum intensity corresponds approximately to

$$J_{\max} = \left(\frac{kT}{2hcB}\right)^{1/2}.$$

Thus, for example, in a vibration and rotation band, where the successive lines of the two branches P and R are separated by B wave numbers, there is an intensity maximum for each of the two branches. The two maxima have an approximately symmetric position around the zero line of the band (cf. Fig. 5), and the separation between them, in wave numbers, is about

$$4BJ_{\max} = \left(\frac{8kTB}{hc}\right)^{1/2}.$$

This relation between the separation of the two intensity maxima and the value of B can be particularly useful in measuring B and therefore the moment of inertia of the molecules, although only approximately. For this we must study the vibration and rotation bands of the molecules, which is possible even in cases where, owing to the large moment of inertia, the individual lines of the band cannot be resolved. In these cases we can still distinguish between the intensity maximum for branch P and for branch R of the band. From their frequency difference for a given temperature, one can calculate B from the preceding formula.

3-3 THE ENTROPY CONSTANT

It is well known that knowledge of the energies of chemical reactions alone is not sufficient to calculate the chemical equilibria between the reacting gases. These energies determine the chemical equilibria only to within certain constants; to obtain these constants thermodynamically, we need the absolute constants of the entropy for the various reacting gases.

In Part III of this book we discuss the problem of the entropy constant for monoatomic gases. This problem is strictly related to the degeneracy responsible for the fact that the specific heat, even of a monoatomic gas, goes to zero at zero absolute temperature. For the entropy of a monoatomic gas whose atoms have a single ground state, we find the following result:

$$S = Nk\left[\tfrac{3}{2}\log T + \log V - \log N + \log\frac{(2\pi mk)^{3/2}e^{5/2}}{h^3}\right] \qquad (6)$$

where N is the number of atoms in the gas, m is their mass, V is the volume of the gas, and e is the base of the natural logarithms.

If, instead of a single gas, we have a mixture of gases, the entropy, as we know from thermodynamics, is simply the sum of the entropies the various constituents would have if each one alone occupied the whole volume of the mixture. This is true only as long as we can consider the gases perfect. Finally, we note that (6) is not valid either at very low temperatures, where degeneracy begins to take place, or at very high temperatures, where the higher energy levels of the atoms can be excited.

We now consider a gas of atoms or molecules having certain energy levels $w_0 = 0$, w_1, w_2, . . . (in the order of increasing values, starting from the ground level $w_0 = 0$ and with each degenerate level counted as many times as its multiplicity, so that the individual w_i's can be treated as simple). If the energy levels are so widely spaced that those higher than the ground level are practically absent in thermal equilibrium, we can still calculate the entropy from Eq. (6). This, of course, happens almost regularly in monoatomic gases, at least when the ground state is not degenerate or multiple. But for molecules, a very low temperature is already sufficient for the thermal excitation of several rotational levels.

If the distribution among the various quantum states of the molecules of our gas, at temperature T, is governed by thermal equilibrium, the number of molecules in the level w_j is given by the Boltzmann law:

$$N_j = N\left[e^{-w_j/kT} \Big/ \sum_i e^{-w_i/kT}\right]. \qquad (7)$$

To compute the entropy constant, we may consider our gas a mixture of several different species of gases, the *i*th component of which consists of the N_i molecules in the state w_i.

It is easy to see that we can calculate the total entropy of the gas by adding the entropies of the individual constituents; these can be calculated by means of Eq. (6), as if each constituent were a simple monoatomic gas. This is because the essential requirement in deriving Eq. (6) is not that the gas be monoatomic, but that all its constituent particles belong to a single quantum state so that the statistical state of each particle is determined completely by specifying its translational motion without specifying its internal state. It is obvious, now, that if we confine our attention to the N_i molecules belonging to the energy level w_i, this condition is certainly satisfied, and therefore we can apply Eq. (6).

The total entropy of our gas is thus

$$S = \sum_{i=0}^{\infty} S_i = \sum_{i=0}^{\infty} kN_i \left[\frac{3}{2} \log T + \log V - \log N_i + \log \frac{(2\pi mk)^{3/2} e^{5/2}}{h^3} \right].$$

Since $\Sigma N_i = N$, we have

$$S = kN \left[\frac{3}{2} \log T + \log V + \log \frac{(2\pi mk)^{3/2} e^{5/2}}{h^3} \right] - k \sum_i N_i \log N_i.$$

From Eq. (7) we also have

$$\begin{aligned} \sum_i N_i \log N_i &= \left(N \Big/ \sum_i e^{-w_i/kT} \right) \sum_i e^{-w_i/kT} \\ &\qquad \left(\log N - \frac{w_i}{kT} - \log \sum_i e^{-w_i/kT} \right) \\ &= N \log N - N \log \sum_i e^{-w_i/kT} \\ &\qquad - \frac{N}{kT} \left(\sum_i w_i e^{-w_i/kT} \Big/ \sum_i e^{-w_i/kT} \right) \\ &= N \log N - N \log \sum_i e^{-w_i/kT} - \frac{N}{kT} \bar{w}, \end{aligned}$$

where $\bar{w}$ is the average energy of the internal states of the molecule.

We finally obtain

$$S = kN\left[\tfrac{3}{2}\log T + \log V - \log N + \log \frac{(2\pi m k)^{3/2} e^{5/2}}{h^3}\right] + kN\left[\frac{\bar{w}}{kT} + \log \sum_i e^{-w_i/kT}\right], \qquad (8)$$

where the last term must be added to the entropy (6) to take into account the thermal equilibrium among the internal states w_i of the molecules.

As an example, we calculate the entropy of a gas of diatomic molecules. To simplify the problem, we assume that the electronic ground state of the molecule is a $^1\Sigma$ term, so that the energy of its Jth rotational level is

$$chBJ(J+1),$$

and the effect of nuclear spin can be neglected. We also assume that kT is large compared to the energy differences between the rotational terms and small compared to the differences between the vibrational or electronic terms. Within these limits, we need consider only the rotational levels.

Since, by hypothesis, kT is large compared to the energy differences between the rotational levels, it is easy to calculate the sum $\Sigma e^{-w_i/kT}$ approximately. Recalling that the state J has the statistical weight $2J+1$, one obtains

$$\sum_i e^{-w_i/kT} = \sum_{j=0}^{\infty} (2J+1)\exp\left[-\frac{chB}{kT}J(J+1)\right].$$

For large values of kT, we may replace the preceding sum by an integral and neglect 1 with respect to J; this gives

$$\sum_i e^{-w_i/kT} = \int_0^{\infty} 2J\exp\left[-\frac{chB}{kT}J^2\right]dJ = \frac{kT}{chB}. \qquad (9)$$

We saw in the preceding sections that, within our hypotheses, the average energy corresponding to the two rotational degrees of freedom of the molecule is $\bar{w} = kT$. Thus we find, by substituting in (8),

$$S = kN\left[\tfrac{5}{2}\log T + \log V - \log N - \log(chB) + \log\frac{(2\pi m)^{3/2}k^{5/2}e^{7/2}}{h^3}\right]. \qquad (10)$$

In this formula, B depends on the moment of inertia of the molecule according to Eq. (4) of Chapter 2.

In deriving Eq. (10), we neglected the nuclear spin. If the nuclei have spins, we must distinguish two cases according to whether the molecule is hetero- or mononuclear. If the two nuclei are different, and have spins I_1 and I_2, it is sufficient to multiply the weight of each state by $(2I_1 + 1)(2I_2 + 1)$, since there are $2I_1 + 1$ possible orientations of the first nucleus and $2I_2 + 1$ orientations of the second. As a consequence, expression (9) is multiplied by the factor $(2I_1 + 1)$ $(2I_2 + 1)$, and the entropy (10) has the additional term

$$kN \log [(2I_1 + 1)(2I_2 + 1)].$$

For a homonuclear molecule whose nuclear spin is I, the statistical weight of the states with even J (or odd J) is $(I + 1)(2I + 1)$, whereas the weight of the states with odd J (or even J) is $I(2I + 1)$, according to the statistics obeyed by the nuclei (cf. Section 2-17). One can easily see that in this case expression (9) must be multiplied, in our approximation, by $(2I + 1)^2/2$, the mean of the two weights.

Therefore, expression (10) for the entropy has the additional term

$$kN[2 \log (2I + 1) - \log 2].$$

Finally, we note that, owing to the simplifications we have introduced, all these formulas are valid only within the temperature interval where the specific heat of the gas is equal to $\frac{5}{2}R$.

4

Polyatomic Molecules

4-1 STRUCTURE OF POLYATOMIC MOLECULES

As we have seen in the previous chapters, the study of the diatomic molecules and of their spectroscopic properties is already in an advanced stage. On the contrary, much less is known of either the experimental or the theoretical properties of polyatomic molecules.

The first problem in the study of these molecules is the determination of their structure, that is, the relative positions and the distances between the nuclei of the atoms which constitute the molecule. The solution of this problem for diatomic molecules is particularly simple, because the only quantity to be determined in this case is the distance between the two nuclei. This quantity can be derived from the moment of inertia of the molecule, and the latter can usually be found from band-spectrum analysis. For polyatomic molecules however, the problem of the structure already presents many more difficulties. Here we review the methods that can be used to determine this structure.

A primary criterion, often essential, for determining the structure of polyatomic molecules is derived from the formulas giving their chemical structure. This criterion, as one would expect, has its most reliable and extended applications in the field of the organic molecules. The theory that the four valences of carbon are arranged in a tetrahedral configuration and are equivalent to each other already gives, in the majority of cases, a precise idea of the relative positions of the various atoms in the molecule; this conclusion must then be tested by other methods. For example, for methane (CH_4) and for its analogs, with halogens occupying the place of the four hydrogens (e.g., CCl_4) the criteria of organic chemistry suggest a tetrahedral structure in which the carbon atom occupies the center of a regular tetrahedron and the four hydrogens (or the four chlorines) the vertices. Other methods must be used to confirm this derived structure and to determine the length of the side of the regular tetrahedron. For compounds of methane in which a single hydrogen is replaced by a halogen (e.g., CH_3Cl), organic chemistry suggests an analogous structure with the difference that now the tetrahedron, whose center is still occupied by carbon, is not necessarily regular. Because of symmetry, the base, occupied by the three hydrogens, is an equilateral triangle, and the three distances from the chlorine to the three hydrogens are equal but different from the lengths of the sides of the triangle.

For more complicated compounds, the structural formulas are still a very useful guide but often lead to ambiguities that are not easily resolved, even by other methods. Thus, for example, for ethane, $H_3C—CH_3$, the chemical formulas suggest the following structure: The two carbons are close to each other, and the six hydrogens are at the vertices of two equilateral identical triangles. The two triangles must lie in planes perpendicular to the line joining the two carbons, but on opposite sides of the carbons and at equal distances from the point midway between the two carbons. But the relative orientation of the two triangles is undetermined in this picture. Benzene, C_6H_6, is similar. Here organic chemistry gives us the well-known hexagonal structure but does not specify the relative position of the hydrogen hexagon with respect to the carbon hexagon.

4-2 X-RAY DIFFRACTION BY MOLECULES*

In spite of these deficiencies the structural formulas are almost always the most reliable guides. Another method that gives useful

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* See numerous articles on this subject by P. Debye, L. Bewilogua, and others in *Z. Physik.*, **28–32** (1927–1931).

results, at least in simple cases, is the diffraction of X rays, which are so useful for analyzing crystals.

When a thin beam of X rays falls on a molecule, the rays scattered by the individual atoms which form the molecule interfere with each other and produce intensity maxima and minima of the scattered radiation in different directions.

In practice, the experiment can be done by sending a thin beam of rays through a vessel containing the substance, in a gaseous state, to be analyzed. The scattered radiation is then studied. The primary beam, of course, encounters molecules having all possible orientations. The intensity of the scattered light in a certain direction is then obtained by averaging the intensities produced in that direction by all the possible orientations of the molecules. As a consequence, the observed diffraction pattern, for instance, on a photographic plate placed perpendicular to the incident beam, consists of concentric rings with their center where the primary beam hits the plate. From the positions and intensity distribution of these rings, one can deduce to some extent the arrangement of the atoms in the molecule.

It is obvious, however, that this method is useful only in relatively simple cases, because several things complicate the phenomenon and obscure its interpretation. First, the atoms themselves are not point centers of the diffraction, since their dimensions are of the order of magnitude of the dimensions of the molecule and of the wavelength of the X rays. This considerably reduces the clarity of the scattering images, so that the details are easily lost. This cannot be improved too much by calculating approximately the effect of the atomic dimensions from the statistical distribution of the electrons in the atoms.

Another phenomenon that also reduces the clarity of the images is the incoherent scattered radiation (Compton effect), which of course, does not give rise to diffraction phenomena and hence produces a uniform diffusion of radiation superposed on the diffraction halos. One should also keep in mind that the light atoms, particularly hydrogen, scatter X rays only very weakly, so that this method is useless for determining their positions. Furthermore, the deformations of the molecules arising from their thermal motions reduce the clarity of the images.

Finally, the following effect complicates the phenomenon even more and, in particular, makes the measurements on liquids useless: When we study X rays scattered by a liquid, even if it is monoatomic (e.g., mercury), we always observe diffused halos with a shape very similar to that produced by molecular scattering. These halos, even in a monoatomic liquid, arise because the centers of the atoms are not distributed at random; there is always a certain order in their distribution, because of the finite extension of the atoms. Thus if the center of an atom is at a certain point at a certain instant, the center of another atom at that instant cannot be closer to this point than twice the atomic radius. The more condensed the body, the more pronounced is this kind of order, which can be shown to be sufficient to explain the halos observed in the X-ray scattering in monoatomic liquids. This order disappears completely in a gas in which the average distance between atoms is large compared to the atomic dimensions; the drawback for gases is that the intensity of the scattered radiation is extremely reduced.

Because of these circumstances, only the observations of X-ray scattering from gases or vapors are of any practical use in determining the structure of molecules. For nongaseous sytems, the halos caused by molecular scattering cannot be clearly distinguished from those arising from the causes discussed above.

Finally, we note that an analogous method for studying the structure of molecules is found in electron diffraction. This method is similar to, and the results can be analyzed in the same way as X-ray diffraction. The advantage of this method lies in the higher intensity of the scattered electrons; however its resolution is inferior to that of X rays.

4-3 ELECTRIC POLARIZABILITY OF MOLECULES

An important source of information about a molecule is the observation of its electric polarizability, from which we can measure its electric moment.

When a molecule is placed in an electric field, the average value of its electric moment in the direction of the field is different from zero and, to a first approximation, it increases with increasing intensity E of the electric field. The "electric polarizability" of the molecule is defined as the ratio α of the average electric moment in the direction of the field to the intensity of the electric field.

The polarizability of a molecule is usually due to the superposition of two essentially different effects. Since any molecule contains negative electrons and positive nuclei, the electric field E exerts a force on the nuclei in the direction of the field and another on the electrons in the opposite direction. Against these forces, which tend to polarize the molecule, there are forces between electrons and nuclei that try to maintain the original shape of the molecule. As a result of these two opposite actions, the molecule becomes electrically polarized, that is, it acquires an electric moment proportional to the field E. One can see that even with an electric field of constant magnitude, the moment produced in the molecule is not always the same but depends on the direction of the field with respect to the axis of the molecule. In other words, the molecule has directions of "easy" polarization and of "difficult" polarization. Since the various molecules of a gas have all possible orientations with respect to the field E, the observed polarizability is the average of the polarizability in all the different directions; we indicate this value as α_0. It is important to note that α_0 is a property of the molecule and does not depend on the temperature.

Besides this polarizability α_0, which we can call the *deformation polarizability* because it corresponds to a real deformation of the molecule (displacement of the positive nuclei with respect to the negative electrons), several molecules can also have another polarizability called *orientation polarizability*, which is due to the following causes: Many molecules, even in the absence of external electric fields, have a permanent electric moment. A typical example is a saline molecule such as NaCl, consisting of two ions of opposite signs. In these molecules the permanent electric moment is simply given by the product of the electric charge of the ions and their separation. Also, a nonpolar diatomic molecule generally has an electric moment, except when the molecule is homonuclear, because then the electric moment is obviously zero for reasons of symmetry. Similarly, polyatomic molecules generally have a permanent electric moment, large or small, as long as the symmetry of the molecule is not incompatible with it.

When a molecule with a permanent electric moment μ is placed in an electric field E, the field tries to align the electric moment parallel to itself. Operating against this tendency is the thermal motion, which tries to disarrange the molecules and to produce a uniform distribution of their electric moments in all possible directions. When thermal equilibrium is reached, the molecules with their moments μ along the field are a little more numerous than those with moments in the opposite direction. The average value of the projection of the electric moment along the field therefore differs from zero; this means that the gas has a net polarization.

While the polarization by deformation is temperature-independent, the polarization by orientation, for the same electric field, is larger for lower temperatures. This can be understood if we recall that the intensity of the thermal motion which opposes the orientation of the molecules decreases with decreasing temperature.

The theory of orientation polarization of molecules can be developed in a manner exactly analogous to that of the Langevin theory of paramagnetism. If the temperature is sufficiently high so that we can neglect the quantization of the rotation of the molecule, the orientation polarizability is given by $\mu^2/3kT$. As one can see, it is inversely proportional to the absolute temperature. One arrives at the same result by applying quantum mechanics.

The total polarizability of a molecule equals the sum of the polarizability by deformation and polarizability by orientation; thus we have

$$\alpha = \alpha_0 + \frac{\mu^2}{3kT}. \tag{1}$$

In a gas we can neglect the perturbations of one molecule on another; the dielectric susceptibility can then be taken as the product $n\alpha$ of the polarizability of the individual molecule and the number n of molecules per unit volume. Therefore the dialectric constant is equal to

$$\epsilon = 1 + 4\pi n\alpha. \tag{2}$$

For a liquid, on the other hand, the perturbation produced by the molecules cannot be neglected. In many cases, however, we can still deduce the molecular polarizability of a liquid from the dielectric constant ϵ through the Clausius-Mossotti formula:

$$\alpha = \frac{3}{4\pi n}\frac{\epsilon - 1}{\epsilon + 2}. \tag{3}$$

4-4 ELECTRIC MOMENT OF A MOLECULE

The previous considerations are very important for an understanding of molecular structure. They allow us to know whether a molecule has a permanent electric moment, and to measure it if it has.

From Eq. (1) we see that, if the permanent moment is zero, the polarizability of the molecule is independent of the temperature and so is the dielectric constant (measured at constant density). If the molecule has a permanent moment, its polarizability decreases with increasing temperature; this is also true of the dielectric constant.

Therefore, if we find that the dielectric constant does not depend on the temperature, we conclude that the permanent moment of the molecule is zero; if the dielectric constant does depend on the temperature, we can calculate the molecular polarizability α as a function of the temperature by means of (2) or (3), depending on the case.

If we plot α as a function of the inverse of T we find, according to Eq. (1), a linear relationship, the slope of which gives immediately the value of the electric moment μ of the molecule.

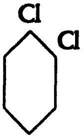
Knowledge of the electric moment, as we mentioned earlier, gives interesting information about the structure of the molecule. Thus, in particular, the absence of an electric moment usually indicates that an electric moment is incompatible with the symmetry of the molecule, since it is unlikely that only by chance does a permanent moment have a value too small to be observed.

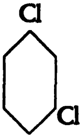
For example, that the molecules CH_4 and CCl_4 have no electric moment confirms the regular tetrahedral structure indicated for these molecules by stereochemistry. If we replace one of the methane hydrogens with a chlorine, we obtain the CH_3Cl molecule, whose structure suggests the existence of an electric moment, which is actually observed. Similarly, the compounds CH_2Cl_2 and $CHCl_3$ also have electric moments.

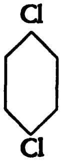
Benzene is interesting. This compound, as suggested by its structural formula, has no electric moment. Its monosubstituted compounds, like C_6H_5Cl for example, do have an electric moment as can be seen from the structural formula (I).

(I)

Of the three bi-substituted compounds, ortho-(II), meta-(III),


(II)


(III)


(IV)

and *para*-dichlorobenzene (IV), one finds, in agreement with the symmetry, that the first two have an electric moment, whereas the last one does not. Let us examine this phenomenon in more detail. We assume that the introduction of Cl in the benzene ring always produces an electric moment that can be represented by a vector going from the center of the molecule to the chlorine atom and whose magnitude is equal to 1.5×10^{-18} esu. According to this hypothesis, C_6H_5Cl should have a moment of 1.5×10^{-18}. Since the total moment of *ortho*-dichlorobenzene is the vector sum of two moments with magnitude 1.5×10^{-18} and an angle of 60° between them, its magnitude should equal $1.5 \times 10^{-18}\sqrt{3} = 2.6 \times 10^{-18}$. The angle between the two component moments in *meta*-dichlorobenzene equals 120°, and therefore the magnitude of the resultant moment is 1.5×10^{-18}. Finally, the two moments in *para*-dichlorobenzene are in opposite directions so that the resulting magnitude equals zero. Thus one obtains Table 3. One sees that in spite of the rough approximation, the agreement is quite satisfactory.

Table 3 Moments of Substituted Benzene Compounds

Compound	Calculated moment, $\times 10^{18}$	Observed moment, $\times 10^{18}$
C_6H_5Cl	1.5	1.6
o-$C_6H_4Cl_2$	2.6	2.25
m-$C_6H_4Cl_2$	1.5	1.4
p-$C_6H_4Cl_2$	0	0

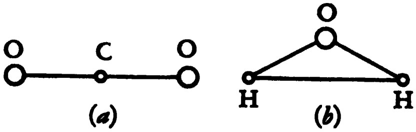


Figure 24

The shapes of some simple molecules can be deduced directly from the absence of an electric moment. Thus, for example, since carbon dioxide (CO_2) has a zero moment, one deduces the structure represented in Fig. 24(*a*), where the carbon atom is at the midpoint of the line joining the two oxygens. This model, which is independently confirmed by other phenomena that we shall discuss later, is the only one whose symmetry excludes an electric moment. An analogous structure can also be assigned to CS_2, which also has no electric moment. As for water (H_2O), the structure suggested by the presence of an electric moment is the one in Fig. 24(*b*); similarly for the molecules SO_2 and SH_2, which also have electric moments.

In the case of ammonia (NH_3), the equivalence of the three hydrogens and the existence of an electric moment suggest a pyramidal structure having as a base an isosceles triangle with the vertices occupied by the hydrogens; the vertex of the pyramid is equidistant from the three hydrogens and is occupied by the nitrogen atom.

4-5 ENERGY LEVELS OF POLYATOMIC MOLECULES

In polyatomic molecules, as in the diatomic ones, one can divide the motions of the constituent particles into the following categories: electronic motions, where, to a first approximation, we may neglect the motions of the nuclei; vibrations of the nuclei around their equilibrium position; rotations of the whole molecule considered, in a first approximation, a rigid body.

But, whereas in the case of diatomic molecules the analysis of the electronic terms and their classification by means of quantum numbers is, at least in simple cases, sufficiently developed, little or nothing is known about the arrangement into series of the electronic terms in polyatomic molecules because of the much greater complexities of the problem.

We shall discuss vibrations in the next section; here we briefly examine rotations.

In polyatomic molecules with a linear structure, like carbon dioxide (cf. Fig. 24) or acetylene $HC{\equiv}CH$, whose four atoms in the equilibrium position are all on one line, the rotation has the same characteristics as those of diatomic molecules. If we assume (usually verified for the ground states of the simpler molecules) that the angular momentum of the electrons in the direction of the molecular axis is zero, we can then directly apply the formulas of the rigid rotator. The energies of the rotational terms are then given, as in the diatomic molecules, by $c\hbar BJ(J+1)$, where B is related to the moment of inertia with respect to the center of mass by Eq. (4) of Chapter 2. Hence, these molecules may exhibit rotational bands or both rotational and vibrational bands and finally rotational Raman effects, with an appearance very similar to that observed in diatomic molecules. For example, in the case of carbon dioxide one finds, from observations of the rotational Raman effect, a moment of inertia of about 70×10^{-40} g-cm^2; from this one calculates that the distance between the carbon and the two oxygen nuclei is equal to 1.16Å.

The case of molecules whose nuclei do not lie in a straight line is more complicated. Relative to the center of mass, these generally have three unequal principal moments of inertia. The problem of the quantization of the rotational motion of these molecules is that of a rigid body rotating around the center of mass. This problem is somewhat complicated, particularly if the three principal moments of inertia I_x, I_y, I_z are all different; in this case there is no closed analytical expression for the energy levels. The problem is considerably simplified if the ellipsoid of inertia is a rotation ellipsoid as, for example, for ammonia. If we assume, for instance, that $I_x = I_y$, we find for the rotational energy levels,

$$W_{\mathrm{rot}} = \frac{\hbar^2}{2}\left[\frac{J(J+1)}{I_x} + \left(\frac{1}{I_z} - \frac{1}{I_x}\right)\Omega^2\right], \tag{4}$$

where Ω can have positive or negative integer values including zero, and J can take on the values $|\Omega|$, $|\Omega| + 1$, $|\Omega| + 2$, ... The experiments performed on ammonia confirm the expression (4) for the energy levels.

4-6 VIBRATIONS OF POLYATOMIC MOLECULES

If a molecule is in a definite electronic state (the only electronic state that has been studied is the ground state), its nuclei can be pictured as bound to each other by elastic-type forces—forces that try to restore the nuclei to their equilibrium positions with intensities which, to a first approximation, are proportional to the displacements from these positions. If we displace the nuclei from their equilibrium positions and then release them, the molecule undergoes elastic vibrations. When the amplitudes of the vibrations are small, they can be described by a superposition of some fundamental harmonic vibrations whose (fundamental) frequencies depend on the masses of the nuclei and on the forces binding them to their equilibrium positions.

If N is the number of nuclei in the molecule, the system has $3N$ degrees of freedom; from these we must subtract the six degrees of freedom of translation and rigid rotation, so that we are left with the $3N - 6$ degrees of freedom corresponding to the possible modes of deformation of the molecule. Associated with each of these $3N - 6$ degrees of freedom is a fundamental frequency. Of course, there are often cases of degeneracy, where two or more fundamental frequencies coincide.

We should also note that, for polyatomic molecules whose atoms in the equilibrium position are arranged in a straight line, the number of fundamental frequencies is $3N - 5$ instead of $3N - 6$; in this case the number of degrees of freedom of translation and rigid rotation is 5 instead of 6 because the rotational degree of freedom around the line along which all the atoms are fixed is, of course, absent.

To determine the fundamental frequencies and the corresponding vibrational modes, we can employ the following general method. We designate with $\xi_1, \xi_2, \ldots, \xi_{3N}$ the $3N$ components of the displacement of the N nuclei. The kinetic energy is then a quadratic orthogonal function of the $\dot{\xi}_i$, which we can write as

$$T = \frac{1}{2} \sum_i m_i \dot{\xi}_i^2. \tag{5}$$

If we consider only oscillations of small amplitude, the potential energy also is a quadratic form of the ξ_i's. We write it in the form

$$V = \frac{1}{2} \sum_{i,k} V_{ik} \xi_i \xi_k. \tag{6}$$

We first change the coordinates ξ_i to

$$\eta_i = \sqrt{m_i}\,\xi_i.$$

The expression for T then assumes the spherical form

$$T = \tfrac{1}{2}\Sigma\dot{\eta}_i^2, \tag{7}$$

and Eq. (6) becomes

$$V = \tfrac{1}{2}\sum_{i,k} v_{ik}\eta_i\eta_k, \tag{8}$$

where $v_{ik} = V_{ik}/\sqrt{m_i m_k}$.

We now change the coordinates again, transforming the η's by a linear orthogonal transformation into new variables (the normal coordinates) u, so that Eq. (8) becomes the normal orthogonal form

$$V = \tfrac{1}{2}\Sigma v_i u_i^2. \tag{9}$$

This can always be done by solving the secular equation of the quadratic form (8) whose roots give directly the coefficients v_i in Eq. (9). Since the transformation is orthogonal, the kinetic energy still has the spherical form $T = \tfrac{1}{2}\Sigma\dot{u}_i^2$ in the new variables. The total energy of the molecule, therefore, has the form

$$W = \sum_i \tfrac{1}{2}(\dot{u}_i^2 + v_i u_i^2), \tag{10}$$

where the individual variables are separated. The energy term corresponding to the variable u_i is of the same form as the energy of a harmonic oscillator whose frequency ν_i is related to the coefficient v_i as follows:

$$4\pi^2\nu_i^2 = v_i. \tag{11}$$

From this relation we can calculate the fundamental frequencies once the v_i's are known from the solution of the secular equation. With this procedure, we obtain $3N$ frequencies (distinct or coincident); six of these, however, are zero because they correspond to the six degrees of freedom without deformation. Each of the remaining $3N - 6$ characteristic frequencies correspond to a particular normal mode of vibration of the molecule. If two (or more) fundamental frequencies are equal, the corresponding vibrational mode remains undetermined, since we can take any linear combination of two (or more) vibrational modes corresponding to that frequency.

Of course, when we are dealing with simple molecules that have a specific type of symmetry, we usually do not have to solve the secular equation completely to determine the characteristic frequencies and the corresponding modes of vibration, because they can easily be obtained by intuitive considerations.

The easiest way to carry out this analysis is the following: First one examines all the elements of symmetry of the molecule and looks for vibrational modes for which the molecule, although deformed, retains all the symmetry elements. Such vibrations, if they exist, are called *totally symmetric.* Once this is done, one eliminates successively some elements of symmetry and looks for motions for which the deformed molecule has only the residual elements of symmetry. One proceeds in the same way until all the vibrational modes have been found.

The fundamental vibrational modes for some of the most common types of molecules are collected in Fig. 25.

1. Molecules of the type CO_2: Here we have three fundamental frequencies ν_1, ν_2, ν_3, corresponding to the vibrational modes illustrated in Fig. 25. Frequencies ν_1 and ν_3 are simple, but ν_2 is double, because the corresponding vibration can take place in the plane of the figure as well as in the plane through the three atoms and perpendicular to that of the figure.

To illustrate with this simple example how we can classify the fundamental modes of vibration with respect to the symmetries of the molecule, we first point out that the symmetry elements of the molecule CO_2 in its equilibrium state can be reduced to the following: three mutually orthogonal planes of symmetry, one of which (α) is perpendicular to the line of the three atoms and contains the carbon atom; the other two (β,γ) interset along the line of three atoms (we can take β as the plane of the figure and γ as the plane perpendicular to it).

Given these three elements of symmetry, the positions of the three atoms of the molecule are obviously determined by only one parameter, that is, the distance between the carbon atom and the two oxygen atoms. Corresponding to the possible variations of this single parameter, there is only one fundamental vibration that is totally symmetric: the one indicated by ν_1 in Fig. 25.

We now look for vibrations during which the molecule, in the de-

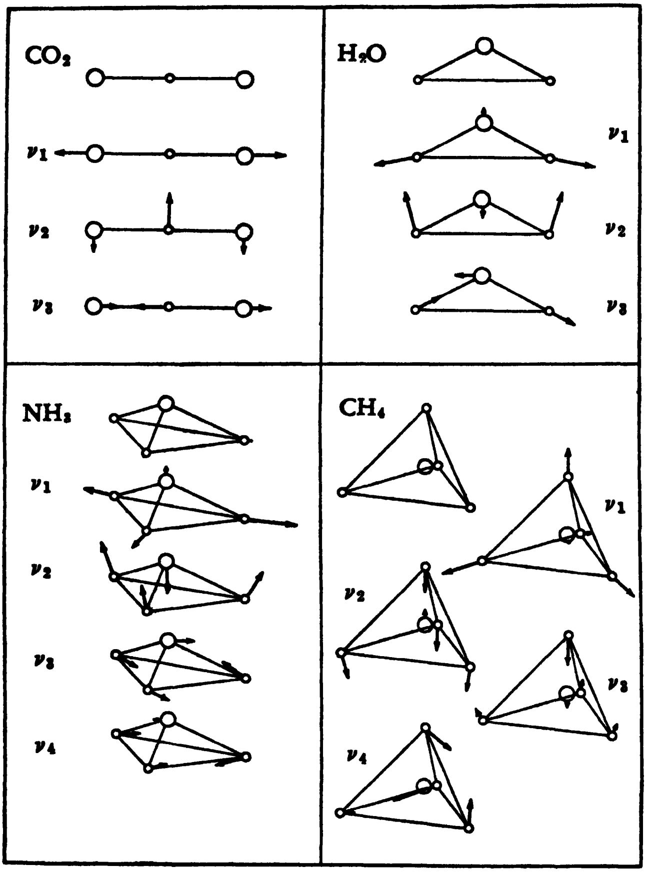


Figure 25

formed state, still retains the planes of symmetry α and β but does not have γ as a plane of symmetry. To be compatible with these elements of symmetry, the carbon atom must remain on the line of intersection of the two planes of symmetry α and β; let χ be its abscissa. The two oxygen atoms, instead, must lie in the plane of the figure (plane β) in symmetric positions with respect to the plane α. Let ξ and η be the coordinates of one of the two atoms in the plane β; knowing these coordinates, we can determine the position of the other oxygen atom. It follows then that, if we know the elements of symmetry α and β, we can determine the vibrational state of the molecule from the three coordinates χ, ξ, η. It would seem, then, that there are three fundamental vibrations having the desired symmetry. But one of these is the totally symmetric vibration mentioned earlier; another is a rigid motion of translation of the molecule in the direction parallel to the line of intersection of the two planes α and β. There remains, therefore, only one motion with the maximum symmetry, described above, which leaves the symmetry elements (α) and (β) unaltered. This motion corresponds to the vibration designated by ν_2 in Fig. 25. If we inspect the motions that have the planes α and γ as elements of symmetry, we arrive, by a similar analysis, at a vibration having the same frequency ν_2; this is why ν_2, as we have already mentioned, is double.

We finally search for vibrations for which only the planes of symmetry β and γ are kept constant. For such motions, all three atoms must lie on the line of intersection of the two planes β and γ. To specify their positions, we need know only their abscissas; thus, only three parameters are needed. It would seem, accordingly, that there are three fundamental motions having the desired symmetry. But of these one is the totally symmetric vibration; another is a motion of rigid translation parallel to the intersection of the two planes β and γ. Therefore, we are left with only one vibration—that indicated by ν_3 in Fig. 25. With this, the analysis of the fundamental vibrations of carbon dioxide is completed.

2. Molecules of the type H_2O: Here we have three fundamental frequencies ν_1, ν_2, ν_3, all simple, which correspond roughly to the three modes of vibration illustrated in the figure. The motions ν_1 and ν_2 are symmetric with respect to the altitude of the isosceles triangle that represents the molecule and therefore have the same symmetry as the molecule: They have maximum symmetry. For ν_3, only one symmetry plane is left invariant.

3. Molecules of the type NH_3: Here we have four distinct fundamental frequencies, ν_1, ν_2, ν_3, ν_4. Of these, ν_1 and ν_2 have a triple symmetry with respect to the altitude of the pyramid that represents the molecule (maximum symmetry and hence the same as the molecule); they have three planes of symmetry: the planes that contain the

altitude or ternary axis of the pyramid and one of the hydrogen atoms. These two frequencies are both simple. The frequencies ν_3 and ν_4, instead, are double.

4. Molecules of the type CH_4: Here we have four distinct frequencies ν_1, ν_2, ν_3, ν_4. The mode of vibration corresponding to ν_1 consists of a homogeneous dilation and contraction of the hydrogen tetrahedron without displacement of the central carbon atom; ν_1 is simple and totally symmetric. Frequencies ν_2 and ν_3 are triples; we can represent them by vibrational modes with a ternary axis through one of the vertices of the tetrahedron with the three planes of symmetry intersecting along this axis. Finally, frequency ν_4 is double; the carbon atom remains fixed, and the distances between the hydrogens and the carbon do not change. Two of the opposite sides of the tetrahedron alternately expand and contract; that is, the atoms at the vertices of the tetrahedron alternately approach and recede from each other in pairs.

4-7 INFRARED SPECTRUM OF POLYATOMIC MOLECULES

The oscillations of the nuclei may be assumed to be harmonic only as long as they have small amplitudes. For larger amplitudes, the forces that restore the molecule to its equilibrium position are not strictly proportional to the displacements. This produces a certain anharmonicity in the oscillations. As long as the oscillations can be considered harmonic, the energy levels corresponding to the different vibrational states can be found in the following way: From the point of view of the oscillations, we can visualize the molecule as a system of $3N - 6$ oscillators with frequencies equal to the fundamental frequencies ν_1, ν_2, ν_3, ... The energy of each oscillator is given by $\frac{1}{2}h\nu_i + v_ih\nu_i$, where v_i is an integer. If we omit the additive constant $\frac{1}{2}h\nu_i$, the vibrational energy of the molecule can be written

$$W_{\text{vibr}} = \Sigma h\nu_i v_i. \tag{12}$$

The molecules can emit or absorb frequencies corresponding to differences between two of these energy levels. One can immediately see that these frequencies are just the fundamental frequencies or harmonics and combinations of these. But one should note that, in the vibrational spectrum of polyatomic molecules just as in that of the diatomic ones, the fundamental frequencies are usually much more intense than their harmonics or their combinations. The reason for this is the same as for this situation in diatomic molecules. The radiation depends on the matrix elements of the electric moment of the molecule for the relevant quantum transitions. If on the other hand, u_1, u_2, . . . are the coordinates representing the various fundamental oscillations into which the oscillatory motion of the molecule can be resolved, the electric moment can be expanded in a series of powers of those coordinates:

$$\mathfrak{M} = \mathfrak{M}_0 + \sum_i \mathfrak{M}_{1i} u_i + \sum_{i,k} \mathfrak{M}_{2ik} u_i u_k + \cdots . \qquad (13)$$

The first term is a constant representing the permanent electric moment of the molecule (which is zero in some cases); this term obviously does not contribute to the vibration radiation. If we stop at the linear terms in u_i and assume, as a first approximation, that the vibrations are exactly harmonic, the matrix elements different from zero are only those for which the transitions correspond to a change of one unit in only one vibrational quantum number. Each of these transitions corresponds, of course, to the emission or the absorption of one of the fundamental frequencies which, for this reason, is very intense. On the other hand, the higher harmonics and the combination frequencies are much less intense because they are due to the anharmonicity of the oscillations and to the presence of quadratic and higher-order terms in expansion (13) of the electric moment.

Of course, we do not usually observe the pure vibrational frequencies, but vibrational and rotational bands quite similar to those observed in diatomic molecules, where they arise because of a simultaneous variation of the vibrational and rotational states. However, the rotational structure of these bands is often somewhat more complicated than that of diatomic molecules, except when the atoms of the molecules lie in a straight line.

The infrared spectrum of polyatomic molecules is usually observed in absorption. With an infrared spectrometer, we first analyze, as a function of the frequency, the intensity distribution of a source of infrared radiations. A new determination of the intensity distribution is then performed, after placing the gas or the vapor to be examined in the path of the rays. By comparing the two, we then deduce the absorption spectrum of the molecule. When the resolving power is insufficient to show the rotational structure of the bands, each band usually appears to consist of two absorption maxima separated by a region of weak absorption. Figure 5 illustrates this situation for the vibrational and rotational band of a diatomic molecule (see also Section 3-2).

The absorption observations sometimes indicate that only transitions between the vibrational ground term and higher terms occur, because at the ordinary temperatures at which the observations are usually made, the higher vibrational terms are not often excited. However, it is by no means exceptional for a molecule to have vibrational frequencies so small that the first and also some other vibrational levels can be thermally excited even at ordinary temperatures. Usually, some of the frequencies of the molecules containing hydrogen are somewhat high (around 3000 cm^{-1}) because of the small mass of the oscillating nucleus. Molecules containing heavy atoms have, instead, much lower frequencies, frequencies that can go below 100 cm^{-1}.

We have already said that the bands with the higher intensities correspond to the fundamental frequencies of the molecule. However, if we observe them in very dense, thick layers of vapors, we are usually confronted with a very complicated and hardly decipherable system of absorptions arising mostly from higher harmonics and combination frequencies. Among these absorptions, it is not easy to recognize those corresponding to the fundamental frequencies, but they can be distinguished by their intensities if we use thin absorbing layers of gases of low density. We can get some idea of the intensity of the absorption corresponding to the fundamental frequencies by noting that the fundamental bands of carbon dioxide arising from the small quantity of carbon dioxide always present in the atmosphere can even be observed in thin layers of air.

The fundamental bands of a molecule are generally by far the most intense in its infrared spectrum; however, one should keep in mind that in several cases of molecules having particular types of symmetry, some of the fundamental frequencies may not appear in absorption. This happens when the corresponding motion, because of its particular symmetry, does not cause the electric moment of the molecule to vary.

To clarify this point, we consider molecules of the types shown in Fig. 25. In molecules of the CO_2 type, the frequencies ν_2 and ν_3 appear in absorption. Indeed, this molecule, which, for reasons of symmetry, has no electric moment in its equilibrium position, loses this symmetry (for which its moment is zero) when it is vibrating with frequencies ν_2 and ν_3; therefore, there is a variation of the electric moment corresponding to these frequencies. However, the motion corresponding to the ν_1 frequency does not change the symmetry of the molecule, so that its electric moment is still zero; the ν_1 frequency, therefore, does not appear in the infrared absorption spectrum or, as it is customary to say, is *inactive* in the infrared. In practice, in the infrared spectrum of carbon dioxide we find two extremely intense bands at wavelengths 15 and 4.3 μ, which correspond to the fundamental frequencies ν_2 and ν_3; besides these, there are many weaker bands corresponding to harmonics and to combination frequencies.

In molecules of the type H_2O, all three fundamental frequencies ν_1, ν_2, ν_3 are inactive in the infrared. Similarly inactive are all the fundamental frequencies ν_1, ν_2, ν_3, ν_4 of molecules of the NH_3 type. Finally, in molecules of the CH_4 type, the frequencies ν_2 and ν_3 are active; the ν_1 frequency, whose motion does not affect the tetrahedral symmetry of the molecule, is inactive. The ν_4 frequency is also inactive, because the corresponding motion, although affecting the symmetry of the molecule, still leaves enough symmetry for the electric moment to vanish.

4-8 RAMAN EFFECT IN POLYATOMIC MOLECULES

One of the most important methods for studying the fundamental frequencies of polyatomic molecules is by analyzing their Raman spectra. This method is often more powerful than the analysis of the infrared absorption; the Raman lines, particularly in gases, are very well-defined, so that accurate measurements of the frequencies can be made. Furthermore, only fundamental frequencies, easily identifiable, are found in the Raman effect.

The theory of the Raman [123] effect can be developed via the Kramers-Heisenberg [106] formula, taking into consideration, besides the two states that combine to give the Raman effect, all the other quantum states of the system. This, however, is not an easy procedure with polyatomic molecules, because the structure of the electronic terms is unknown. It is more convenient, instead, to use the following approximate arguments, valid when the Raman frequency is small with respect to the exciting frequency and the electronic frequencies of the molecule; these hypotheses are abundantly verified in practice.

When a molecule is exposed to primary light, it is subject to the rapidly varying electric field E of the light waves. The field E induces in the molecule an electric moment proportional to E, because E polarizes the molecule; the proportionality coefficient α represents, of course, only the deformation polarizability, and not the orientation polarizability, because the vibrations of E occur too fast for the molecule to orient itself with respect to the field. Furthermore, α is not necessarily equal to the deformation polarizability that would be induced by static fields; it may differ from that value more or less, according to the difference between the incident light frequency and the anomalous dispersion frequencies of the molecule. If the molecule is optically isotropic, the induced electric moment M is parallel to the field E. In general, however, the induced electric moment is not parallel to E, and α is a tensor; α_{xy} is the coefficient of the proportionality between the component M_y of the induced moment in the direction y and the field E, assumed to be in the direction x. x and y specify any two directions, which occasionally may coincide. If we deform the molecule by displacing the nuclei from their equilibrium positions, the polarizability is, of course, affected; therefore, if the molecule oscillates, α changes during the different phases of the oscillation. If $u_1, u_2, \ldots$ are the coordinates of the fundamental oscillations, α_{xy} is thus a function of the u's. We can write, expanding α in a power series,

$$\alpha_{xy} = \alpha_{xy0} + \sum_j \alpha_{xyj} u_j + \sum_{jk} \alpha_{xyjk} u_j u_k + \cdots \tag{14}$$

For simplicity we now neglect the effect of the rotation of the molecule, to which we shall return later.

We can easily understand the conditions that are necessary for the vibrational Raman effect by means of a classical argument that can be quite easily translated into the quantum language of the Dirac theory [81] of radiation.

The electric moment M_y in the direction y, induced in the molecule by the electric field E of the light, is given, according to what we have just said, by

$$M_y = \alpha_{xy}E. \tag{15}$$

The field E oscillates with the frequency ν of the primary light; thus we can write

$$E = E_0 \cos 2\pi\nu t.$$

For α_{xy}, we can substitute its series expansion (14) terminated at the first-order term. Since the coordinate u_j oscillates with its own fundamental frequency ν_j, we can write

$$u_j = u_{j0} \cos\,(2\pi\nu_j t + \beta_j),$$

and finally obtain

$$M_y = [\alpha_{xy0} + \sum \alpha_{xyj}u_{j0} \cos\,(2\pi\nu_j t + \beta_j)]E_0 \cos 2\pi\nu t. \tag{16}$$

It is immediately obvious from this expression (by transforming the product of the two cosines into the cosine of the sum and the difference) that M_y can be decomposed into a component with the frequency ν of the primary light plus two other components with frequencies $\nu \pm \nu_j$:

$$M_y = \alpha_{xy0}E_0 \cos 2\pi\nu t + \frac{E_0}{2}\sum \alpha_{xyj}u_{j0}\{\cos[2\pi(\nu + \nu_j)t + \beta_j] + \cos\,[2\pi(\nu - \nu_j)t - \beta_j]\}.$$

To each one of these harmonic components there corresponds, according to the electromagnetic theory, radiation with the same frequency; this is the light emitted by the molecule. In the light emitted by the molecule, besides a component with the frequency ν of the primary light (Tyndall effect), we also find components with modified frequencies (Raman effect). The latter have frequencies $\nu \pm \nu_j$, that is, the same as the frequency of the primary light, increased or decreased by one of the fundamental frequencies. The component $\nu + \nu_j$ represents the anti-Stokes-Raman effect, whereas $\nu - \nu_j$ represents the Stokes-Raman effect.

In this analysis we have introduced some simplifications and approximations whose effects we now discuss. First, we have used classical instead of quantum-mechanical arguments; this does not change the result insofar as the calculation of frequencies goes. The only important difference is in the relative intensities of the Stokes and anti-Stokes components, which, in the classical derivation, are equal. The quantum calculation, instead, predicts much higher intensities for the Stokes lines than for the anti-Stokes lines, in perfect agreement with observation; this difference is larger the lower the temperature and the higher the fundamental frequency (cf. Section 7-3).

Furthermore, we have neglected the effect of the rotation of the molecule. Owing to this rotation, rotational bands are produced around the line with the unchanged frequency and around those with the modified frequencies, analogous to those discussed for the Raman effect in diatomic molecules. These are often observed, but not always resolved, around the unchanged line, whereas they are generally much too faint to appear around the vibrational Raman lines.

Finally, we have neglected the higher-order terms in expansion (14). Indeed, these terms are usually much less important than those of first order. They would give rise to Raman lines with frequencies that differ from the unchanged line frequency by the sum of the two fundamental frequencies of the molecule or by twice their values; in higher approximations they produce frequencies equal to a linear combination of the fundamental ones. In practice, there are a few cases where these "harmonics" are observed as extremely faint Raman lines. The ratios of the intensities of these very faint lines to those of the normal Raman lines are of the same order of magnitude as the ratios of the intensities of the latter to the intensity of the unmodified line.

4-9 SELECTION RULES FOR THE VIBRATIONAL RAMAN EFFECT

We may thus conclude that in the Raman effect the only transitions that give rise to lines of considerable intensity are those for which one of the vibrational quantum numbers differs by one while the others do not change. In other words, as long as the fundamental vibrational frequencies are observed, it is only with a much smaller intensity that their higher harmonics and the combination frequencies are observed, if at all.

However, it frequently happens that for the Raman effect, as for the infrared spectrum, some of the fundamental frequencies are forbidden because of the particular symmetry of the molecules. We recall that a fundamental frequency shows up very intensely in the Raman effect only if the corresponding vibration induces a first-order alteration (in the direction of the elongation) in the molecule's polarizability (that is, if the corresponding α_{xyj} of (14) is not equal to 0). We thus immediately deduce the following selection rule: If a fundamental frequency is to appear in the Raman effect when the corresponding oscillation is excited, the molecule must be so deformed as to have different polarizabilities at opposite phases of the oscillation. Indeed, it is obvious that the perturbation of the polarizability with respect to the elongation otherwise appears only in an order higher than the first.

From this point of view one can distinguish between even and odd oscillations.

We consider a molecule oscillating with the fundamental frequency under study, and we compare the two deformed states α and β when the molecule is at opposite phases of its oscillation. We say that the oscillation is even if the two following conditions are simultaneously satisfied: (1) the two deformed states α and β are identical (they can be superposed) or they are mirror images of one another, and (2) the deformed molecule in the two states α and β must retain parallel elements of symmetry which furthermore must be sufficient to identify the orientation of the axes of an ellipsoid (that is, two planes of symmetry or at least a ternary axis). If both conditions are not satisfied, the oscillation is said to be odd. In the Raman effect only the odd fundamental vibrations appear with high intensity.

We can better illustrate the distinction between even and odd vibrations by some examples (see Fig. 25).

1. Molecules of the type CO_2. Here the frequency ν_1 is odd; indeed at opposite phases the dimensions of the molecule are different; the molecule is longer in one phase than in the other and therefore different. Frequency ν_2 is even; the two states in opposite phases can be converted into each other by a 180° rotation around the line passing through the three atoms in their equilibrium position. Symmetry planes and axes in the two deformed states are obviously coincident. Similarly, frequency ν_3 is even; the two states of opposite phase are symmetric with respect to the plane perpendicular to the axis of the molecule through the equilibrium position of the carbon atom. Also, the axis along which the three atoms lie remains fixed. As a result, frequencies ν_2 and ν_3 are forbidden in the Raman effect.

2. Molecules of the type H_2O. Here all three fundamental frequencies are odd.

3. Molecules of the type NH_3. Here all four fundamental frequencies are odd.

4. Molecules of the type CH_4. All four frequencies odd.

The Raman spectrum is frequently complicated by accidental degeneracies or quasi-degeneracies among the vibrational energy levels. These cases can easily occur because of the considerable number of possible modes of oscillation in polyatomic molecules.

The Raman spectrum of the carbon dioxide molecule is a typical example of this. We said that, of the three fundamental frequencies of this molecule, only ν_1 is odd; we would therefore expect a Raman spectrum with only one line. We observe, instead, two intense lines separated from two very faint ones. Leaving the two faint lines aside, for the moment, we may account for the two intense lines as follows: From infrared observations we know that the fundamental frequencies ν_2 and ν_3 of this molecule are 670 and 2350 cm^{-1}, respectively. The order of magnitude of the fundamental frequency ν_1 active in the Raman effect but not in the infrared can be deduced from the mechanics of the problem; we find that ν_1 is close to 1300 cm^{-1} and therefore lies in the vicinity of the two intense Raman lines with frequencies 1285 and 1388 cm^{-1}; furthermore, by accident, ν_1 also lies near $2\nu_2 = 1340$. Because of this accidental degeneracy, two Raman lines appear instead of only one. This is because the two energy levels with vibrational quantum numbers v_1, v_2, v_3 equal to (100) and (020) are almost coincident and therefore perturb each other very strongly under the action of the anharmonic terms of the potential energy. The perturbed eigenfunctions are linear combinations of the eigenfunctions (100) and (020); and since (100) combines very strongly in the Raman effect with the ground level (000), both perturbed eigenfunctions combine with the ground state because both contain a noticeable percentage of the unperturbed eigenfunction (100) that is active in the Raman effect.

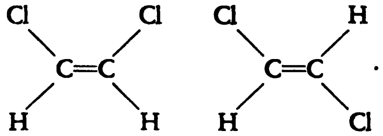
The two faint Raman lines accompanying the two intense ones can be explained analogously as a Raman effect of the molecules, which are thermally excited, with a quantum of the fundamental frequency $\nu_2 = 760$ cm^{-1}. The ratios of the intensities to the positions of these lines confirm the above interpretation.

4-10 PECULIARITIES OF THE VIBRATIONAL LEVELS OF POLYATOMIC MOLECULES

The vibrational states of polyatomic molecules exhibit, at times, structural characteristics that have no counterparts in diatomic molecules; we briefly mention them below.

We can represent the motion of a molecule as a superposition of some fundamental harmonic vibrations only if the amplitude of the motion is very small. Whereas in classical mechanics we may always introduce vibrations with arbitrarily small amplitudes, this is not permissible in quantum mechanics. Indeed, even in the vibrational state of lowest energy, there is already a positive amount of energy, the so-called zero-point energy. In some cases this energy may already be so large that the corresponding vibrations cannot be considered harmonic, and, possibly, they do not even have the characteristics of oscillatory motion.

An example of this is found in the so-called free rotatability of certain radicals. We consider, for example, ethane H_3C—CH_3. This molecule consists of two methyl radicals connected to each other by a simple C—C bond. Plausible chemical arguments suggest that the two radicals rotate freely (or almost freely) with respect to each other around the line joining the two carbon atoms; this is not true for two radicals connected by a double bond. That this is so can be inferred, for example, from the existence of only one doubly substituted compound of the type ClH_2C—CH_2Cl while the corresponding compound of ethylene has two possible forms (*cis* and *trans*):



The existence of these two different compounds demonstrates that, in the case of the double bond, considerable energy is needed to rotate the two radicals 180° with respect to each other around the double bond in order to transform the *cis* into the *trans* form, and vice versa. In ClH_2C—CH_2Cl, instead, the absence of isomeric forms indicates that the energies necessary to rotate the two radicals with respect to each other are very small. They are presumably smaller than the zero-state energy for the corresponding degree of freedom, so that no real oscillation exists for this state, but rather there is a distribution of energy levels corresponding to a rotation. Until now it has been impossible to verify experimentally the positions of these energy levels.

One peculiarity of the structure of the vibrational levels that has been accurately observed, is the following, which we illustrate with ammonia as an example, because this molecule has been studied in detail.

The NH_3 molecule, as we have already said, has the shape of a regular pyramid with the nitrogen atom at the vertex. Let the potential energy U of the molecule be a function of the distance x of the nitrogen nucleus from the plane of the three hydrogens; for the moment, let the sides of the triangle of the hydrogens be constant. Let x_0 be the value of x in the equilibrium configuration (the height of the pyramid when the molecule is in equilibrium). The potential energy $U(x)$ thus has a minimum for $x = x_0$. It is obvious, on the other hand, that $U(x)$ is symmetric with respect to $x = 0$. Its behavior as a function of x is therefore something like that shown in Fig. 26.

We can represent the vibrations of the molecule schematically, particularly those of the type ν_2 (see Fig. 25), as the motion of a point along a line, subject to a force that can be derived from a potential of the type represented in Fig. 26. We must give this point a mass equal to the reduced mass of the nitrogen atom and the three hydrogens.

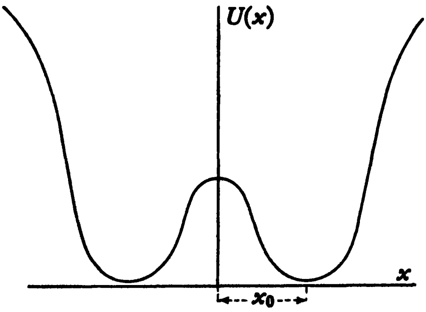


Figure 26

In Section 2-14 we discussed the structure of the eigenfunctions and energy levels in such a case. We concluded that, when the potential barrier between the two wells is very high and wide, so that the two wells can be considered separate, the point can oscillate in either well and, corresponding to these two possibilities, each eigenvalue is double. However, since the potential barrier is finite, this degeneracy actually disappears and the two eigenvalues are unequal; the deepest one corresponds to an eigenfunction symmetric with respect to $x = 0$ and the other to an antisymmetric eigenfunction. Also, we see that the difference between these two eigenvalues, divided by h, is the frequency with which the first point jumps from one well to the other across the barrier. Thus one can understand how this frequency (that is, the eigenvalue difference) changes for the various vibrational levels; it is larger for the higher levels because the point is then near the top of the barrier and therefore has a higher probability of crossing it.

The doubling of vibrational levels has been studied carefully for the quantum-number-1 level of the ν_2 vibration of ammonia (Fig. 25). In the corresponding absorption bands all the lines are double, with a frequency difference of about 30 cm^{-1}. The effect has also been observed, for the same level, in the Raman spectrum. Finally, the doubling has also been observed for an excited quantum state of frequency ν_1 (Fig. 25); the separation for this level is somewhat smaller, as is to be expected theoretically. For the ground level, the doubling is very small and corresponds to about 0.9 cm^{-1}. Such a frequency, equivalent to a wavelength of 1.1 cm, can be produced with a magnetron of very small dimensions; the selective absorption of electromagnetic waves of this wavelength by ammonia has been observed by Williams and Carlson.

Similar phenomena also occur in many other molecules whenever the nuclei are in stable equilibrium for two different positions. The molecule can then oscillate about one or the other of the two equilibrium positions; however, whereas in classical mechanics a certain minimum energy is always needed for a transition from one to the other of the two equilibrium configurations, this is not necessarily the case in quantum mechanics. There is always a finite probability, however small, for a transition from one to the other configuration.

Thus, in particular, all the optically active molecules have two isomeric forms, a dextro- and levorotatory one. There is always a finite probability for a spontaneous transition between these two configurations; if this probability is small, each form is relatively stable and can be obtained and kept in a pure state for a long time. If the transition probability is high, the two optical isomers continually change into each other, so that the only thing we can obtain is the racemic product.

PART II

Crystals

The theory of crystals will be discussed here from the molecular and atomic points of view. We shall give only very brief accounts of the true crystallographic properties. Similarly, we shall not discuss the laws of the macroscopic physics of anisotropic bodies, except incidentally. Instead, we shall concentrate on how the atomic structure of solid bodies and the geometric arrangement of crystal atoms give a clue to the understanding of the fundamental properties of these bodies. However, we shall exclude from this program the discussion of the properties of metals.

All solid bodies, except those in an amorphous state, which are more properly compared to liquids (from which they differ only in their much higher viscosity), are in a crystalline or microcrystalline state. Hence from the atomic point of view, the study of crystals is identical with the study of solid bodies.

5

Geometry of Crystal Lattices

5-1 SIMPLE AND COMPOUND LATTICES

The study of the crystalline state of matter entered a new phase after Laue [110] (in 1913) discovered that one can obtain X-ray interference or diffraction patterns from the atomic lattices that constitute the crystals. This discovery is of fundamental importance, both for the study of X rays, because it is an easy and precise tool for their spectral analysis, and for the study of crystals, because the positions of the different atoms in a crystal lattice, even in complex cases, can be determined by analyzing the diffraction of X rays.

The hypothesis that the atoms and molecules of a crystal are ordered in three-dimensional lattices was introduced in crystallography by Haüy [97] at the end of the eighteenth century; this hypothesis was later revived (about 60 years before Laue's discovery [110]) by Bravais.[76] Definite confirmation of this hypothesis came with the discovery of X-ray diffraction.

Before beginning the study of crystals, we introduce some fundamental definitions related to crystal lattices.

We consider three families of planes, each formed by an infinite number of parallel and equally spaced planes. The ensemble of points, each determined by the intersection of any three planes, taken from the three different families, is called a *simple spatial lattice of points.* We illustrate this definition in Fig. 27, which represents a lattice in a plane instead of in space (in place of three families of planes, there are two families of parallel and equidistant lines).

A simple lattice can also be built in the following way: Let **a**, **b**, and **c** be three vectors (fundamental vectors) not parallel to the same plane. Starting from a fixed point P_0, we move a distance given by the vector

$$l\mathbf{a} + m\mathbf{b} + n\mathbf{c}, \tag{1}$$

where l, m, and n are three integers that can be positive, negative, or zero. The sum, of course, is a vector sum. After this displacement, we reach a new point P_{lmn}. If all possible values are given to the three integers l, m, n, the points P_{lmn} describe a simple lattice of points.

Finally, a third equivalent method for defining a simple lattice is the following: We take a cartesian system of axes, either rectangular or oblique, and choose for each axis a unit of distance which need not be the same for the three axes. The simple lattice is the ensemble of all points with integer coordinates (positive, negative, or zero) in this coordinate system.

It is important to note that each point of a simple lattice is surrounded by the other points of the lattice in exactly the same way; all points of a simple lattice are thus equivalent with respect to the lattice.

The parallelepiped that has one of the points of the lattice as a vertex

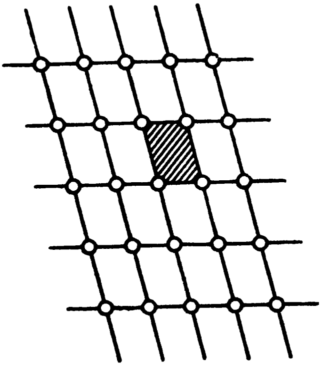


Figure 27

and the three fundamental vectors **a**, **b**, and **c** that start from that point as its three edges is called the *cell* of the lattice. In the two-dimensional representation of Fig. 27 the cross-hatched parallelogram represents one cell. Notice, however, that, given a simple lattice, the choice of the three fundamental vectors and consequently also the definition of the cell remain largely undetermined. This is shown, again for the two-dimensional case in Fig. 28. The lattice represented in the figure can be described either by the fundamental vectors **a**, **b** or by **a**′, **b**′. In the latter case the cross-hatched area must be taken as the cell.

We call the ensemble of two or more identical simple lattices displaced with respect to each other by a translation (not a rotation) a *composite lattice*. Such a lattice can be produced in the following way: We take a certain number of points P_0, P'_0, P''_0, . . . (as many as there are simple lattices) and also three fundamental vectors **a**, **b**, **c**. We then move from the points P_0, P'_0, P''_0, . . . a distance given by the vector (1), where l, m, n are again integers. We thus arrive at other points which we label P_{lmn}, P'_{lmn}, P''_{lmn}, ... If we take for l, m, n all possible triads of integers (positive, negative and zero), these new points describe the composite lattice.

Notice that, although all points in a simple lattice are in equivalent positions with respect to the lattice, different points in a composite lattice are not necessarily equivalent. In general, only points belonging to the same simple lattice inside the composite one are equivalent. This is shown again in Fig. 29 for the two-dimensional case, where we

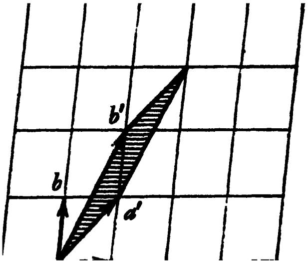


Figure 28

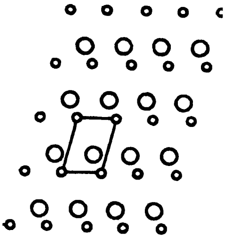


Figure 29

see a composite lattice made of two simple lattices (small and large circles). All the small circles are equivalent with respect to the composite lattice; the same is true of the large circles. But the small circles as a group are displaced with respect to the large ones.

It is often convenient to describe a composite lattice by isolating a cell belonging to one of its simple lattices. Inside or on the surface of this cell we can always find, for each constituent simple lattice, at least one point belonging to that lattice. Specifically, we find only one point if it lies inside the cell, two (on the two opposite faces) if the points are on the surface, four (on the four parallel edges) if on a side, eight if in a corner. The composite lattice is completely specified if the elementary cell we start with is defined and the coordinates of all the points of all the other simple lattices lying in or on this cell are given with respect to the cell. Thus, for example, it is sufficient in the case of Fig. 29 to give the position of the outlined cell together with the position within this cell of the large circle.

The atoms of crystals are arranged exactly like the points of simple or composite lattices; more precisely, the equilibrium positions of the atoms are at the points of the lattice, and the atoms, owing to the thermal motion, oscillate around these equilibrium positions.

If a crystal consists of identical atoms (which are arranged in a simple lattice), we say that the crystal is *monoatomic;* if, instead, the atoms form a composite lattice, the crystal is called *polyatomic* (di-, tri-, quadriatomic, according to the number of the constituent simple lattices).

In a crystal that contains different atoms the crystal lattice consists of many simple lattices, each containing atoms of the same type; on the other hand, there may be several simple lattices composed of the same type of atoms.

We may define a molecule of the crystal as the smallest ensemble of atoms each of which represents one of the simple lattices. It should be noticed that the concept of a molecule in a crystal is considerably different from the concept of a molecule in a gas or a liquid. Owing to the thermal motion, the molecules in a fluid wander over the entire volume occupied by the fluid; we may therefore treat them as real particles which retain their identity during the motion. This molecular concept obviously loses all meaning in a crystal, where the thermal motion consists of vibrations of each atom around its equilibrium position; we should then, according to the previous point of view, consider the whole crystal a single large molecule. However, in a narrower sense, we can also define a crystal molecule as an ensemble of atoms, one for each of the simple lattices which constitute the crystal and so chosen that they lie as closely grouped together as possible. It is clear that this definition contains a certain amount of arbitrariness which, by means of simplifying criteria, we can reduce but never quite eliminate.

5-2 SYMMETRIES OF CRYSTAL LATTICES

The symmetry characteristics of a crystal are determined by the symmetries of its crystal lattice, simple or composite. Bravais[76] and Schönfliess have demonstrated that only a few types of simple lattices need be considered to obtain the symmetries of the different crystal systems. All the simple lattices can be classified into the 14 types of Bravais lattices listed in Table 4; a, b, c represent the lengths of the three fundamental vectors; $\widehat{bc}$, $\widehat{ca}$, $\widehat{ab}$ the angles between them. All 14 lattices are simple, even those of types 5, 7, 11, 13, and 14, which are not described by their own fundamental vectors but by those of a preceding lattice. Thus, for example, the two monometric lattices, the "cubic body-centered" and the "cubic face-centered," can be constructed with the following fundamental vectors of their own:

cubic body-centered:

$$a = b; \qquad c = (\sqrt{3}/2)a; \qquad \widehat{ab} = \pi/2; \qquad \widehat{ac} = \widehat{bc};$$

$$\sin \widehat{ac} = \sqrt{\tfrac{2}{3}}; \qquad \cos \widehat{ac} = \sqrt{\tfrac{1}{3}};$$

Table 4 Bravais Lattices

	Lattice type	Crystal system
1.	The most general spatial lattice: $a \neq b \neq c$; $\widehat{ab} \neq \widehat{bc} \neq \widehat{ca}$	Triclinic
2.	$a = b$; $\widehat{ac} = \widehat{bc}$	Monoclinic
3.	$\widehat{ab} = \widehat{ac} = \pi/2$	Monoclinic
4.	$a = b$; $\widehat{ac} = \widehat{bc} = \pi/2$	Rhombic
5.	Same as above, with a point in the center of each elementary parallelepiped (body-centered)	Rhombic
6.	$\widehat{ab} = \widehat{bc} = \widehat{ca} = \pi/2$	Rhombic
7.	Same as 6, with a point in the center of each elementary parallelepiped (body-centered)	Rhombic
8.	$a = b = c$; $\widehat{ab} = \widehat{bc} = \widehat{ca}$	Trigonal
9.	$a = b$; $\widehat{ab} = \pi/6$; $\widehat{ac} = \widehat{bc} = \pi/2$	Hexagonal
10.	$a = b$; $\widehat{ab} = \widehat{bc} = \widehat{ca} = \pi/2$	Tetragonal
11.	Same as 10, with a point in the center of each elementary parallelepiped (body-centered)	Tetragonal
12.	Simple cubic lattice $a = b = c$; $\widehat{ab} = \widehat{bc} = \widehat{ca} = \pi/2$	Monometric
13.	Cubic body-centered lattice: like 12, with a point in the center of each cube (body-centered)	Monometric
14.	Face-centered lattice: like 12, with a point in the center of each face	Monometric

cubic face-centered:

$$b = c; \qquad a = b/\sqrt{2}; \qquad \widehat{bc} = \widehat{ac} = \pi/4; \qquad \widehat{ab} = \pi/2.$$

In spite of this, it is usually simpler to represent these two types by means of a cubic cell. The cubic cells of the three simple monometric lattices, cubic, cubic body-centered, and cubic face-centered, are shown in Fig. 30.

The symmetry of a crystal consisting of a composite lattice is determined by the symmetries of its simple lattices. According to the different relative positions of the simple lattices, there are different symmetry classes for the crystal system. With a proper arrangement of

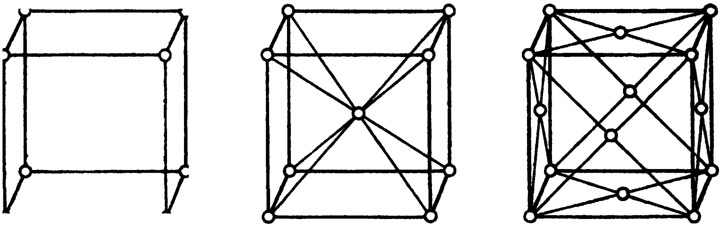


Figure 30

the simple lattices, the symmetry of a crystal can be less complex than that of the simple lattice.

5-3 ANALYSIS OF THE CRYSTAL LATTICES

The criteria applied to the analysis of crystals by X rays are briefly reviewed in this section. The various methods for observing X-ray diffraction and X-ray spectroscopy are described in another part of this volume.

We merely note here that, when a beam of X rays strikes the face of a crystal, the individual planes occupied by the atoms and parallel to the face of the crystal reflect the X rays. The rays reflected by the various parallel planes of atoms at different depths interfere with each other. This interference gives rise to strong reflection maxima when Bragg's relation [7] is satisfied:

$$n\lambda = 2d \cos \vartheta, \tag{2}$$

where λ is the wavelength of the X rays, n is an integer called the *order of the reflection*. ϑ is the incident angle, and d is the distance between successive parallel planes belonging to the crystal lattice, if it is simple, or to any of the constituent simple lattices, if the crystal lattice is composite.

The problem of determining the structure of the crystal lattice can be separated into two parts: (1) determining the shape of the simple lattice or of the different simple lattices which constitute the crystal;

(2) determining the relative positions of the different simple lattices (if the lattice is composite).

The solution of the first problem is usually simple enough. Once the system to which the crystal belongs is known from crystallography, the choice is limited to a few types of simple lattices (among those shown in Table 4). The type can be determined and the fundamental vectors measured by observing the reflection of X rays from a few faces of the crystal.

With an X-ray spectrograph, one can measure the angle for which the Bragg reflections of the various orders occur; knowing the wavelength of the X rays that have been used, one then can apply Eq. (2) to calculate the distance d between successive planes of the simple lattices. From the values of d relative to certain faces, we can easily deduce the structure of the simple lattice.

Let us examine, as an example, a monometric crystal. As we see from Table 4, there are only three types of simple lattices belonging to this crystal; the cubic, the cubic body-centered, and the cubic face-centered (see Fig. 30).

To decide among these three possibilities, it is sufficient to measure the spacing between the parallel planes that pass through the lattice points for the three faces (100), and (110), and (111) of the crystal. These correspond to the face of the cube itself, to the face perpendicular to a surface diagonal, and to the face perpendicular to a space diagonal. From Fig. 30 we see that if a is the edge of the cubic cell, the spacings between these three sets of parallel planes are the following:

$$\text{cubic:}\quad d_{100} = a; \qquad d_{110} = \frac{a}{\sqrt{2}}; \qquad d_{111} = \frac{a}{\sqrt{3}}$$

$$\text{body-centered cubic:}\quad d_{100} = \frac{a}{2}; \qquad d_{110} = \frac{a}{\sqrt{2}}; \qquad d_{111} = \frac{a}{2\sqrt{3}}$$

$$\text{face-centered cubic:}\quad d_{100} = \frac{a}{2}; \qquad d_{110} = \frac{a}{2\sqrt{2}}; \qquad d_{111} = \frac{a}{\sqrt{3}}.$$

From the ratios $d_{100}:d_{110}:d_{111}$, we can then determine the crystal type. The three types of monometric crystals have the following ratios:

$$\text{simple cubic:}\quad d_{100}:d_{110}:d_{111} = 1:\frac{1}{\sqrt{2}}:\frac{1}{\sqrt{3}},$$

$$\text{body-centered cubic:}\quad d_{100}:d_{110}:d_{111} = 1:\sqrt{2}:\frac{1}{\sqrt{3}},$$

$$\text{face-centered cubic:}\quad d_{100}:d_{110}:d_{111} = 1:\frac{1}{\sqrt{2}}:\frac{2}{\sqrt{3}}.$$

In each case the length a of the edge of the elementary cubic cell of the crystal can be calculated from the values of a, and the simple lattice can be completely determined.

5-4 STRUCTURE OF CRYSTALS WITH A COMPOSITE LATTICE

If the crystal consists of a simple lattice, its structure is completely known if the dimensions of an elementary cell are measured. But the problem of determining the structure is more complicated, if the crystal consists of more than one simple lattice. First, after determining the shape of the simple lattice, one calculates the volume of the cell. Knowing the density of the crystal, we can then deduce the mass of a cell; from the latter, by means of the chemical composition of the substance and the atomic weights, one obtains the number of different atoms per cell, that is, the number of simple lattices that constitute the crystal.

No general criteria are available for determining the arrangement of simple lattices. The knowledge of the number of atoms of the various types which belong to the cell and the symmetry of the crystal are often useful for fixing the positions, or the limits on the positions, of some of the atoms. In some simple cases this may even completely determine the structure.

Usually, however, further data are necessary. A method that can give very useful information for determining the structure consists of comparing the intensities of the reflections of the various orders from the faces of the crystal. If the crystal consists of a single simple lattice, all the parallel lattice planes are equivalent, and they therefore reflect the X rays with the same intensity; in this case the maximum reflection intensities for the various orders decrease regularly with increasing order. But if the lattice is not simple, there are, parallel to each face of the crystal, successions of planes with different densities of atoms or with different types of atoms. These successive planes are spaced periodically with the period d of the simple lattice to which they belong. In this case the maximum reflection intensity variations in the different orders are irregular. This is analogous to what happens when light is diffracted by an ordinary grating; the positions of the diffraction images for the various orders depend exclusively on the grating constant, that is, on the distance between the successive lines, but the intensities of the various images are strongly influenced by the shape of the grating line; for certain particular shapes, for instance, the second-order may be more intense than the first.

We can make these points more precise in the following way: We assume, for simplicity, that there are two different reflecting planes parallel to a certain face of a crystal; let K and K' be their reflecting powers. Let the outer surface of the crystal be a K plane. The distance from this surface to any K plane is md (m integer); if δ is the distance between a K plane and the adjacent K' plane, the distance of any K' plane from the outer surface is $md + \delta$.

We consider the reflection of a parallel beam of X rays incident on the face of the crystal. The difference in optical-path length between the waves reflected from the first plane and those reflected from a plane at a distance p is obviously given by $AO + OB = 2p \cos \vartheta$ (see Fig. 31); the phase difference between the two waves is thus

$$2\pi \frac{2p \cos \vartheta}{\lambda}.$$

The amplitude of the wave reflected from the K plane at a distance md is proportional to the real part of

$$\sqrt{K} \exp\left[2\pi i\left(\nu t - \frac{2md \cos \vartheta}{\lambda}\right)\right],$$

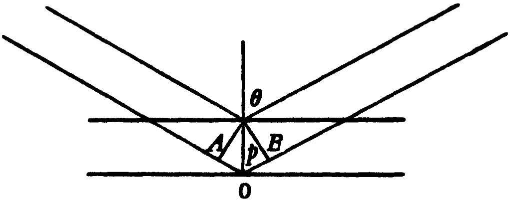


Figure 31

and the corresponding amplitude for the wave reflected from the K' plane at a distance $md + \delta$ is proportional to the real part of

$$\sqrt{K'} \exp \left\{ 2\pi i \left[\nu t - \frac{2(md + \delta) \cos \vartheta}{\lambda} \right] \right\}.$$

If N is the number of planes, the combined amplitude is

$$\left(\sqrt{K} + \sqrt{K'} \exp \left[-2\pi i \frac{2\delta \cos \vartheta}{\lambda} \right] \right) \exp (2\pi i \nu t) \sum_{m=0}^{N-1} \exp \left(-2\pi i \frac{2md \cos \vartheta}{\lambda} \right).$$

Summing the geometric progression, one finds for the total amplitude

$$\left(\sqrt{K} + \sqrt{K'} \exp \left[-2\pi i \frac{2\delta \cos \vartheta}{\lambda} \right] \right) \exp (2\pi i \nu t) \frac{1 - \exp \left(-2\pi i \frac{2Nd \cos \vartheta}{\lambda} \right)}{1 - \exp \left(-2\pi i \frac{2d \cos \vartheta}{\lambda} \right)}.$$

We calculate the total intensity of the reflected beam by multiplying this expression for the amplitude by its complex conjugate. We thus find that the intensity is proportional to

$$\left\{ K + K' + 2 \sqrt{KK'} \cos \frac{4\pi\delta \cos \vartheta}{\lambda} \right\} \frac{\sin^2 [(2\pi N d \cos \vartheta)/\lambda]}{\sin^2 [(2\pi d \cos \vartheta)/\lambda]} \qquad (3)$$

Since N is a very large number, the second factor in (3) is appreciably different from zero only when the denominator vanishes, that is, when

$$\frac{2\pi d \cos \vartheta}{\lambda} = n\pi,$$

which is equivalent to the Bragg relation

$$n\lambda = 2d \cos \vartheta.$$

Under these conditions, the intensity variation from order to order is determined by the factor between the parenthesis in (3); if we introduce the Bragg relation, this becomes

$$K + K' + 2\sqrt{KK'}\left(\cos 2\pi n \frac{\delta}{d}\right). \tag{4}$$

If we introduce the observed intensities of the various orders into this formula, we derive the ratios K'/K and δ/d. In this theory we have neglected the effect of such factors as the finite extension of the atoms, the irregularities of the crystal, and the thermal motion, which introduce, even in a crystal with a simple lattice, a uniform decrease in intensity for successive orders; one must, of course, take this into account before applying (4).

Since the intensity with which a crystal plane reflects X rays is roughly proportional to the electron density in that plane, the ratio K'/K gives us the ratio of the electron densities of the two planes. From this ratio we obtain information about the type and number of atoms that lie on the two planes. For example, if $\delta/d = \frac{1}{2}$, (4) shows that the orders with n even are more intense than those with n odd, whereas for $K = K'$, and $\delta/d = \frac{1}{4}$, the intensities of the successive orders, as given by (4), are in the ratios:

$$1:0:1:2:1:0:1:2: \cdots .$$

It is evident that this method is applicable in principle to the analysis of crystals with any number of periodically recurring parallel planes and not just two. However, in complicated cases, the uncertainty in the measurements and the uniform decrease of intensity from order to order (because of the finite size of the atoms and the thermal motion) make a thorough application of the theory practically impossible.

Once we have determined, with this method, the structure of the largest possible number of series of parallel planes in the crystal, the best thing is to find by trial and error a configuration of the atoms in the molecule that can give the observed reflections. In this procedure we are often helped by chemical considerations; these may indicate which groups of atoms are likely to be near each other and which far apart. Crystallographic symmetry conditions are also useful.

This method, in the typical form described above, can be applied only to crystals large enough so that the Bragg method can be applied to the reflections from all faces of the crystals. To analyze minerals with a microcrystalline structure or crystal powders, one must use the method of Debye and Scherrer,[79] which gives good results, at least in cases that are not too complicated. Another useful method for the analysis of the crystal structures is that of the Laue photographs, which give on one single plate the reflections from all the internal (virtual) faces of the crystal.

5-5 SOME EXAMPLES OF CRYSTAL STRUCTURE

We review in this section some of the better known crystal lattice structures.

Among the monoatomic crystals of the monometric system are the metal crystals of copper and silver, easily obtainable as large specimens; they have a cubic body-centered lattice (see Fig. 30). The side of the cubic cell is 3.597 Å for copper, 4.079 Å for silver.

Diamond is another important example of a monoatomic substance with crystals belonging to the monometric system. The carbon atoms are so arranged in the diamond crystal lattice (Fig. 32) that each atom is at the center of a regular tetrahedron whose vertices are occupied by four other carbon atoms. The diamond lattice is not simple. We can picture it as composed of two cubic face-centered lattices displaced, with respect to each other, in the direction of one of the principal diagonals of the cubic cell (see Fig. 30), by a distance equal to one-quarter the diagonal.

Other examples of monometric crystals are rock salt and fluorite. The rock-salt lattice (Fig. 33) is most simply described as a cubic lattice whose points are alternately occupied by atoms of chlorine and sodium. Each chlorine atom has, as nearest neighbors, six sodium atoms, and vice versa. Even though the atoms in sodium chloride occupy the points of a simple cubic lattice, the NaCl lattice is not simple, because the atoms in this cubic lattice are not all of the same type but are alternately chlorine and sodium. The NaCl lattice must thus be described as a composite lattice, formed by two cubic face-centered lattices, one consisting of Cl atoms, the other of Na atoms, displaced by half the side of the cubic cell with respect to each other.

Fluorspar, CaF_2, can be described as a simple cubic lattice with fluorine atoms at the vertices. A calcium atom lies at the center of every cube so that these atoms form a cubic face-centered lattice with

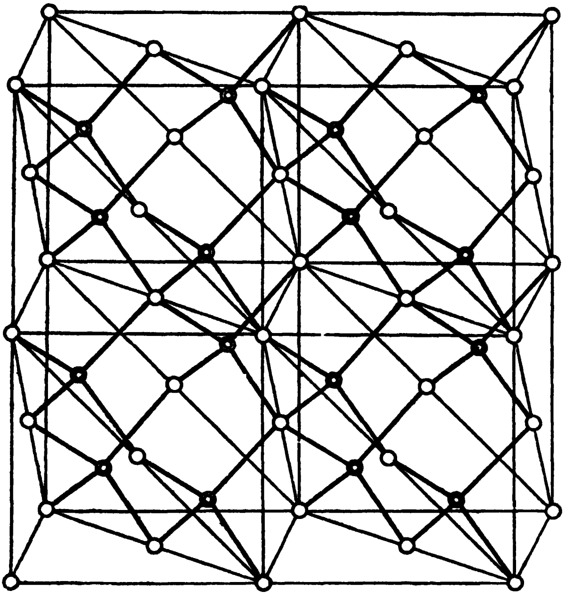


Figure 32

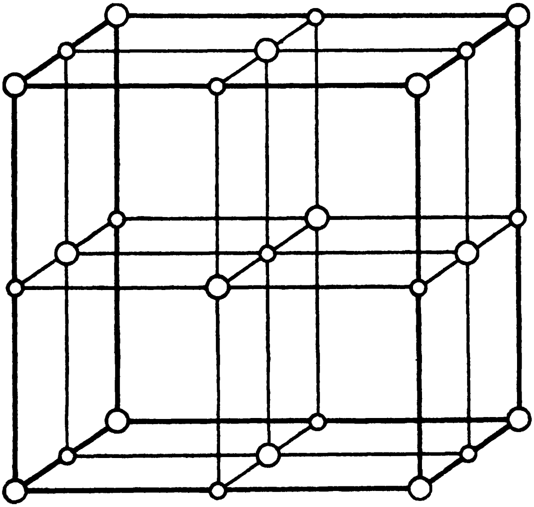


Figure 33

an edge twice the length of the edge of the simple cubic lattice of the fluorine atoms (see Fig. 34). The CaF_2 lattice is thus a composite lattice consisting of three simple cubic face-centered lattices, two of them occupied by fluorine atoms displaced by one-half an edge length with respect to each other and one by calcium atoms displaced with respect to the former by one-quarter of the spatial diagonal.

Figure 35 shows the fundamental lattice cell of calcite, $CaCO_3$, which is an example of a somewhat more complicated crystal structure. This crystal, which belongs to the trigonal system, consists of simple lattices of type 8 in Table 4. The structure of this lattice can be easily understood in the following way: We neglect, for the moment, the internal structure of the CO_3 radical and assume that the three oxygen atoms and the carbon form a simple unit. The structure of the lattice formed by the ions, Ca and CO_3, can then be thought of as analogous to that of rock salt but so contracted in the direction of one of the principal diagonals of the cubic cell as to become a trigonal structure. The three oxygen atoms of the CO_3 ion are arranged around the carbon atom in a small equilateral triangle which lies in a plane through the carbon atom and is perpendicular to the ternary symmetry axis. In

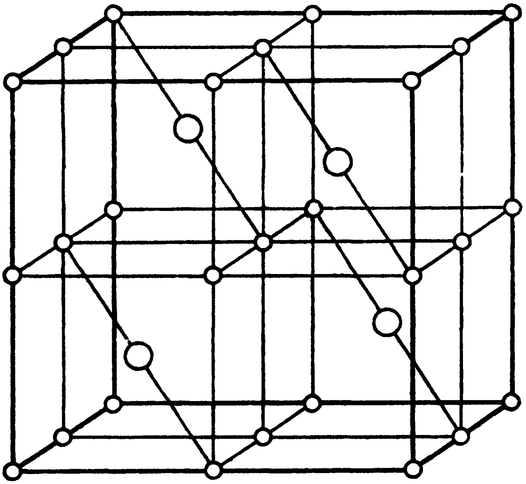


Figure 34

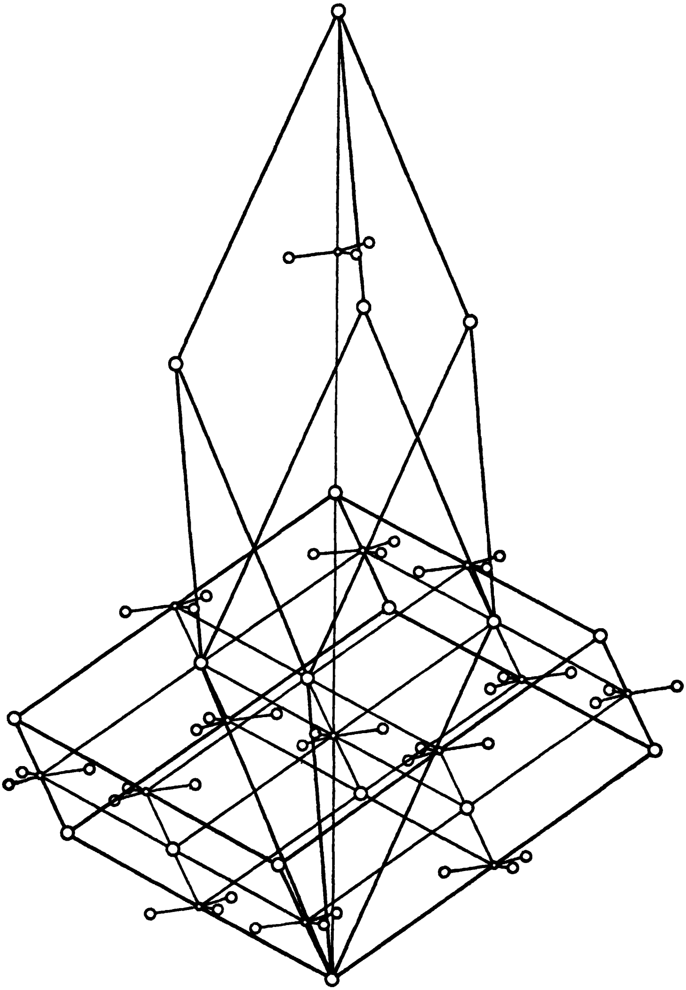


Figure 35

the figure one can also see the crystal cell, represented by the extended rhombohedron.

As seen in the figure, the angle bisectors of the small triangles are parallel to the faces of the rhombohedric cell; their vertices alternately point in opposite directions.

APPENDIX 1. APPLICATION OF X-RAY, ELECTRON-, AND NEUTRON-DIFFRACTION THEORY TO CRYSTAL STRUCTURE; X-RAY DIFFRACTION

It should be pointed out that a great deal of work has been done in the structure analysis of crystals, amorphous bodies, and liquids, since the Italian edition of this book was published. For a complete discussion of this topic, see the *Encyclopedia of Physics*, Vol. XXXII (S. Flügge, ed.), Springer, Berlin, 1957, particularly the articles by Guinier and Von Eller [21] and by Bouman [6] and Fournet.[16] A complete bibliography is given in these articles.

The essential element in the recent treatments of structural analysis by X-ray diffraction is the following basic principle: The scattering of X rays by an atom gives us a Fourier analysis of the electron density surrounding the atom. Hence the scattering of X rays by a crystal is equivalent to the Fourier analysis of the crystal.

It also follows from this that the scattering of X rays from amorphous bodies and liquids gives us a Fourier analysis of the molecular structure of the constituent molecules. This has been of extreme importance in the recent analysis of the molecular structure of DNA and RNA molecules in chromosomes.[96, 139]

We may outline this procedure briefly as follows: Let

$$\mathbf{r} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$$

be the vector from some lattice point 0, taken as the origin, to any other lattice point where $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ are the basic vectors of the lattice, and n_1, n_2, n_3 are integers. If $\mathbf{s}$ is then a unit vector in the direction of an incident beam of radiation and $\mathbf{s}_0$ a unit vector in the direction of the scattered beam, the diffracted ray will be observed if

$$\frac{\mathbf{r}_1 \cdot (\mathbf{s} - \mathbf{s}_0)}{\lambda} = n_1h + n_2k + n_3l,$$

where h, k, l are positive or negative integers and λ is the wavelength of the X ray.

If an arbitrary origin is chosen and the coordinates of any atom in this coordinate system are x, y, z, then we write the condition for diffraction in the form

$$\mathbf{r} \cdot \mathbf{r}^* = hx + ky + lz,$$

where we have placed

$$\mathbf{r}^* = (\mathbf{s} - \mathbf{s}_0)/\lambda.$$

Let $e\rho\, dv$ be the electric charge in an element of volume dv at the point $\mathbf{r}$, where e is the charge on an electron and ρ is the electron density. Then the scattering factor f of the atom is defined as

$$\begin{aligned} f &= \textstyle\iiint \rho\, dv\, e^{2\pi i \mathbf{r} \cdot \mathbf{r}^*} \\ &= \textstyle\iiint \rho\, dv\, e^{2\pi i(hx+ky+lz)}. \end{aligned}$$

On the other hand, the electron density ρ of an atom, a molecule, or a single cell can be written as a Fourier integral:

$$v\rho(x,y,z) = \iiint_{-\infty}^{\infty} T(h',k',l')e^{-2\pi i(h'x+k'y+l'z)}\, dh'\, dk'\, dl',$$

where v is the volume of the cell. We then have

$$T(h',k',l') = \iiint_{-\infty}^{\infty} \rho(x,y,z)ve^{2\pi i(h'x+k'y+l'z)}\, dx\, dy\, dz,$$

so that $T(h',k',l')$ is the Fourier transform of the electron density. We now introduce the reciprocal space of the lattice (the reciprocal lattice) whose lattice points are defined by the vector $\mathbf{r}^*$ from an origin 0^* such that

$$\mathbf{a}^* = A\frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot [\mathbf{b} \times \mathbf{c}]},$$

$$\mathbf{b}^* = A\frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot [\mathbf{b} \times \mathbf{c}]},$$

$$\mathbf{c}^* = A\frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot [\mathbf{b} \times \mathbf{c}]},$$

where A is an arbitrary constant we may place equal to 1. We note that

$$\mathbf{r}^* \cdot \mathbf{r} = (h'\mathbf{a}^* + k'\mathbf{b}^* + l'\mathbf{c}^*) \cdot (x\mathbf{a} + y\mathbf{b} + z\mathbf{c})$$
$$= h'x + k'y + l'z.$$

We also define

$$dv^* = v^*\, dh'\, dk'\, dl' = \frac{1}{v}\, dh'\, dk'\, dl'.$$

We now observe from the previous expressions that

$$\rho(\mathbf{r}) = \iiint\limits_{-\infty}^{\infty} T(\mathbf{r}^*) e^{2\pi i \mathbf{r}^* \cdot \mathbf{r}}\, dv^*$$

and

$$T(\mathbf{r}^*) = \iiint\limits_{-\infty}^{\infty} \rho(\mathbf{r}) e^{2\pi i \mathbf{r}^* \cdot \mathbf{r}}\, dv.$$

We see from this that the Fourier transform of the atom, the cell, or the molecule is equal to the atomic scattering factor. This is the basis of structural analysis.

If the intensity of X rays scattered by an arbitrary body is observed, one has the Fourier analysis of the electron density. From this the electron density can be found, and thus the atomic, molecular, or crystal structure can be inferred. See also Refs. 32, 53.

Electron Diffraction and Interference

The theory of the diffraction of waves by crystals can be applied not only to X rays but also to electron waves [48,52] so that the scattering of electrons from crystals can be used for structure analysis just as X rays are. The procedure is quite similar to that described above, with some slight modifications.

Let the spherical electron wave scattered by an atom have the amplitude

$$f(\theta) \frac{e^{ikr}}{r}$$

at a point defined by the spherical coordinates r, θ, ϕ where $\mathbf{k}$, the wave vector of the electron, has the magnitude $mv/\hbar = 2\pi/\lambda$, m being the electron mass and v its velocity. The number of electrons scattered by the atom (placed at the origin of the coordinate system) in the direction θ, ϕ, and passing per unit time through an element of surface ds at the distance r, is just $|f(\theta)|^2 v(ds/r^2)$. We call $f(\theta)$ the atomic scattering factor for electrons.

If $\psi_0(r)$ is the incident plane wave of the electron and $v(r)$ is the potential field of the atom, then one can show, to the Born approximation, that

$$f(\theta) = -\frac{m}{2\hbar^2}\int e^{-i(\mathbf{s}\cdot\mathbf{r}')}V(r')\psi_0(r')\,d\tau',$$

where $\mathbf{s}$ is a unit vector in the direction of the scattered wave.

Let $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ be the unit vectors of our lattice, let $\mathbf{s}_0$ be a unit vector in the direction of propagation of the incident electron wave striking the lattice, and let $\mathbf{s}$ be a unit vector of the scattered wave in the direction OP. If $\mathbf{r}$ is the vector from the origin to an arbitrary lattice point that scatters waves to P just as the lattice point at the origin does, the path difference between the two scattered waves is just $R - \mathbf{r}\cdot\mathbf{s} + \mathbf{r}\cdot\mathbf{s}_0$, where R is the distance from 0, the origin, to P.

If the amplitude scattered from 0 to P is

$$\frac{f}{R}\exp\left[2\pi i\left(\nu t - \frac{R}{\lambda}\right)\right],$$

the amplitude scattered from the arbitrary lattice point is

$$\frac{f}{R}\exp\left(2\pi i\left\{\nu t - \frac{R}{\lambda} + \frac{1}{\lambda}[\mathbf{r}\cdot(\mathbf{s}-\mathbf{s}_0)]\right\}\right),$$

where f is the atomic scattering factor. Summing over all points of the lattice, one then obtains

$$\frac{f}{R}\exp\left[2\pi i\left(\nu t - \frac{R}{\lambda}\right)\right]\sum_{x,y,z}^{N_1N_2N_3}\exp\left\{\frac{2\pi i}{\lambda}[\mathbf{r}\cdot(\mathbf{s}-\mathbf{s}_0)]\right\}.$$

The intensity of the diffracted waves at any point on the screen is now given by the interference function

$$I = \frac{f^2}{R^2}\frac{\sin^2 A_1N_1}{\sin^2 A_1}\frac{\sin^2 A_2N_2}{\sin^2 A_2}\frac{\sin^2 A_3N_3}{\sin^2 A_3},$$

where

$$A_1 = \frac{\pi}{\lambda}[\mathbf{a}\cdot(\mathbf{s}-\mathbf{s}_0)]; \qquad A_2 = \frac{\pi}{\lambda}[\mathbf{b}\cdot(\mathbf{s}-\mathbf{s}_0)];$$

$$A_3 = \frac{\pi}{\lambda}[\mathbf{c}\cdot(\mathbf{s}-\mathbf{s}_0)].$$

We obtain interference maxima if $A_1 = n_1\pi$, $A_2 = n_2\pi$, $A_3 = n_3\pi$, or $[\mathbf{a}\cdot(\mathbf{s}-\mathbf{s}_0)] = h\lambda$, $[\mathbf{b}\cdot(\mathbf{s}-\mathbf{s}_0)] = k\lambda$, $[\mathbf{c}\cdot(\mathbf{s}-\mathbf{s}_0)] = l\lambda$, where $h, k, l, \ldots$ are the integers 1, 2, 3, ...

The structure factor of the crystal is now given by

$$\left|\sum_i f_i \cos 2\pi(hx_i + ky_i + lz_i)\right|^2 + \left|\sum_i f_i \sin 2\pi(hx_i + ky_i + lz_i)\right|^2,$$

where the summation extends over all particles in the crystal. Since it can be shown that h, k, l (the positions of the interference maxima) are the lattice points of the reciprocal lattice defined in our discussion of X-ray diffraction, it is clear that, given the interference pattern, one can obtain important information about the structure of the crystal.

Neutron Diffraction

The theory outlined above for the diffraction and scattering of X rays and electrons by crystals can be applied with some slight modification to the scattering and diffraction of neutrons. Here we outline the development as given by Ringo.[54] Using the previous results, we find that the amplitude at a distance R from a unit cell of an X-ray beam scattered by this cell is

$$A = \frac{A_0}{R}\left(\frac{e^2}{mc^2}\right)\left(\frac{1+\cos^2 2\theta}{2}\right)^{1/2} \sum_{\text{cell}} f_j e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{r}_j}$$

where A_0 is the amplitude of the incident wave, e is the charge on the electron, m is its mass, θ is one-half the angle between the direction of the incident beam and the direction of scattered beam, $\mathbf{k}$ is the wave vector of the incident beam, $\mathbf{k}'$ is the wave vector of the scattered beam, f_j is the atomic scattering factor of the jth atom in the cell, and $\mathbf{r}_j$ is the vector from a reference point in the cell to the jth atom. Since only elastic scattering is considered, $\mathbf{k}$ and $\mathbf{k}'$ both have the same magnitude, $2\pi/\lambda$; they define the scattering vector:

$$\boldsymbol{\kappa} = \mathbf{k}' - \mathbf{k}.$$

The summation in the above expression defines the structure factor F of the cell:

$$F = \sum_j f_j e^{i\boldsymbol{\kappa}\cdot\mathbf{r}_j}.$$

Thermal vibrations can be included by introducing the Debye-Waller temperature factor e^{-W_j} for each atom. Thus

$$F = \sum_j f_j e^{-W_j} e^{i\boldsymbol{\kappa}\cdot\mathbf{r}_j}.$$

For X-ray scattering, a sufficiently good approximation for W_j is

$$W_j = 8\pi^2 u_{j\kappa}^2 \frac{\sin^2\theta}{\lambda^2},$$

where $u_{j\kappa}^2$ is the mean-square displacement of the jth atom in the direction of $\boldsymbol{\kappa}$ because of thermal motion.

We can carry this analysis over to neutron scattering by writing

$$A_n = \frac{A_{0n}}{R} F_n$$

for the amplitude of the scattered neutron wave, where the cell structure factor for neutron scattering is given by

$$F_n = \sum_j f_{jn} e^{-W_{jn}} e^{i\boldsymbol{\kappa}\cdot\mathbf{r}_j}.$$

Here f_{jn} is the atomic neutron scattering factor for the jth atom in the cell. We note that this differs from the X-ray scattering formula by the absence of the polarization factor $[(1 + \cos^2 2\theta)/2]^2$, since this equals 1 for neutrons. The factor corresponding to the square of the classical radius of the electron (the electron scattering factor) has been incorporated in f_{jn}. Hence F_n is of the order of 10^{-12}, whereas F is of the order of 1. Here nuclear spins are neglected.

To pass from the scattering from a single cell to the scattering from a complete crystal, we write

$$A_n = \frac{A_{0n}}{R} F_n \sum_L e^{i\boldsymbol{\kappa}\cdot\mathbf{A}_L},$$

where $\mathbf{A}_L$ is the vector from some reference point in the crystal to the Lth unit cell.

For the intensity of the scattered wave, we obtain

$$I_n = I_{0n} \frac{|F_n|^2}{R^2} \frac{\sin^2(\frac{1}{2}n_a\boldsymbol{\kappa}\cdot\mathbf{a})}{\sin^2(\frac{1}{2}\boldsymbol{\kappa}\cdot\mathbf{a})} \frac{\sin^2[\frac{1}{2}(n_b\boldsymbol{\kappa}\cdot\mathbf{b})]}{\sin^2(\frac{1}{2}\boldsymbol{\kappa}\cdot\mathbf{b})} \frac{\sin^2[(\frac{1}{2}n_c\boldsymbol{\kappa}\cdot\mathbf{c})]}{\sin^2(\frac{1}{2}\boldsymbol{\kappa}\cdot\mathbf{c})},$$

where I_{0n} is the intensity of the incident wave, **a**, **b**, **c** are the fundamental lattice vectors that define the unit cell, and $n_a\mathbf{a}$, etc., are the dimensions of the crystal in the direction **a**, etc. The interference maxima are now given by

$$\frac{\boldsymbol{\kappa}\cdot\mathbf{a}}{2\pi} = h,$$

$$\frac{\boldsymbol{\kappa}\cdot\mathbf{b}}{2\pi} = k,$$

$$\frac{\boldsymbol{\kappa}\cdot\mathbf{c}}{2\pi} = l,$$

where h, k, l are integers, the so-called Miller indices of the crystal planes. Finally, we may write, for the structure factor for neutron scattering at the interference maxima,

$$F_n(h,k,l) = \sum_j f_j e^{-W_j} e^{2\pi i(hx_j+ky_j+lz_j)},$$

where

$$x_j = \mathbf{r}_j\cdot\mathbf{a}; \qquad y_j = \mathbf{r}_j\cdot\mathbf{b}; \qquad z_j = \mathbf{r}_j\cdot\mathbf{c}.$$

For an actual crystal, this analysis must be altered slightly to take into account nuclear spin I and the possible presence of different isotopes i at the lattice points of the crystal. To take into account the latter, we introduce an average nuclear scattering factor for nuclei at the jth site of each cell

$$f_j = \frac{1}{N}\sum_L f_j^L,$$

where the summation is over the N cells. We then have the mean structure factor

$$\bar{F} = \frac{1}{N} \sum_L F_L$$

and

$$|\bar{F}|^2 = \frac{1}{N} \sum_L F_L^2.$$

To take into account nuclear spin, we have for the coherent scattering amplitude

$$\bar{f}_j = \sum_i w_i \left[\frac{I+1}{2I+1} f_i(+) + \frac{I}{2I+1} f_i(-1) \right],$$

where w_i is the fraction of nuclei of isotope type i of nuclear spin I, $f_i(+)$ is the scattering amplitude of isotope i for parallel neutron and isotope spins, and $f_i(-1)$ is the amplitude for antiparallel spins. For incoherent scattering, we use the scattering amplitude given by

$$|f_i|^2 = \sum_i w_i \left[\frac{I+1}{2I+1} f_i^2(+) + \frac{1}{2I+1} f_i^2(-) \right].$$

For a detailed discussion of all of these points, see the article by Ringo [54] and Refs. 29, 91, and 94.

APPENDIX 2. MÖSSBAUER EFFECT AND CRYSTALS

When properly analyzed, the resonant emission or absorption of gamma rays by nuclei bound in crystals can give important information about the structure and dynamic properties of crystals. Three quantities associated with resonance absorption appear to be of particular interest in structure analysis: (1) the "no-phonon" absorption cross section, (2) the "one-phonon" absorption cross section, and (3) the second-order Doppler shift.

The first of these processes is what one ordinarily defines as the Mössbauer [114–116] effect, for in the no-phonon absorption processes, only the internal state of the nucleus changes, and no energy is interchanged between the nucleus and the crystal in which it is bound. In this "recoilless absorption" (or emission) of a gamma ray, the vibrational energy of the crystal is the same after the processes as it was before the process.

In the one-photon process, the recoil momentum of the emitted gamma ray is transferred to the nucleus in a single quantum and is then transferred to the crystal as a single quantum of vibrational energy. The third process arises because the change in mass of the emitting (or absorbing) nucleus induces a change in the vibrational energy of the crystal, which, in turn, changes the frequency of the emitted gamma ray.

To understand the Mössbauer effect, we consider a few simple equations. If an atom or a nucleus goes from an initial excited state B to the ground state A, which differs in energy from A by E_r, a photon of energy E_γ is emitted. In general $E_\gamma < E_r$, because the emitting system must have a recoil momentum equal and opposite to the momentum of the emitted photon. If $E_\gamma = E_r$, we then have resonance emission (or absorption).

If **p** is the momentum of the emitted photon and **P** that of the recoiling nucleus, we must have (nonrelativistic approximation)

$$R = \frac{P^2}{2M} = \frac{p^2}{2M} = \frac{E_\gamma^2}{2Mc^2}$$

where R is the recoil energy. Conservation of energy now gives us

$$E_r = E_\gamma + R \qquad \text{or} \qquad E_\gamma = E_r - R.$$

To a first approximation, we may write

$$R \cong \frac{E_r^2}{2Mc^2},$$

since, in general, $R \ll E_\gamma$.

Now, if Γ is the energy of the excited state B and τ is its lifetime, we have, from the uncertainty principle,

$$\tau \cdot \Gamma = \hbar.$$

Because of this, the energy of the decay processes cannot be represented as a sharply defined energy E_r but rather as a distribution around E_r. (Note that the ground state is infinitely sharp because its lifetime is infinite.) Hence the energies of the emitted photons are not all equal to $E_r - R$ but are distributed about this value.

If a photon of energy E_γ and momentum p strikes a target and is absorbed, all the momentum of the photon is transferred to the center of mass of the target which then has kinetic energy R, so that only the energy $E_\gamma - R$ can excite the absorbing atom or nucleus. Hence to excite the absorbing atom we must have

$$E_\gamma - R = E_r \qquad \text{or} \qquad E_\gamma = E_r + R.$$

Since the energies of the photons emitted by an excited system are distributed around a value $E_r - R$ and the energies of the absorbed photons that can excite the absorbing atom or nucleus are distributed around the value $E_r + R$, only photons in an overlapping region of magnitude $2R$ of the emission and absorption spectra can give rise to resonance absorption. But this overlapping can occur only if the width Γ of the level is large enough for overlapping to occur. In fact, we must have $\Gamma \gtrsim 2R$.

Now, in general, this condition is not fulfilled, but we can still obtain resonance absorption by moving the source with respect to the observer to compensate for the recoil-energy loss, either with the aid of an ultracentrifuge or by increasing the thermal motion of the emitting and absorbing systems (Doppler broadening of the line). One can also try to reduce R by fixing the emitting and absorbing nuclei in a massive crystal lattice at low temperature. This last procedure is the basis of the Mössbauer effect.

If the emitting or absorbing system has momentum $\mathbf{P}_i$ before the emitting (or absorbing) process, the energy transferred to the emitting system is just

$$R' = \frac{(\mathbf{P}_i - \mathbf{p})^2}{2M} - \frac{\mathbf{P}_i^2}{2M} = \frac{p^2}{2M} - \frac{\mathbf{p} \cdot \mathbf{P}_i}{2M}.$$

The first term is just R, as we had before, but the second term represents the Doppler broadening. If we place $\epsilon = P_i^2/2M$ (the kinetic energy of the emitting system before the emission) and let θ be the angle between the initial momentum of the emitting system and the momentum of the photon, we obtain

$$R' = \frac{p^2}{2M} - 2\left(\frac{p^2P_i^2}{4M^2}\right)^{1/2}\cos\theta$$
$$= R - 2(\epsilon R)^{1/2}\cos\theta.$$

The photon energy is thus

$$E_\gamma = E_r - R' = E_r - R + 2(\epsilon R)^{1/2}\cos\theta,$$

and we have an additional Doppler broadening superposed on the natural line width.

Now, if Γ is the total line width (the sum of the widths associated with all possible modes by which the excited nucleus can return to the ground state; here the contributions to the width by thermal motions, etc., are neglected) and Γ_γ is the gamma-ray width, then the scattering cross section at energy E is given by

$$\sigma_{\text{scatt}}(E) = \sigma_0 \frac{\Gamma_\gamma^2}{4(E - E_r)^2 + \Gamma^2}$$

and the absorption cross section is given by

$$\sigma_{\text{abs}}(E) = \sigma_0 \frac{\Gamma\Gamma_\gamma}{4(E - E_r)^2 + \Gamma^2},$$

where σ_0 is the maximum resonance cross section. If I_A is the total spin of the system in state A and I_B is its total spin in state B, then

$$\sigma_0 = \frac{2I_B + 1}{2I_A + 1}\frac{\lambda^2}{2\pi},$$

where λ is the wavelength of the gamma ray.

Since in this analysis the only important competing modes for transitions to the ground state are γ-ray emission and internal conversion (emission of an atomic electron), we have $\Gamma = \Gamma_\gamma + \alpha\Gamma_\gamma$, where α is the coefficient of internal conversion. Hence

$$\Gamma_\gamma = \frac{1}{1 + \alpha}\Gamma.$$

To obtain the effective absorption or scattering cross section, we must multiply $\sigma(E)$ by the energy distribution $I(E)\,dE$ of the incident radiation and integrate over all energy. If, now, the energy spectrum $I(E)$ of the incident gamma radiation is

$$\frac{\Gamma}{2\pi}\frac{1}{(E-E_r)^2+(\Gamma/2)^2},$$

where Γ is exactly equal to the total width of the absorbing state of the nucleus and E_r is the energy of this state, and if R, the recoil energy, is very small or zero, then

$$\sigma_{\text{eff abs}}=\sigma_0\frac{\Gamma_\gamma}{2\Gamma}=\frac{\sigma_0}{2(1+\alpha)}.$$

This is the maximum value of the resonance absorption cross section. If Doppler broadening is present because of thermal motion, we find that

$$\sigma_{\text{abs}}^{\text{Dop}}\cong\sigma_0\Gamma_\gamma/2(\epsilon R)^{1/2}.$$

We see that if α is very small (internal conversion negligible), the Doppler broadening can reduce the cross section considerably below its maximum value. In 1957, Mössbauer [114–116] investigated the resonance scattering at room temperature of 129-keV-I_r^{191} gamma rays. Since $R = 0.05$ eV for these rays and the Doppler absorption-line width at room temperature is 0.1 eV, the width of the line is just about equal to $2R$, and resonance scattering is observed. The thermal motion compensates for the recoil-energy loss.

Mössbauer reasoned that this scattering would therefore be reduced if both the source and absorber were cooled, because the Doppler width would then be so small that the emission and absorption spectra would no longer overlap. However, he found a larger scattering than at room temperature. Mössbauer explained this unexpected increase in the nuclear resonance absorption by using Lamb's theory [109] of the absorption of slow neutrons by a lattice. From this theory one finds that the binding of the crystal lattice allows the solid, as a whole, to take up the recoil momentum for a fraction of the gamma transitions, so that the vibrational state of the crystal lattice is not changed. Hence the emission and absorption spectra contain very strong lines of natural width superimposed on broad lines arising from the thermal motion of the atoms in the lattice.

According to Lamb, the cross section for resonance absorption by a nucleus in a crystal is

$$\sigma(E) = \frac{\Gamma^2}{4}\sigma_0 W_a(E),$$

where Γ is the total width of the resonance level, E is the energy of the incident gamma photons, and σ_0 is the cross section at exact resonance. $W_a(E)$ gives the position and the shape of the absorption line:

$$W_a(E) = (2/\Gamma)\,\mathrm{Re}\left\{\int_0^\infty d\mu \exp\left[i\mu\left(E - E_0 + \frac{i\Gamma}{2}\right) + g_a(\mu)\right]\right\},$$

where

$$g_a(\mu) = \sum_s \frac{(\mathbf{p}\cdot\mathbf{e}_s)^2}{2M\hbar\omega_s N}\left[(\bar{n}_s + 1)e^{-i\mu\hbar\omega_s} + n_s e^{i\mu\hbar\omega_s} - 1 - 2\bar{n}_s\right].$$

Here E_0 is the resonance energy, ω_s the frequency of the sth mode of the crystal, M the mass of the absorbing nucleus, $\mathbf{p}$ the momentum of the photon, $\mathbf{e}$ the unit polarization vector, $3N$ the number of degrees of freedom of the crystal, and $\bar{n}_s$ the average occupation number of the sth oscillator state

$$\bar{n}_s = (e^{\hbar\omega_s/kT} - 1)^{-1}.$$

We obtain a similar expression for $W_e(E)$ for the emission line with $g_e(\mu)$ replacing $g_a(\mu)$ in the integral. $g_e(\mu)$ is obtained from $g_a(\mu)$ by interchanging the coefficients of $(\bar{n}_s + 1)$ and $\bar{n}_s$ in $g_a(\mu)$.

One now evaluates the integrals for $W_a(E)$ and $W_e(E)$ in the Debye approximation with the Debye temperatures for the transverse and longitudinal modes equated. For $\mu k\Theta \ll 1$,

$$g_a(\mu) \approx -i\mu R - \mu^2 R\epsilon,$$

$$g_e(\mu) \approx i\mu R - \mu^2 R\epsilon,$$

where R is the recoil energy previously introduced and ϵ is the average energy per vibrational degree of freedom of the crystal:

$$\epsilon(T) = kT^* = 3kT\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T}\left(\frac{1}{e^t - 1} + \frac{1}{2}\right)t^3\,dt.$$

For $\mu k\Theta \gg 1$,

$$g_e(\infty;T) = g_a(\infty;T) = -\left(\frac{6R}{k\Theta}\right)\left(\frac{T}{\Theta}\right)^2 \int_0^{\Theta/T}\left(\frac{1}{e^t - 1} + \frac{1}{2}\right)t\,dt.$$

To obtain the average cross section $\bar{\sigma}_r(T_q;T_a)$, where T_q and T_a are the temperature of the source and absorber, respectively, we must multiply $\sigma(E)$ by the normalized distribution function $W_e(E)$ of the emitted photons and integrate over all energies:

$$\begin{aligned}\bar{\sigma}_r &= \int_0^\infty \sigma(E)\left(\frac{\Gamma}{2\pi}\right)W_e(E)\,dE\\ &= \frac{\Gamma^3}{8\pi}\sigma_0\int_0^\infty W_a(E)W_e(E)\,dE,\end{aligned}$$

where

$$\Gamma/2\pi\int_0^\infty W_e(E)\,dE = 1.$$

Depending on the value of $|E - E_0|$ as compared to Γ, one obtains different values for $W(E)$. For $E \cong E_0$ (near resonance),

$$W_e(E) = \frac{4}{\Gamma^2}\psi(\xi_e;x_e) + \frac{\exp\,[g_\infty(T_q)]}{(E - E_0)^2 + (\Gamma^2/4)},$$

$$W_a(E) = \frac{4}{\Gamma^2}\psi(\xi_a;x_a) + \frac{\exp\,[g_\infty(T_a)]}{(E - E_0)^2 + (\Gamma^2/4)},$$

where

$$\begin{aligned}\psi(\xi,x) &= \tfrac{1}{2}\sqrt{\pi}\,\xi\exp\,[-\xi^2x^2/4],\\ x &= 2(E - E_0 + R)/\Gamma,\\ \xi &= \Gamma/\Delta\end{aligned}$$

and Δ is just the Doppler width.

From the expressions for W_e, W_a, and $\bar{\sigma}_r$, we see that the absorption cross section has two nonnegligible terms, one of which dominates at high temperatures (the Doppler broadening) and the other of which dominates at low temperatures (the natural line width). This last term accounts for the Mössbauer effect.

For a complete discussion see *The Mössbauer Effect*, edited by Frauenfelder.[20] This contains an elementary presentation and has the original papers of Lamb and of Mössbauer with sections of the latter translated into English. See also Refs. 64, 65, and 113.

6

Physical Properties of Crystal Lattices

6-1 SPECIFIC HEATS OF SOLID BODIES

The study of the dynamics of crystal lattices and, in particular, of their vibrations was developed in parallel with the theory of the specific heats of solid bodies. In our treatment also, we study the two problems together.

For the study of the specific heats of solid bodies, the Dulong-Petit law is of fundamental importance. This law states that the specific heat, referred to a gram-atom, has the same value for all elements in the solid state: about 6 cal/deg. There are some notable exceptions to the Dulong-Petit law (e.g., carbon and boron), nor is it valid for the other elements at low temperatures; there the specific heat is always below the value required by the law. Opposite deviations occur at high temperatures.

We shall discuss these phenomena in a moment. We first note that the Dulong-Petit law can be immediately interpreted by classical statistics. According to the principle of equipartition of energy, each degree of freedom of the system (in thermal equilibrium) has an average kinetic energy $kT/2$. Each atom of the body therefore has on the average the kinetic energy $3kT/2$. On the other hand, we know that in a system oscillating under the action of elastic forces, the average kinetic energy is equal to the potential energy; since the atoms of a body can be considered material points which, to a first approximation, at least, exert elastic-type forces on each other, we have, besides the average kinetic energy $3kT/2$, an equal amount of potential energy. The total energy of the body, referred to one atom, is thus $3kT$; referred to 1 gram-atom, it is

$$W = 3RT. \tag{1}$$

From this expression for the thermal energy we can immediately derive the specific heat:

$$C = \frac{dW}{dT} = 3R. \tag{2}$$

Since the constant R, in calories, is almost exactly 2, the specific heat for each gram-atom is about 6, which is indeed the value required by the Dulong-Petit law.

We have already mentioned deviations from the Dulong-Petit law, which occur at very low temperatures. We first examine the effect of very high temperatures, which can be easily understood without leaving classical statistics. The increase in specific heat above the Dulong-Petit value, observed at high temperatures, depends, according to Born and Brody,[73] on the nonelasticity of the forces between the atoms of a body: When the relative displacements of the atoms exceed certain limits, the proportionality between force and displacement begins to disappear. Thus, although in the case of exactly elastic forces the average kinetic energy and the potential energy are the same, this, of course, is not true if the forces are only quasi-elastic. The differences are more noticeable the larger the amplitudes of the vibrations, because the deviations from the laws of elasticity are then more pronounced. One can demonstrate that the deviations from the laws of elasticity in the solid bodies act in a direction such that the average potential energy exceeds the average kinetic energy. The thermal energy is thus larger than the value given by (1), and the atomic heat exceeds the Dulong-Petit value [Eq. (2)]. The effect becomes noticeable only at high temperatures, where the amplitudes of the thermal vibrations of the atoms are large.

More important and more interesting are the low-temperature deviations from the Dulong-Petit law. The behavior of the specific heat at low temperatures is represented in Fig. 36. The absolute temperature is given along the abscissa and the specific heat along the ordinate.

In the region of normal temperatures the atomic heat has the value $3R$ (it is larger at very high temperatures for the reasons mentioned above); at low temperatures the atomic heat decreases, going toward zero for zero absolute temperature. The temperatures at which the specific heat begins to drop appreciably below the Dulong-Petit value are not the same for all elements; usually they are sufficiently below the ordinary temperature so that the values of the specific heats measured at ordinary temperature agree with the law. Only exceptionally do some elements such as boron and carbon have specific heats below the Dulong-Petit value even at temperatures higher than the ordinary, so that at ordinary temperatures the specific heats of these elements are smaller than those predicted by the law.

The explanation of the low-temperature deviations from the Dulong-Petit law was first given by Einstein,[83] in 1907, and was one of the first experimental confirmations of the quantum theory, which at that time was in its early stage. Einstein used a very rough model of a solid body in his analysis. He assumed each atom to be independent of all others and subject to an elastic force which restored it to its equilibrium position. Each atom was allowed to vibrate in the directions of the three axes, thus corresponding to three harmonic oscillators. A body

Figure 36

of this sort, containing N atoms, thus corresponds to $3N$ oscillators, all of which have the same frequency ν.

According to classical statistics, each harmonic oscillator has, in thermal equilibrium, the same energy kT ($kT/2$ for the kinetic energy and the same amount for the potential energy). The energy of the $3N$ oscillators of the body is then, according to this theory, $3NkT$, giving a specific heat in agreement with the Dulong-Petit law. But according to quantum statistics,* the average energy of an oscillator depends not only on the temperature but also on the frequency of the oscillator.

We have

$$w = \frac{h\nu}{e^{h\nu/kT} - 1}. \tag{3}$$

This expression, at high temperatures, approaches the classical value of kT asymptotically, whereas it is always smaller for low temperatures.

The thermal energy of the solid body must then be taken, according to Einstein, as $3N$ times the energy (3):

$$W = \frac{3Nh\nu}{e^{h\nu/kT} - 1}. \tag{4}$$

From this we obtain the specific heat:

$$C = \frac{dW}{dT} = \frac{3Nh\nu}{(e^{h\nu/kT} - 1)^2} \frac{h\nu}{kT^2}. \tag{5}$$

This formula shows that the qualitative behavior of c as a function of temperature is not different from that given in Fig. 36. Also the frequency of the $3N$ oscillators, which we can derive by comparing Eq. (5) with the observed specific heats, coincides in order of magnitude with the vibrational frequencies of the atoms of the solid body observable in the infrared. We can say, therefore, that the Einstein theory of specific heats, in spite of its very rough assumptions, already represents a reasonable approximation to reality.

However, there are serious discrepancies between Eq. (5) and experiment, particularly at very low temperatures. According to (5), the specific heat at very low temperatures should go to zero much faster than it actually does.

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* For quantum statistics see Part III of this volume.

6-2 THE DEBYE THEORY OF SPECIFIC HEATS

The discrepancies between theory and experiment disappear in the Debye theory [78] which takes into account that a body can vibrate with a large number of characteristic frequencies and not with only one, as assumed in the Einstein theory. However, in the Debye theory, also, the problem must be simplified and developed schematically as follows:

We completely neglect, at first, the atomic structure of the solid body and consider it a continuous elastic body as is usually done in the classical theory of elasticity. We know that an elastic body of definite shape with definite dimensions, elastic modulus, and density can vibrate with an infinite number of well-defined frequencies, just as a stretched string can vibrate with infinitely many frequencies (the fundamental and all its multiples).

If c_1 and c_2 are the propagation velocities of the elastic transverse and longitudinal waves inside the body (assumed isotropic), the number of characteristic frequencies of the body between ν and $\nu + d\nu$ is given asymptomatically, that is, for large values of ν, by

$$dn = 4\pi\left(\frac{2}{c_1^3} + \frac{1}{c_2^3}\right)V\nu^2\,d\nu, \tag{6}$$

where V is the volume of the body.

According to this equation, the body has an infinite number of characteristic frequencies; they correspond to the infinite number of degrees of freedom of a continuous elastic body. But all bodies contain only a finite number N of atoms and therefore have only $3N$ degrees of freedom, and hence a maximum of $3N$ characteristic frequencies. It follows, therefore, that some of the frequencies given by (6), in effect, the higher ones, are not present because of the atomic structure of the body. Indeed we shall see later that the atomic structure modifies the formula for the propagation of elastic waves with a wavelength of the order of the distances between atoms; in effect, Eq. (6) is not valid at high frequencies.

Debye assumed a model of a solid with the following properties: Each solid body has a maximum frequency $\nu_{\max}$ beyond which there are no other characteristic frequencies. Below $\nu_{\max}$ the distribution of the characteristic frequencies is still given by Eq. (6). We shall see later that we can justify, at least in part, these assumptions which are sufficient for dealing with the problem of specific heats.

The frequency ν_{max} can be calculated from the condition that the number of frequencies below it, as computed from (6), must equal the number of degrees of freedom of the body—$3N$. We must therefore have*

$$3N = \int_0^{\nu_{\mathrm{max}}} 4\pi\left(\frac{2}{c_1^3} + \frac{1}{c_2^3}\right)V\nu^2\,d\nu = \frac{4\pi V}{3}\left(\frac{2}{c_1^3} + \frac{1}{c_2}\right)\nu^3{}_{\mathrm{max}}. \tag{7}$$

To calculate the thermal energy of the body, we can now, according to Debye, assign to each characteristic frequency an energy given by Eq. (3). This means assigning to this frequency the average energy derived from quantum statistics for an oscillator with the same frequency.

With dn frequencies in the interval $d\nu$, the thermal energy of the body is

$$W = \int \frac{h\nu}{e^{h\nu/kT} - 1}\,dn = 4\pi V\left(\frac{2}{c_1^3} + \frac{1}{c_2^3}\right)\int_0^{\nu_{\mathrm{max}}} \frac{h\nu^3\,d\nu}{e^{h\nu/kT} - 1}.$$

Taking $x = h\nu/kT$ as a new variable and using Eq. (7), we then find

$$W = 3Nk\frac{3T^4}{\Theta^3}\int_0^{\Theta/T} \frac{x^3\,dx}{e^x - 1}, \tag{8}$$

where we have put

$$\Theta = \frac{h\nu_{\mathrm{max}}}{k}. \tag{9}$$

Θ has the dimensions of a temperature and is a characteristic constant of each substance. We can calculate it from (7) and (9) if we know the elastic properties of the substance.

From Eq. (8), taking the derivative with respect to T, one obtains the thermal capacity of the body

$$C = 3NKD\left(\frac{T}{\Theta}\right), \tag{10}$$

where D is the following function:

$$D(\xi) = 12\xi^3\int_0^{1/\xi} \frac{x^3\,dx}{e^x - 1} - \frac{3/\xi}{e^{1/\xi} - 1}. \tag{11}$$

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* *Editor's note:* See the material appended to this chapter for a criticism of the Debye theory.

Notice, in particular, that the function D introduced here is completely independent of the nature of the substance; the properties of the substance enter only through the characteristic temperature Θ.

It is interesting to study the two extreme cases: $T \gg \Theta$ and $T \ll \Theta$. From (11) we obtain

$$\lim_{\xi \to \infty} D(\xi) = 1;$$

for $\xi < 1$, making use of integral

$$\int_0^\infty \frac{x^3\,dx}{e^x - 1} = \frac{\pi^4}{15},$$

we have the asymptotic expression

$$D(\xi) = \frac{4\pi^4}{5}\,\xi^3.$$

Since $Nk = R$ for a gram-mole, we have from (10), in the limiting case of very high temperatures

$$C = 3R,$$

that is, the Dulong-Petit law. In the limiting case of very low temperatures, the result, instead, is

$$C = \frac{12\pi^4}{5}\,\frac{R}{\Theta^3}\,T^3 \tag{12}$$

at low temperatures; therefore, the specific heat is proportional to the third power of the absolute temperature.

The theory is found to be in excellent agreement with experimental results; this is remarkable since the constant Θ in (10) is calculated solely from measurements of the elastic constants without any thermal data.*

In agreement with theory, experiments show that the specific heat at very low temperatures is proportional to T^3. As predicted by Eq. (10), the curves of the atomic heats of two different solids as functions of T are identical if the temperature units are properly chosen (property of corresponding states).

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* *Editor's note:* See appended material for a discussion of this point in terms of recent developments.

6-3 ELASTIC PROPERTIES OF A ONE-DIMENSIONAL LATTICE

In the Debye theory of specific heats, the atomic structure of matter appears only through the somewhat arbitrary cut-off of the vibrational frequencies of the body at $\nu_{\max}$. In this section we shall discuss more precisely the effect of the atomic structure on the propagation of the elastic waves through a body.

We start by considering a very simple model which, however, gives insight into the more complex real picture. We consider a line of identical atoms, arranged at regular intervals in a row. Each atom can be thought of as being bound to the two adjacent atoms by an elastic force which acts to keep them at their equilibrium positions, separated by the distance a. Thus we have a simple model of a one-dimensional crystal (simple unidimensional lattice). We shall study the elastic properties of such a model.

Let us displace the atoms of the row from their equilibrium positions, but always along the row. Call ξ_n the displacement of the nth atom. Two forces act on the nth atom, owing to the elastic bonds connecting it to the $(n+1)$th and $(n-1)$th atom. Since the relative displacements are $\xi_{n+1} - \xi_n$ and $\xi_{n-1} - \xi_n$, the two elastic forces are $k(\xi_{n+1} - \xi_n)$ and $k(\xi_{n-1} - \xi_n)$, where k is the coefficient of the elastic binding between each atom. Thus the force acting on the nth atom is $k(\xi_{n+1} + \xi_{n-1} - 2\xi_n)$. If m is the mass of the atom, its motion is determined by the equation

$$m\ddot{\xi}_n = k(\xi_{n+1} + \xi_{n-1} - 2\xi_n). \tag{13}$$

If the row of atoms extends to infinity on both sides, we have an infinite system of equations of the form (13), where n takes on integer values (positive, negative, or zero).

One can easily solve this system of equations and obtain the elastic waves that propagate along the line of atoms. We introduce

$$\xi_n = A \cos 2\pi(\nu t - gn) \tag{14}$$

into Eq. (13) and find that (14) is a solution if the following condition is satisfied:

$$\nu = \frac{1}{\pi}\sqrt{\frac{k}{m}} \sin \pi g. \tag{15}$$

Equation (14) represents an elastic wave that propagates along the line. The wavelength λ is simply

$$\lambda = \frac{a}{g}, \tag{16}$$

since a is the distance between two adjacent atoms. Using this relation, we can rewrite (15) as

$$\nu = \frac{1}{\pi}\sqrt{\frac{k}{m}}\sin\frac{\pi a}{\lambda}. \tag{17}$$

From the last equation we can already see that

$$\nu \leq \frac{1}{\pi}\sqrt{\frac{k}{m}},$$

that is, no elastic waves exist propagating along the line at a frequency higher than $(1/\pi)\sqrt{k/m}$. The existence of this maximum frequency somewhat justifies the introduction of a limiting frequency in Debye's theory.

Multiplying Eq. (17) by λ and recalling that $\nu\lambda$ is equal to v, the propagation velocity of the waves, we have

$$v = \frac{1}{\pi}\sqrt{\frac{k}{m}}\lambda\sin\frac{\pi a}{\lambda}. \tag{18}$$

The propagation velocity, therefore, depends on the wavelength. This is typical of the propagation of elastic waves in a medium with an atomic structure; in a continuous elastic medium, instead, it is well-known that the propagation velocity is a constant which does not depend on the wavelength.

For sufficiently large values of $\lambda(\lambda \gg a)$, we can replace the sine by the arc in (18) and obtain

$$v = a\sqrt{\frac{k}{m}}.$$

In this limiting case, which corresponds to the ordinary theory of elasticity, where the atomic structure does not enter, one finds, indeed, that the propagation velocity is independent of the wavelength. For wavelengths of the order of the interatomic distance, instead, the propagation velocity is smaller.

From the point of view of the dynamics of crystal lattices, it is particularly interesting to determine the characteristic frequencies of a body of finite size. As a one-dimensional model of this we can take a row of N atoms of finite length. We may assume, as boundary conditions, that the two extremities of the row are fixed; this, however, would introduce complications in the motion near the ends of the row and make the analytic treatment of the problem more difficult. We thus prefer, in this and similar problems, to replace the preceding condition by another, which although physically equivalent, can be treated more easily mathematically. We consider an infinite row with the following periodicity condition: Atoms differing by N places must have, at any moment, the same displacement. We see immediately that the properties of an infinite array subject to the above condition correspond to those of a line of N atoms. Notice that if the N atoms are so arranged that the two extremities of the row meet, as, for example, when the N atoms are on the circumference of a circle, the condition of periodicity is automatically valid. Indeed, the order of each atom in the closed row is determined only up to an integer multiple of N. The analytical advantage of this is that the extremities of the row are eliminated.

We must now determine the characteristic frequencies of a row. For this we must find those solutions of Eqs. (13) which represent the atoms vibrating with frequency ν. We can take

$$\xi_n = \eta_n \cos (2\pi\nu t + \beta), \tag{19}$$

where η_n is independent of time and satisfies the periodicity condition

$$\eta_n = \eta_{n+N}. \tag{20}$$

Substituting (19) in Eq. (13), we have

$$-4\pi^2\nu^2 m\eta_n = k(\eta_{n+1} + \eta_{n-1} - 2\eta_n). \tag{21}$$

This system of equations can be solved by either

$$\eta_n = \cos \pi g n \qquad \text{or} \qquad \eta_n = \sin \pi g n. \tag{22}$$

If we substitute these in Eqs. (21), we can easily verify that Eqs. (21) are satisfied only if

$$\nu = \frac{1}{\pi}\sqrt{\frac{k}{m}} \sin \pi g, \tag{23}$$

which is identical to (15). It is clear that, since Eqs. (21) are linear in the η's, any linear combination of the two fundamental solutions (22) also satisfies (21).

We still have to impose the periodicity condition (20). If the two fundamental equations (22), and, of course, any linear combination of them are to satisfy (20), it is obviously necessary and sufficient that

$$gN = 2f, \tag{24}$$

where f is an integer. The two fundamental solutions (22) then become

$$\eta_n = \cos\frac{2\pi f}{N}n \qquad \text{and} \qquad \eta_n = \sin\frac{2\pi f}{N}n. \tag{25}$$

There are two linearly independent solutions for each value of f. Notice, however, that the solutions corresponding to values of f whose difference or sum is an integer multiple of N are, in effect, identical (they are equal, apart from sign). Therefore it is sufficient to consider the integer values of f from 0 to $N/2$. More precisely, if N is even, f can take on the values

$$f = 0, 1, 2, \ldots, \frac{N}{2},$$

and, if N is odd,

$$f = 0, 1, 2, \ldots, \frac{N-1}{2}.$$

Only one of the solutions (25) exists if f equals 0 or $N/2$, because the second solution is then identically zero. For all other values of f there are two independent solutions so that there is a total of N independent solutions for both N even and N odd.

We obtain the corresponding frequencies by inserting into Eq. (23) the value of g from Eq. (24):

$$\nu = \frac{1}{\pi}\sqrt{\frac{k}{m}}\sin\frac{2\pi f}{N}. \tag{26}$$

For each value of f, from 0 to $N/2$, there is a characteristic frequency which, except for the cases $f = 0$ and $f = N/2$, can be considered double because it corresponds to the two distinct solutions (25).

6-4 VIBRATIONS OF SIMPLE AND COMPOSITE LATTICES

The analysis in the previous section can be generalized to the case of a spatial crystal whose atoms occupy the points of a simple lattice. One finds that elastic waves can propagate in such a crystal. If the wavelength and the direction of propagation of the waves (the crystal is anisotropic) are given, the frequency can be determined. The propagation velocity, as in the case of the linear array of atoms, depends on the wavelength. This dependency is particularly noticeable for wavelengths of the order of the interatomic distances; but for large wavelengths, the ordinary laws of propagation of elastic waves in continuous media are valid.

Things are rather different in a crystal with a composite lattice. This can easily be seen by examining the possible vibrations with infinite wavelength (those for which all the atoms of the same simple lattice are vibrating in the same phase). If the crystal consists of a single simple lattice, the only motion corresponding to an infinite wavelength is a translation motion of the whole crystal; obviously this motion has zero frequency. But if the crystal lattice consists, for example, of two simple lattices, the motions with infinite wavelength are not necessarily only translational motions. Indeed, motion in which each of the two simple lattices undergoes a translation and the two lattices oscillate with respect to each other has an infinite wavelength. Similarly, if we have more than two simple lattices, we can have different vibrations in which each simple lattice oscillates with respect to the others without changing its shape; all these vibrations have infinite wavelength. We call these vibrations with infinite wavelength *principal* or *fundamental* vibrations and the corresponding frequencies *fundamental* frequencies.

One can demonstrate that in a crystal whose lattice consists of r simple lattices there are usually $3r$ frequencies (some of them may coincide) for each wavelength and propagation direction of the elastic waves. When the wavelength approaches infinity, three of these frequencies, which we may call the *acoustic* frequencies, go smoothly to zero; for a wavelength long with respect to the interatomic distances, the three corresponding motions coincide with the three elastic waves derived from the ordinary theory of elasticity, where the discontinuous structure of the crystal is neglected. (Usually, in an anisotropic body, there are three waves with different frequencies; but for an isotropic

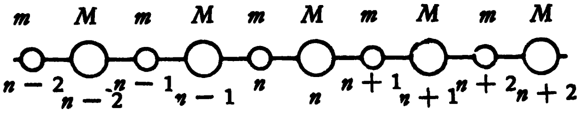

Figure 37

body, two of them, the transverse waves polarized along two different directions, have equal frequencies, different from the frequency of the longitudinal wave of equal wavelength.)

The remaining $3r - 3$ frequencies, when the wavelength becomes infinite, go over smoothly to the principal frequencies of which there are, in fact, $3r - 3$, some of which may coincide.

These points can be illustrated by a simple example of a one-dimensional composite lattice. We consider a row of atoms on a straight line with the equilibrium distance between successive atoms equal to a. We assume that there are two different kinds of atoms, with masses m and M, in alternate positions along the line. As in the case of the row in Section 6-3, we assume that each atom is elastically connected to the two adjacent atoms. We want to study the propagation of elastic waves in this one-dimensional model of a composite lattice.

We assign to the successive atoms of type m serial numbers n and assign the same numbers to the atoms M, in such a way that the atom m with number n has the atom M with number $n - 1$ on one side of it and the atom M with number n on the other side of it (see Fig. 37). In the same way, the atom M with number n is surrounded by the atoms m with numbers n and $n + 1$. Let ξ_n be the displacement of the nth atom m and η_n the displacement of the nth atom M. The force exerted on the nth atom m by the two elastic bonds which connect it with the two adjacent atoms M is given by

$$k(\eta_n + \eta_{n-1} - 2\xi_n),$$

where k is the elastic coefficient of the bond; similarly, the force exerted on the nth atom M is

$$k(\xi_{n+1} + \xi_n - 2\eta_n),$$

Therefore, the equations of motion of the two atoms are:

$$\begin{aligned} m\ddot{\xi}_n &= k(\eta_n + \eta_{n-1} - 2\xi_n), \\ M\ddot{\eta}_n &= k(\xi_{n+1} + \xi_n - 2\eta_n). \end{aligned} \tag{27}$$

When n assumes all the integer values (positive, negative, or zero), the system of equations we obtain describes the motion of the row of atoms. We are interested in those solutions which describe the propagation of elastic waves along the row. Let us try to satisfy Eqs. (27) with the following substitutions:

$$\begin{aligned} \xi_n &= Ae^{2\pi i(\nu t - gn)}, \\ \eta_n &= Be^{2\pi i(\nu t - gn)}. \end{aligned} \tag{28}$$

Here we have used exponentials in place of trigonometric functions to simplify the calculations. Equations (28) describe the propagation of elastic waves with a wavelength

$$\lambda = \frac{2a}{g} \tag{29}$$

(notice that the period of the lattice is $2a$, and not a). Substituting Eqs. (28) in (27) we find, after a few easy reductions,

$$\begin{aligned} -4\pi^2\nu^2 mA &= k[B(1 + e^{2\pi i g}) - 2A], \\ -4\pi^2\nu^2 MB &= k[A(1 + e^{-2\pi i g}) - 2B]. \end{aligned} \tag{30}$$

This system of linear homogeneous equations in A and B has solutions different from zero only if its determinant is zero:

$$\begin{vmatrix} 4\pi^2\nu^2 m - 2k & k(1 + e^{2\pi i g}) \\ k(1 + e^{-2\pi i g}) & 4\pi^2\nu^2 M - 2k \end{vmatrix} = 0.$$

This equation, after a few transformations and with the aid of Eq. (29), can be written in the form

$$(4\pi^2\nu^2)^2 - 2k\,\frac{m + M}{mM}\,(4\pi^2\nu^2) + \frac{4k^2}{mM}\sin^2\frac{2\pi a}{\lambda} = 0. \tag{31}$$

From this last equation we obtain a relation between the frequency

ν and the wavelength λ. Solving (31) for $4\pi^2\nu^2$, we find

$$4\pi^2\nu^2 = \frac{k}{mM}\left[m + M \pm \sqrt{m^2 + M^2 + 2mM\cos\frac{4\pi a}{\lambda}}\right]. \quad (31')$$

For each value of λ there are two values of ν (apart from the sign); in the one-dimensional model of a simple lattice we found, instead, only one frequency for each wavelength.

The dependence of the frequency on the wavelength is shown in Fig. 38. The inverse wavelengths (the wave numbers) are plotted along the abscissa and the frequencies along the ordinate.

In the limiting case of $\lambda = \infty$, that is, $1/\lambda = 0$, the two solutions (31′) become

$$4\pi^2\nu_\infty^2 = \begin{cases} \dfrac{2k(m + M)}{mM}, \\ 0. \end{cases} \quad (32)$$

Thus, one of the two frequencies (31′) goes to zero (acoustic frequency) and the other approaches a nonzero finite limit as $\lambda \to \infty$. This limit is the only principal or fundamental frequency of our model. We see

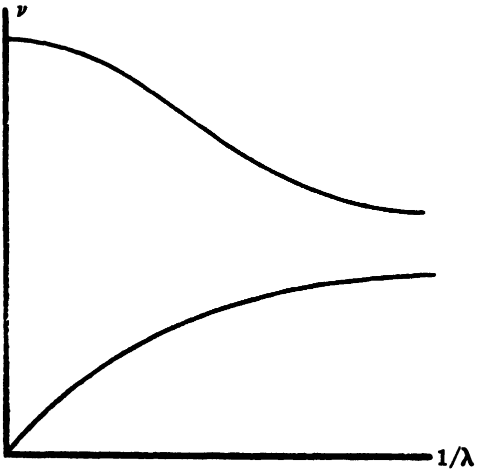

Figure 38

that the corresponding motion is a vibration in which the row of *m* atoms oscillates as a group relative to the row of *M* atoms as a group without the distances between any two *m* atoms or between any two *M* atoms changing.

6-5 INFRARED FREQUENCIES AND RESIDUAL RAYS

The principal frequencies of a crystal can be measured by observing its infrared absorptions. The best procedure is to analyze the absorption of the infrared radiation by a very thin layer of the crystal. In many cases, however, the residual-rays method is preferred because it is easier.

The infrared radiation emitted by a source with a continuous spectrum is reflected a few times from the surface of the crystal and is then analyzed by a prism or an infrared grating. Its spectral distribution is then measured photometrically with a thermocouple. Anomalies can then be observed in the reflected intensity near the principal frequencies of the crystal.

It is easy to see from the following considerations that only the principal frequencies of the crystal, and not all the other very numerous characteristic frequencies, are observed in the infrared absorption. Since the infrared wavelength is much larger than the interatomic distances, we can always concentrate on a portion of the crystal that is small with respect to the wavelength of the infrared light but large enough to contain many atoms. It is well-known that the emission or the absorption of a system whose dimensions are small with respect to the wavelength, as in the case of our portion of the crystal, is determined by the variations of the electric moment of the system. When one of the characteristic frequencies is excited, the crystal suffers a deformation; if the vibration is a principal one, all the parts of the crystal oscillate in phase, so that, in general, there is a variation of the over-all electric moment of the crystal, owing either to the displacement of the electric charges inside the atoms or to the displacement of the ions if the crystal lattice consists of ions. The frequency of the variation of the electric moment is, of course, the same as that of the corresponding principal vibration. The principal frequencies can thus be observed in the infrared.

If, instead, a characteristic frequency other than a principal one is excited, different regions in the crystal oscillate with different phases and produce variations in the partial electric moments that are out of phase. As a consequence, the average variation of the total electric moment over the whole crystal is zero, and our frequency will not be observed in the infrared. In many cases, of course, the symmetry of the crystal is such that some of the principal frequencies are inactive in the infrared, because the corresponding vibrations do not produce a variation of the electric moment.

We can illustrate these points with fluorite, whose lattice (See Fig. 34) consists of three face-centered cubic lattices; one is occupied by calcium atoms; the other two, which together constitute a simple cubic lattice with its cell side equal to half the cell side of the face-centered lattice, are occupied by fluorine atoms. It is easily seen that this composite lattice has two distinct principal frequencies; the corresponding vibrations can be described in the following way.

ν_1 is the frequency of vibration of the Ca lattice with respect to the two F lattices, which remain fixed with respect to each other. Since the calcium fluoride lattice is an ionic lattice, composed of the Ca^{++} and F^- ions, the displacement of the calcium ions with respect to the fluorine ions produces an electric moment; thus the frequency ν_1 is active in the infrared.

ν_2 is the vibrational frequency of the two fluorine lattices moving alternately in opposite directions while the Ca lattice remains fixed. It is clear, for reasons of symmetry, that this vibration does not produce an electric moment; thus the frequency ν_2 is inactive in the infrared.

The sodium chloride lattice (Fig. 33) has only one principal frequency: that of the vibration of the two simple lattices of chlorine and of sodium with respect to each other. This frequency is obviously active in the infrared, because the corresponding motion produces a variable electric moment in the crystal.

The diamond lattice (Fig. 32) also has only one principal frequency: that of the vibration of the two face-centered lattices which constitute the diamond, relative to each other. This vibration, however, is inactive in the infrared because, for obvious reasons of symmetry, the corresponding displacement does not produce an electric moment.

One should note that the resolving powers of the methods used to observe the infrared frequencies are often quite small and not always very useful for the exact determination of the principal frequencies of crystals.

6-6 RAMAN EFFECT IN CRYSTALS

In many cases the principal frequencies of a crystal can be obtained much more accurately by combining the results obtained from infrared absorption with observations of the Raman effect. The Raman spectrum of a crystal consists, in general, of one or more usually well-defined lines. The differences between the frequencies of the Raman lines and the frequency of the exciting line are normally the principal frequencies of the crystal. The Raman lines of crystals usually have polarization characteristics which depend on the orientation, with respect to the crystallographic planes, of the plane of polarization of the primary light and of the direction of observation.

The Raman effect in crystals can be analyzed theoretically by methods analogous to those developed in Section 4-8, for the Raman effect in polyatomic molecules. The effect is determined by the periodic variations of the polarizability of the crystal which occur when the crystal is set vibrating. One can show to a first approximation that, in the Raman effect in a crystal, only those frequencies occur for which the wavelengths of the corresponding elastic vibrations are of the same order of magnitude as those of the light waves. Since the latter are always much larger than the interatomic distances, the corresponding elastic frequencies are practically the principal or fundamental frequencies of the crystal.

This can be easily understood if we consider, as we did for the infrared, a portion of the crystal small with respect to the wavelength of the light but large enough to contain a great number of atoms. The light diffusion is then determined by the variations of the electric moment M induced in the crystal by the electric field E of the primary light. M depends on the polarizability α of the crystal according to the formula

$$M = \alpha E \tag{33}$$

(in general, α is a tensor instead of a scalar, and refers to the unit volume).

The polarizability of the crystal for some elastic oscillations is not the same all over the crystal, because the polarizability is influenced by the deformations of the vibrating crystal, which differ from place to place. To a first approximation, the change in the polarizability at a given point can be taken as proportional to the elastic deformation at that point. The effect then of an elastic wave of short wavelength, to this approximation, is equal and opposite in regions of opposite phase and vanishes when averaged over the whole crystal. There is an average variation of the polarizability different from zero only if the whole crystal oscillates in the same phase. This happens when the elastic wavelength is practically infinite with respect to the interatomic distances; consequently, there is a variation in the average value of the polarizability only when one of the principal frequencies is excited. In this case, periodic vibrations of the polarizability α occur with the frequency ν of the principal vibration. Since the electric field E oscillates with the frequency ν_0 of the primary light, the analysis of the electric moment M into harmonic components shows, by way of Eq. (33), that a large component with frequency ν_0 is present. This gives rise to the scattered light with unmodified frequency and the components with frequencies $\nu_0 \pm \nu$ corresponding to the Stokes and anti-Stokes Raman lines.

These classical considerations can be translated into quantum language, and we still find that only the principal frequencies appear in the Raman effect, at least when we do not go beyond the first approximation.

In crystals, as in polyatomic molecules, some of the principal frequencies are inactive in the Raman effect because of a particular symmetry. This happens when the corresponding vibration does not produce, to a first approximation, a variation of the electric polarizability of the crystal. Thus, for example, in fluorspar, whose principal frequencies ν_1 and ν_2 were described in the previous section, the frequency ν_1 is active in the infrared but inactive in the Raman effect. It is clear, indeed, that the symmetry of the vibration ν_1 is such that, in situations of opposite phase, the crystal has the same polarizability, that is, it is quadratic in the displacement from equilibrium. Therefore, at least in the first order, the polarizability is not influenced by this vibration. The frequency ν_2, instead, is inactive in the infrared but active in the Raman effect. In fact, it is observed in the Raman spectrum of fluorite, which consists of only one line with frequency 321 cm^{-1}.

In certain cases there are no crystal frequencies active in the Raman effect, at least to a first approximation. This happens for all crystals having a simple lattice, because in this case there are obviously no principal frequencies. It may also happen that all the principal frequencies of a crystal with a composite lattice are inactive in the Raman effect. Let us consider, for example, rock salt, whose lattice is shown in Fig. 33. This crystal has only one fundamental frequency corresponding to the vibration of the two lattices (chlorine and sodium) relative to each other. This frequency, as we said in the previous section, is active in the infrared but inactive in the Raman effect. It is clear, indeed, that the vibrating crystal has identical polarizability in two positions with opposite phase; the polarizability, therefore, is not influenced by the vibration, at least up to terms of the first order.

In effect, if we observe with the usual methods the light diffused in a crystal of rock salt, we do not find any Raman line. Only by using special arrangements which greatly increase the intensity did Rasetti [124–126] observe a Raman effect in rock salt. This effect, however, is very different from the usual Raman effects observed in crystals; it consists not of discrete lines but of a continuous spectrum with a somewhat irregular intensity distribution which extends up to a frequency of about 365 cm^{-1}.

The Raman effect in rock salt is a second-order effect. Its origin can be understood by observing that the electric polarizability α, to a first approximation, depends linearly on the elastic deformation. In the second-order approximation, the quadratic terms must also be taken into account. We consider a characteristic vibration that is not a fundamental vibration. For this vibration the linear terms in the dependence of α on the deformation vanish, on the average, over the whole crystal, because regions of the crystal that vibrate in opposite phase contribute terms of opposite sign which cancel each other. The quadratic terms, instead, although much smaller, have an average value different from zero and therefore affect the diffusion of the light, thereby producing a Raman effect. Whereas the frequencies observed in the first-order Raman effect are only the fundamental ones, which produce a Raman spectrum with isolated lines, all the characteristic frequencies are active in the second-order Raman effect so that in this case the Raman spectrum is continuous.

A more accurate analysis shows that the second-order Raman effect must extend up to twice the maximum vibrational frequency of the crystal and justifies, at least qualitatively, the apparent random distribution of the maxima and minima of the intensity.

6-7 THERMAL EXPANSION AND HEAT CONDUCTION IN CRYSTALS

In this section we briefly discuss, in a qualitative way, the basic features of the thermal expansion of and heat conduction in crystals. In particular, we shall limit our considerations of heat conduction to the electrically nonconducting crystals; heat conduction in electrical conductors is closely connected to the subject of electrical conductivity.

Both thermal expansion and heat conduction (in the electrically nonconducting crystals) are closely related to the fact that the forces binding the atoms of the crystal lattice are not exactly elastic. These forces are proportional to the displacement only as long as the latter is small; for larger displacements, the quadratic and higher terms become appreciable.

We first discuss thermal expansion. To understand it qualitatively it is better to limit our considerations to two atoms—a diatomic molecule. We want to show that the increase in temperature produces an increase in the average separation of the two atoms. In a crystal, the thermal-expansion mechanism is obviously analogous to this; the thermal motion tends to increase the average distance between adjacent atoms, thus resulting in an over-all expansion of the crystal.

We consider two atoms, A and B, and let a be their equilibrium separation. We further simplify the problem by constraining the two atoms to move along a fixed line. Owing to the thermal motion, they oscillate about their equilibrium positions, and we call $a + \xi$ the distance between them at a certain instant. The force that restores the two atoms to their equilibrium positions is approximately equal to

$$f = -\alpha\xi + \beta\xi^2, \tag{34}$$

where α and β are constants. The first term, proportional to the displacement ξ, is an elastic force and is the principal term (the negative coefficient means that the force is attractive). The second term is quadratic, usually much smaller than the first, and gives the deviations from the laws of elasticity. In a further approximation, one should take into account also higher-order terms, which, however, are not important for these qualitative considerations.

We do not need quantum mechanics for this problem; classical mechanics and statistics are sufficient. As long as the oscillations of the two atoms around their equilibrium configuration are very small, the first approximation, that is, the elastic term $-\alpha\xi$ alone, gives reliable results. The corresponding potential energy is

$$\tfrac{1}{2}\alpha\xi^2.$$

According to the principle of equipartition of energy, the kinetic energy of the relative motion of the two atoms at the temperature T is $kT/2$ (notice that the relative motion has only one degree of freedom because the two atoms are constrained to move along a fixed line). On the other hand, we know that, as long as the attractive force can be considered elastic, the kinetic and potential energies have the same average value. Therefore, to this approximation, we can write

$$\tfrac{1}{2}\alpha\overline{\xi^2} = \tfrac{1}{2}kT,$$

where the overbar indicates the average value. Hence,

$$\overline{\xi^2} = \frac{kT}{\alpha}. \tag{35}$$

The average value of the force f between the atoms must obviously vanish in the stationary state of the thermal oscillations; otherwise the two atoms would either become attached to one another or would be completely separated, depending on the sign of $\bar{f}$. Therefore, from Eq. (34), we obtain

$$-\alpha\bar{\xi} + \beta\overline{\xi^2} = 0,$$

which gives

$$\bar{\xi} = \frac{\beta}{\alpha}\,\overline{\xi^2}.$$

We can introduce the approximate expression (35) on the right side of the previous equation. Since β is a very small quantity, the error introduced is negligible (of the order of β^2). We thus find

$$\xi = \frac{\beta k}{\alpha^2} T. \tag{36}$$

The result we seek is contained in this formula. We see, indeed, that the average distance between the two atoms is proportional to the temperature T. The expansion coefficient (the increase in length of a rod, per unit of initial length, per degree of temperature) is given, through (36), by

$$\chi = \frac{\xi}{aT} = \frac{\beta k}{a\alpha^2}. \tag{37}$$

We have thus obtained a qualitative model for thermal expansion. We can also show that with plausible values for the constants α and β in Eq. (34), the resulting values for the expansion coefficients χ have the correct order of magnitude. Let us consider a case that is close to reality, for example, when the force between two atoms A and B is of the polar type; A and B are then two ions (monovalent) with opposite sign. The Coulomb attraction $(-e^2/r^2)$ is then the force between them; in addition, there is a repulsive force which is important only when the atoms are very near each other and which, as we shall see in a moment, can be derived with sufficient accuracy from a potential inversely proportional to the ninth power of the distance. The repulsive force is then γ/r^{10} with γ constant. This constant is determined by the condition that the equilibrium distance between the two ions is a; that is, for $r = a$ the attractive and repulsive forces must balance:

$$\frac{e^2}{a^2} = \frac{\gamma}{a^{10}},$$

from which

$$\gamma = e^2 a^8.$$

The force between the two atoms is thus

$$f = -\frac{e^2}{r^2} + \frac{e^2 a^8}{r^{10}}.$$

Now, introducing $r = a + \xi$, we can expand f in a series with respect to ξ; we find

$$f = -\frac{8e^2}{a^3}\xi + \frac{52e^2}{a^4}\xi^2 + \cdots .$$

Comparing this with Eq. (34), we obtain

$$\alpha = \frac{8e^2}{a^3}, \qquad \beta = \frac{52e^2}{a^4}.$$

Substituting these values in Eq. (37), we find

$$\chi = \frac{52}{64}\frac{ak}{e^2}.$$

This formula, of course, is significant only as an order of magnitude. Introducing $k = 1.36 \times 10^{-16}$ and $e = 4.77 \times 10^{-10}$, and using for a the order of magnitude of the distances between adjacent atoms in crystals ($a = 3 \times 10^{-8}$), we obtain $\chi = 1.4 \times 10^{-5}$. The order of magnitude here is correct.

We now examine heat conduction in electrically nonconducting crystals. We saw in the previous sections that elastic waves, that is, acoustic waves, with wavelengths ranging right down to interatomic distances, propagate unhindered through a crystal lattice. We have also seen that the thermal motion of the crystal can be represented as a superposition of these elastic waves whose amplitudes increase with increasing temperature. According to this scheme, the heat conduction in the crystal should be exceedingly large and should, indeed, have entirely different characteristics from those actually observed. As an example, we study a crystal part of which is at a certain temperature T and another part at absolute zero. In the part at the temperature T, elastic waves are excited whose propagation velocity is of the same order of magnitude as that of the acoustic waves (a few hundred or thousand meters per second). They should thus fill the whole crystal in a very short time and bring it to a uniform temperature in a fraction of a second.

That thermal conduction in a crystal does not have these characteristics at all is due, as we have already mentioned, to the slight nonelasticity of the forces between the atoms of the crystal. The propagation of elastic waves in the crystal was derived by assuming that these forces were proportional to the relative displacement of the atoms. The neglected inelastic terms introduce a kind of scattering of the waves as they move through the crystal, so that their amplitudes decrease and their energy is transformed into new elastic waves which propagate in all directions with wavelengths generally different from those of the original waves. This kind of scattering is not very pronounced for large wavelengths, whereas it is definitely important when the wavelength is of the order of magnitude of the interatomic distances; it increases further when the amplitude of the vibration increases.

Because of this phenomenon, we can introduce a sort of mean free path of the waves in the crystal; in a rough schematization we can think of the wave, after moving a certain distance through the crystal, as changing direction suddenly. It then follows that the propagation of the thermal motion from a hot to a cold region of the crystal is greatly impeded; instead of moving in a straight line, the elastic waves follow a circuitous pattern and therefore require a much longer time. The phenomenon is analogous, from a certain point of view, to heat propagation in a gas. We first neglect collisions between gas molecules, which will then be able to move through the vessel containing the gas in straight lines and reach the other side of it in a very short time. If at a certain instant there are temperature differences between the various portions of the gas, the molecules will all be intermixed, after a fraction of a second, and temperature equilibrium will be reestablished. If, instead, the molecules collide with each other, so that their mean freepath is small compared to the vessel's size, the molecules slowly diffuse from one side to the other, their motion being a complicated series of sharp turns. Hence, thermal equilibrium occurs only after a much longer time.

This qualitative discussion of thermal conductivity in crystals is very difficult to develop quantitatively; it has been impossible, up to now, to develop a really complete theory of this phenomenon.* The analysis given above, however, is sufficient to derive the order of magnitude of the thermal conductivity observed in electrically nonconducting crystals.

6-8 IONIC LATTICES

In discussing the chemical bond between the atoms of a molecule, we distinguished between polar and homopolar molecules. The first can be considered to consist of ions of opposite sign, kept together by the electrostatic attraction; the second can be thought of, instead,

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* *Editor's note:* See the material in the appendix to this chapter.

as composed of neutral atoms between which attractive resonance forces exist, according to the mechanism proposed by Heitler and London for the chemical bond of the hydrogen molecule.

The forces that keep the atoms of a crystal together can be classified in the same way, but the mechanism of the homopolar forces, although analogous to that of molecules, is not as well-known. The binding forces in polar crystals, on the other hand, where the ions have different signs, are much simpler and better known.

The salt crystals are usually composed of ionic lattices where, as in the salt molecules, the metal component is the positive ion and the radical or nonmetallic ion is the negative ion. Rock salt is a typical example of a polar crystal with positive sodium and negative chlorine ions.

In addition to the electrostatic forces between the ions of a polar crystal, one must also take into account the repulsive forces between atoms or ions when they are very near each other. These forces, whose origin has already been discussed in connection with the chemical bond of the molecule, decrease very rapidly with the distance between the two atoms or ions; on the other hand, they become very strong when the electronic clouds surrounding the ions begin to overlap. In the theory of polar crystals one usually assumes empirically that the repulsive force between two ions can be derived from a potential inversely proportional to some power of the distance; this power varies from case to case but is usually near 9. These forces are therefore important only between adjacent ions of the lattice, whereas the electrostatic forces have a considerable effect even between ions that are far from each other.

The fundamental problem in the study of the ionic lattices is to determine the electrostatic potential of the lattice itself. We first consider a simple lattice whose points are occupied by the same kind of atoms. If this lattice were infinite, its potential would clearly be infinite at all points. Indeed it would be given by

$$e \sum_{l} \frac{1}{r_l}, \tag{38}$$

where e is the charge of the individual ions and r_l is the distance of the lth ion from the point where the potential is calculated. Now, it is clear that the sum in (38) diverges if it is taken over all points of an infinite simple lattice. A polar crystal, of course, never consists of a simple lattice, because to be electrically neutral it has to contain at least two ions of opposite sign.

For a composite lattice we designate the various simple lattices with the index k. Let e_k be the electric charge of the ions of the kth lattice. We then designate with the index l the various cells of the crystal (l really represents a triplet l_1, l_2, l_3 of indices): r_{lk} is the distance from the point P, where we want to calculate the potential, to the ion of the crystal belonging to the lth cell of the kth simple lattice. The potential at the point P is given by

$$V_P = \sum_l \mathop{\text{S}}_k \frac{e_k}{r_{lk}}, \tag{38'}$$

where the symbol $\sum\limits_l$ represents the sum (of infinite terms) taken over all the cells of the lattice, while the symbol $\mathop{\text{S}}\limits_k$ represents the sum taken over the finite number of simple lattices which constitute the crystal.

But the sum in (38′) does not converge unconditionally, that is, for all arrangements of its terms. One can, however, define the potential of the lattice unambiguously by using, for example, the following artifice: In place of (38′) we consider the expression

$$V_{P\alpha} = \sum_l \mathop{\text{S}}_k \frac{e_k}{r_{lk}} e^{-\alpha r_{lk}} \tag{39}$$

where α is a positive constant. Expression (39) differs from (38′) in the factors $e^{-\alpha r_{lk}}$, which make it converge unconditionally, that is, independently of the way the terms are arranged. In the limit $\alpha \rightarrow 0$, the exponential factors reduce to unity so that (39) formally coincides with (38′). We may then define

$$V_P = \lim_{\alpha = 0} V_{P\alpha}, \tag{40}$$

and thus obtain an unambiguous expression for the potential of the lattice. Another procedure which leads to a precise definition of V_P and does not have the arbitrariness of the one mentioned above, is the following:

The potential V must satisfy the Laplace equation

$$\Delta V = 0, \tag{41}$$

at all points of the space, except those occupied by the ions. Furthermore, in the vicinity of an ion (l,k), it must clearly tend to infinity like e_k/r_{lk}. To these two conditions on the function V, which alone would not suffice for its complete determination, we now add another one, namely, that V be periodic with respect to the crystal cell, i.e., its values be the same at corresponding points of different cells. One can easily demonstrate that these conditions are sufficient to determine V up to an inessential additive constant, which can be suitably fixed, for example, by the condition that the average value of V be zero. It is clear that this definition is equivalent to (40).

We now expand the potential V in a Fourier series. To simplify the analysis, we imagine our crystal as consisting of a certain number of simple cubic lattices with cell size equal to a. All the crystals of the monometric system can be represented as such, even if their individual simple lattices are cubic body-centered or face-centered. The latter can indeed again be considered ensembles of simple cubic lattices. It is easy to extend to noncubic crystal lattices the analysis we now apply.

Let ρ be the density of the electric charges. Since ρ is periodic in the cubic cell, we can expand it in a triple Fourier series:

$$\rho(r) = \sum_{l} b_l e^{(2\pi i/a)\mathbf{l}\cdot\mathbf{r}}, \tag{42}$$

where $\mathbf{l}$ represents the triplet of indices l_1, l_2, l_3 (positive, negative, or zero integers), $\mathbf{r}$ is the vector radius of the point where the charge density ρ is taken and, $\mathbf{l}\cdot\mathbf{r} = l_1 r_x + l_2 r_y + l_3 r_z$ is the scalar product of $\mathbf{r}$ and the vector $\mathbf{l} = l_1, l_2, l_3$. The expansion coefficients in (42) can be calculated by the usual rule, taking into account that the electric charges are point-like (charge e_k concentrated in the point defined by the vector radius $\mathbf{r}_k$): they are

$$b_l = \frac{1}{a^3}\int_{\text{cell}} \rho e^{-(2\pi i/a)\mathbf{l}\cdot\mathbf{r}}\, d\tau = \frac{1}{a^3}\mathop{S}_{k} e_k e^{-(2\pi i/a)\mathbf{l}\cdot\mathbf{r}_k}, \tag{43}$$

where the symbol S represents, as usual, the sum over the individual atoms of a cell.

Since the potential V is periodic inside the cell, we can expand it in a Fourier series of the type (42):

$$V = \sum_{l} c_l e^{(2\pi i/a)\mathbf{l}\cdot\mathbf{r}}. \tag{44}$$

The coefficients c_l can be determined by means of the Poisson equation

$$\Delta V = -4\pi\rho.$$

Substituting (44) and (42) in the above expression, we immediately obtain

$$-\frac{4\pi^2}{a^2}(l_1^2 + l_2^2 + l_3^2)\, c_l = -4\pi b_l,$$

from which

$$c_l = \frac{a^2}{\pi}\frac{b_l}{l_1^2 + l_2^2 + l_3^2}. \tag{45}$$

Using (45) and (43), we obtain for the expansion (44) of the potential at the point defined by the radius vector $\mathbf{r}$ the expression

$$V(r) = \mathop{\mathsf{S}}_{k} e_k B(\mathbf{r} - \mathbf{r}_k), \tag{46}$$

where

$$B(\mathbf{r}) = \frac{1}{\pi a}\sum_{l}{}' \frac{e^{(2\pi i/a)\mathbf{l}\cdot\mathbf{r}}}{l_1^2 + l_2^2 + l_3^2}. \tag{47}$$

The accent on Σ indicates the term $l_1 = l_2 = l_3 = 0$ must be dropped from the sum [this term disappears in (46) because $\mathsf{S}_k\, e_k = 0$, since the crystal is electrically neutral].

The calculation of the potential of the crystal, regardless of the number and distribution of ions in the cell, is thus reduced, for the monometric lattices, to the evaluation of the function (47) only. Generalizing to other lattices, one finds that the function to be evaluated is of the same form as $B(\mathbf{r})$ but a different one for each given ratio between the crystallographic axes and for each inclination between them. Expression (47) for B is not very convenient for numerical calculations; however, by artifices which we shall not describe, one can easily transform it into a rapidly convergent expression.

We can easily find the physical significance of B. If we interpret B as the potential generated by a distribution of charges with density ρ^*, the Poisson equation gives

$$\rho^* = -\frac{1}{4\pi}\,\Delta B = \frac{1}{a^3}\sum{}' e^{(2\pi i/a)\mathbf{l}\cdot\mathbf{r}} = \frac{1}{a^3}\sum e^{(2\pi i/a)\mathbf{l}\cdot\mathbf{r}} - \frac{1}{a^3}. \tag{48}$$

Notice now that

$$\frac{1}{a^3}\sum e^{(2\pi i/a)\mathbf{l}\cdot\mathbf{r}} \tag{49}$$

is the Fourier expansion of an improper function with values different from zero only at the vertices of the simple cubic lattice of side a; its integral taken over a region containing only one vertex, has the value 1. Therefore, (49) represents the number of electric charges equal to $+1$ concentrated in the vertices of the lattice.

The other term, $-1/a^3$, represents, instead, a uniform distribution of negative electricity with a density equal to $-1/a^3$, that is, such that inside the cell there is a quantity of electricity equal to -1, exactly what is needed to neutralize the charge $+1$ concentrated in the vertices.

6-9 ELECTROSTATIC ENERGY OF IONIC LATTICES

The calculation of the electrostatic energy of an ionic lattice is important for many applications in the physics and chemistry of crystals; if the energy of the repulsive forces between adjacent ions (usually a small percentage of the preceding energy, because of the small range of these forces) is added to this, we obtain the total heat of formation of the crystal, that is, the heat released when the crystal is formed from the individual ions.

The calculation of the electrostatic energy for any crystal having certain determined crystallographic axes is governed by only one characteristic function, regardless of the number and arrangement of the ions in the cell. In particular, only one function is needed for all the crystals of the monometric system; for simplicity we limit our considerations to this system. Further, we use the Born [3, 5, 72] method of the *fundamental potential.*

Let a be the side of the cubic cell of our lattice. With n as an integer, we consider a new lattice with cell side equal to a/n, so that the cell of the first lattice contains n^3 cells of the second. If n is sufficiently large, the positions of all the ions of the crystal coincide, to a sufficient approximation, with one of the vertices of the second lattice. In practice, even a small value of n is sufficient in many cases, because frequently the ion coordinates and a stand in a simple rational ratio to each other.

Having chosen a suitable value of n, we can describe the points of the second lattice by means of the two sets of indices l_1, l_2, l_3 and k_1, k_2, k_3 (abbreviated l and k) with l_1, l_2, l_3 assuming all positive, negative, or zero values and defining the cell of the first lattice (with side a), whereas k_1, k_2, k_3, which assume only integer values from 0 to $n - 1$, define the position of the point within the cell. The corresponding vector radius is

$$\mathbf{r}_{lk} = \frac{a}{n}(n\mathbf{l} + \mathbf{k}), \tag{50}$$

where $\mathbf{l}$ and $\mathbf{k}$ are the vectors with components l_1, l_2, l_3 and k_1, k_2, k_3.

Let e_k be the electric charge of the ion at the point $(\mathbf{l},\mathbf{k})$; e_k does not depend on the index l, because of the periodic occurrence of the same ions in the cells (of side a). If there is no ion at the point $(\mathbf{l}, \mathbf{k})$, we set $e_k = 0$.

Whatever the values of e_k, we can always take

$$e_k = \mathop{\mathrm{S}}_{h} \xi_h e^{(2\pi i/n)\mathbf{h}\cdot\mathbf{k}}, \tag{51}$$

where $\mathbf{h}$ represents, as usual, a triplet of indices (h_1,h_2,h_3) defined modulo n; $\mathbf{h} \cdot \mathbf{k}$ is the scalar product $(h_1k_1 + h_2k_2 + h_3k_3)$ and the n^3 quantities ξ_h are completely analogous to the coefficients of a Fourier series expansion:

$$\xi_h = \frac{1}{n^3} \mathop{\mathrm{S}}_{k} e_k e^{-(2\pi i/n)\mathbf{h}\cdot\mathbf{k}}. \tag{52}$$

To calculate the electrostatic energy of the lattice, we must first find the potential produced at the position of a given ion, for example, the ion k' of the cell $l_1 = l_2 = l_3 = 0$, by all the other ions of the crystal.

This potential is evidently

$$\varphi_{k'} = \sum_{l}{}' \mathop{S}_{k} \frac{e_k}{|\mathbf{r}_{lk} - \mathbf{r}_{0k'}|}. \tag{53}$$

The prime on Σ means that the term ($l_1 = l_2 = l_3 = 0$, $k = k'$) must be excluded from the sum. Taking into account (50) and (51), we can write

$$\begin{aligned}\varphi_{k'} &= \sum_{l}{}' \mathop{S}_{kh} \xi_h \frac{e^{(2\pi i/n)\mathbf{h}\cdot\mathbf{k}}}{(a/n)|n\mathbf{l} + \mathbf{k} - \mathbf{k}'|} \\ &= \frac{n}{a} \mathop{S}_{h} \xi_h e^{(2\pi i/n)\mathbf{h}\cdot\mathbf{k}'} \sum_{l}{}' \mathop{S}_{k} \frac{e^{(2\pi i/n)[\mathbf{h}\cdot(n\mathbf{l}+\mathbf{k}-\mathbf{k}')]}}{|n\mathbf{l} + \mathbf{k} - \mathbf{k}'|}. \end{aligned} \tag{54}$$

Note that in the sum with respect to the indices l, k, the vector $n\mathbf{l} + \mathbf{k} - \mathbf{k}'$ has as its components all possible triplets (positive and negative) of integers except (0, 0, 0). We can therefore replace the two sums with respect to $\mathbf{l}$ and $\mathbf{k}$ by a single sum with respect to only one vector $\mathbf{l}$ with integer components, and write

$$\begin{aligned}\sum_{l}{}' \mathop{S}_{k} \frac{e^{(2\pi i/n)[\mathbf{h}\cdot(n\mathbf{l}+\mathbf{k}-\mathbf{k}')]}}{|n\mathbf{l} + \mathbf{k} - \mathbf{k}'|} &= \prod\left(\frac{h_1}{n}, \frac{h_2}{n}, \frac{h_3}{n}\right) \\ &= \prod\left(\frac{\mathbf{h}}{n}\right),\end{aligned}$$

where

$$\prod(\mathbf{p}) = \sum_{l}{}' \frac{e^{2\pi i(\mathbf{p}\cdot\mathbf{l})}}{|l|} = \sum_{l}{}' \frac{\cos 2\pi(\mathbf{p}\cdot\mathbf{l})}{|l|}. \tag{55}$$

The prime on the summation symbol means that the triplet $l \equiv (0,0,0)$ is to be excluded. Notice also that the series that defines the function Π is convergent and does not depend on the order of the terms; for example, the terms can be arranged in such a way that the magnitude of the vector $\mathbf{l}$ increases monotonically.

The function Π, named the fundamental potential by Born, has been calculated numerically by Emersleben.[85] We see from its definition that this function is symmetric with respect to the three components p_1, p_2, p_3 of the vector $\mathbf{p}$; furthermore it is periodic with unit period with respect to these arguments, and its value does not change under permutations of the arguments. Because of this property, it is sufficient to evaluate it in the domain:

$$\tfrac{1}{2} \geq p_1 \geq p_2 \geq p_3 \geq 0.$$

Equation (54) can now be written

$$\varphi_{k'} = \frac{n}{a} \mathop{\mathrm{S}}_{h} \xi_h e^{(2\pi i/n)\mathbf{h}\cdot\mathbf{k}'} \prod\left(\frac{\mathbf{h}}{n}\right). \tag{56}$$

[Notice that the summation in (56) extends only over a finite number of terms.] The electrostatic energy of the crystal, referred to one cell, is then

$$W_{\mathrm{el}} = \tfrac{1}{2} \mathop{\mathrm{S}}_{k'} e_{k'}\varphi_{k'}, \tag{57}$$

that is, taking into account (51) and (56),

$$W_{\mathrm{el}} = \frac{n}{2a} \mathop{\mathrm{S}}_{hh'k'} \xi_h \xi_{h'} e^{(2\pi i/n)(\mathbf{h}+\mathbf{h}')\cdot\mathbf{k}'} \prod\left(\frac{\mathbf{h}}{n}\right).$$

The sum with respect to k' can be evaluated immediately. It is different from zero only if $h' = -h$; therefore

$$W_{\mathrm{el}} = \frac{n^4}{2a} \mathop{\mathrm{S}}_{h} \xi_h \xi_{-h} \prod\left(\frac{\mathbf{h}}{n}\right). \tag{58}$$

One can further transform this expression by means of (52) and obtain

$$W_{\mathrm{el}} = \frac{1}{2an^2} \mathop{\mathrm{S}}_{kk'h} e_k e_{k'} e^{(2\pi i/n)(\mathbf{k}'-\mathbf{k})\cdot\mathbf{h}} \prod\left(\frac{\mathbf{h}}{n}\right). \tag{59}$$

To compute the electrostatic energy with either (58) or (59) we must evaluate a sum over a finite number of terms.

For the crystals of the type of NaCl (cf. Fig. 33), the electrostatic energy for each cell (i.e., 4 molecules) has the value:

$$W_{\mathrm{el}} = -10.17\frac{e^2}{a} \qquad (\mathrm{NaCl}). \tag{60}$$

For the crystals of the type of fluorite, the electrostatic energy of a cubic cell (4 molecules; see Fig. 34), is equal to

$$W_{\mathrm{el}} = -46.5\frac{e^2}{a} \qquad (\mathrm{CaF_2}). \tag{61}$$

For dimensional reasons, the electrostatic energy always of course has the same form:

$$W_{\mathrm{el}} = -\beta\frac{e^2}{a}, \tag{62}$$

where β is a dimensionless numerical constant, which can be calculated by analyzing the lattice potential.

6-10 REPULSIVE FORCES; COMPARISON WITH EXPERIMENT

We have mentioned several times that, when the atoms or the ions of a crystal get closer to each other than a certain limiting distance, repulsive forces occur between them. These forces increase very rapidly with a further approach of the two particles. In Part I of this volume, we gave a qualitative discussion of the origin of these forces: They arise in part from a purely electrostatic repulsion and in part from a quantum resonance effect. However, to calculate the law of repulsion by a direct application of these phenomena is not very feasible. It is more convenient, at the present stage of our knowledge, to use an empirical formula that expresses the repulsive force as an inverse function of the distance to some power.

According to Born,[3, 5] the best way to determine the exponent of this power law is from the data on the compressibility of the crystal. Again let a be the side of the cubic cell of the crystal in the equilibrium configuration. Under the action of an external pressure p the crystal contracts in all directions and its cell side becomes $a(1 - \epsilon)$. If the crystal consists of N cubic cells, its volume in the equilibrium configuration is given by

$$V_0 = Na^3.$$

When the crystal contracts under the external pressure, its volume decreases to

$$V = Na^3(1 - \epsilon)^3 \cong Na^3(1 - 3\epsilon) \tag{63}$$

up to terms of the order of ϵ^2. The crystal compressibility χ is given by the ratio of the relative contraction of the volume to the pressure which produces such a contraction:

$$\chi = \frac{3\epsilon}{p}.$$

The electrostatic energy of the crystal can then be obtained from (62) by substituting $a(1 - \epsilon)$ for a and multiplying by the number N of cells; thus we obtain

$$-\beta N \frac{e^2}{a(1-\epsilon)}.$$

If we then assume that the repulsive forces can be derived from a potential inversely proportional to the nth power of the distance, the corresponding energy of the N cells of our crystal can evidently be written

$$N \frac{A}{a^n(1-\epsilon)^n},$$

where A is a constant. Thus, the total energy of the lattice is

$$E = N\left[-\beta \frac{e^2}{a(1-\epsilon)} + \frac{A}{a^n(1-\epsilon)^n}\right]. \tag{64}$$

To determine the two constants A and n, we note that, when there is no external pressure, the crystal is in its equilibrium configuration when its cell side equals a; that is, (64) must have a minimum for $\epsilon = 0$:

$$\left(\frac{dE}{d\epsilon}\right)_{\epsilon=0} = 0.$$

From this we immediately obtain

$$A = \beta \frac{e^2}{n} a^{n-1},$$

and Eq. (64) becomes

$$E = -N\frac{\beta e^2}{a}\left[\frac{1}{1-\epsilon} - \frac{1}{n(1-\epsilon)^n}\right],$$

or, expanding in a series and dropping terms above ϵ^2, we have

$$E = -N\frac{\beta e^2}{a}\left(1 - \frac{1}{n}\right) + N\frac{\beta e^2}{a}\frac{n-1}{2}\epsilon^2. \tag{65}$$

Let p be the external pressure on the crystal. For a virtual variation of the parameter ϵ, the pressure p performs the virtual work

$$-p\delta V = 3Na^3p\,\delta\epsilon,$$

which must equal

$$\delta E = N\frac{\beta e^2}{a}(n-1)\epsilon\,\delta\epsilon,$$

the virtual variation of the energy. Equating the two expressions, we find the compressibility

$$\chi = \frac{3\epsilon}{p} = \frac{9a^4}{\beta e^2(n-1)}. \tag{66}$$

Using this formula, we can express the coefficient n of the repulsive forces in terms of known quantities:

$$n = 1 + \frac{9a^4}{\beta e^2\chi}. \tag{67}$$

The values computed in this way for different crystals of the cubic system cluster around 9. For this reason the value $n = 9$ is usually assumed.

Notice that for $\epsilon = 0$, that is, for the normal state of the crystal, the energy of the N cells of the lattice can be obtained from Eq. (65) by placing $n = 9$ in (65). Thus

$$E_0 = -N\frac{\beta e^2}{a}\left(1 - \frac{1}{n}\right) = -\frac{8}{9}N\frac{\beta e^2}{a},$$

so that the total energy of the ionic lattice is about equal to $\frac{8}{9}$ of the electrostatic energy.

The experimental measurement of the energy formation of an ionic lattice starting from the free constituent ions cannot be made directly; we can however, use an indirect method called the Born cyclic process.[3, 5, 72] We take, for example, the sodium chloride lattice. From thermochemical measurements, one knows the heat of formation of rock salt starting from metallic sodium and diatomic chlorine vapor.

This formation process, on the other hand, can be decomposed into a succession of simpler processes, namely: (1) transformation of the metallic sodium into monoatomic sodium vapor (for this we must supply an amount of energy equivalent to the sodium heat of sublimation); (2) dissociation of the Cl_2 molecules into separated atoms (for this the chlorine dissociation energy is needed); (3) formation of positive sodium ions and negative chlorine ions, by transporting one electron from each sodium atom to a chlorine atom (the energy necessary for this process is given by the difference between the sodium ionization energy and the chlorine electronic affinity); and (4) once the Na^+ and Cl^- ions have been formed, we are left with the last process, consisting of the arrangement of these ions in the rock-salt lattice.

The energy freed in this last process can thus be obtained as the difference between energy of formation of rock salt from the solid metal and diatomic chlorine, and the sum of the energies of processes 1, 2, and 3.

Table 5, reproduced from Born,[3, 5] gives the lattice energies of various crystals as calculated from the theory of lattice potentials and as ob-

Table 5 Lattice Energies[a]

Compound	Experimental	Theoretical
NaCl	183	182
NaBr	170	171
NaJ	159	158
CaF_2		609
CaJ_2		422
KCl	165	162
KBr	154	155
KJ	144	144
$CaCl_2$		480
ZnS		738
RbCl	161	155
RbBr	151	148
RbJ	141	138
$CaBr_2$		452

[a] Energies in calories per gram-mole.

tained empirically by methods of the type just described. All the energies are in calories per gram-mole. We see that the agreement between theory and experiment is very good.

6-11 PROPAGATION OF ELECTROMAGNETIC WAVES IN CRYSTALS

The theory of lattice potentials can be developed not only for the ordinary electrostatic potential, but also for a variable electromagnetic field. A case of practical importance is the propagation of a plane electromagnetic wave through the crystal. An analysis of this phenomenon leads, on the one hand, to an understanding of the properties of the optical anisotropy of the crystal and, on the other hand, to a complete explanation of the diffraction of X rays. Since we cannot discuss these theories in detail here, we give only a brief account.

When an electromagnetic wave penetrates a crystal, the electric field of the wave polarizes the atoms of the substance. If the crystal can be pictured as consisting of neutral atoms, the electric displacement of each atom is essentially determined by the displacement of the electrons with respect to the nucleus of the atom. If, instead, we have an ionic lattice, the over-all displacement of the ion itself can also be very important. This is particularly true at low infrared frequencies, because the ions, owing to their relatively large mass, can oscillate with considerable amplitude only under the action of low-frequency fields.

The electric polarization of the crystal atoms generates in turn an electromagnetic field which, superposed on the original wave, modifies it. If the crystal is not monometric, the field produced by the atomic polarizations has, in general, a direction different from that of the electric moments of the atoms themselves; thus it produces an anisotropy in both the dielectric constant and the index of refraction.

We first consider the dielectric constant, which, of course, can still be analyzed by simple electrostatics. We assume for this that our crystal lattice is subject to a uniform external electric field E_e. Each atom is then in a field E which is the sum,

$$E_e + E_i,$$

of the external field E_e and the field E_i produced by the action of the electric moments of the surrounding atoms. The over-all field E determines the atomic polarization and, as the simplest hypothesis, we assume that the electric moment produced in each atom is given by

$$\mu = \alpha E$$

(it is proportional to and has the same direction as E). We further simplify the problem by referring to a lattice of neutral atoms, so as not to be burdened with the translational motion of the particles that occur in ionic lattices.

The field E_i of the electric moments induced in the surrounding atoms can be derived from a potential V_i of the form

$$V_i = \sum{}' \frac{\mu \cos \vartheta}{r^2},$$

where the sum must be extended to all atoms except the one being considered; r is the distance of this atom from the reference point in the lattice, and ϑ is the angle between the directions of r and μ.

The sum V_i can be evaluated numerically by procedures analogous to those used to calculate the potential in ionic lattices. After determining the field E_i, one can immediately derive the relation between the electric moment and the external field E_e. For nonmonometric crystals, one usually finds a tensor relation that expresses the anisotropy of the polarizability and therefore of the dielectric constant of the crystal.

To the anisotropy of the dielectric constant there corresponds, of course, an anisotropy of the optical properties and in particular of the index of refraction; birefraction phenomena can thus be interpreted. For a more accurate calculation, we must also take into account that electromagnetic interactions are propagated from one atom to the other via retarded potentials. This is especially important for the case of small wavelengths and in particular for X rays. Ewald,[14, 15] who has carefully investigated this problem, gave a satisfactory theoretical interpretation of the small deviations from the Bragg law observed in the reflection of X rays.

We conclude this subject by noting that the electromagnetic-potential theory of lattices has also led to a satisfactory interpretation of the rotatory polarization phenomena; in crystals having convenient symmetry properties, these phenomena can be attributed to the reciprocal actions between the electric moments of the atoms which have been polarized by the electric field of the light.

6-12 OPTICAL ABSORPTION IN CRYSTALS

Many crystals appear colored because they absorb the light of the various colors differently. Their absorption spectra contain absorption bands that vary considerably in number and width from case to case. The most typical case is that of the rare-earth salts, where one observes large numbers of bands; these bands are so narrow that they can almost be considered real absorption lines. They are usually sharper when the absorption occurs at a very low temperature. Similar absorption bands, although not as sharp, are also observed in other crystals, for example, in many chromium and manganese salts.

Optical absorption in a crystal is due to the quantum transitions of the electrons in the crystal. To understand the structure of the energy levels of an electron inside a crystal, we use the simple model of an electron moving in a field defined by a triply periodic potential. This is equivalent to disregarding the interactions of the individual electrons among themselves and to representing the action of all the other electrons on a particular one as a screening of the nuclear charges. Furthermore, by doing this we neglect the irregularities of the crystal lattice arising from both the thermal motions and the permanent distortions of the crystal.

The potential of the forces acting on the electron can be described as a system of potential wells arranged next to each other like the cells of the lattice and separated by potential barriers. A one-dimensional representation of this potential is given in Fig. 39. To study the energy levels of an electron moving in the field of this potential it is convenient to distinguish two extreme cases, 1 and 2. The first has been discussed, in particular, by Bloch,[62, 68] the second by Peierls.[121]

Case 1: We assume that the energy level of the electron is considerably lower than the potential energy separating the different potential wells (level *a* in Fig. 39). In this case, according to classical mechanics, the electron cannot leave the potential well in which it is moving. But according to quantum mechanics, the electron has a small probability of moving from one well to another by passing through the

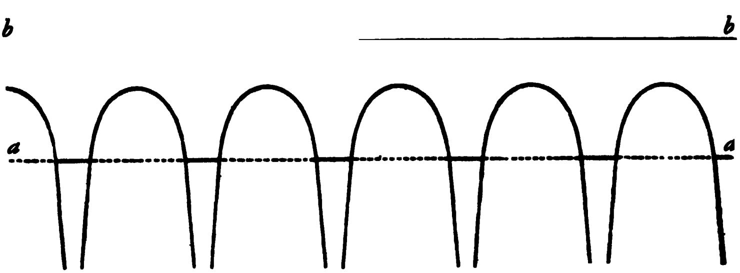

Figure 39

potential barriers that separate them. We may suppose, however, as a first approximation in the analysis of this problem, that the potential wells are independent of each other (which corresponds to dealing with isolated crystal atoms); we shall consider the perturbation of the wells on each other only as a second approximation.

Case 2: This case is valid when the electron energy is much higher than the potential energy maxima (level b in the figure). In this case it is convenient to start with a free electron as a first approximation, and consider the effect of the periodic irregularities of the potential as a perturbation.

We limit ourselves, for simplicity, to only one dimension (let x be the abscissa of the point). One can easily demonstrate that, if the potential is a periodic function of x with period a, the eigenfunctions can always be written in the form

$$\psi(x) = e^{(2\pi i/a)qx}v(x),$$

where $v(x)$ is a periodic function with period a, and q is a constant whose absolute value can always be taken less than or equal to $\frac{1}{2}$.

In case 1, Bloch has demonstrated that, to a first approximation, we can write

$$v(x) = \sum_{-\infty}^{\infty} u(x - na), \tag{68}$$

where $u(x)$ is the eigenfunction of the electron when it is in the potential well near $x = 0$ and far from the other potential wells (eigenfunction of the isolated atom). The eigenvalue corresponding to the eigenfunction (68) is given to a first approximation, by

$$E = A + \beta \cos 2\pi q, \tag{69}$$

where A and β are constants. The value of A is close to the eigenvalue of the isolated atom; the smaller the difference between the electron energy and the potential energy maxima that separate the different wells, the larger is the value of β.

Since q takes on all values between $-\frac{1}{2}$ and $+\frac{1}{2}$, Eq. (69) represents a continuous strip of eigenvalues, having a width of 2β and going from $A - \beta$ to $A + \beta$. The width of this strip is small for low states whose corresponding isolated-atom eigenfunctions have a small extension. It gradually increases for orbits which are tightly bound. This behavior is illustrated in Fig. 40: On the left the eigenvalues for the isolated atom are represented, and on the right are the strips of the continuous spectrum of eigenvalues into which each eigenvalue of the isolated atom expands when it is in the crystal.

Figure 41 refers to case 2. Here we take for our unperturbed eigenfunction that of a free electron; this can be written in the form

$$e^{(2\pi i/a)qx}.$$

The energy corresponding to this eigenfunction for the unperturbed

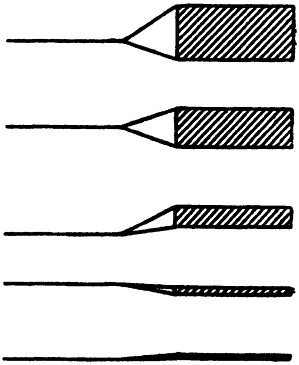

Figure 40

problem (when the potential is neglected) is

$$E = \frac{h^2}{2ma^2} q^2, \tag{70}$$

where m is the mass of the electron. Graphically, Eq. (70) is represented by a parabola. The perturbation deforms this parabola in the way indicated in Fig. 41. The breaks occur in places corresponding to $q = \pm\frac{1}{2}, \pm 1, \pm\frac{3}{2}, \ldots$. The energy levels are shown at the right side of the figure. We see here that there is also a continuous spectrum of eigenvalues; it consists of broad strips, separated by narrow intervals.

What we have said for the one-dimensional case holds, with minor modifications, for the three-dimensional case. Also here, for both cases 1 and 2, the spectrum consists of strips whose width increases for the higher levels and which correspond more or less exactly to eigenvalues of the isolated atom. In the three-dimensional case, however, in contrast to what happens in one dimension, some of the strips partly overlap.

We now return to the original problem, namely, that of optical absorption by solid bodies. The previous analysis tells us why the absorption spectrum of solid bodies consists of continuous strips. We must, of course, keep in mind that the width of these strips is increased by the thermal motion of the crystal.

In the rare-earth salts, as we have said, the absorption bands are so

exp $(2x/a)$

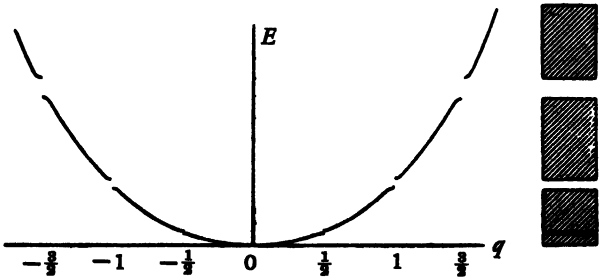

Figure 41

narrow that they look like lines. The reason for this is found in the particular structure of the rare-earth ions, which contain an incomplete shell of 4*f* electrons. Electrons in these orbits have very little binding energy and hence can be excited to unoccupied states by small amounts of energy. But these orbits lie so very deep inside the atom that the broadening of the spectral terms produced by the ion's being in the crystal is very small, and hence the observed absorption bands are very narrow. The multiplicity of the energy levels of rare-earth crystals is partly due to the various relative orientations the orbits of the 4*f* electrons can have; it is also partly due to their possible orientations with respect to the crystallographic axes. Each ion, in fact, lies in an electric field which, owing to the surrounding ions, has a symmetry dependent on the crystal symmetry. This field produces a splitting of the terms, studied in detail by Bethe,[67] which is analogous to the Stark effect and may considerably increase the multiplicity of the spectrum, even producing differences (usually not very large) between the spectra of the same rare earth in different salts.

We further note that, in the isolated atom, the transitions between energy levels differing only in the relative orientation of the 4*f* orbits are forbidden by the Laporte rule. They are allowed in a crystal because of the perturbing action of the electric field, but even so (confirming that this is a perturbation effect), these transitions involve only a small number of dispersion electrons per atom (of the order of magnitude of 10^{-8}) as determined from the magnetic rotation near these lines. We also note that the Zeeman effect has been observed in these absorptions; complicated anomalous Zeeman patterns have been observed.

Last, the structure of the energy levels of an electron in a crystal is confirmed, according to Kronig,[62] by the fine structure of the absorption limits of the X-ray spectrum. In the absorption of X rays, electrons are knocked out of deep atomic orbits and thrown into unoccupied energy levels. Since the high-energy levels of an electron in a crystal do not form a continuous array but are arranged irregularly with spaces between them, there are corresponding irregularities in the absorption spectrum near the absorption limit. The fine structure of the spectrum for the same element differs from crystal to crystal and corresponds qualitatively to the energy-level structure of the electron in the different types of crystal lattices.

APPENDIX 1. ON DEVIATIONS FROM AND CORRECTIONS TO THE DEBYE THEORY

That deviations from the Debye theory are to be expected was first pointed out by Eucken,[18] who published an extensive survey of the experimental and theoretical results in 1929. There were two obvious discrepancies. On the one hand, we cannot represent all the data for a given crystal in terms of a single value of Θ. If one plots Θ against T, the result is not a straight line. However, the deviation from a straight line rarely exceeds 20 per cent, and in a good many cases does not exceed 10 per cent. Thus the Debye theory is in reasonably good agreement with experiment, at least for monoatomic crystals.

The second discrepancy between the Debye theory and experimental data is found in the difference in the value of Θ as calculated from specific heats and from elastic data. The values obtained from the elastic data are consistently larger than those found from the specific heats.

The reason for the discrepancy between Debye theory and experiment is that the Debye theory is essentially a continuum theory, whereas the crystal is a point lattice. The vibration spectra of crystals are so markedly different from a Debye spectrum, that deviations from the Debye theory are hardly to be wondered at. Once the lattice structure of the crystal is taken into account, the discrepancy between theory and experiment disappears.

Blackman[1] has given a complete discussion of the lattice theory of specific heats as developed by Born, von Karman, and others. In the Born and von Karman[74] theory, and as later expanded by Born[5, 70], the vibrational modes of a crystal lattice are calculated from the solutions of the equations of motion (with proper boundary conditions) of the particles (atoms) at the lattice points. One then obtains the energy spectrum and also an expression for the total energy of the crystal as an integral over all vibrational modes, and the specific heat is then obtained in the usual way. In this treatment, elastic forces are assumed between the particles, but there is no valid reason for such an assumption. However, the agreement between theory and observation is as good as can be expected at the present time.

For a complete bibliography of recent work in this field see Blackman.[1]

APPENDIX 2. HEAT CONDUCTION

A great deal of work has been done on the thermal conductivity of crystals since Fermi published his book. A detailed discussion of the recent work in this field is given in the article by Leibfried.[39] One defines the total energy or heat-flow density as

$$q = \frac{1}{V} \sum_{\mathbf{k},s} \epsilon_s^{\mathbf{k}} \mathbf{v}_s^{\mathbf{k}},$$

where the summation is extended over all lattice waves defined by the propagation vector $\mathbf{k}$. Here V is the volume of a single fundamental cell containing N atoms, $\epsilon_s^{\mathbf{k}}$ is the energy in the wave defined by $\mathbf{k}$ and polarized in the direction s (which takes on the values 1, 2, 3) and $\mathbf{v}_s^{\mathbf{k}}$ is the group velocity with which this energy is transported:

$$\mathbf{v}_s^{\mathbf{k}} = \frac{\partial \omega_s^{\mathbf{k}}}{\partial \mathbf{k}}, \qquad \omega_s^{\mathbf{k}} = 2\pi \nu_s^{\mathbf{k}}.$$

Since the $\epsilon_s^{\mathbf{k}}$ are not sharply defined, we must introduce mean values

$$\bar{\epsilon}_{s,T}^{\mathbf{k}} = \epsilon(\omega_s^{\mathbf{k}}, T)$$

for a given temperature T.

One now places

$$\epsilon_s^{\mathbf{k}} = \hbar\omega_s^{\mathbf{k}}(\bar{N}_{s,T}^{\mathbf{k}} + \tfrac{1}{2}),$$

where $\bar{N}_{s,T}^{\mathbf{k}}$ is the mean number of waves with energy $\hbar\omega_s^{\mathbf{k}}$ and is given by the Einstein-Bose distribution function:

$$\bar{N}_{s,T}^{\mathbf{k}} = [e^{\hbar\omega_s^{\mathbf{k}}/kT} - 1]^{-1}.$$

For the thermal equilibrium there is no transport of heat, but for a small departure from the equilibrium state we have a steady-state heat flow arising from the small temperature gradient. This heat flow is caused by the deviation of the actual distribution $\bar{N}_s^{\mathbf{k}}$ of the lattice waves from the equilibrium distribution $\bar{N}_{s,T}^{\mathbf{k}}$. Thus

$$\bar{N}_s^{\mathbf{k}} = \bar{N}_{s,T}^{\mathbf{k}} + n_s^{\mathbf{k}}.$$

Only the $\bar{n}_s^{\mathbf{k}}$ enter into the heat flow. Thus the heat flow is given by

$$\mathbf{q} = \frac{1}{V} \sum_{\mathbf{k},s} \hbar\omega_s^{\mathbf{k}} n_s^{\mathbf{k}} \mathbf{v}_s^{\mathbf{k}}.$$

The problem here is to calculate $n_s^{\mathbf{k}}$, which is proportional to the temperature gradient

$$n_s^{\mathbf{k}} = - \sum_l \alpha_{s,l}^{\mathbf{k}} \frac{\partial T}{\partial x_l}.$$

From this we obtain the components of the heat flow

$$q_k = \frac{1}{V} \sum_{\mathbf{k},s,l} \hbar\omega_s^{\mathbf{k}} \alpha_{s,l}^{\mathbf{k}} v_{s,k}^{\mathbf{k}} \frac{\partial T}{\partial x_l}$$

or

$$q_k = - \sum \lambda_{kl} \frac{\partial T}{\partial x_l},$$

where

$$\lambda_{kl} = \frac{1}{V} \sum_{\mathbf{k},s} \hbar\omega_s^{\mathbf{k}} \alpha_{s,l}^{\mathbf{k}} v_{s,k}^{\mathbf{k}}$$

is the tensor of heat conductivity.

One can now obtain various expressions for the coefficient of heat conductivity by introducing more or less simple models of the forces between the atoms in a crystal. For high temperatures, one finds, for example, that

$$\lambda = \text{const} \frac{N}{V} \frac{M^3 \omega_D{}^5 v^2}{T g^2},$$

where M is the mass of an atom in the crystal, ω_D is the maximum lattice frequency according to the Debye theory, and g is the coefficient of anharmonicity. For a detailed bibliography, see Leibfried.[39]

PART III

Quantum Statistics

7

Statistical Equilibrium Between Quantum States

7-1 EXTENSION OF THE BOLTZMANN LAW

In the statistical treatment of classical problems, a characteristic difficulty is often encountered. To assign a finite, discrete number of possible or favorable states to a system, it is necessary to divide the velocity or phase space into arbitrary, finite (although small) cells of equal volume (such cells have no physical significance).

The statistical treatment of quantum systems is much more suited to this type of analysis, since the discontinuity necessary for probability considerations is already present as a consequence of the quantization. For the small phase-space cells of classical statistics, we substitute in quantum statistics the various quantum states of the system.

The fundamental problem of quantum statistics is completely analogous to that of classical physics. A system (atom, molecule, . . .) in thermodynamic equilibrium at the absolute temperature T and with quantum energy levels w_1, w_2, w_3, . . . is given. What is the probability of finding the system in a certain energy level w_1?

This problem is of course equivalent to the following: Given a very large number of independent systems (atoms, molecules, . . .), all equal and capable of being in the energy states $w_1, w_2, w_3, \ldots$, how many of these systems in thermal equilibrium at the temperature T are in the ith quantum state?

The problem is solved in exactly the same way as if it were classical; we seek the law of distribution of a large number of systems among all their possible states. The result can be found from the following considerations: Each of the energy levels

$$w_1, w_2, w_3, \ldots \tag{1}$$

of the systems is assumed, for simplicity, to correspond to a single nondegenerate quantum state, which means that we count each degenerate level as many times as its degree of degeneracy. If, for instance, states 1 and 2 happen to have the same energy, we have $w_1 = w_2$ in the sequence (1). Then the probability of finding the system in the ith state is proportional to

$$e^{-w_i/kT}. \tag{2}$$

This is the obvious extension of the Boltzmann distribution law of classical statistics applied to the quantum case. Distribution law (2) can be derived by methods identical to those used in classical statistics. We may, for instance, proceed as follows:

A very large number N of systems identical to the one being considered is assumed to be in thermal equilibrium. Let the numbers of these systems found in the various states (1) be

$$N_1, N_2, N_3, \ldots, \tag{3}$$

respectively. We say that (3) defines a partition or distribution of the N systems among the possible energy levels (1). We must first find the number of ways in which the partition (3) can be realized; the most probable partition is then the one that can be realized in the maximum number of ways. Just as in the analogous classical case, this procedure is not rigorous, since we have assumed that all the quantum states are equally probable. Nevertheless, we adopt it because of its simplicity.

The number Π of ways of realizing (3) can be calculated as follows. From the N systems given, we first choose N_1 to assign to the level w_1; this can be done in $\binom{N}{N_1}$ ways. From the remaining $N - N_1$

systems we choose N_2 for the energy level w_2, and this we can do in $\binom{N - N_1}{N_2}$ ways. The N_3 systems can then be chosen from the remaining $N - N_1 - N_2$, in $\binom{N - N_2 - N_2}{N_3}$ ways, and so on, until no systems remain. Thus the number of ways in which partition (3) can be realized is equal to the product

$$\Pi = \binom{N}{N_1}\binom{N - N_1}{N_2}\binom{N - N - N_2}{N_3}\cdots$$

$$= \frac{N!}{N_1!(N - N_1)!}\,\frac{(N - N_1)!}{N_2!(N - N_1 - N_2)!}\,\frac{(N - N_1 - N_2)!}{N_3!(N - N_1 - N_2 - N_3)!}\cdots$$

$$= \frac{N!}{N_1!N_2!N_3!\cdots}. \tag{4}$$

We have still to take into account that the sum of the numbers N_1, N_2, N_3, . . . equals the total number N of systems:

$$\begin{aligned}\sum_i N_i &= N_1 + N_2 + N_3 + \cdots \\ &= N.\end{aligned} \tag{5}$$

We also have

$$\sum_i N_i w_i = N_1 w_1 + N_2 w_2 + \cdots = W, \tag{6}$$

where W is the total energy of the N systems. To obtain the most probable partition, we must now determine which combination of numbers N_1, N_2, N_3, . . . , satisfying (5) and (6), maximizes (4).

This problem is solved just as in classical statistics. Instead of maximizing Π, we maximize $\log \Pi$, which leads to the same final result. The factorials appearing in Π are first transformed by Stirling's formula, which, in the case of very large numbers, can be written

$$\log N! = N(\log N - 1).$$

From (4) and (5), we thus obtain

$$\begin{aligned}\log \Pi &= N(\log N - 1) - \sum_i N_i(\log N_i - 1) \\ &= N \log N - \sum_i N_i \log N_i.\end{aligned}$$

We seek the maximum of this expression with the supplementary conditions (5) and (6). By applying the method of undetermined multipliers, we reduce the problem to that of finding the maximum (without supplementary conditions) of the expression

$$N \log N - \sum_i N_i \log N_i - \alpha \sum_i N_i - \beta \sum_i N_i w_i,$$

where α and β are parameters independent of the N_i. Taking the partial derivative of the preceding expression with respect to N_i and equating it to zero, we find

$$-\log N_i - 1 - \alpha - \beta w_i = 0.$$

From this we get

$$N_i = e^{-1-\alpha} e^{-\beta w_i},$$

or, introducing the new constant

$$A = e^{-1-\alpha},$$

we have

$$N_i = A e^{-\beta w_i}. \tag{7}$$

The constants A and β are to be determined so that conditions (5) and (6) are fulfilled.

The constant β, as in classical statistics, is connected to the absolute temperature by the relation

$$\beta = \frac{1}{kT}, \tag{8}$$

where k is the Boltzmann constant ($k = 1.36 \times 10^{-16}$ erg deg^{-1}). This can be seen very easily if we first note that (8) is certainly valid in classical statistics. Then the correspondence principle states that (8) is also true for large quantum numbers. But β is independent of the quantum number. Hence if (8) is verified for large quantum numbers, it must hold for any quantum number.

Using Eq. (8), we can write Eq. (7) as

$$N_i = A e^{-w_i/kT}. \tag{9}$$

From Eq. (5) we then derive

$$N = A \sum_j e^{-w_j/kT},$$

from which we obtain the value of A:

$$A = N \Big/ \sum_j e^{-w_j/kT}. \tag{10}$$

Substituting in Eq. (9), we obtain

$$N_i = N e^{-w_i/kT} \Big/ \sum_j e^{-w_j/kT}. \tag{11}$$

Thus the probability for one of the systems to be in the *i*th state is

$$\Pi_i = e^{-w_i/kT} \Big/ \sum_j e^{-w_j/kT}. \tag{12}$$

7-2 THERMAL EQUILIBRIUM AMONG THE QUANTUM STATES OF AN ATOM OR A MOLECULE

The extension of the Boltzmann distribution law to quantum theory leads to interesting applications for atoms.

We consider two quantum states, 1 and 2, of an atom whose energies are w_1 and w_2, respectively and whose internal quantum numbers are J_1, J_2. State 1 is then $2J_1 + 1$ times degenerate, and state 2 is $2J_2 + 1$ times. Let N_1 and N_2 be the numbers of atoms in the energy levels w_1 and w_2, respectively, at temperature T. Since level w_1 consists of $2J_1 + 1$ coincident levels and level w_2 of $2J_2 + 1$ levels, N_1 and N_2 are proportional to $(2J_1 + 1)e^{-w_1/kT}$ and $(2J_2 + 1)e^{-w_2/kT}$, respectively. We have, therefore,

$$\frac{N_2}{N_1} = \frac{2J_2 + 1}{2J_1 + 1} e^{-(w_2-w_1)/kT}. \tag{13}$$

We apply Eq. (13) numerically to sodium vapor to calculate the ratio of atoms N_1 and N_2 that are in thermal equilibrium, in the ground state $3\,^2S_{1/2}$ and in the state $3\,^2P_{3/2}$, respectively. The transition between these two states produces the D_1 line with wavelength 5890 Å and frequency $\nu = 5.1 \times 10^{14}$. The difference in energy between the two states is therefore

$$w_2 - w_1 = h\nu = 3.34 \times 10^{-12} \text{ erg.}$$

In our case,

$$J_1 = \tfrac{1}{2}, \qquad J_2 = \tfrac{3}{2};$$

therefore we find, applying (13),

$$\frac{N_2}{N_1} = \frac{4}{2} e^{-(3.34\times 10^{-12})/kT} = e^{-24,500/T} = 2 \times 10^{-10,680/T}.$$

Values of this ratio for different temperatures are given in Table 6.

We conclude therefore that, even at very high temperatures, the number of atoms in the state $3\,{}^2P_{3/2}$ is always a very small fraction of the atoms in the ground state; this sufficiently justifies the name *ground state* given to the deeper energy level. We should of course keep in mind that all this applies to states in thermal equilibrium, for if this equilibrium is perturbed, these results are not valid. Thus, for instance, when an electric discharge is produced through the vapor, many more atoms may appear in excited states than are predicted for thermal equilibrium; this is because collisions with ions accelerated by the electric field to velocities much higher than thermal velocities excite many of the atoms to states of higher energy.

Similar phenomena are observed for the atoms of several other elements; up to very high temperatures, almost all the atoms are in the ground state in thermal equilibrium. There are other atoms, however, with energy levels very near the ground state. Thus, for instance,

Table 6 Population of the $3^2P_{3/2}$ Excited State of Na

Temperature, T	N_2/N_1
273	2×10^{-39}
1000	4.7×10^{-11}
2000 (common temp of several flames)	9.7×10^{-6}
4000 (temp of electric arc crater)	0.0044
10,000	0.173
∞	2

the ground state in the alkali earth metals is a ${}^2P_{1/2}$ term and, very near it, lies the other member of the doublet ${}^2P_{3/2}$. For aluminum, the separation between these two terms is 15 wave numbers, corresponding to an energy difference $w_2 - w_1 = 15hc = 2.95 \times 10^{-15}$ erg. We see that in this case, even at ordinary temperatures, the exponential factor in (13) is almost 1; thus, the ratio of the numbers of atoms in the two states is approximately equal to the ratio of the weights of the two states. (For aluminum this ratio is 2.) The ground term of thallium is an intermediate case similar to that of aluminum; but for thallium the energy difference between the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ terms is about 8000 cm^{-1}, and hence larger than for aluminum. At low temperatures, therefore, a very small percentage of thallium atoms is in the ${}^2P_{3/2}$ state, whereas at temperatures around 1000 and 1200°C, many of these atoms are excited to this state. This can be observed experimentally by looking at the absorption lines in the Tl spectrum. At low temperatures, only those absorption lines that belong to the series which has the ground state ${}^2P_{1/2}$ as its lowest term are very intense. At higher temperatures, some lines starting from the ${}^2P_{3/2}$ state also begin to appear with increasing intensity. The ratio of the anomalous dispersion coefficients for two absorption lines, one starting from the ${}^2P_{1/2}$ state, and the other from the ${}^2P_{3/2}$ state, have been measured at various temperatures; from this one can verify the Boltzmann distribution law between the two quantum states ${}^2P_{1/2}$ and ${}^2P_{3/2}$ for this case.

We should note the following difficulties in our derivation of the equilibrium distribution among the various quantum states of an atom. When the principal quantum number approaches infinity, the energy w approaches zero and therefore the Boltzmann factor $e^{-w/kT}$ approaches 1. It follows that the sum (over the infinite number of states) in the denominator of Eqs. (11) and (12) diverges; therefore, if this formula were correct, the probability of finding the atom in any quantum state would be zero.

The reason for this apparent contradiction is that the Boltzmann distribution law has been extended to quantum states on the assumption that the atoms do not perturb each other. This is generally true for the quantum states of an atom which are not too high above the ground state. But the higher quantum states have very extended orbits, and consequently they are strongly perturbed in collisions with other atoms of the gas. This means that the sum in the denominator of (11) and (12) must not be extended over all quantum states; it is sufficient to sum only over those states the dimensions of whose orbits are smaller than the mean distance between the atoms of the gas. Thus the sum remains finite.

Gas molecules, like atoms, are also distributed among the various quantum states according to the Boltzmann law. There is a difference, however, in that the ground state of an atom almost always lies rather far from all the other energy levels of the atom. Thus almost all atoms are in their ground states when the temperature is not exceedingly high. Molecules, on the other hand, have many rotational levels not very far from the ground state. Hence, molecules in thermal equilibrium are distributed among these levels according to Boltzmann's law. Frequently, a vibrational level is also excited, particularly in the heavier molecules, even at ordinary temperatures.

7-3 ANTI-STOKES LINES IN FLUORESCENCE AND IN THE RAMAN EFFECT

The so-called anti-Stokes lines in fluorescent light and in the Raman effect have their origin in the thermal equilibrium among the various quantum states.

Normally, the frequency of fluorescent light is lower than that of the primary light (Stokes law). This is because the majority of the fluorescent atoms are in the ground state (*a*), Fig. 42. When the atoms are illuminated with light of the appropriate frequency ν, they absorb one quantum $h\nu$ and reach the excited level (*b*). From this level they may fall back into a lower level (*c*), emitting one quantum $h\nu'$ of fluorescent light with frequency ν'. From the figure one can see that $\nu' \leq \nu$, as predicted by Stokes law. However, exceptions to this law are often observed: for example, fluorescence lines or Raman effect lines with a frequency slightly higher than that of the primary light. These lines are called *anti-Stokes lines*.

Anti-Stokes lines appear when the fluorescent atom (or molecule) has an energy level (*c*) not far from the ground state (*a*); therefore, in thermal equilibrium, several atoms will be in state (*c*). Then fluorescence may also occur by the absorption of a quantum $h\nu'$, which brings the atom from (*c*) to (*b*). From (*b*) the atom can then fall back

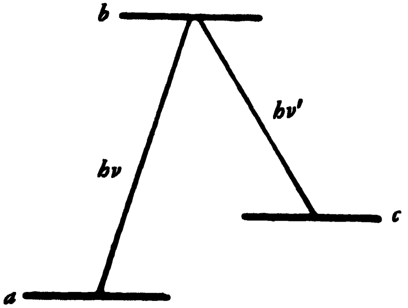

Figure 42

to (*a*), emitting one quantum $h\nu$ of fluorescent light. Since $\nu' < \nu$, the emitted lines are anti-Stokes. A similar mechanism gives rise to the Stokes and anti-Stokes Raman effect lines.

An appreciable number of atoms can be thermally excited to a given level only if the energy difference between this level and the ground state is not much larger than kT; therefore, the frequency difference between the anti-Stokes and the primary exciting line cannot be much larger than kT/h. This difference, actually, is rarely found to exceed 500 or 600 cm^{-1} at normal temperatures.

7-4 AVERAGE OSCILLATOR ENERGY

We now compute the average energy of a harmonic oscillator at the temperature T by applying the Boltzmann law. The energy levels of an oscillator are represented by the formula $w_n = h\nu(n + \frac{1}{2})$; here ν is the oscillator frequency and n is an integer which can assume the values 0, 1, 2, ... Since the energy scale is determined except for an arbitrary additive constant, we subtract $h\nu/2$ from the energy levels so that all energies are counted from the ground state. With this convention, the energy levels of the oscillator become

$$w_n = nh\nu \qquad (n = 0, 1, 2, \ldots). \tag{14}$$

The probability of finding the oscillator in thermal equilibrium, in the nth state, is given, according to Eq. (12), by

$$\Pi_n = e^{-(h\nu/kT)n} \Big/ \sum_{j=0}^{\infty} e^{-(h\nu/kT)j}.$$

The denominator is just the geometric series, which can be easily summed:

$$\sum_{j=0}^{\infty} e^{-(h\nu/kT)j} = \frac{1}{1 - e^{-h\nu/kT}}. \tag{15}$$

Hence,

$$\Pi_n = (1 - e^{-h\nu/kT})e^{-(h\nu/kT)n}. \tag{16}$$

We can now calculate the average oscillator energy, which is

$$\bar{w} = \sum_0^{\infty} w_n \Pi_n = (1 - e^{-h\nu/kT})h\nu \sum_0^{\infty} ne^{-(h\nu/kT)n}.$$

To sum this series we differentiate both sides of (15) with respect to ν. We obtain

$$-\frac{h}{kT}\sum_{j=0}^{\infty} je^{-(h\nu/kT)j} = -\frac{(h/kT)e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2}.$$

Hence,

$$\sum_{j=0}^{\infty} je^{-(h\nu/kT)j} = \frac{e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2}. \tag{17}$$

If we substitute this into the expression for $\bar{w}$ we finally obtain

$$\bar{w} = \frac{h\nu}{e^{h\nu/kT} - 1}. \tag{18}$$

This fundamental formula was derived and applied for the first time by Planck in his classical investigation of the spectrum of blackbody radiation; it led him to the quantum theory of radiation.

It is of interest to compare (18) with the results obtained from classical statistics. According to the classical principle of equipartition of energy, the average kinetic energy of the oscillator should be $kT/2$. Furthermore, the average values of the kinetic and potential energies of a harmonic oscillator are the same; hence the average potential energy must also equal $kT/2$. Thus, according to classical statistics, the average total energy is

$$w_{\mathrm{Cl}} = kT. \tag{19}$$

We note that for very high temperatures, such that $(h\nu/kT) \ll 1$, both the classical and quantum theories give practically the same result. If we expand the denominator of (18) up to the second term, we obtain

$$w = \frac{h\nu}{(1 + (h\nu/kT) + \cdots) - 1} = \frac{h\nu}{h\nu/kT} = kT,$$

which is the classical result (19). There are important differences, however, between the two equations at lower temperatures. Figure 43 illustrates these differences; the average energy as computed by the two equations is plotted as a function of T. We see that the differences are very pronounced for temperatures of the order of magnitude of, or smaller than,

$$T_0 = \frac{h\nu}{k}. \tag{20}$$

This shows us that, for an oscillator of macroscopic frequency, the differences would become noticeable only at temperatures too low to

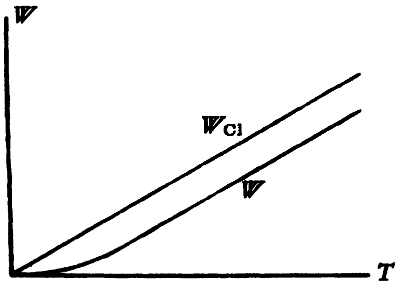

Figure 43

be reached. In contrast to this, the differences for atomic oscillators are very pronounced, even at ordinary temperatures.

Equation (18) is of great importance in the study of the specific heats of the solids (cf. Sections 6-1 and 6-2); it is applied to the vibrations of the atoms of a solid body around their equilibrium positions and leads to a complete explanation of the behavior of the specific heats as a function of temperature. Following Planck, we shall apply this formula to the analysis of blackbody radiation.

7-5 SPECTRUM OF BLACKBODY RADIATION

All bodies, when heated to a sufficiently high temperature, become incandescent and emit radiation at a certain rate. Of course, cool bodies at ordinary temperatures also emit a considerable amount of radiant energy but at a rate much smaller than that of a very hot body. If the body is at room temperature, it does not get cooler as it emits energy, because it absorbs energy from its surroundings at the same rate as it radiates energy to the surroundings.

The radiation emitted by a body at a certain temperature T usually has a continuous spectrum. Let $e(\nu)\,d\nu$ be the radiant energy emitted by the body per unit time and unit surface, in the frequency interval between ν and $\nu + d\nu$. The function $e(\nu)$ is called emissive power of the body at temperature T. The emissive power depends not only on the body properties but also on the temperature. Whenever we wish to stress this temperature dependence, we write $e(\nu,T)$.

The total emissive power is often introduced: that is, the total energy radiated by the body per unit time and unit surface in all frequencies. The total emissive power is thus given by

$$e_{\text{tot}}(T) = \int_0^\infty e(\nu,T)\,d\nu. \tag{21}$$

Generally, e_{tot} is a rapidly increasing function of the temperature.

When radiant energy strikes the surface of a body, part of it is absorbed; the rest is reflected or, if the body is partially transparent, it is transmitted through the body. We call the absorbing power of a body the ratio a of the energy absorbed to the incident energy.

The absorbing power of a body depends on several factors. First, on the nature of the body, especially on its surface. There are bodies that absorb almost all of the incident radiant energy (for example, lamp black) and bodies that reflect it almost entirely (for instance, a good silvered surface). Furthermore, the absorbing power depends on the frequency of the incident radiation. Several bodies absorb certain frequencies strongly, whereas they reflect or transmit others almost entirely. We know, for example, that the color of a body is due to the wavelengths that are primarily reflected from its surface. The absorbing power may also depend, to some extent, on the body temperature. And, finally, it depends on the angle of incidence of the radiation. In this chapter we shall always consider the absorption of isotropic incident radiation, that is, radiation of the same intensity in all directions. For a given body, therefore, the absorbing power is taken as a function of ν and T only:

$$a = a(\nu,T).$$

By definition, the value of a can never exceed unity. The value $a = 1$ corresponds to a perfect absorber, that is, a body which completely absorbs all the radiant energy, regardless of frequency, incident on its surface. Such a body is called a *perfect blackbody;* all the blackbodies in nature are only approximations, however good, to a perfect blackbody.

There is an important relation (Kirchhoff's law) between the emissive and the absorbing power of any body: The ratio of the emissive to the absorbing power of a body depends only on the frequency and temperature of the body and is independent of its nature:

$$\frac{e}{a} = E(\nu,T), \tag{22}$$

where $E(\nu,T)$ is a universal function (i.e., the same for all bodies).

We can see the physical significance of the function $E(\nu,T)$ by applying Eq. (22) to a perfect blackbody (by placing $a = 1$). We then have $e = E(\nu,T)$, which means that the universal function $E(\nu,T)$ is the emissive power of a perfect blackbody. We can therefore express Kirchhoff's law as follows: The ratio of the emissive to the absorbing power of any body at a given temperature for a given frequency equals the emissive power for that frequency of a perfect blackbody at the same temperature. From this we clearly see the importance of determining the emissive power of a perfect blackbody, or as it is usually referred to, the ***blackbody spectrum***—the function $E(\nu,T)$.

The best practical and theoretical way of representing a black surface is by a small hole in the wall of a very large cavity. A ray of light which enters the cavity through the hole is reflected many times against the inner walls of the cavity before whatever is left of it gets out again; since it is absorbed almost completely during these multiple reflections, we may place the absorbing power of the hole equal to 1. This is why the entrance of a church or the orifice of a large cave appears black when viewed from the outside.

The inside of the cavity always contains a certain density of radiant energy, because the walls, being at temperature T, continuously emit radiation; but then the same walls also absorb part of the same radiation. The density of the radiation reaches its equilibrium value when the walls absorb as much energy per second as they emit per second. Here we may neglect the presence of the hole, because of its very small dimensions with respect to those of the cavity.

However, a small part of the radiation that fills the cavity flows continuously through the hole. The hole thus behaves as a source of radiation. Furthermore, since the hole behaves as a blackbody, the spectral intensity distribution of the emitted radiation must be the same as that of a blackbody at temperature T.

We designate the density of the radiant energy with frequency between ν and $\nu + d\nu$ in the cavity as $u(\nu,T)\,d\nu$ and calculate that part of it that escapes per unit time through the small hole AB of area S (Fig. 44). To do this we calculate the radiation in the frequency interval $d\nu$ which flows per second through AB within the solid angle $d\omega$ in a direction that makes an angle ϑ with the normal to the cavity surface. This is obviously the amount of radiation that is contained initially in the oblique cylinder $ABCD$ and is moving in the direction defined by $d\omega$. The base of the cylinder is the aperture of the hole and the side AD is equal to c, the velocity of light. Since the volume of the cylinder is $Sc \cos \vartheta$, the energy in the frequency interval ν to $\nu + d\nu$ contained in it is

$$u(\nu,T)Sc \cos \vartheta \, d\nu.$$

Since this radiation is isotropic, the fraction of it moving in the direction

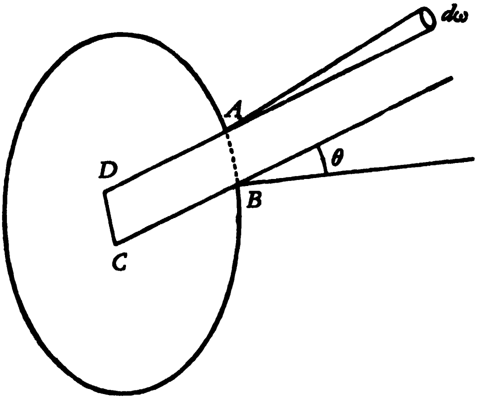

Figure 44

defined by $d\omega$ is

$$\frac{d\omega}{4\pi}\, u(\nu,T)Sc \cos\vartheta \, d\nu.$$

The total radiation in the frequency interval $d\nu$ emitted by the hole per unit time is given by the integral of the previous expression over the solid angle; the integration must be extended over the half-sphere corresponding to the outgoing directions from the cavity. Since

$$\int_{\text{half sphere}} \cos\vartheta \, d\omega = 2\pi \int_0^{\pi/2} \cos\vartheta \sin\vartheta \, d\vartheta = \pi,$$

one finds that the energy radiated per unit time is

$$\frac{Sc}{4}\, u(\nu,T)\, d\nu. \tag{23}$$

On the other hand, since the aperture is equivalent to a perfect black surface, its emitting power is given by $E(\nu,T)$: therefore the emitted energy (23) must also be given by $SE(\nu,T)\, d\nu$. Comparing the two expressions, one obtains

$$E(\nu,T) = \frac{c}{4}\, u(\nu,T). \tag{24}$$

This is the desired relation between the emitting power of a blackbody and the density of radiant energy in equilibrium at temperature T with the walls of a cavity.

In particular, we note from (24) that, since $E(\nu,T)$ is a function only of the frequency and the temperature, the function $u(\nu,T)$ depends only on ν and T. As a consequence, the radiation in thermal equilibrium inside a cavity (with or without black walls) has a density and a spectral distribution that depend only on the temperature of the walls and not on the material of which they are made. This property can also be derived from direct thermodynamic considerations.

7-6 PLANCK'S EQUATION

Equation (24) reduces the problem of the theoretical determination of the blackbody spectrum to an analysis of the radiation inside a cavity; more precisely, to finding the function $u(\nu,T)$. We may now use different procedures, not all of them completely acceptable. From thermodynamics we can derive only two laws: Stefan's and Wien's. Later we shall discuss the significance of these laws which restrict the shape of the function $u(\nu,T)$ but which are insufficient for a complete determination of the function. For this we must rely on statistical arguments. In the early studies, classical statistical mechanics was employed, but the results were unacceptable. Thus, the Rayleigh-Jeans law, based on classical statistics, requires the total density of radiant energy in thermal equilibrium to be infinite at any temperature.

Out of this failure of classical methods came Planck's inspiration to introduce a completely new idea: the hypothesis that the energy values of an oscillator form a discrete and not a continuous set. This was the beginning of the quantum theory. Its first result was the Planck radiation formula which, in very good agreement with experiment, describes the blackbody spectrum.

One of the simplest ways to deduce the Planck formula is the following (later we shall consider other methods based on different criteria). We consider the radiation contained inside a cavity of volume Ω and with completely reflecting walls. The electromagnetic field inside this cavity has properties very similar to those of an elastic body. In particular, it can oscillate with certain characteristic frequencies that depend on the shape and dimensions of the cavity.

We can show* that the frequency distribution is an asymptotic function of the volume of the cavity only: The frequency interval between ν and $\nu + d\nu$ contains

$$dN = \Omega \frac{8\pi}{c^3} \nu^2 \, d\nu \tag{25}$$

* A very simple although not completely rigorous method of deriving Eq. (25) is the following: We suppose that the cavity has the shape of a cube of side a. For each characteristic frequency, a stationary wave system exists. If λ is the wavelength and α, β, γ are the direction cosines of the wave system, the following three conditions must be imposed for stationary waves to exist in the directions parallel to the three edges of the cube:

$$a = \frac{\lambda}{\alpha} \frac{n_1}{2}; \qquad a = \frac{\lambda}{\beta} \frac{n_2}{2}; \qquad a = \frac{\lambda}{\gamma} \frac{n_3}{2},$$

where n_1, n_2, n_3 are three integers.

Since $\alpha^2 + \beta^2 + \gamma^2 = 1$, we can deduce from the preceding equation that

$$n_1^2 + n_2^2 + N_3^2 = \frac{4a^2}{\lambda^2}. \tag{a}$$

A system of stationary waves can be found corresponding to each triad of positive integers satisfying this condition. To find how many of these correspond to frequencies in the interval $d\nu$, we consider a cartesian coordinate system having n_1, n_2, n_3 as coordinates. According to (a), the distance R of the point n_1, n_2, n_3 from the origin is

$$R = \frac{2a}{\lambda} = \frac{2a}{c} \nu$$

Hence the frequencies between ν and $\nu + d\nu$ correspond to those points with integer coordinates that lie in the positive octant between the two spheres with their centers at the origin and with radii $(2a/c)\nu$ and $(2a/c)(\nu + d\nu)$. The corresponding volume is

$$\frac{1}{8} 4\pi \left(\frac{2a\nu}{c}\right)^2 \frac{2a}{c} \, d\nu = \frac{4\pi a^3}{c^3} \nu^2 \, d\nu.$$

Since in each unit cell (one unit of length on a side) there is just one point of the required kind, this volume, on the average, is obviously equal to the number of points with integer coordinates inside it. This then gives the number of stationary wave systems belonging to the frequency interval $d\nu$. We must also take into account that there are two kinds of characteristic oscillations for each stationary wave system: one for each polarization. Hence, the number of characteristic frequencies is twice that of the number of stationary waves. The resulting number is then $(8\pi a^3/c^3)\nu^2 \, d\nu$, which coincides with (25) because the volume of the cavity is $\Omega = a^3$

characteristic frequencies. Each one of these exhibits all the properties of a harmonic oscillator of the same frequency. Owing to this, which is completely justified by the quantum theory of the radiation, the electromagnetic field inside the cavity can be pictured as a system of many oscillators, each one corresponding to one of the characteristic frequencies.

Since each oscillator of the radiation field is similar in all respects to an ordinary mechanical oscillator, its average energy in thermal equilibrium at temperature T is given by (18). Hence the total energy of the dN oscillators with frequencies in the range $d\nu$ is, from (25),

$$\Omega \frac{8\pi}{c^3} \frac{h\nu^3}{e^{h\nu/kT} - 1} d\nu.$$

This same energy can also be written $\Omega u(\nu,T)\, d\nu$, from which we find

$$u(\nu,T) = \frac{8\pi}{c^3} \frac{h\nu^3}{e^{h\nu/kT} - 1}. \tag{26}$$

This is Planck's equation. From (24) we obtain an equivalent expression for the emissive power of a blackbody:

$$E(\nu,T) = \frac{2\pi}{c^2} \frac{h\nu^3}{e^{h\nu/kT} - 1}. \tag{27}$$

Figure 45 shows the behavior of the function (26) for a given value of the temperature. The radiation density has a maximum at some frequency $\nu_{\max}$, which can be found by solving the equation obtained when the derivative of (26) with respect to ν is equated to zero. After

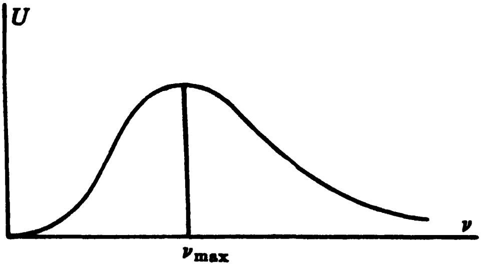

Figure 45

a few simple algebraic transformations, we obtain

$$\nu_{\max} = \alpha \frac{k}{h} T, \tag{28}$$

where α is the root of the equation

$$(3 - \alpha)e^{\alpha} = 3.$$

This equation has a root very near 2.77. We therefore get

$$\nu_{\max} = 5.8 \times 10^{10} T. \tag{29}$$

Equation (29) is Wien's displacement law and could also have been deduced directly from the laws of thermodynamics applied to the radiation. It tells us that the frequency corresponding to the maximum intensity or density of blackbody radiation is proportional to the absolute temperature of the radiation.

This law [Eq. (29)] has important applications in astrophysics, where it is used to determine stellar surface temperatures. To a sufficient approximation, we may consider the surfaces of most stars to be blackbodies radiating at their surface temperatures. From the continuous spectrum of the radiation emitted by a star, we can find the frequency of the most intense part of the spectrum (the most intense color). We can then apply (29) to find the corresponding surface temperature of the star.

From the Planck equation, we can easily deduce Stefan's law, which also can be obtained by thermodynamic arguments alone. We compute the energy density $u(T)$ of the radiation in the cavity, for all frequencies. We have

$$u(T) = \int_0^\infty u(\nu,T)\,d\nu = \frac{8\pi}{c^3}\int_0^\infty \frac{h\nu^3\,d\nu}{e^{h\nu/kT} - 1} = \frac{8\pi k^4 T^4}{c^3 h^3}\int_0^\infty \frac{x^3\,dx}{e^x - 1}.$$

The value of the last integral is $\pi^4/15$. Therefore we obtain

$$u(T) = \frac{8\pi^5 k^4}{15 c^3 h^3} T^4. \tag{30}$$

Thus the total energy density (for all frequencies) is proportional to the fourth power of the absolute temperature (Stefan's law).

Through (30) we can also immediately derive the total emissive power of the blackbody; from (24), we have

$$E(T) = \frac{c}{4}u(T) = \frac{2\pi^5k^4}{15c^2h^3}T^4 = 5.55 \times 10^{-5}T^4 \text{ erg cm}^{-2}\text{ sec}^{-1}. \tag{31}$$

This result, also, is in very good agreement with experiment; both the fourth-power dependence and the value of the coefficient in (31) are found to be correct.

7-7 STATISTICAL EQUILIBRIUM BETWEEN ATOMS AND BLACKBODY RADIATION

We consider an atom inside a cavity whose walls are at temperature T. Let the energy levels of the atom, which for simplicity we take as nondegenerate, be w_1 and w_2; furthermore let $w_1 < w_2$. Since the cavity is filled with blackbody radiation at temperature T, two inverse processes can occur:

(1) If the atom is in the excited state w_2, it can jump down to state w_1 by emitting one quantum of frequency

$$\nu = \frac{w_2 - w_1}{h}.$$

(2) If the atom is in quantum state w_1, it can absorb one photon of frequency ν from the cavity and thereby jump to the excited state w_2.

Obviously, in thermal equilibrium, the average probabilities of these two inverse processes are necessarily equal. Let P_1 and P_2 be the probabilities of finding the atom in the states w_1 and w_2, respectively. The Boltzmann law then gives us

$$\frac{P_1}{P_2} = e^{(w_2-w_1)/kT} = e^{h\nu/kT}. \tag{32}$$

The probability for an atom in state w_1 to absorb one quantum of frequency ν and thus jump to state w_2 is proportional to the density of radiation of frequency ν: It is given by $Bu(\nu,T)$. The probability per unit time for process (2) is then equal to $P_1Bu(\nu,T)$.

If the atom is initially in the excited state w_2, it can jump down to the state w_1 either spontaneously or through the influence of radiation of frequency ν. We therefore write, for the probability per unit time of the transition from w_2 to w_1, the expression

$$A + Cu(\nu,T). \tag{33}$$

The second term represents the transitions induced by the radiation which, as we shall see, must be included to ensure statistical equilibrium. The probability per unit time for process (1) is given by

$$P_2[A + Cu(\nu,T)]$$

To ensure statistical equilibrium, as we mentioned, the two processes (1) and (2) must occur with the same frequency. Therefore,

$$P_1Bu(\nu,T) = P_2[A + Cu(\nu,T)].$$

From this we obtain, through Eq. (32),

$$e^{h\nu/kT} = \frac{A}{Bu(\nu,T)} + \frac{C}{B}. \tag{34}$$

If we now substitute Planck's formula (26) in this equation, we obtain

$$e^{h\nu/kT} = \frac{A}{(8\pi h\nu^3/c^3)B}\,(e^{h\nu/kT} - 1) + \frac{C}{B}.$$

Since this equality must be valid at all temperatures, we must have

$$A = \frac{8\pi h\nu^3}{c^3}\,B \tag{35}$$

and

$$B = C. \tag{36}$$

These important relations among A, B, and C are due to Einstein.[84] They establish a useful relationship between the probability A for spontaneous emission and the absorption coefficient B [Eq. (35)]. Furthermore they tell us that radiation can induce both transitions from the lower to the higher level and vice versa; Eq. (36) shows that the probabilities for these two processes, $Bu(\nu,T)$ and $Cu(\nu,T)$ are, indeed, equal.

We may also reverse the above chain of reasoning and deduce the Planck equation from relations (35) and (36). The argument is the following: From Dirac's[82] quantum theory of radiation, without any statistical considerations, we can derive relations (35) and (36) among the coefficients A, B, and C directly. By the same arguments as those used above, we obtain Eq. (34), which, using Eqs. (35) and (36), we now write as

$$e^{h\nu/kT} = \frac{8\pi h\nu^3}{c^3}\frac{1}{u(\nu,T)} + 1.$$

From this we get

$$u(\nu,T) = \frac{8\pi}{c^3}\frac{h\nu^3}{e^{h\nu/kT} - 1},$$

which is the Planck equation.

7-8 QUANTUM THEORY OF PARAMAGNETIC GASES

Langevin [111] developed a theory of the paramagnetism of gases by applying classical statistical mechanics to gases. In this theory he assigned to each gas molecule (or atom) its own magnetic moment.

If, then, a magnetic field is imposed, the magnetic moments of all the molecules tend to align themselves parallel to the field. But the thermal motion tends to destroy this alignment and to produce a random distribution of moments in all directions. These two opposing actions produce statistical equilibrium; individual moments are oriented in all directions, but more of them point in the direction of the field than in any other direction. On the average, there is thus an over-all magnetization of the gas in the direction of the field which accounts for the phenomenon of paramagnetism in gases.

The quantum modification of this paramagnetic theory consists essentially of introducing space quantization. This means that the component of the magnetic moment along the field can only assume certain discrete values; the limiting values of these components (the largest positive and largest negative values) correspond to the parallel and antiparallel orientations of the moment with respect to the field.

More precisely, let J be the internal quantum number of the atom; the magnetic quantum number m, that is, the projection of J along the field, can then have the values J, $J - 1$, . . . , $-(J - 1)$, $-J$. If μ is the magnetic moment, its component along the field is

$$\mu\frac{m}{J}, \qquad (37)$$

and its magnetic energy equals

$$-H\mu\frac{m}{J}, \tag{38}$$

where H is the magnetic field intensity. We assume, for simplicity, that the ground level of the atom is very far from all other energy levels, so that the influence of the latter may be neglected.

Thermal equilibrium, in accordance with the Boltzmann law, then occurs among the magnetic levels (38) into which the ground state is split. The probability of finding the atom in the state with magnetic quantum number m is given, according to Eq. (12), by

$$\Pi_m = e^{(H\mu/kTJ)m} \bigg/ \sum_{m=-J}^{m=J} e^{(H\mu/kTJ)m}.$$

The average value of the magnetic moment in the direction of the field is then given, according to Eq. (37), by

$$\bar{\mu} = \frac{\mu}{J}\sum_{m=-J}^{m=J} m\Pi_m = (\mu/J)\sum_{m=-J}^{m=J} me^{(H\mu/kTJ)m} \bigg/ \sum_{m=-J}^{m=J} e^{(H\mu/kTJ)m}.$$

One can easily evaluate the two sums in this expression. The denominator is the sum of a geometric progression with ratio equal to $e^{H\mu/kTJ}$; this gives immediately

$$\sum_{m=-J}^{m=J} e^{(H\mu/kTJ)m} = \frac{\sinh\,[H\mu(J+\frac{1}{2})/kTJ]}{\sinh\,(H\mu/2kTJ)}.$$

The other sum is also easily obtained by taking the derivative of both sides of the previous equation with respect to the argument $H\mu/kTJ$. The result is

$$\sum_{m=-J}^{m=J} me^{(H\mu/kTJ)m} = \left[(J+\tfrac{1}{2})\sinh\frac{H\mu}{2kTJ}\cosh\frac{H\mu}{kTJ}(J+\tfrac{1}{2}) - \tfrac{1}{2}\sinh\frac{H\mu}{kTJ}(J+\tfrac{1}{2})\cosh\frac{H\mu}{2kTJ}\right] \bigg/ \sinh^2\frac{\mu H}{2kTJ}.$$

We now obtain from the last two equations the mean value of the magnetic moment:

$$\bar{\mu} = \frac{\mu}{J}\left[(J+\tfrac{1}{2})\coth\frac{H\mu(J+\frac{1}{2})}{kTJ} - \tfrac{1}{2}\coth\frac{h\mu}{2kTJ}\right]. \tag{39}$$

If H is not too large, the previous expression can be expanded in a series up to the linear term in H; thus we have

$$\bar{\mu} = \frac{\mu^2}{3kT}\frac{J+1}{J}H, \tag{40}$$

from which we obtain the following expression for the magnetic susceptibility (per atom):

$$\chi = \frac{\bar{\mu}}{H} = \frac{\mu^2}{3kT}\frac{J+1}{J}. \tag{41}$$

The magnetic susceptibility is thus inversely proportional to the absolute temperature (Curie law) as in Langevin's theory.

The Langevin result is obtained from (41) as the limiting case for $J = \infty$; space-quantization then has no effect, and we obtain:

$$\chi = \frac{\mu^2}{3kT}. \tag{42}$$

Equation (42) is usually employed to define the effective magnetic moment of an atom, even when the conditions for its validity are not satisfied; by definition,

$$\mu^* = \sqrt{3\chi kT}. \tag{43}$$

We write μ^* in place of μ to stress that μ^* in general does not give the magnetic moment of the atom; it is rather a convenient, though quite arbitrary, quantity to characterize the observed magnetic properties of the atom. The relation between μ and μ^* is easily obtained from Eqs. (41) and (43):

$$\mu^* = \mu\sqrt{\frac{J+1}{J}}. \tag{44}$$

The effective moment μ^* is very often measured in Weiss magnetons (equivalent to about $\frac{1}{5}$ of the Bohr magneton), because some physicists believe that μ^* in solids and solutions is always a multiple of the Weiss magneton. There is, however, no theoretical justification for this, and it is by no means clearly supported by experimental results.

Expression (41) for the magnetic susceptibility of gases has been verified experimentally only for sodium vapor ($\mu = 1$ Bohr magneton, $J = \frac{1}{2}$) and is in very good agreement with the Gerlach [98] measurements. The equation has also been extensively applied to calculate the paramagnetic properties of ions in a solution; here, of course, the conditions for the validity of (41) are only approximately satisfied. Further, only in a few special cases can the magnetic properties of the isolated ion of a gas (properties known through spectroscopic analysis) be identified with those it acquires in solution.

However, these conditions are sufficiently well-satisfied for the equation to apply to the trivalent ions of the rare earths. The reason for this is that these ions have closed electronic shells, which therefore do not exhibit magnetic effects, plus a certain number of electrons in the incomplete $4f$ shells (1 for Ce, 2 for Pr, . . . , 14 for Cp) which are responsible for the magnetic properties. Since these shells are restricted to a deep inner region of the atom, they are unaffected by external perturbations; the magnetic properties of these ions are thus practically unaffected by the molecules of the solvent, and are therefore, to a very good approximation, the same as in the gaseous state. The rare earth ions have been analyzed theoretically, principally by Sommerfield [131] and Van Vleck.[60]

The theoretical values of μ and J can be substituted into (41), and a correction can then be applied to include the perturbations of the energy levels nearest the ground state, which we neglected in our derivation. Figure 46 illustrates the very good agreement found in this way between theory and experiment; the various elements appear along

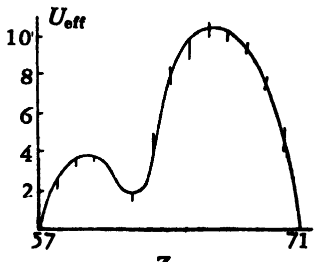

Figure 46

the abscissa, whereas the effective magnetic moments μ^* are plotted along the ordinate. The continuous curve represents the theoretical values, the vertical lines the experimental results; the probable errors in the measurements are given by the lengths of the lines.

Similar calculations have also been attempted for other elements, in particular, the iron group. However, the agreement in these cases is not nearly so good. This certainly arises, in great part, because the magnetic shells of these ions are much more exposed (not as deep lying) to external perturbations than are those of the equivalent ions of the rare earths; hence, the perturbations of the surrounding molecules of the solvent are much more effective.

7-9 THE PRINCIPAL THERMODYNAMIC QUANTITIES

By extending the Boltzmann law to quantized systems, we can derive not only their statistical but also their thermodynamic properties if we know their energy levels. In this section we calculate the principal thermodynamic quantities as functions of the energy levels. We consider a system of N atoms (or molecules) all equal and independent; let the energy levels of each atom be w_0, w_1, w_2, . . . , listed in increasing order. We measure the energy of each level relative to the ground state so that we place

$$w_0 = 0. \tag{45}$$

We further assume that the atoms do not perturb each other, so that we can apply the Boltzmann law to calculate their statistical distribution.

The function

$$Z(\beta) = \sum_{j=0}^{\infty} e^{-\beta w_j}, \tag{46}$$

referred to as the *sum of the states* or the *partition function* is very important for future considerations. We can calculate it once we know the energy levels w_j.

Taking the derivative of (46) with respect to β, we obtain

$$Z'(\beta) = -\sum_{j=0}^{\infty} w_j e^{-\beta w_j}. \tag{47}$$

The number N_j of the systems in the state j is given, from Eq. (11), by

$$N_j = Ne^{-w_j/kT} \Big/ Z\left(\frac{1}{kT}\right),$$

and since each of these has the energy w_j, their total energy is $N_j w_j$. The total energy of all N atoms is, therefore,

$$W = \sum w_j N_j = N \sum_{j=0}^{\infty} w_j e^{-w_j/kT} \Big/ Z\left(\frac{1}{kT}\right).$$

Using Eq. (47) and placing

$$\beta = \frac{1}{kT}, \tag{48}$$

we may write

$$W = -N\frac{Z'(\beta)}{Z(\beta)} = -N\frac{d}{d\beta}\log Z(\beta), \tag{49}$$

which gives us the thermal energy of the system as a function of β, that is, of the temperature.

We now calculate the entropy S of the system of atoms. Since the system does no external work, we have

$$S = \int \frac{dW}{T}. \tag{50}$$

Considering Eqs. (48) and (49), we obtain

$$\begin{aligned}\int \frac{dW}{T} &= k\int \beta\, dW = k\beta W - k\int W\, d\beta \\ &= k\beta W + kN\int \frac{d}{d\beta}\log Z(\beta)\, d\beta \\ &= k\beta W + kN\log Z(\beta),\end{aligned}$$

$$S = kN\left[\log Z(\beta) - \beta\frac{d}{d\beta}\log Z(\beta)\right]. \tag{51}$$

This expression for the entropy has been derived from the thermodynamic definition (50). We can also derive it by applying the Boltzmann relation between entropy and probability:

$$S = k\log \Pi.$$

To do this one uses the Stirling equation to calculate the logarithm of expression (4) for the probability and then uses (11) for the populations in the various states. We shall not carry out this calculation here.

From (51) and (49) we also obtain immediately the expression for the free energy

$$F = W - TS = -NkT \log Z(\beta). \tag{52}$$

In the same way all the other thermodynamic quantities can be expressed in terms of the function $Z(\beta)$.

7-10 THE NERNST PRINCIPLE OR THE THIRD LAW OF THERMODYNAMICS

In the usual thermodynamic definition the entropy, [Eq. (50)], is determined only to within an arbitrary additive constant. This indeterminacy in the entropy means that results obtained with it involve constants whose values have to be determined experimentally. This is clearly so when the state of equilibrium among different substances is determined thermodynamically as, for instance, the state of chemical equilibrium between gaseous substances or between the saturated vapor and the condensed liquid state below it. The undetermined constants in the final results stem from the additive constants present in the individual entropies of the components that are interacting in the equilibrium state.

With this in mind, Nernst[46] introduced a third law of thermodynamics which enables us to evaluate the entropy constant. The Nernst principle affirms that the entropy of any substance is zero at zero absolute temperature.

If this principle is valid, the constant of the entropy is not an undetermined quantity, since the integral defining the entropy must be taken between definite limits: The lower limit is the absolute zero temperature and the upper limit the temperature of the equilibrium state. The entropy thus is given by

$$S = \int_0^T \frac{dQ}{T}, \tag{53}$$

where dQ is the infinitesimal amount of heat that the system absorbs reversibly at temperature T.

Important relations exist between the Nernst principle and quantum statistics. Here we discuss them briefly, without considering their applications to chemical equilibria, which is treated elsewhere.

To define the entropy, we use, instead of the thermodynamic definition, the statistical one:

$$S = k \log \Pi. \tag{54}$$

Here the entropy is expressed in terms of the probability Π of the state. Stated precisely, Π is not a probability but is the number of different ways in which the state can be realized. Thus, it is proportional to the probability of the state that is obtained by dividing Π by the total number of possible states that can occur.

In classical statistics the definition of the number Π necessarily contains several arbitrary elements. To define Π we must, in fact, subdivide the phase-space of the atoms into an arbitrary number of small cells of equal volume; a state is then defined when the number of atoms per cell is given. Obviously, the number of ways in which a certain state can occur is a function of the size chosen for each cell; the smaller the volume, the smaller is Π. We see that, when the cell volume is altered, Π is also altered by a multiplicative factor. Consequently its logarithm, and hence the entropy (54) of the system, vary by an additive constant. Therefore in classical statistical mechanics the entropy is characterized by the presence of an arbitrary additive constant, as in the usual thermodynamic definition.

In contrast to this, all arbitrariness in the cell size disappears in quantum statistics. Instead of cells we introduce quantum states, so that the number of ways in which a state of the system can be realized (the state being defined by the number of atoms in each quantum state) has a well-defined value given by (4). Equation (54) then unambiguously defines the value of the entropy for the given state.

To relate this to the Nernst principle, we assume first that the lowest state of our system is a single state. At zero absolute temperature, all the atoms are in the lowest state; the over-all state of the system then corresponds to the atoms all being in a single quantum state. Obviously this state can occur in only one way, as we can also see from (4). We thus have $\Pi = 1$ and, from (54), $S = 0$ in agreement with the Nernst principle.

In some cases, however, the Nernst principle may not be valid. Let us assume, for instance, that the ground level of the atoms of our system is r times degenerate. At absolute zero the N atoms are distributed among the r degenerate single quantum states belonging to the ground level. Obviously, for the most probable distribution there are N/r atoms in each of these states. In accordance with (4), the number of ways in which this distribution can occur is

$$\Pi = \frac{N!}{\left[\left(\frac{N}{r}\right)!\right]^r}.$$

If we use Stirling's formula in the approximation

$$\log n! = n(\log n - 1)$$

to evaluate $\log \Pi$, we obtain

$$\log \Pi = N(\log N - 1) - r\frac{N}{r}\left(\log \frac{N}{r} - 1\right) = N \log r.$$

From (54) we then find that the value of the entropy at absolute zero is

$$S = kN \log r, \tag{55}$$

which is different from zero if $r > 1$.

This result does not necessarily mean that the Nernst principle is not universally valid, since we derived it by considering all the atoms to be completely independent of each other; in reality there is always a certain amount of coupling, however weak, among them, which reduces the degree of degeneracy of the ground state. The entropy at absolute zero is then very small, if not exactly zero. We shall see later that, for gases, certain peculiar degeneracy phenomena occur which further reduce the entropy. In spite of these considerations, we cannot exclude the possibility that there may be systems for which the Nernst principle is not valid; i.e., systems for which the entropy is not zero at absolute zero. However, at least for the simplest systems, this does not happen.

According to classical statistics, the specific heat of all systems should differ from zero even at absolute zero. The principle of the conservation of energy requires the mean kinetic energy of the atoms to be proportional to T; hence its derivative with respect to T must be a constant. The contribution of the kinetic energy to the specific heat is therefore constant and cannot vanish at absolute zero. This implies complete disagreement between the Nernst principle and classical statistics. If C is the thermal capacity of the system, the integral defining the entropy can be written

$$S = \int \frac{dQ}{T} = \int C \frac{dT}{T}.$$

If C is different from zero at absolute zero, this integral diverges logarithmically for $T = 0$, and we cannot take zero as its lower limit. Hence the specific heat of all substances must be zero at $T = 0$, and this is what actually happens for quantized systems. See, for example, the case of the oscillator in Fig. 43: from the shape of the two curves we see that, at $T = 0$, $dw/dT = 0$, whereas $(dw_{cl}/dT) > 0$, showing that the specific heat vanishes in the quantum theory but not in the classical one.

We can understand quantitatively why the specific heat of any quantum system vanishes at absolute zero by noticing that, at very low temperatures, the energy of thermal motion (of the order of kT) is too small to raise the system even to the first excited level. Therefore, all the components of the system are in the ground state and their energy is independent of the temperature; consequently the specific heat must be zero. From this it follows that the closer together the two energy levels are near the ground state, the more slowly does the specific heat go to zero as $T \rightarrow 0$. The specific heat in the classical case, which may be considered the limit of the quantum case when the energy levels are infinitely close together, can never go to zero, since even slight increases in the temperature increase the energy of the system.

The behavior of the specific heats of quantized systems is studied in Section 3-1 (for molecular rotations) and in Sections 6-1 and 6-2 (for solids).

8

The Quantum Statistics of Gases

8-1 PHASE-SPACE CELLS FOR A PERFECT GAS

This chapter deals with the quantization of the translational motion of molecules in gases. The quantization of the rotational motions and, in general, of the relative motions of the various atoms or constituents of the molecules does not exhibit any characteristics that are of special interest from the statistical point of view.

To simplify the problem, we consider, for the time being, an ideal gas whose molecules may be approximated by mass points without internal structure. We also assume that the effect of collisions among the molecules can be neglected, and that, when a molecule hits the container wall, it is reflected elastically.

Let N be the number of molecules inside a vessel of volume V. Since the system has $3N$ degrees of freedom, its average kinetic energy is, according to the principle of equipartition,

$$W_{cl} = \frac{3NkT}{2}; \tag{1}$$

in the absence of potential energy, (1) is the total thermal energy of the gas. The thermal capacity from (1) is,

$$C_{cl} = \frac{dW_{cl}}{dT} = \frac{3Nk}{2}. \tag{2}$$

As is well known, the thermal capacity does not depend on the temperature. We have already seen that this is incompatible with the Nernst principle, which demands that the specific heat vanish at absolute zero. If we assume the Nernst principle to be valid, we must also assume that the translational motion of the molecules of a gas follows the quantum laws.

Tetrode,[129, 134] as early as 1913, first attempted to introduce quantization into gas statistics. He tried to build a statistical theory of perfect gases based on the Boltzmann law with the additional assumption of a fixed size for the phase-space cells. He assigned the volume h^3 to each cell, where h is the Planck constant.

We may justify this hypothesis, according to the rules of quantization, as follows: We assume that the gas is in a cube whose edge length is a. Since we neglect collisions among the molecules, each molecule moves in straight lines inside the cube, bouncing back and forth between opposite walls. Either wave mechanics or the Sommerfeld conditions can be used to quantize this motion. The result in both cases is that the energy of any stationary state (which is the same as the kinetic energy, since the potential energy is zero) is given by

$$L_{n_1,n_2,n_3} = \frac{h^2}{8ma^2}(n_1^2 + n_2^2 + n_3^2), \tag{3}$$

where n_1, n_2, n_3 are three nonnegative integers. If a is macroscopic as in our case (a^3 is the volume of the container), the energy levels written above are so dense that they practically form a continuous distribution. We can easily compute how many states have energies between L and $L + dL$. We represent each state by a point with nonnegative integer coordinates (n_1,n_2,n_3); the states of the system then define a cubic lattice of unit size in the positive octant. The states with energies between L and $L + dL$ are those for which

$$\frac{8ma^2}{h^2}L < n_1^2 + n_2^2 + n_3^2 < \frac{8ma^2}{h^2}(L + dL).$$

The points representing these states are those belonging to the positive octant contained in the interspace between the two spheres of radius

$$\sqrt{\frac{8ma^2}{h^2}}\sqrt{L}$$

and

$$\sqrt{\frac{8ma^2}{h^2}}\sqrt{L+dL}=\sqrt{\frac{8ma^2}{h^2}}\left(\sqrt{L}+\frac{dL}{2\sqrt{L}}\right).$$

In the limit of very large L, the number of these states is manifestly given by the volume of the space between the two spheres belonging to the positive octant, that is, by

$$dQ=\frac{1}{8}4\pi\frac{8ma^2}{h^2}L\sqrt{\frac{8ma^2}{h^2}}\frac{dL}{2\sqrt{L}}.$$

Remembering that a^3 is the volume V of the container, we can now derive the number of those kinetic energy states which belong to the interval dL:

$$dQ=\frac{2\pi V}{h^3}(2m)^{3/2}\sqrt{L}\,dL. \tag{4}$$

This is equivalent to placing the volume of each phase-space cell equal to h^3. To see this, note that from the relation between the momentum and kinetic energy of a molecule $L = p^2/2m$ we find that the momenta lying between $p = \sqrt{2mL}$ and $p + dp = \sqrt{2m(L+dL)} = \sqrt{2mL} + \sqrt{m/2L}\,dL$ correspond to kinetic energies between L and $L + dL$. The interval dL of kinetic energies thus corresponds to the space between the spheres with radii p and $p + dp$ in momentum-space; the volume of this interspace is

$$d\omega = 4\pi p^2\,dp = 2\pi(2m)^{3/2}\sqrt{L}\,dL.$$

Since the total number of states in this volume element in momentum-space is dQ, given by (4), the density of states in momentum-space is

$$\frac{dQ}{d\omega}=\frac{V}{h^3}.$$

But an element $d\omega$ of momentum-space corresponds to an element $d\tau = V\,d\omega$ in phase-space (the molecules are free to move within the volume V). Hence, the phase-space volume belonging to each state is

$$\frac{d\tau}{dQ}=\frac{V d\omega}{dQ}=h^3,$$

that is, each phase-space cell has a volume h^3.

Finally, there is a correlation between cell size in the phase-space and the Heisenberg uncertainty principle. We consider, for simplicity, only one degree of freedom: a point that moves along a line. According to Heisenberg, the following relation exists between the accuracy Δq and the accuracy Δp, to which the coordinate and the momentum of the particle can be known:

$$\Delta q \Delta p \sim h.$$

This means that the position of the point in its phase-space is determined only to within a small area of the order of magnitude of h. The analog in three dimensions is found to be a phase-space volume equal to h^3. Therefore, if we imagine the phase-space subdivided into cells having this volume, we may determine in which cell the point lies but, in accordance with the Heisenberg principle, it is meaningless to try to determine its position more accurately inside the cell. According to quantum mechanics, assigning the point to a particular cell does, indeed, represent the maximum that can be known about the state of the system.

Once we define in this way the phase-space volume of cells, the number Π of ways in which a certain state can be realized is also defined; hence, from the Boltzmann relation $S = k \log \Pi$, we obtain the value of the entropy of the perfect gas without any undetermined constant. If we followed this procedure rigorously however, our results would be unacceptable. We would find, indeed, that the entropy of a certain amount of gas at a given pressure and temperature is not proportional to the amount of gas, but instead grows very quickly as the number of molecules in the gas increases. Nevertheless, owing to a fortuitous incompleteness in his treatment, Tetrode obtained a correct expression for the entropy; this expression was then confirmed by further investigations, both experimental and theoretical.

Since the work of Tetrode, many papers have been published in an attempt to justify his result; almost all, however, contain more or less explicit violations of the principles of Boltzmann statistics. This is not surprising since, as we now know, Boltzmann statistics is not applicable to gases. In its place quantum statistics (either Bose-Einstein or Fermi statistics) must be used. The results obtained with quantum statistics coincide with those derived from Boltzmann statistics only for high temperatures and low gas densities; for low temperatures and large densities, so-called degeneracy phenomena (deviations from the classical laws), occur and can be explained only with quantum statistics.

8-2 THE ENTROPY CONSTANT FOR GASES

We can obtain the entropy constant of gases correctly, even without using quantum statistics, if we follow Stern's [182] procedure. With conventional thermodynamics we can calculate the vapor pressure of a saturated vapor, that is, the condition for thermodynamic equilibrium between a vapor and its condensed phase. The result contains an undetermined constant that depends on the entropy constant of the gas. On the other hand, we may also derive the condition for equilibrium between the condensed phase and its vapor from a statistical treatment based upon certain appropriate hypotheses; by this method the vapor pressure can be completely determined, and a comparison of the two results then gives the entropy constant.

We assume that there are N molecules in a container of volume V and consider the molecular mass points without structure. We assume, further, that n of the N molecules belong to the gaseous phase and $N - n$ to the condensed phase. We now calculate the conditions for the statistical equilibrium between the two phases.

We introduce a few simplifying hypotheses about the properties of the condensed phase in order not to complicate the problem unnecessarily. In particular, we assume that:

1. The volume of the solid phase is negligible compared to the volume V of the container.
2. The binding of the molecules to each other in the solid phase is so strong that no thermal vibrations are excited at the given temperatures; consequently, both the thermal energy and the specific heat of the solid phase can be neglected up to the temperatures that we are interested in.
3. To remove a molecule from the solid phase, a certain constant energy w is necessary.

To find the condition for statistical equilibrium between the two phases, we first compute the probability that n molecules are in the gas phase and $N - n$ in the solid phase and then find the value of n which makes this probability a maximum.

The complex system of N molecules with n of these molecules in the gas phase and $N - n$ in the solid phase has a large number of quantum states. These states are determined by the various ways of choosing n gas molecules from the total available number N, while the remaining $N - n$ molecules are arranged in various ways within the solid lattice as well as by the ways in which the velocities of the individual molecules are assigned to the different quantum states of the translational motion (see Section 8-11). Let W_{nj} be the energy of a quantum state of the total system of N molecules, where n is the number of molecules belonging to the gaseous phase in this quantum state and j specifies this particular quantum state from among the many possible ones with n molecules in the gaseous phase and $N - n$ in the solid phase.

The probability for this state according to the Boltzmann law is proportional to $P_{nj} = e^{-W_{nj}/kT}$. Hence the total probability for states with n molecules in the gaseous and $N - n$ in the solid phase is proportional to

$$P_n = \sum_j P_{n_j} = \sum_j e^{-W_{nj}/kT}. \tag{5}$$

We want to calculate P_n and the value of n for which this is a maximum. The various quantum states corresponding to a given n are obtained as follows: From the N molecules we choose n for the gaseous phase; this can be done in $\binom{N}{n}$ ways, all obviously equivalent to one another. The $N - n$ remaining molecules can be arranged in the lattice of the solid phase in $(N - n)!$ different ways, all equivalent to one another. According to hypothesis 2, we must assign a single quantum state of the solid phase to all these arrangements of the molecules inside the solid, because the higher-energy levels of the solid are never excited at our temperatures.

We must now distinguish among the n gas molecules by assigning to each a kinetic energy permitted by the quantization of its translational motion. Thus if the kinetic energies corresponding to the quantum states of the translational motion of the molecule are

$$L_1, L_2, \ldots, L_r, \ldots,$$

the total kinetic energy of the n molecules is

$$\sum_{i=1}^{n} L_{r_i},$$

where L_{r_i} is the kinetic energy of the ith molecule which is in the rth quantum state in the gaseous phase. The total energy of the n gas molecules is obtained by adding to their kinetic energy the energy nw required to remove them from the solid (hypothesis 3). On the other hand, hypothesis 2 requires the energy of the $N - n$ molecules of the solid phase to be zero. Therefore the total energy of the state is

$$W_{nj} = nw + \sum_{i=1}^{n} L_{r_i}.$$

As we said above, this energy level is

$$\binom{N}{n}(N-n)! = \left(\frac{N!}{n!}\right) - \text{fold}$$

degenerate, corresponding to the $\binom{N}{n}$ ways of choosing the gas molecules and the $(N - n)!$ ways of arranging the $N - n$ solid molecules within their crystal lattice.

Expression (5) then becomes

$$P_n = \frac{N!}{n!} \sum_{r_1, r_2, \ldots, r_n = 0}^{\infty} \exp\left[-\frac{1}{kT}\left(nw + \sum_{i=1}^{n} L_{r_i}\right)\right]$$

$$= \frac{N!}{n!} \exp\left[-\frac{nw}{kT}\right]\left(\sum_{r=0}^{\infty} e^{-L_r/kT}\right)^n. \tag{6}$$

Note that the last expression is correct only if the various gas molecules are free to distribute themselves among the translational quantum states in a completely uncorrelated way so that the probability of any molecule's being in a particular quantum state is independent of the presence of any other molecule in that state. This hypothesis, characteristic of Boltzmann statistics, is not valid in quantum statistics. To a first approximation, however, we may consider it still valid if the gas density is sufficiently small.

To calculate the sum in (6), we recall that the number of translational quantum states of a molecule with kinetic energy between L and $L + dL$ is given by Eq. (4):

$$dQ = \frac{2\pi V}{h^3}(2m)^{3/2}\sqrt{L}\,dL. \tag{7}$$

Using this relation, we may replace the sum on the right side of (6) by the integral

$$\frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty e^{-L/kT}\sqrt{L}\,dL.$$

Integrating, we obtain

$$\sum_{r=0}^{\infty} e^{-L_r/kT} = \frac{V}{h^3}(2\pi mkT)^{3/2}. \tag{8}$$

On substituting this into (6), we have

$$P_n = \frac{N!}{n!}e^{-nw/kT}\frac{V^n}{h^{3n}}(2\pi mkT)^{3n/2}. \tag{9}$$

Our problem is now to find the value of n for which P_n is a maximum. In practice it is easier to find the maximum of $\log P_n$. Since the logarithm of the factorial terms can be approximated by Stirling's formula

$$\log n! = n(\log n - 1),$$

we obtain

$$\log P_n = N(\log N - 1) + n\left[1 - \log n - \frac{w}{kT} + \log\frac{V(2\pi mkT)^{3/2}}{h^3}\right].$$

We now equate to zero the derivative of this expression with respect to n:

$$1 - \log n - \frac{w}{kT} + \log\frac{V(2\pi mkT)^{3/2}}{h^3} - 1 = 0.$$

This immediately gives

$$\frac{n}{V} = \frac{(2\pi mkT)^{3/2}}{h^3}e^{-w/kT}. \tag{10}$$

This formula represents the complete solution of our problem: it gives the density n/V of molecules in the gaseous phase (really a saturated vapor) in equilibrium with the condensed phase of the system at the temperature T.

As we said at the beginning of the paragraph, we have derived formula (10) not because of its intrinsic interest (which is not great, since we made assumptions about the solid phase which do not correspond at all to the properties of a real solid), but only to compare it with the corresponding thermodynamic result. In this way we can deduce the entropy constant for a gas. For this we still must calculate the condition for thermodynamic equilibrium between the gaseous and the condensed phase.

We recall that hypothesis 2 requires the internal energy and the specific heat of the solid phase to be zero. Consequently, as demanded by Nernst's principle, the entropy, together with the free energy, should also be zero. The total free energy F of the system is then reduced to the free energy of the gaseous phase alone.

The energy of the n molecules belonging to the gaseous phase equals the sum of the energy nw necessary to separate them from the solid phase and the energy of their thermal motion, $\frac{3}{2}nkT$; that is, $n(w + \frac{3}{2}kT)$. The entropy S is a function of V, T, and the number n of molecules:

$$S = S(n,V,T);$$

therefore, the free energy is given by

$$F = n(w + \tfrac{3}{2}kT) - TS(n,V,T).$$

When the free energy is a minimum, the system is in thermodynamic equilibrium; this happens when

$$0 = \frac{\partial F}{\partial n} = w + \tfrac{3}{2}kT - T\frac{\partial S}{\partial n}.$$

Replacing w in this equation by its value from (10), we have

$$\frac{\partial S}{\partial n} = -k \log n + \frac{3k}{2} + k \log \frac{V(2\pi mkT)^{3/2}}{h^3}.$$

On integrating with respect to n, we find the entropy. The integration constant, which is still a function of V and T, is uniquely determined by the obvious condition that the entropy must vanish for

$n = 0$, that is, when there is no gaseous phase. We have

$$S = \int_0^n \left[-k \log n + \frac{3k}{2} + k \log \frac{V(2\pi mkT)^{3/2}}{h^3} \right] dn$$

$$= -kn(\log n - 1) + \frac{3kn}{2} + kn \log \frac{V(2\pi mkT)^{3/2}}{h^3}$$

$$= kn \left\{ \frac{3}{2} \log T - \log \frac{n}{V} + \log \frac{(2\pi mk)^{3/2} e^{5/2}}{h^3} \right\}, \qquad (11)$$

where e is the base of the natural logarithms. Equation (11) gives the entropy of our gas without any undetermined constant.

We have deduced (11) for gas molecules that are point masses with no inner structure. This is a good approximation only for a monoatomic gas and only if the temperature is so low that all the atoms are in the ground state, which is also assumed to be nondegenerate. If the ground state is p-fold degenerate, we find, by analogous arguments, that

$$S = nk \left[\frac{3}{2} \log T - \log \frac{n}{V} + \log \frac{(2\pi mk)^{3/2} p e^{5/2}}{h^3} \right]. \qquad (12)$$

We discussed the problem of the entropy constant for a diatomic gas in Section 3-3.

8-3 CONDITION FOR EQUILIBRIUM IN THERMAL IONIZATION; THERMIONIC EFFECT

The results of the preceding section have important and extensive applications to the thermodynamics of chemical reactions, of vaporization, etc. Here we shall discuss only the application of the dissociation of atoms into ions and electrons to high-temperature phenomena. We shall also study the thermionic effect.

Starting with the first of these two problems, we consider a monoatomic vapor composed of a certain kind A of atoms. At high temperatures, some of the atoms become ionized, that is, they lose one electron and become ions A^+. The phenomenon is similar to a chemical reaction that can be symbolically written

$$A \rightleftharpoons A^+ + e^-,$$

where e^- stands for the electron. We want to calculate the percentage of ionized atoms at a given temperature.

We assume that at the beginning there are n atoms in a container of unit volume. Let N be the degree of ionization at temperature T (nx is the number of ionized atoms). The container then contains $n(1-x)$ neutral atoms A, nx ions A$^+$, and nx electrons. Thus we have a mixture of three gases; an atomic gas, an electron gas, and an ionic gas. The free energy of the system is

$$F = W - TS.$$

As we know, the condition for thermodynamic equilibrium is that F be a minimum.

The energy W of the system is the sum of the kinetic energies of all the particles and the ionization energy of nx ionized atoms. All together, there are $n(1-x) + nx + nx = n(1+x)$ particles, each with an average kinetic energy $\frac{3}{2}kT$. The total kinetic energy is then

$$\tfrac{3}{2}nkT(1+x).$$

If w is the ionization energy of an atom, the ionization energy of the n ionized atoms is nwx. The total energy of the system is then

$$W = \tfrac{3}{2}nkT(1+x) + nwx.$$

To obtain the entropy of the mixture we must sum the separate entropies of the individual components. Let m_A be the mass of an atom, practically identical with that of an ion. Let m be the mass of the electron, and let p_A and p_J be the statistical weights of the ground states of the atoms and the ions, respectively. The statistical weight of the electrons is equal to 2, owing to the two possible spin orientations. We can then write

$$\begin{aligned} S = nk(1-x)&\left\{\tfrac{3}{2}\log T - \log n(1-x) + \log\frac{p_A(2\pi m_A k)^{3/2}e^{5/2}}{h^3}\right\} \\ &+ nkx\left\{\tfrac{3}{2}\log T - \log nx + \log\frac{p_J(2\pi m_A k)^{3/2}e^{5/2}}{h^3}\right\} \\ &+ nkx\left\{\tfrac{3}{2}\log T - \log nx + \log\frac{2(2\pi m k)^{3/2}e^{5/2}}{h^3}\right\}, \end{aligned}$$

and, for the free energy,

$$F = \tfrac{3}{2}nkT(1 + x) + nwx - nkT(1 + x)\log\frac{(2\pi kT)^{3/2}e^{5/2}}{nh^3}$$
$$+ nkT\{\log(1 - x) - \log m_A{}^{3/2}p_A\}$$
$$+ nkTx\left\{\log\frac{x^2}{1 - x} - \log\frac{2p_J m^{3/2}}{p_A}\right\}.$$

We can obtain the degree of ionization at thermodynamic equilibrium from the condition that the free energy F be a minimum:

$$\frac{\partial F}{\partial x} = 0.$$

This gives

$$n\frac{x^2}{1 - x} = \frac{2p_J}{p_A}\frac{(2\pi mk)^{3/2}}{h^3}T^{3/2}e^{-w/kT}. \tag{13}$$

The degree of ionization x can be derived from this equation. Notice, in particular, that (13) includes the law of mass action. The first member can indeed be written $nx \cdot nx/n(1 - x)$, and hence is equal to the product of the ion abundance and the electron abundance divided by the atom abundance.

As a numerical example we apply this equation to the ionization of sodium vapor. The ionization potential of sodium is 5.12 volts, corresponding to an energy of $w = 8.15 \times 10^{-12}$ erg. For the sodium atom we have $p_A = 2$ (ground state ${}^2S_{1/2}$) and for the ion $p_J = 1$ (ground state ${}^1S_0$, with a noble gas structure). Therefore we find from (13), inserting the values of constants and using exponentials to the base 10, that

$$\frac{nx^2}{1 - x} = 2.42 \times 10^{15}T^{3/2}10^{26,000/T}.$$

For $T = 4000$, which is approximately the temperature in the crater of an arc discharge, we have

$$\frac{nx^2}{1 - x} = 1.94 \times 10^{14}.$$

Let $n = 3.5 \times 10^{16}$, that is, an atomic density that gives a pressure of about 1 mm Hg at ordinary temperatures. Then

$$\frac{x^2}{1 - x} = 5.5 \times 10^{-3},$$

which gives $x = 0.071$. Under the above conditions the degree of ionization is about 7 per cent.

The theory of thermal ionization as developed above is due to the Indian physicist Saha,[40] who first applied it to the study of ionization in stellar atmospheres.[17,18]

We now present the theory of the thermionic effect as another application of Eq. (12). All metals, when heated to high enough temperatures, emit electrons from their surfaces. The metallic walls of a cavity within a bloc of metal at a uniform temperature T thus emit electrons so that the cavity is filled with an "electron gas." The density of this gas does not grow without limit, of course, since the metallic walls, in addition to continuously emitting electrons, reabsorb some of the electrons of the electron gas which strike them. Eventually, statistical equilibrium is reached, and the number of electrons emitted per second by the walls is then equal to the number per second reabsorbed. We shall now calculate the density of the electron gas when it is in equilibrium with the metal walls at a temperature T.

For simplicity, we take a metal-surrounded cavity of unit volume and assume that there are n electrons in equilibrium inside the cavity. To find n we must calculate the free energy of our system (metal + electron gas) and impose the condition that it be a minimum. That is, we seek the value of n that makes the free energy a minimum. The free energy is given by the sum of the free energies of the metal and of the electron gas. The metal free energy does not depend on n. This is not obvious a priori; indeed, the thermal properties of the metal may well be altered by the loss of n electrons. However, this is not observed to be the case; in fact, the electrons (free or bound) in a metal do not contribute especially to the specific heat (and hence neither to the energy, nor to the free energy and the entropy). This agrees very well with the quantum theories of the structure of metals, according to which the electrons bound in the metal—as well as the free electrons—are quantized and contribute to the specific heat only at very high temperatures. Since we are interested in the minimum of the free energy with respect to the variable n, we may neglect the free energy of the metal because it does not depend on n. We are thus left with only the free energy of the electron gas. To calculate this we first find the total energy of the electron gas, which is the sum of the kinetic energy of the n electrons, $\frac{3}{2}nkT$, and the energy necessary to extract the n electrons from the metal, nw, if w is the energy necessary to remove one electron. Thus the total gas energy is

$$U = wn + \tfrac{3}{2}nkT.$$

To calculate the free energy $F = U - TS$, we still need the entropy; this we obtain from Eq. (12) with $V = 1$ and $p = 2$. We then find

$$F = wn + \tfrac{3}{2}nkT - nkT\left[\tfrac{3}{2}\log T - \log n + \log\frac{2(2\pi mk)^{3/2}e^{5/2}}{h^3}\right].$$

We now find the value of n for which this expression is a minimum by equating to zero its derivative with respect to n:

$$0 = w + \tfrac{3}{2}kT - kT\left[\tfrac{3}{2}\log T - \log n + \log\frac{2(2\pi mk)^{3/2}e^{5/2}}{h^3}\right] + kT.$$

Hence

$$n = \frac{2(2\pi mk)^{3/2}}{h^3}\,T^{3/2}e^{-w/kT}$$

This is the desired expression for the density of an electron gas in equilibrium with the surface of a metal at a temperature T. Notice that the only metallic constant that appears in the expression for n is the work function w of the metal (that is, the extraction energy per electron); we can find its value directly from the limiting frequency in the photoelectric effect without knowing anything about the thermionic effect.

The number N of electrons emitted per unit time from a unit surface area of the heated metal is of much greater practical importance than n. From N, we can immediately calculate the thermionic saturation current.

We can deduce the order of magnitude of N from a knowledge of n. Because of the thermal motion of the electrons in the electron gas, the surface of the metal is continuously struck by electrons. From the kinetic theory of gases, we find that the number of electronic collisions occurring per unit time against a unit area is

$$n\sqrt{\frac{kT}{2m\pi}}.$$

Some of the electrons are reflected after colliding with the wall, while others penetrate into the metal. If ϑ is the probability that an electron penetrates the surface of the metal, the number of electrons entering the metal per unit time per unit area is then

$$\vartheta n\sqrt{\frac{kT}{2\pi m}}.$$

At equilibrium this number must equal the number N of electrons leaving a unit area of the metal per unit time. Therefore

$$N = 2\vartheta\,\frac{2\pi mk^2}{h^3}\,T^2 e^{-w/kT}.$$

In this equation, ϑ is still undetermined, but since the order of magnitude of ϑ is 1, the formula gives us the order of magnitude of N. To determine ϑ completely, we require hypotheses about the shape of the potential at the metal boundary; we shall not pursue this point further.

8-4 QUANTUM STATISTICS

The application of the Boltzmann distribution law to quantized systems as carried out in Section 7-1 is valid only for a system of identical particles that are independent of each other. For example, we may apply it immediately to calculate the statistical distribution of a system of identical and completely separated atoms among all their possible internal quantum states but not among the quantized states of their translational motion.

The situation is quite different, however, in dealing with the statistical properties of a gas. We assume for a moment that the gas consists of identical particles with no forces between them (a perfect gas). If each molecule were the only occupant of the container, any of the translational quantum states would be available to it (see Section 8-1); its total energy, consisting only of its kinetic energy, would then have any of the values given by (3):

$$L_1, L_2, L_3, \ldots, L_r, \ldots \tag{14}$$

We now consider two molecules moving around in the same container. Because the gas is a perfect gas, these molecules do not exert forces on each other, and each one should be free to move in any one of the energy levels (14). However, this is not the case, because, even though the two molecules do not interact with each other, they cannot be considered independent. Indeed, owing to the Pauli exclusion principle, there is an interaction between the two molecules; if one occupies a certain quantum state, the other must necessarily be in a different state. The same applies to N molecules in the container. If there are N identical molecules in the container and the Pauli principle is valid, we may always assign any one molecule to any one of the energy levels (14), provided however, that the N quantum states, occupied by the N molecules, all differ from each other. The situation is analogous to the distribution of the electrons inside an atom. That only two electrons are allowed in the lowest energy level, the K shell, has nothing to do with mechanical actions between the electrons but is a consequence of the Pauli principle which states that only two electrons can occupy the two available quantum states, one in each state of the K shell.

The interdependence of the translational quantum states of motion of the molecules of a gas is a notable example of an interaction between particles that is not due to forces between the molecules but to the Pauli principle. The statistics of a gas whose molecules obey the Pauli principle is called Fermi [88] statistics. We shall also deal, later, with a different type of interdependence between gas molecules which is the basis of Bose-Einstein statistics.[74, 84]

Using quantum-mechanical concepts, Dirac [81] has shown how to derive the statistical distribution of the molecules of a gas and what the origin of the differences between classical Boltzmann statistics and quantum statistics is. From such considerations, Dirac was also able to deduce independently the Fermi statistics.[17, 18]

Let x_1 be the coordinates of the first molecule (x_1 stands for x_1, y_1, z_1), x_2 the coordinates of the second molecule, x_N those of the Nth, and let

$$\psi_1(x), \qquad \psi_2(x), \qquad \psi_3(x), \ . \ . \ . \ , \psi_r(x) \tag{15}$$

be the eigenfunctions corresponding to the energy levels (14).

Thus, if the kth molecule occupies the quantum state r_m, its eigenfunction is $\psi_{r_m}(x_k)$. If, then, the first molecule occupies state r_1, the second state r_2, . . . , the Nth state r_N, the over-all eigenfunction of the system of N molecules is given by the product, (since the molecules exert no forces on each other)

$$\psi_{r_1}(x_1)\psi_{r_2}(x_2) \cdot \cdot \cdot \psi_{r_N}(x_N) \tag{16}$$

of the eigenfunctions of the individual molecules. This corresponds to the energy

$$L_{r_1} + L_{r_2} + \cdot \cdot \cdot + L_{r_N}. \tag{17}$$

Since the molecules are identical, this energy level has what is called a *resonance* or *exchange* degeneracy. This means that the system can be in the same energy level (17) by having its molecules assigned to the same quantum states r_1, r_2, . . . , r_N, but in a different order. Let P be one of the $N!$ possible permutations of the indices 1, 2, . . . , N, and let P_1, P_2, . . . , P_N, be the new arrangement of the indices when we apply the permutation P to the original arrangement 1, 2, . . . , N. Then to the eigenvalue (17) there belong not only the eigenfunction (16) but all the $N!$ eigenfunctions:

$$\psi_P = \psi_{r_1}(x_{P_1})\psi_{r_2}(x_{P_2}) \cdot \cdot \cdot \psi_{r_N}(x_{P_N}). \tag{18}$$

If the quantum states r_1, r_2, . . . , r_N are all different from each other, then the $N!$ eigenfunctions (18) are all different; the energy level (17) is then $N!$-fold degenerate. If, instead, some of the indices r_1, r_2, . . . , r_N coincide (this cannot happen if the Pauli principle is valid, because then two or more particles cannot be in the same quantum state), some of the eigenfunctions (18) are the same and the degree of degeneracy of the energy level (17) is less than $N!$. Specifically, we assume that the indices r_1, r_2, . . . , r_N are divided into s groups which contain respectively N_1, N_2, . . . , N_s identical indices. The sum $N_1 + N_2 + \cdot \cdot \cdot + N_s$ must of course equal N and some of the numbers N_1, N_2, . . . , N_s may equal unity. The number of distinct eigenfunctions (18) is then obviously equal to the number of ways in which N objects can be divided into groups of $N_1, N_2, \ldots, N_s$, that is,

$$\frac{N!}{N_1!N_2! \cdots N_s!}. \tag{19}$$

Any linear combination of the degenerate eigenfunctions (18) is also an eigenfunction belonging to the same eigenvalue (17). We know that these linear combinations can be classified according to their symmetry properties under a permutation of the coordinates of the particles; whatever perturbations may be applied to the system, the eigenfunctions of one symmetry do not become eigenfunctions of a different symmetry. Two types of eigenfunctions are important in physics: the symmetric (the eigenfunctions do not change sign under any permutation of the coordinates of the particles) and the antisymmetric (the eigenfunctions retain their same absolute values under an arbitrary permutation of the coordinates of the particles, but they change their signs if the permutation is odd and do not change signs if the permutation is even). A symmetric combination can be obtained simply by adding all the $N!$ eigenfunctions (18) obtained by applying the permutations P. We have,

$$\psi_{\text{sym}} = \sum_{(P)} \psi_P \tag{20}$$

An antisymmetric linear combination on the other hand, is given by the sum

$$\psi_{\text{ant}} = \sum_{(P)} \pm \psi_P, \tag{21}$$

where the sign is taken as + or − according to whether the permutation is even or odd. We may also write the antisymmetric eigenfunction (21) as a determinant

$$\begin{vmatrix} \psi_{r_1}(x_1) & \psi_{r_1}(x_2) & \cdots & \psi_{r_1}(x_N) \\ \psi_{r_2}(x_1) & \psi_{r_2}(x_2) & \cdots & \psi_{r_2}(x_N) \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \psi_{r_N}(x_1) & \psi_{r_N}(x_2) & \cdots & \psi_{r_N}(x_N) \end{vmatrix}. \tag{22}$$

In nature there are particles whose eigenfunctions are always of the antisymmetric kind and particles whose eigenfunctions are always of the symmetric kind. To the first category belong, for example, electrons and protons, to the second helium nuclei (insofar as they can be considered particles) and photons.

We also know that the particles with antisymmetric eigenfunctions obey the Pauli principle. This is easily seen from the form (22) of the antisymmetric eigenfunction: If one of the quantum states is occupied by two molecules, two of the indices $r_1, r_2, \cdots, r_N$ are identical. Consequently, two rows of the determinant (77) are equal, and the determinant itself is identically zero.

If the eigenfunctions of the gas particles are of the symmetric kind, we shall say that the particles obey Bose-Einstein statistics; indeed, as we shall see later, this is the statistics that applies to all systems with symmetric eigenfunctions. We must now find in which states a system can be if it obeys either Bose-Einstein statistics or the Pauli principle (Fermi statistics) or, finally, in the ideal case, if all eigenfunctions (18) are possible quantum states of the system. The last case, which is never realized in nature, corresponds to classical Boltzmann statistics.

We suppose that a state of the gas is completely defined when the numbers

$$N_1, N_2, N_3, \ldots, N_r, \ldots \tag{23}$$

of molecules which occupy the successive energy levels are known. We always have

$$N_1 + N_2 + \cdots + N_r + \cdots = N.$$

Here N_1 of the indices $r_1, r_2, \ldots, r_N$ is taken equal to 1, N_2 equal to 2, $\ldots$, N_r equal to r, $\ldots$.

We first consider Bose-Einstein statistics. One and only one symmetric eigenfunction exists for the system of N molecules, and it is given by (20). Only one quantum state of the system corresponds to configuration (23); the configuration therefore can be realized in only one way.

We now consider the Pauli principle. If none of the numbers (23) is larger than 1 (that is, their values are either 1 or 0), there is an antisymmetric eigenfunction belonging to configuration (23), and it is given by (22). The eigenfunction is unique, and hence the configuration can be realized in only one way. If, instead, at least one of the numbers (23) is larger than 1, configuration (23) contradicts the Pauli principle and cannot occur; no antisymmetric eigenfunction exists for such a configuration.

Finally, in the unrealistic case for which all the eigenfunctions (18) correspond to real quantum states, the number of quantum states corresponding to configuration (23) would be, according to (19),

$$\frac{N!}{N_1!N_2!N_3!\cdots},$$

which is just the number of ways in which a particular distribution can be realized, according to Boltzmann statistics.

We now illustrate the different ways of counting states for the three different statistics (Bose-Einstein, Fermi, and Boltzmann) by a very simple numerical example. Let our system consist of two identical molecules, each of which we assume, can be in any one of just three translational quantum states. We represent these states by the three cells in Fig. 47. The numbers N_1, N_2, N_3, the sum of which must be 2, can have the following six values:

$$(2,0,0)\quad(0,2,0)\quad(0,0,2)\quad(0,1,1)\quad(1,0,1)\quad(1,1,0).$$

Figure 47 shows how these states are realized.

In the scheme corresponding to the Boltzmann statistics, the two molecules are represented by two different letters *a* and *b*, because states in which *a* and *b* are in different cells are different if one of these states can be obtained from the other by interchanging *a* and *b*. On the other hand, the same symbol *a* is used for both molecules in quantum statistics, since the two molecules are completely identical and no distinction can be made between them.

8-5 BOSE-EINSTEIN STATISTICS

The principal characteristic of Bose-Einstein statistics[75, 85] is that each distribution of the molecules has a unit weight, a distribution being defined by the number of molecules which are found in the first, second, . . . translation quantum state. With this, we can now calculate the law governing the statistical distribution of N molecules that obey Bose-Einstein statistics.

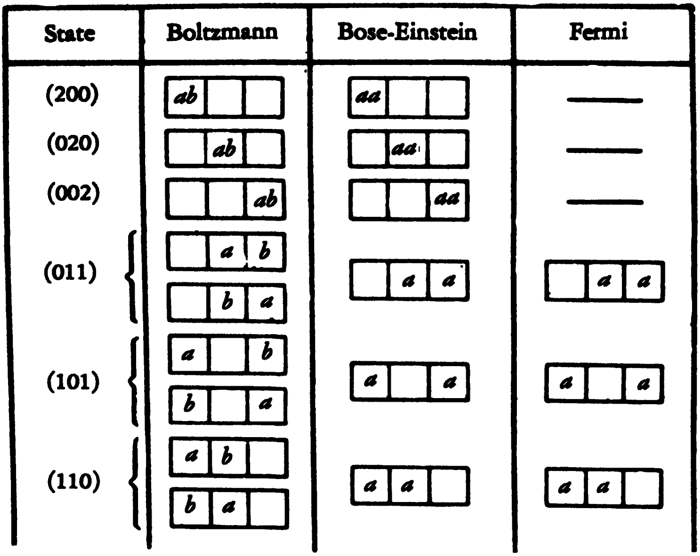

Figure 47

To this end, we first note that Eq. (4) gives the number of translational quantum states for a molecule whose kinetic energy lies between L and $L + dL$. The larger the volume of the container, the larger is the density of the energy levels. For a container with macroscopic dimensions, the distribution is almost continuous. We divide the energies L that the molecules can have into small intervals: from 0 to L_1, from L_1 to L_2, . . . , from L_n to L_{n+1}, ... These intervals need not be equal, but each one must be very small with respect to the average energy of the molecules, and yet sufficiently large to contain many translational energy levels, so that each one is well-populated with molecules.

Let Q_r be the number of translational energy levels in the interval L_{r-1} to L_r. According to Eq. (7) this number is given (to a good approximation, since $L_r - L_{r-1}$ is practically a differential) by

$$Q_r = \frac{2\pi V}{h^3}(2m)^{3/2}\sqrt{L_r}\,(L_r - L_{r-1}). \tag{24}$$

Let n_1 be the number of molecules in the energy interval 0 to L_1, n_2 those in the interval L_1 to L_2, . . . , and n_r those in the interval L_{r-1} to L_r, ... We now calculate the number of ways according to the Bose-Einstein statistics, that the distribution

$$n_1, n_2, \ldots, n_r, \ldots \tag{25}$$

can occur. First we calculate in how many ways n_r molecules can be distributed among the Q_r quantum states in the interval L_r to L_{r-1}. Each solution of the equation

$$x_1 + x_2 + \cdots + x_{Q_r} = n_r \qquad (x_i = 0, 1, 2, \ldots) \tag{26}$$

with integer values of the x's equal to or larger than zero gives a possible distribution of the n_r molecules that obey Bose-Einstein statistics. Indeed, given a solution of Eq. (26), we may consider $x_1, x_2, \ldots, x_{Q_r}$ molecules, respectively, in the first, second, . . . , Q_rth state of the Q_r states in the interval L_r to L_{r-1}. It is easy to demonstrate[*] that Eq. (26) has

$$\frac{(n_r + Q_r - 1)!}{n_r!(Q_r - 1)!} \tag{27}$$

integer solutions.

The total number of ways in which distribution (25) can occur is thus given by the product

$$\Pi = \frac{(n_1 + Q_1 - 1)!}{n_1!(Q_1 - 1)!} \frac{(n_2 + Q_2 - 1)!}{n_2!(Q_2 - 1)!} \cdots \frac{(n_r + Q_r - 1)!}{n_r!(Q_r - 1)!}. \tag{28}$$

[*] One of the easiest ways is the following: Figure 48 shows n_r circles and $Q_r - 1$ vertical lines arranged in a certain way. In our case $n_r = 6$ and $Q_r = 5$. Each of the $(n_r + Q_r - 1)!$ permutations of the $(n_r + Q_r - 1)$ objects represented by the circles and vertical lines is a solution of (26).

It is sufficient, indeed, to take x_1 equal to the number of circles to the left of the first vertical line, x_2 equal to the number of circles between the first and second vertical line, x_3 equal to the number of circles between the second and third vertical line, . . . , x_{Q_r} equal to the number of circles to the right of the last vertical line. In our example, we have $x_1 = 3$, $x_2 = 2$, $x_3 = 0$, $x_4 = 2$. However, these $(n_r + Q_r - 1)!$ solutions of (26) are not all distinct; it is clear that we obtain the same solution by permuting in any way the n_r circles among themselves and the $Q_r - 1$ vertical lines among themselves. Each solution, therefore, is repeated $n_r!(Q_r - 1)!$ times. The number of different solutions is thus equal to (27).

Figure 48

The most probable distribution is the one for which (28) is a maximum. But the numbers (25) are not all independent. They are bound by the relation

$$n_1 + n_2 + \cdots + n_r + \cdots = N, \tag{29}$$

which says that the total number of molecules is N, and also by the relation

$$n_1L_1 + n_2L_2 + \cdots + n_rL_r + \cdots = W, \tag{30}$$

which gives the total energy W (since $L_r - L_{r-1}$ is very small, we may, without too large an error, assign the energy L_r to all the n_r molecules that really have energies between L_{r-1} and L_r).

Since by hypothesis the numbers n_r and Q_r are very large, we may approximate the factorials in the usual way by the Stirling formula

$$\log n! = n(\log n - 1).$$

Furthermore, we may neglect 1 compared with Q_r and write

$$\log \Pi = \sum_{r=1}^{\infty} [(n_r + Q_r) \log (n_r + Q_r) - n_r \log n_r - Q_r \log Q_r]. \tag{31}$$

Instead of maximizing Π we may maximize $\log \Pi$. We incorporate the two conditions (29) and (30) into our procedure by using lagrangian multipliers; we maximize (with no auxiliary conditions) the expression obtained by subtracting from (31) expressions (29) and (30) multiplied by the undetermined coefficients (lagrangian multipliers) α and β. Equating the derivative of this expression to zero with respect to n_r gives

$$\log \frac{n_r + Q_r}{n_r} - \alpha - \beta L_r = 0.$$

From this we immediately obtain

$$n_r = \frac{Q_r}{Ae^{\beta L_r} - 1}, \tag{32}$$

where $A = e^{\alpha}$ is a new constant introduced in place of α.

Equation (32) gives the values of n_r for the most probable distribution. The two constants A and β can be determined so as to satisfy conditions (29) and (30). We see at once that (32) can be expressed in an equivalent form. The fraction n_r/Q_r is the average number of molecules in any of the Q_r quantum states between L_{r-1} and L_r. The average number of molecules ρ in a given quantum state is, then (neglecting the index r for simplicity),

$$\rho = \frac{1}{Ae^{\beta L} - 1}. \tag{33}$$

Equations (32) or (33) are almost the same as the Boltzmann law; indeed, they would be exactly the same if the denominator did not contain the term -1. If L is very large, then $Ae^{\beta L}$ also is very large, so that the term -1 can be neglected. Equation (33) then becomes the Boltzmann law, if we place

$$\beta = \frac{1}{kT}. \tag{34}$$

Since β is a constant, this relation—once verified for large L—must be true for all values of L. We may therefore write Eqs. (32) and (33) in the form

$$n_r = \frac{Q_r}{Ae^{L_r/kT} - 1}; \qquad \rho = \frac{1}{Ae^{L/kT} - 1}, \tag{35}$$

where only A remains undetermined; we can evaluate it by noting that N is the total number of molecules see [Eq. (29)].

We can also derive the relation (34) between β and the temperature by first calculating the entropy from $S = k \log \Pi$ with Π substituted from (31) and (32), and then calculating the energy W from Eqs. (30) and (35). The temperature is then obtained from the thermodynamic relation

$$\frac{1}{T} = \frac{\partial S}{\partial W}. \tag{36}$$

This procedure gives Eq. (32) with $\beta = 1/kT$.

8-6 THE DEGENERACY OF THE EINSTEIN GAS

Since we derived Eq. (35) without introducing either Eq. (24) or its equivalent [Eq. (7)], the equilibrium distribution defined by (35) is valid independently of these equations.

We now use (7) to derive the properties of a gas governed by Bose-Einstein statistics (we call this gas an Einstein [85] gas).

Since ρ is the number of molecules per energy level, we may replace it by dn/dQ in the second Eq. (35) and introduce the expression for dQ from Eq. (7); therefore the total number of molecules with energies between L and $L + dL$ is

$$dn = \frac{dQ}{Ae^{L/kT} - 1} = \frac{2\pi V(2m)^{3/2}}{h^3} \frac{\sqrt{L}\, dL}{Ae^{L/kT} - 1}. \tag{37}$$

This equation for the distribution of velocities in a gas obeying Bose-Einstein statistics is the analog of the Maxwell distribution law in a gas obeying Boltzmann statistics. One can easily show that the deviations of Eq. (37) from the Maxwell law are negligible when the temperature is not too low and the gas not too compressed. Equation (37) then becomes the Maxwell law, because the term -1 in the denominator is negligible with respect to the term $Ae^{L/kT}$.

The constant A can be determined from the condition that the total number of molecules must be N; we have

$$N = \int dn = \frac{2\pi V(2m)^{3/2}}{h^3} \int_0^\infty \frac{\sqrt{L}\, dL}{Ae^{L/kT} - 1}. \tag{38}$$

We shall study the special case $A \gg 1$; in this case the differences between (37) and the Maxwell law are very small, and the Einstein gas is then governed to a good approximation by the ordinary laws of perfect gases.

The integral (38) can be easily expanded in powers of $1/A$; we find

$$\frac{N}{V} = \frac{(2\pi mkT)^{3/2}}{Ah^3}\left[1 + \frac{1}{2^{3/2}A} + \frac{1}{3^{3/2}A^2} + \cdots\right]. \tag{39}$$

Since $A \gg 1$, we may drop all terms in this series beyond the first and solve the resulting equation for A. We then substitute this value for A in the square brackets and obtain

$$A = \frac{V}{N}\frac{(2\pi mkT)^{3/2}}{h^3}\left[1 + \frac{Nh^3}{2^{3/2}V(2\pi mkT)^{3/2}} + \cdots\right]. \tag{40}$$

Since each of the dn molecules (37) has energy L, the total energy of the gas is

$$W = \int L\, dn = \frac{2\pi V(2m)^{3/2}}{h^3} \int_0^\infty \frac{L^{3/2}\, dL}{Ae^{L/kT} - 1}. \tag{41}$$

We expand this integral also in powers of $1/A$ and find

$$W = \frac{3}{2} VkT \frac{(2\pi mkT)^{3/2}}{Ah^3} \left[1 + \frac{1}{2^{5/2}A} + \frac{1}{3^{5/2}A^2} + \cdots \right]. \tag{42}$$

Substituting (40) for A in this equation, we find, in our approximation,

$$W = \tfrac{3}{2} NkT \left[1 - \frac{Nh^3}{2^{5/2}V(2\pi mkT)^{3/2}} + \cdots \right]. \tag{43}$$

Notice that, to a first approximation, the energy is $\frac{3}{2}NkT$, the same as in classical physics; the terms in the parenthesis give the deviations from the classical laws. These deviations are larger the larger the quantity

$$D = \frac{Nh^3}{V(2\pi mkT)^{3/2}} \frac{1}{2^{5/2}} \tag{44}$$

is. We call D the degeneracy parameter. From (44) we see that the degeneracy parameter increases when the density of the gas increases or its temperature decreases, or both. Furthermore, it decreases with increasing molecular weight of the gas.

From (43) we can immediately derive the equation of state of the gas. We apply the virial theorem, which relates the pressure P to the kinetic energy W of the translation motion of the molecules:

$$PV = \tfrac{2}{3}W. \tag{45}$$

From (43), we then have

$$PV = NkT \left[1 - \frac{Nh^3}{2^{5/2}V(2\pi mkT)^{3/2}} + \cdots \right]. \tag{46}$$

To a first approximation, we find the classical equation of state of a perfect gas, $PV = NkT$; the degeneracy reduces the pressure of a gas below the classical value.

In most ordinary gases the degeneracy effects discussed above are always very small; they are masked by other deviations from the perfect gas law, such as those caused by the van der Waals forces and the finite extension of the molecules. An ordinary gas for which the degeneracy is more appreciable is helium (small atomic weight, possibility of lowering the temperature without condensation, etc.). Since helium obeys Bose-Einstein statistics, we may apply Eq. (46) to calculate its degeneracy. If, for example, $T = 4°$ and $N/V = 10^{21}$, the degeneracy parameter D equals 0.08, so that the pressure is 8 per cent lower than one expects from the ordinary equation of state of a gas with the same pressure and density. We see that deviation is not so small, and we could detect it very easily if it were not for other deviations from the classical laws of perfect gases.

8-7 THE BOSE PHOTON GAS

Of more interest is the application of Bose-Einstein statistics to photons considered to be particles. We can derive Planck's law, using the properties of the photons exclusively, without introducing any of their wave characteristics.

The energy L and momentum p of a photon are related to its frequency by the equations

$$L = h\nu; \qquad p = \frac{h\nu}{c}. \tag{47}$$

It follows that the volume in momentum-space for photons with frequencies between ν and $\nu + d\nu$ is,

$$4\pi p^2\,dp = 4\pi\,\frac{h^3}{c^3}\,\nu^2\,d\nu.$$

If V is the volume of the container, the hypervolume in the phase-space corresponding to the frequency interval $d\nu$ equals

$$V\frac{4\pi h^3}{c^3}\,\nu^2\,d\nu.$$

We treat the photons in the volume V as a gas of particles. Since the phase-space of this gas can be subdivided into small cells of hypervolume h^3, there are then $(4\pi/c^3)V\nu^2\,d\nu$ small cells in the frequency interval $d\nu$. Furthermore, since each photon has two possible states of polarization, we must multiply by two the number of photon states belonging to the frequency interval $d\nu$. The number of such states is then

$$dQ = \frac{8\pi}{c^3}\,V\nu^2\,d\nu. \tag{48}$$

Let the photons in the volume V be in thermal equilibrium and obey

Bose-Einstein statistics. We wish to calculate their distribution. We can proceed as we did in Section 8-5 to derive (35).

We subdivide the frequency interval from 0 to ∞ into very small contiguous intervals

$$d\nu_1, d\nu_2, \ldots, d\nu_r, \ldots \tag{49}$$

and suppose that

$$n_1, n_2, \ldots, n_r, \ldots \tag{50}$$

are the numbers of photons with frequencies lying in the above intervals.

The number Π of ways in which the photon distribution (50) can occur can be derived exactly as we derived Eqs. (28) and (31). In line with Eq. (48), we write for the photons

$$Q_r = \frac{8\pi}{c^3} \nu_r^2 \, d\nu_r. \tag{51}$$

In complete analogy with (31), we find

$$\log \Pi = \sum_{r=1}^{\infty} [(n_r + Q_r) \log (n_r + Q_r) - n_r \log n_r - Q_r \log Q_r]. \tag{52}$$

We now seek the photon distribution [that is, the set of numbers in (50)] that maximizes Π or, equivalently, $\log \Pi$. We must keep in mind, of course, that the numbers n_r are not independent; a relation of the form (30) expressing the conservation of energy holds here also. Thus for photons we have

$$h\nu_1 n_1 + h\nu_2 n_2 + \cdots + h\nu_r n_r = W. \tag{53}$$

In contrast to a gas of particles we do not have a relation here of the form (29) expressing the conservation of particles. The number of photons inside the volume V cannot be fixed; in contrast to atoms, it may increase or decrease.

The most probable photon distribution is then found by maximizing $\log \Pi$ with the condition (53). As usual, we eliminate the condition by maximizing the expression

$$\log \Pi - \beta W,$$

where β, the lagrangian multiplier, is introduced to take into account Eq. (53). Equating to zero the derivative of the previous expression with respect to n_r, we find

$$\log \frac{n_r + Q_r}{n_r} - \beta L_r = 0,$$

from which we obtain

$$n_r = \frac{Q_r}{e^{\beta L_r} - 1}. \tag{54}$$

The constant β depends on the temperature in the usual way:

$$\beta = \frac{1}{kT},$$

as can be demonstrated by the thermodynamic arguments at the end of Section 8-5. Taking this into account, together with Eqs. (51) and (47), we obtain from (54)

$$n_r = \frac{8\pi V}{c^3} \frac{\nu_r^2 \, d\nu_r}{e^{h\nu_r/kT} - 1}. \tag{55}$$

Since each of these n_r photons has energy $h\nu_r$, the total energy in the frequency interval $d\nu$ can now be written, dropping the subscript r, as

$$dW = V \frac{8\pi}{c^3} \frac{h\nu^3}{e^{h\nu/kT} - 1} \, d\nu.$$

From this equation we obtain the density of radiant energy $u(\nu,T)$, in agreement with Planck's equation, by placing

$$\frac{dW}{V} = u(\nu,T) \, d\nu.$$

8-8 FERMI STATISTICS

We now study the properties of a gas whose molecules obey Fermi statistics. Whereas Bose-Einstein statistics is applied principally to the photon gas, Fermi [88] statistics is applied principally to electron gases and, in particular, to the study of the electrical properties of metals, because these depend on the behavior of the free electrons in metals.

The analysis of the Fermi statistics is quite similar to that of the Bose-Einstein statistics, which we treated in Section 8-5. We assume that there are N monatomic molecules governed by Fermi statistics in a volume V. However, in view of the applications to an electron gas, we consider a slightly more general case and assume that the ground state of our atoms is g-fold degenerate. (In the application to the electron gas, $g = 2$, owing to the two possible spin orientations of an electron.)

To derive the distribution law for our particles we divide all the kinetic energies L, from 0 to ∞, into intervals

$$dL_1, dL_2, \ldots, dL_r, \ldots.$$

These intervals must be small enough to be treated as differentials. Let

$$n_1, n_2, \ldots, n_r, \ldots$$

be the numbers of molecules with energies in the above intervals. The total number of molecules is to be so great that $n_1, n_2, \ldots, n_r, \ldots$ are all large numbers.

As usual, let Q_r be the number of states of a single molecule with energy in the interval dL_r. The number of phase-space cells in the kinetic energy interval dL_r is given by Eq. (7):

$$\frac{2\pi V}{h^3}(2m)^{3/2}\sqrt{L_r}\,dL_r.$$

Since the ground state of our particles is g-fold degenerate, there are g states in each of these cells. We then have

$$Q_r = \frac{2\pi g V}{h^3}(2m)^{3/2}\sqrt{L_r}\,dL_r. \tag{56}$$

To calculate the probability of the distribution (55), we must first find the number of ways in which n_r particles in the energy interval dL_r can be distributed among the Q_r available states. Since the Pauli principle applies to these particles, only one particle, at most, can be in any one of the Q_r states. The number of distributions of the n_r particles is then equal to the number of ways in which n_r occupied states can be chosen from among the Q_r available states, that is,

$$\binom{Q_r}{n_r}.$$

The total number of ways in which the distribution (55) can be realized is then obviously given by the product

$$\Pi = \binom{Q_1}{n_1}\binom{Q_2}{n_2}\cdots\binom{Q_r}{n_r}\cdots \tag{57}$$

Note that, because the particles cannot be distinguished, we must not differentiate between states that can be transformed into each other by a simple permutation of the particles among themselves. This is particularly evident from the quantum-mechanical point of view. Owing to the Pauli exclusion principle, the eigenfunctions of two states differing only by a permutation of the particles are either equal or of opposite sign, according to whether the permutation is even or odd. Consequently, the two eigenfunctions differ at most by a constant factor equal to -1, and therefore, according to quantum mechanics, they represent the same quantum state. Hence we shall not consider distinct two states that differ only by a permutation of the particles.

The most probable distribution is that which maximizes Π or, $\log \Pi$. With the usual Stirling formula approximation, we have

$$\begin{aligned}\log\binom{Q_r}{n_r} &= \log Q_r! - \log n_r! - \log(Q_r - n_r)!\\ &= Q_r \log Q_r - n_r \log n_r - (Q_r - n_r)\log(Q_r - n_r),\end{aligned}$$

and, from Eq. (57),

$$\log \Pi = \sum_{r=1}^{\infty} \{Q_r \log Q_r - n_r \log n_r - (Q_r - n_r)\log(Q_r - n_r)\}. \tag{58}$$

The numbers n_r are not independent. They are subject to the two usual conditions

$$\begin{aligned}\Sigma n_r &= N,\\ \Sigma n_r L_r &= W,\end{aligned} \tag{59}$$

which express the conservation of the total number and the total energy of the particles.

We seek then the maximum of (58) under conditions (59). We may, as usual, apply the method of undetermined coefficients and calculate the maximum of the expression

$$\log \Pi - \alpha N - \beta W$$

without conditions, where the constants α and β must then be so determined as to satisfy the relations (59).

We equate to zero the derivative with respect to n_r of the above expression:

$$\log \frac{Q_r - n_r}{n_r} - \alpha - \beta L_r = 0.$$

From this, and introducing the new constant $A = e^\alpha$ in place of α, we obtain

$$n_r = \frac{Q_r}{Ae^{\beta L_r} + 1}. \tag{60}$$

This formula solves our problem. It is the analog in the Fermi statistics of Eq. (32) in the Bose-Einstein statistics. Formally, it is very similar to (32), differing from it only by a + sign in the denominator instead of a − sign. Equation (60) also reduces to the classical Boltzmann distribution when the term +1 in the denominator is neglected with respect to $Ae^{\beta L}$. This is always the case for large values of L, and we then have, on comparing our formula with the Boltzmann formula,

$$\beta = \frac{1}{kT}.$$

Although we have derived this for large values of L, it is valid for any value of L, since β does not depend on L. On the other hand, we may also verify the preceding relation by a thermodynamic argument identical to the one at the end of Section 8-5. Finally, we can write (60) as

$$n_r = \frac{Q_r}{Ae^{L_r/kT} + 1}. \tag{61}$$

The average number ρ of molecules occupying a certain quantum state is obviously given by $\rho = n/Q_r$. We can then write, dropping the superfluous subscript r,

$$\rho = \frac{1}{Ae^{L/kT} + 1}. \tag{62}$$

Notice, in particular, that ρ is always less than 1, as it must be in view of the Pauli principle.

8-9 STATISTICAL PROPERTIES OF THE FERMI GAS

We immediately obtain the law of distribution of the molecules among the various kinetic energies from Eq. (61) by introducing for Q_r its expression (56). Dropping the subscript r, we find that the number of molecules with energies between L and $L + dL$ (specified as n_r above) is

$$dN = \frac{2\pi g V}{h^3} (2m)^{3/2} \frac{\sqrt{L}\, dL}{Ae^{L/kT} + 1}. \tag{63}$$

This distribution law replaces the Maxwell law for a gas governed by the Fermi statistics. Distribution (63) coincides with the Maxwell law when $A \gg 1$, so that the term $+1$ in the denominator can be neglected in comparison with $Ae^{L/kT}$ (weak degeneracy). To determine A, we note that the total number of molecules is given by

$$N = \int dN = \frac{2\pi g V (2m)^{3/2}}{h^3} \int_0^\infty \frac{\sqrt{L}\, dL}{Ae^{L/kT} + 1}.$$

In place of the total number of particles N contained in the volume V, we deal with their density

$$n = \frac{N}{V}. \tag{64}$$

We now define a function $F(A)$ as the definite integral

$$F(A) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{x}\, dx}{Ae^x + 1}. \tag{65}$$

Thus we have

$$n = g \frac{(2\pi m k T)^{3/2}}{h^3} F(A). \tag{66}$$

To calculate the total kinetic energy W of our N molecules, we note that the kinetic energy of the dN molecules (63) is $L\, dN$; the total kinetic energy of the gas is thus

$$W = \int L\,dN = \frac{2\pi g V(2m)^{3/2}}{h^3}\int_0^\infty \frac{L^{3/2}\,dL}{Ae^{L/kT}+1}$$
$$= \tfrac{3}{2}kT\frac{gV(2\pi mkT)^{3/2}}{h^3}\,G(A), \tag{67}$$

where $G(A)$ is defined as the definite integral

$$G(A) = \frac{4}{3\sqrt{\pi}}\int_0^\infty \frac{x^{3/2}\,dx}{Ae^x+1}. \tag{68}$$

The average kinetic energy of a molecule, taking into account Eqs. (64) and (66), is given by

$$\bar{L} = \frac{W}{nV} = \tfrac{3}{2}kT\frac{G(A)}{F(A)}. \tag{69}$$

Finally, with the virial theorem, we can calculate the pressure; from Eqs. (45) and (69), we obtain

$$P = \frac{2}{3}\frac{W}{V} = nkT\frac{G(A)}{F(A)}. \tag{70}$$

Eliminating the parameter A between (70) and (66), we obtain the equation of state. Before doing this, however, we write down, without proof, some of the mathematical properties of the functions $F(A)$ and $G(A)$.

For $A \geq 1$, F and G can be represented by the convergent series

$$\begin{aligned} F(A) &= \frac{1}{A} - \frac{1}{2^{3/2}A^2} + \frac{1}{3^{3/2}A^3} - \cdots, \\ G(A) &= \frac{1}{A} - \frac{1}{2^{5/2}A^2} + \frac{1}{3^{5/2}A^3} - \cdots. \end{aligned} \tag{71}$$

For small values of A, the following asymptotic expressions are valid:

$$\begin{aligned} F(A) &= \frac{4}{3\sqrt{\pi}}(-\log A)^{3/2}\left[1 + \frac{\pi^2}{8(\log A)^2} + \cdots\right], \\ G(A) &= \frac{8}{15\sqrt{\pi}}(-\log A)^{5/2}\left[1 + \frac{5\pi^2}{8(\log A)^2} + \cdots\right]. \end{aligned} \tag{72}$$

The following relation is also easily verified:

$$\frac{dG(A)}{F(A)} = -d\log A. \tag{73}$$

We now introduce a new function $R(\Theta)$ defined by the two relations

$$R(\Theta) = \Theta\frac{G(A)}{F(A)}; \qquad F(A) = \frac{1}{\Theta^{3/2}}. \tag{74}$$

According to whether $\Theta \gg 1$ or $\Theta \ll 1$, the following asymptotic expressions are valid for $R(\Theta)$:

$$\begin{aligned} R(\Theta) &= \Theta\left(1 + \frac{1}{2^{5/2}\Theta^{3/2}} + \cdots\right), \\ R(\Theta) &= \frac{3^{2/3}\pi^{1/3}}{5\cdot 2^{1/3}}\left(1 + \frac{5\cdot 2^{2/3}\pi^{4/3}}{3^{7/3}}\Theta^2 + \cdots\right). \end{aligned} \tag{75}$$

By using equation (74), one can easily demonstrate that

$$\int_0^\Theta \frac{dR(\Theta)}{\Theta} = \frac{5}{3}\frac{G(A)}{F(A)} + \tfrac{2}{3}\log A. \tag{76}$$

Using the function $R(\Theta)$, we can now easily write the equation of state of the gas in explicit form. Taking into account Eqs. (74), we eliminate the parameter A between (70) and (66) and obtain

$$P = \frac{h^2 n^{5/3}}{2\pi m g^{2/3}} R\left(\frac{2\pi m g^{2/3} kT}{h^2 n^{2/3}}\right). \tag{77}$$

Analogously, from (69) we obtain the average kinetic energy of the molecules:

$$\bar{L} = \frac{3}{2}\frac{h^2 n^{2/3}}{2\pi m g^{2/3}} R\left(\frac{2\pi m g^{2/3} kT}{h^2 n^{2/3}}\right). \tag{78}$$

In the limiting case of weak degeneracy (high temperature, small density), Eqs. (77) and (78) become, with the aid of the first of Eqs. (75),

$$\begin{aligned} P &= nkT\left[1 + \frac{1}{2^{5/2}}\frac{h^3 n}{(2\pi mkT)^{3/2} g} + \cdots\right], \\ \bar{L} &= \tfrac{3}{2}kT\left[1 + \frac{1}{2^{5/2}}\frac{h^3 n}{(2\pi mkT)^{3/2} g} + \cdots\right]. \end{aligned} \tag{79}$$

To a first approximation we have, of course, the classical equation of state ($P = nkT$) and the principle of equipartition of energy ($\bar{L} = \frac{3}{2}kT$). The degeneracy increases both the pressure and the average kinetic energy of the molecules above their classical values. However, as in the case of the Bose-Einstein statistics, the effect is very small for ordinary gases.

The limiting case of strong degeneracy (small T, large n) is more interesting to the physicist, because of its applications to the electron theory of metals.[43, 44, 131]

Introducing the second of Eqs. (75) into (77) and (78), we obtain in this case

$$P = \frac{1}{20}\left(\frac{6}{\pi}\right)^{2/3} \frac{h^2 n^{5/3}}{m g^{2/3}} + \frac{2^{4/3}\pi^{8/3}}{3^{5/3}} \frac{m g^{2/3} n^{1/3} k^2 T^2}{h^2} + \cdots, \tag{80}$$

$$\bar{L} = \frac{3}{40}\left(\frac{6}{\pi}\right)^{2/3} \frac{h^2 n^{2/3}}{m g^{2/3}} + \frac{2^{1/3}\pi^{8/3}}{3^{2/3}} \frac{m g^{2/3} k^2 T^2}{h^2 n^{2/3}} + \cdots. \tag{81}$$

We see that, even for $T = 0$, neither the pressure nor the average kinetic energy of the molecules of our gas is zero. But this is not surprising if we note that, in a quantized system such as our gas, it often happens that the particles of the system are not at rest in the lowest energy state, even if the system is at absolute zero. Thus, for instance, the electrons in an atom, even in their ground states, move at high speeds in their orbital motions when the atom is at absolute zero. We shall see in the next section how to demonstrate in a simple way that systems can have a nonzero pressure and kinetic energy at absolute zero.

The quantity

$$D = \frac{h^3 n}{g(2\pi mkT)^{3/2}} \tag{82}$$

is known as the *degeneracy parameter*, since it is a measure of the strength of the degeneracy of the gas. For $D \ll 1$, as we can see from Eqs. (79), the degeneracy is small, that is, the pressure and average kinetic energy of the molecules have almost their classical values. When $D \gg 1$ instead, we see from Eqs. (80) and (81) that the degeneracy is very strong: P and L have values close to those corresponding to the values at absolute zero. The degeneracy parameter is always very small for ordinary gases under conditions which can be realized in practice. But it can be very large for an electron gas. Indeed, in this case the electron density (n) of the gas can be very large, as for example in metals; furthermore, all other conditions being the same, the degeneracy parameter increases rapidly when the mass of the particles decreases.

Let us assume, for instance, that the number of "free electrons" in a metal is of the order of magnitude of one per atom. This is certainly plausible, at least for the more typical metals such as the alkali or copper group metals. The density of the electron gas is then, for example, for silver,

$$n = 5.9 \times 10^{22}.$$

From (82), putting $T = 300°$, we then obtain for the degeneracy parameter ($g = 2$, because of the two possible spin orientations):

$$D = 2330.$$

Under these conditions D is, indeed, very much larger than 1, so that the electron gas inside the metal is highly degenerate.

The specific heat of a degenerate gas is less than the classical specific heat ($\frac{3}{2}k$ per molecule of a monatomic gas). From Eq. (81) we obtain, in the case of strong degeneracy and in the limit of low temperatures, the following value for the specific heat per molecule:

$$C_v = \frac{d\bar{L}}{dT} = \frac{2^{4/3}\pi^{8/3}}{3^{2/3}} \frac{mg^{2/3}k^2T}{h^2n^{2/3}} + \cdots \cdot \tag{83}$$

The specific heat is thus zero at absolute zero (in agreement with the Nernst principle); at low temperatures it is proportional to the absolute temperature.

The vanishing of the specific heat at $T = 0$ has an interesting application to the theory of metals. This phenomenon explains why the "free electrons" of the metal do not contribute to the specific heat of the metal in the proportion required by the principle of the equipartition of energy. Thus, for instance, the contribution of the electron gas to the specific heat of silver, owing to the degeneracy, has about $\frac{1}{80}$ the classical value and is practically negligible.

We now use the Nernst principle to compute the entropy of our gas. We heat the gas, at constant volume, and bring it from absolute zero to temperature T. Since, according to the Nernst principle, the entropy is zero at $T = 0$, the entropy at the temperature T is

$$S = N \int_0^T \frac{d\bar{L}}{T}.$$

Introducing the value of $d\bar{L}$ from (78) and noticing that Θ is just the argument of R in (78), we obtain, with the aid of Eq. (76),

$$S = \tfrac{3}{2}Nk \int_0^\Theta \frac{dR(\Theta)}{\Theta} = Nk\left[\frac{5}{2}\frac{F(A)}{G(A)} + \log A\right], \tag{84}$$

where A can be derived from (66). In the limiting case of no degeneracy ($A \gg 1$), we have, according to (71),

$$F(A) = \frac{1}{A}, \qquad G(A) = \frac{1}{A}.$$

From equation (66), taking (64) into account, we then obtain in the first approximation

$$A = \frac{gV}{N}\frac{(2\pi mkT)^{3/2}}{h^3}.$$

Equation (84) then gives

$$S = Nk\left[\tfrac{3}{2}\log T - \log\frac{N}{V} + \log\frac{(2\pi mk)^{3/2}ge^{5/2}}{h^3}\right],$$

in agreement with (12).

8-10 PROPERTIES OF A HIGHLY DEGENERATE GAS

In view of its applications to the theory of metals, we devote this section to the study of a highly degenerate gas which obeys the Fermi statistics.

We saw, in the previous section, that the pressure and the kinetic energy of the gas, at low temperatures, instead of going to zero, approach finite nonzero limits. We can explain this as follows: We first assume that our gas, occupying the volume V, consists of only one molecule. At absolute zero this molecule is in the translational quantum state of lowest energy. If we now add a second molecule to the gas, the Pauli principle prevents this molecule from being in the same state as the first molecule. Therefore, the second energy state is also occupied at absolute zero. A third molecule would occupy the third state, and so on. We can understand now why only the first molecule is allowed to occupy the zero energy state, while all the others must occupy states of higher energy. This explains why the molecules of a degenerate gas must have an average kinetic energy different from zero even at absolute zero. As a consequence, owing to the collisions of the molecules against the walls, there is a pressure even at absolute zero.

Hence, at absolute zero, the kinetic energies of the molecules have values ranging from zero to a well-defined maximum. Each of the translational quantum states, up to the Nth, in order of increasing energy, is occupied by one of the N molecules, whereas all the higher translational levels are empty.

We may describe this phenomenon in momentum space by noting that the cells in this space have a volume equal to h^3/V. If g is the degree of degeneracy of the ground level, there are g states in each cell. The density of possible states in momentum space is then

$$\frac{gV}{h^3} \tag{85}$$

states per unit volume of momentum space. At absolute zero, the N gas molecules fill up these translational states in order of increasing kinetic energy, starting with the zero-energy ground state. The molecular density of our gas in momentum space is therefore given by (85), and the molecules occupy a sphere with its center at the origin and with a volume large enough to contain N states. The radius $p_{\max}$ of this sphere just equals the maximum momentum of the molecules. Since the volume of a sphere of radius $p_{\max}$ is just $(4\pi/3)p_{\max}^3$, the number of quantum states it contains is, according to (85),

$$\frac{gV}{h^3}\frac{4\pi}{3}p_{\max}^3.$$

We then find

$$\frac{4\pi}{3}\frac{gV}{h^3}p_{\max}^3 = N. \tag{86}$$

From this we can derive the maximum momentum and velocity of the particles:

$$p_{\max} = \left(\frac{3}{4\pi}\right)^{1/3} \frac{h}{g^{1/3}} \left(\frac{N}{V}\right)^{1/3}; \qquad v_{\max} = \frac{p_{\max}}{m} = \left(\frac{3}{4\pi}\right)^{1/3} \frac{h}{mg^{1/3}} \left(\frac{N}{V}\right)^{1/3}. \tag{87}$$

Notice that $p_{\max}$ and $v_{\max}$ depend, as they should, on the ratio N/V, that is, on the concentration of the molecules. Thus, in the case of silver (cf. Section 8-9) we find for the maximum velocity of the free electrons at absolute zero

$$v_{\max} = 1.39 \times 10^8 \text{ cm sec}^{-1},$$

corresponding to 5.5 eV.

Figure 49 shows graphically the distribution law of the velocities at different temperatures. The momentum p is plotted along the abscissa; the ordinate represents the density of occupied states in momentum space. This density, of course, cannot exceed the value given by (85). At $T = 0$, as we said, the density has this maximum value and retains it up to the value $p_{\max}$ of the momentum; then it abruptly becomes zero. The graph representing this distribution is shown in the figure as the two perpendicular straight lines. At a slightly higher temperature T_1, the corner between the two lines becomes smoother. At an even higher temperature T_2, the distribution curve has the continuous shape shown in the figure; this shape, at higher temperatures, looks more and more like the one corresponding to the Maxwell distribution.

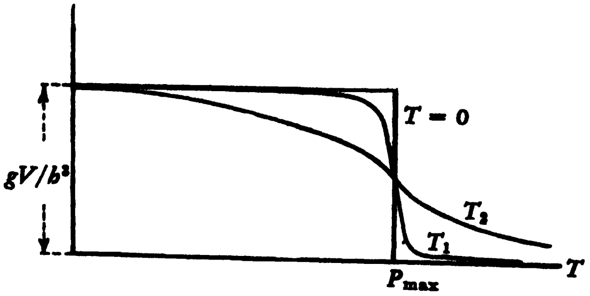

Figure 49

It is always interesting, in the case of complete degeneracy (that is, at $T = 0$), to study how our gas behaves when an external force acts on the particles. Let U be the potential of this force. If ordinary Boltzmann statistics were valid, we would find the molecules concentrated in regions of minimum potential; their density at any point would be proportional to $e^{-U/kT}$. We want to find the law that replaces this when the gas is completely degenerate.

To do this, we first note that, if n is the density of the degenerate gas at a certain point, the maximum momentum of the molecules at that point is given by Eq. (87) with $n = N/V$. The maximum value of the kinetic energy is given by

$$L_{\max} = \frac{p^2_{\max}}{2m} = \frac{1}{2}\left(\frac{3}{4\pi}\right)^{2/3} \frac{h^2}{mg^{2/3}} n^{2/3}.$$

The maximum molecular energy is the sum of the potential energy U and the Maximum kinetic energy $L_{\max}$:

$$w = U + \frac{1}{2}\left(\frac{3}{4\pi}\right)^{2/3} \frac{h^2}{mg^{2/3}} n^{2/3}. \tag{88}$$

It is obvious that w must have the same value everywhere in the gas; otherwise there would be a flux of molecules from the regions with large w to those where w is smaller. From (88) we obtain

$$n = \frac{2^{7/2}\pi g m^{3/2}}{3h^3} (w - U)^{3/2}. \tag{89}$$

This formula is the solution of our problem. The constant w is obtained from the condition

$$\int n \, d\tau = N \tag{90}$$

($d\tau$ = volume element), where the integral is extended over all the space occupied by the gas. This condition tells us that the total number of molecules is N. Equation (89) is valid for regions where $w - U > 0$. In regions where $w - U < 0$, the right side of Eq. (89) is imaginary, and the result is meaningless, but it is also obvious that in these regions, $n = 0$; that is, there are no molecules. If there were a molecule (even at rest) in this region, its energy would have to be larger than the maximum value w for (89) to be real.

8-11 THE STATISTICAL DISTRIBUTION OF ELECTRONS IN AN ATOM

Thomas[135] and Fermi[89, 90] independently, have applied the above theory to the analysis of the distribution of electrons inside an atom.

In an atom containing several electrons we may, to a first approximation, ignore the motions of the single electrons and treat them all as a gas surrounding the nucleus and held there by the electrostatic attraction. It is easy to see that, at ordinary temperatures, this electron gas is always completely degenerate. If we calculate the order of magnitude of the degeneracy parameter (82), we obtain very large values in all cases. We may therefore apply the results of the preceding section to calculate the distribution of the cloud of electrons around the nucleus. We shall determine the density variation in the electron cloud as a function of the distance r from the nucleus.

Let $V(r)$ be the electric potential (determined by the charge on the nucleus and on the electrons), and let $-e$ be the electron charge. We then have $U = -eV$. Since $g = 2$ for electrons, we obtain from (89)

$$n = \frac{2^{9/2}\pi m^{3/2}e^{3/2}}{3h^3} V^{3/2}, \tag{91}$$

where we have incorporated the constant w into the arbitrary constant of the electric potential.

Since the electric charge density is $-en$, the Poisson equation gives

$$\Delta V = \frac{d^2V}{dr^2} + \frac{2}{r}\frac{dV}{dr} = 4\pi en. \tag{92}$$

Therefore, we have for V the differential equation

$$\frac{d^2V}{dr^2} + \frac{2}{r}\frac{dV}{dr} = \frac{2^{13/2}m^{3/2}e^{5/2}}{3h^3} V^{3/2}. \tag{93}$$

In the vicinity of the nucleus, where the screening action of the electrons vanishes, the expression for V must approach the limit Ze/r (Z is the atomic number). Hence we obtain the first condition on V:

$$\lim_{r=0} rV = eZ. \tag{94}$$

We obtain a second condition by noting that the total number of electrons is Z:

$$Z = \int n\, d\tau = \frac{2^{13/2}\pi^2 m^{3/2} e^{3/2}}{3h^3} \int_0^\infty V^{3/2} r^2\, dr. \tag{95}$$

The electrostatic potential of the atom is therefore determined by the differential equation (93) with the two conditions (94) and (95).

We define:

$$x = r/\mu; \qquad \varphi = xV/\gamma, \tag{96}$$

where

$$\mu = \frac{3^{2/3} h^2}{2^{13/2}\pi^{4/3} m e^2 Z^{1/3}}; \qquad \gamma = \frac{2^{13/2}\pi^{4/3} m e^3 Z^{4/3}}{3^{2/3} h^2}. \tag{97}$$

Equation (93) may then be written

$$\frac{d^2\varphi}{dx^2} = \frac{\varphi^{3/2}}{\sqrt{x}}. \tag{98}$$

Equation (94) becomes

$$\varphi(0) = 1 \tag{99}$$

and (95)

$$\int_0^\infty \varphi^{3/2} \sqrt{x}\, dx = 1.$$

We can easily verify that this last condition is equivalent to the boundary condition:

$$\varphi(\infty) = 0. \tag{100}$$

The function $\varphi(x)$ is thus defined by the differential equation (98) plus the two boundary conditions (99) and (100). These conditions are sufficient to determine the function completely, as can be easily shown.

The function $\varphi(x)$ has been calculated numerically; its values are given in Table 7.

Our problem is therefore completely solved. The electric potential at a distance r from the nucleus is given by

$$V = \frac{Ze}{r}\varphi\left(\frac{r}{\mu}\right), \tag{101}$$

and the electron density (91) by

$$n = \frac{2^{9/2}\pi m^{3/2} Z^{3/2} e^3}{3h^3}\frac{1}{r^{3/2}}\varphi^{3/2}\left(\frac{r}{\mu}\right). \tag{102}$$

Table 7 Numerical Values of the Function $\phi(x)$

x	$\varphi(x)$	x	$\varphi(x)$	x	$\varphi(x)$	x	$\varphi(x)$
0.00	1.000	.8	.485	8	.037	38	.0013
.01	.985	.9	.453	9	.029	40	.0011
.02	.972	1.0	.425	10	.024	45	.00079
.03	.959	1.2	.375	12	.017	50	.00061
.04	.947	1.4	.333	14	.012	55	.00049
.05	.935	1.6	.297	16	.0093	60	.00039
.10	.882	1.8	.268	18	.0072	65	.00031
.15	.836	2.0	.244	20	.0056	70	.00026
.20	.793	2.5	.194	22	.0045	75	.00022
.25	.758	3.0	.157	24	.0037	80	.00018
.30	.721	3.5	.130	26	.0031	85	.00015
.35	.691	4.0	.108	28	.0026	90	.00012
.40	.660	4.5	.093	30	.0022	95	.00011
.5	.607	5.0	.079	32	.0019	100	.00010
.6	.562	6	.059	34	.0017		
.7	.521	7	.046	36	.0015		

Notice, in particular, that V and n are both determined by only one function; this function is calculated numerically once and for all, independently of the atomic number.

This statistical method of finding the potential has often been applied to the approximate numerical calculations of several atomic properties. In particular, it has been used to calculate the optical or Roentgen terms, the formation of atomic groups in the periodic system, etc.

Owing to its statistical nature, the method is particularly appropriate when properties varying regularly with the atomic number have to be represented. But properties which depend only sporadically on Z are represented far less well. We cannot enter into these applications here; they can be found in the bibliography, together with discussions concerning the improvements that have been introduced into these statistical methods.

Bibliografia

Parte I

MOLECULE

Opere generali recenti:

R. de L. Kronig, *Band Spectra and Molecular Structure*, Cambridge, 1930.

W. Weizel, *Bandenspektren*, in Wien-Harms, "Handbuch der Experimentalphysik," Lipsia, 1931.

R. Mecke, *Bandenspektren*, in Geiger-Scheel, "Handbuch der Physik," Vol. XXI, Lipsia, 1929.

"Handbuch der Radiologie" (Redatto da Marx), Vol. XI, Parte II, Seconda Ediz., Lipsia, 1934 (Articoli di R. de L. Kronig, P. Debye e H. Sack, G. Placzek, F. Bloch, W. Heitler).

K. F. Herzfeld, *Grösse und Bau der Moleküle*, in Geiger-Scheel "Handbuch der Physik," Vol. XXIV, Parte II, Seconda Ediz., Berlino, 1933.

Capitolo I. *Il legame chimico*

W. Kossel, *Ann. Phys.*, 1916, **49**, 229.

A. E. van Arkel e J. H. de Boer, *Chemische Bindung als elektrostatische Erscheinung*, Lipsia, 1931 (Legame polare).

W. Heitler e F. London, *Z. Phys.* (1927), **44**, 455.

M. Born, Chemische Bindung und Quantenmechanik, *Ergeb. exakt. Naturw.* (1931), **10**, 287 (Legame omeopolare).

Capitolo II. *Spettri delle molecule biatomiche*

R. S. Mulliken, *Rev. Mod. Physics* (1930), **2**, 60, 506; (1931), **3**, 90; (1931), **4**, 1.

Articoli generali ai quali si rimanda anche per indicazioni bibliografiche dettagliate.

C. Schäfer e F. Matossi, *Das infrarote Spektrum*, Berlino, 1930.

J. Lecomte, *Le spectre infrarouge*, Parigi, 1928.

G. Herzberg, *Die Prädissoziation und verwandte Erscheinungen*, *Ergeb. exakt. Naturw.* (1931), **10**, 207.

F. Hund, Molekelbau, *Ergeb. exakt. Naturw.* (1929), 8, 147.
K. W. F. Kohlrausch, *Der Smekal-Raman Effekt*, Berlino, 1931.
F. Rasetti, *Nuovo Cimento* (1929), 6, 356.

Capitolo IV. *Molecole poliatomiche*

P. Debye, *Polare Molekeln*, Lipsia, 1929.
P. Debye, *Struktur der materie, Vier Vorträge*, Lipsia, 1933.
D. M. Dennison, *Rev. Mod. Phys.* (1931), 3, 280.
Kramers e Ittmann, *Z. Phys.* (1929), 53, 553; (1929), 58. 217; (1930), 60, 663.
Wang, *Phys. Rev.* (1929), 34, 243 (Livelli rotazionali delle molecole asimmetriche).

Per gli spettri infrarossi e Raman delle molecole poliatomiche cfr. le op. cit. per gli argomenti analoghi al Cap. II.

Cfr. anche gli articoli: G. Placzek e F. Rasetti, in *Leipziger Vorträge*, Lipsia, 1931; E. Fermi, L'effetto Raman nelle molecole e nei cristalli, *Mem. R. Accad. d'Italia* (1932).

Parte II

CRISTALLI

Capitolo I. *Geometria dei reticoli cristallini*

P. Niggli, *Kristallographische und Strukturtheoretische Grundbegriffe*, in Wien-Harms, "Handbuch der Experimentalphysik," Lipsia, 1928.
P. P. Ewald, *Kristalle und Röntgenstrahlen*, Berlino, 1923.
P. P. Ewald, *Der Aufbau festen Materie und seine Erforschung durch Röntgenstrahlen*, in Geiger-Scheel, "Handbuch der Physik," Vol. XXIV, Lipsia, 1927.
W. H. e W. L. Bragg, *The Crystalline State*, Londra, 1933.

Capitolo II. *Proprieta fisiche dei reticoli cristallini*

M. Born, *Atomtheorie des festen Zustandes*, Lipsia, 1923.
G. Heckmann, Die Gittertheorie der festen Körper, *Ergeb. exakt. Naturw.*, Lipsia, 1925.
C. J. Brester, Kristallsymmetrie und Reststrahlen, *Dissert. Utrecht* (1923).
R. Peierls, *Ann. Phys.* (1929), 3, 1055 (Conduzione termica).

Parte III

LA STATISTICA DELLA TEORIA DEI QUANTI

Opere generali:

L. Brillouin, *Les statistiques quantiques et leurs applications*, Parigi, 1930.
R. H. Fowler, *Statistical Mechanics*, Cambridge, 1929.

Capitolo I. *Equilibrio statistico tra gli stati quantici*

M. Planck, *Vorlesungen über die Theorie der Wärmestrahlung*, Lipsia, 1923.

M. Planck, *Einführung in die theoretische Physik*, Vol. V: *Theorie der Wärme*, Lipsia, 1930.

J. H. van Vleck, *The Theory of electric and magnetic susceptibilities*, Oxford, 1932.

A. Eucken, Der Nernstche Wärmesatz, *Ergeb. exakt. Naturw.* (1922), **1**, 120.

F. Simon, Fünfundzwanzig Jahre Nernstschen Wärmesatzes, *Ergeb. exakt. Naturw.*, (1930), **9**, 222.

F. Simon, in Geiger-Scheel, "Handbuch der Physik," Vol. X, Lipsia, 1926.

Capitolo II. *La quantizzazione dei gas*

R. H. Fowler e T. E. Sterne, *Rev. Mod. Phys.* (1932), **4**, 635.

S. Dushman, Thermionic emission, *Rev. Mod. Phys.* (1930), **2**, 381.

E. Bloch, *Les phémonènes thermoioniques*, Parigi, 1923.

L. Nordheim, Die Theorie der Elektronenemission der Metalle, *Phys. Z.* (1929), **30**, 177.

E. Fermi, In *Leipziger Vorträge*, 1928 (Atomo statistico). Cfr. anche alcune note dello stesso autore in Lincei Rend., 1927, 1928.

References

1. M. Blackman, "Theory of Specific Heats of Solids," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1955, Vol. VII, p. 325; *Rept. Progr. Phys.*, **8**, 11 (1941).
2. E. Bloch, *Thermionic Phenomena* (J. R. Clarke, transl.), Dutton, New York, 1927.
3. M. Born, *Atomtheorie des festen Zustandes*, Teubner, Leipzig, 1923.
4. M. Born, Chemische Bindung und Quantenmechanik, *Ergeb. Exakt. Naturw.* **10**, 287 (1931) (the homopolar bond).
5. M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Clarendon Press, Oxford, 1954.
6. J. Bouman, "Theoretical Principles of Structural Research by X-Rays," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1957, Vol. XXXII, p. 97.
7. W. H. Bragg and W. L. Bragg, *The Crystalline State*, Macmillan, London, 1933.
8. L. Brillouin, *Les Statistiques quantiques et leurs applications*, Presses Universitaires, Paris, 1930.
9. P. J. W. Debye, *Polare Moleküle*, Hirzel, Leipzig, 1929.
10. P. J. W. Debye, *Structure of Matter, Four Lectures* (F. M. Denton, transl.), Univ. New Mexico Press, Albuquerque, N.M., 1934.
11. D. M. Dennison, *Rev. Mod. Phys.*, **3**, 280 (1931).
12. S. Dushman, Thermionic Emission, *Rev. Mod. Phys.*, **2**, 381 (1930).
13. A. Eucken, *Handbuch der Experimental Physik* (W. Wien and F. Harms, eds.), Akademische-Gesellschaft, Leipzig, 1929, Bd. 6(1).
14. P. P. Ewald, *Krystalle und Röntgenstrahlen*, Springer, Berlin, 1923.
15. P. P. Ewald, "Der Aufbau fester Materie und seine Erforschung durch Röntgenstrahlen," in *Handbuch der Physik* (H. Geiger and K. Scheel, eds.), Springer, Berlin, 1927, Vol. XXIV.
16. G. Fournet, "Etude de la structure des fluides et des substances amorphes au moyen de la diffusion de rayons-X," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1957, Vol. XXXII, p. 238.

17. R. H. Fowler, *Statistical Mechanics*, 2nd ed., Cambridge, New York, 1936.
18. R. H. Fowler and E. A. Guggenheim, *Statistical Mechanics*, Cambridge, New York, 1939.
19. R. H. Fowler and T. E. Sterne, *Rev. Mod. Phys.*, **4**, 635 (1932).
20. H. Frauenfelder, *The Mössbauer Effect*, Benjamin, New York, 1962.
21. A. Guinier and G. von Eller, "Les Methodes experimentales des determinations des structures cristallines," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1957, Vol. XXXII, p. 1.
22. G. Heckmann, Die Gittertheorie der festen Körper, *Ergeb. Exakt. Naturw.*, **4**, 100 (1925).
23. N. M. F. Henry, H. Lipson, and W. A. Wooster, *The Interpretation of X-Ray Diffraction Photographs*, Macmillan, London, 1953.
24. G. Herzberg, *Molecular Spectra and Molecular Structures*, Prentice Hall, New York, 1939, Vols. I and II.
25. G. Herzberg, *Infra-red and Raman Spectra*, Van Nostrand, Princeton, N.J., 1950.
26. G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand, Princeton, N.J., 1950.
27. K. F. Herzfeld, "Grösse und Bau der Moleküle," in *Handbuch der Physik*, 2nd ed. (H. Geiger and K. Scheel, eds.), Springer, Berlin, 1933, Vol. XXIV, Part II.
28. H. Hönl, A. W. Maue, and K. Westpfahl, "Theorie der Beugung," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1961, Vol. XXV/1, p. 218.
29. D. J. Hughes, *Neutron Optics*, Wiley-Interscience, New York, 1954.
30. F. Hund, Molekülbau, *Ergeb. Exakt. Naturw.*, **8**, 147 (1929).
31. F. Hund, "Allgemeine Quantenmechanik, des Atom und Molekülbaues," in *Handbuch der Physik* (H. Geiger and K. Scheel, eds.), Springer, Berlin, 1934, Vol. XXIV/1.
32. H. Jagodzinski, "Kristallographie," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1955, Vol. VII/1, p. 1.
33. P. G. Klemens, "Thermal Conductivity of Solids at Low Temperature," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1956, Vol. XIV, p. 198.
34. H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, Wiley, New York, 1954.
35. K. W. F. Kohlrausch, *Der Smekal-Raman Effekt*, Springer, Berlin, 1931.
36. M. Kotani, K. Ohno, and K. Kayama, "Quantum Mechanics of Electron Structures," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1961, Vol. XXXVII/2, p. 1.

37. R. de L. Kronig, *Band Spectra and Molecular Structure*, Cambridge, New York, 1930.
38. J. Lecomte, *Le Spectre infrarouge*, Hermann, Paris, 1928.
39. G. Leibfried, "Mechanische und Thermische Eigenschaften der Kristalle," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1955, Vol. VII/1, p. 1.
40. H. Lipson and W. Cochran, *Determination of Crystal Structure*, Bell, London, 1953.
41. P. Löwdin, *A Theoretical Investigation into Some Properties of Ionic Crystals*, Heinmann, New York, 1948.
42. D. K. C. MacDonald, "Electrical Conductivity of Metals at Low Temperatures," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1956, Vol. XIV, p. 137.
43. R. Mecke, "Bandenspektren," in *Handbuch der Physik* (H. Geiger and K. Scheel, eds.), Springer, Leipzig, 1929, Vol. XXI.
44. N. F. Mott and H. Jones, *The Theory and Properties of Metals and Alloys*, Clarendon Press, Oxford, 1936.
45. R. S. Mulliken, *Rev. Mod. Phys.*, **2**, 60, 506 (1930); **3**, 90 (1931); **4**, 1 (1932).
46. W. Nernst, *The New Heat Theorem*, Dutton, New York, 1926.
47. P. Niggli, "Kristallographische und Strukturtheoretische Grundbegriffe," in *Handbuch der Experimental Physik* (W. Wien and F. Harms, eds.), Akademische Verlag, Leipzig, 1928.
48. Z. G. Pinsker, *Electron Diffraction*, Butterworth, London, 1953.
49. M. Planck, *Vorlesungen über die Theorie der Wärmestrahlung*, J. A. Barth, Leipzig, 1923.
50. M. Planck, Einführung in die theoretische Physik, *Theorie der Wärme*, S. Hirzel, Leipzig, 1930, Vol. V.
51. J. R. Platt, "Chemical Bond and the Distribution of Electrons in Molecules," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1961, Vol. XXXVII/2, p. 173.
52. H. Raether, "Elektroneninterferenz," in *Handbuch der Physik* (S. Flügge, ed.), Springer, Berlin, 1957, Vol. XXXII, p. 443.
53. G. N. Ramachandran and S. Ramaseshan, "Crystal Optics," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1961, Vol. XXV/1, p. 1.
54. G. R. Ringo, "Neutron Diffraction," in *Encyclopedia of Physics* (S. Flügge, ed.), Springer, Berlin, 1957, Vol. XXXII, p. 552.
55. C. Schäfer and F. Matossi, *Das infrarote Spektrum*, Springer, Berlin, 1920.
56. F. Simon, in *Handbuch der Physik* (H. Geiger and K. Scheel, eds.), Springer, Leipzig, 1926, Vol. X.

57. F. Simon, Fünfundzwanzig Jahre Nernstschen Wärmesatzes, *Ergeb. Exakt. Naturw.*, **9**, 222 (1930).
58. J. C. Slater, *Quantum Theory of Matter*, McGraw-Hill, New York, 1951.
59. A. E. van Arkel and J. H. de Boer, *Chemische Bindung als elektrostatische Erscheinung*, S. Hirzel, Leipzig, 1931 (polar bond).
60. J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford, New York, 1932.
61. W. Weizel, in *Handbuch der Physik* (H. Geiger and K. Scheel, eds.), Springer, Berlin, 1931.
62. *Handbuch der Radiologie* (E. Marx, ed.), Vol. XI, Part II, 2nd ed., Leipzig, 1934 (articles by R. de L. Kronig, P. Debye and H. Sack, G. Placzek, F. Bloch, and W. Heitler).
63. Compare also the following articles: G. Placzek and F. Rasetti, in *Leipziger Vorträge*, Leipzig, 1931; E. Fermi, L'effetto Raman nelle molecole e nei cristalli, *Mem. R. Accad. d'Italia*, **3** (3), 5–22 (1932).
64. D. M. J. Compton and A. H. Schoen, *Proc. 2nd Intern. Conf. Mössbauer Effect*, Wiley, New York, 1961.
65. Third Intern. Conf. Mössbauer Effect (A. J. Bearden, ed.), *Rev. Mod. Phys.*, **36** (1, part 2), 333 (1964).
66. R. Berman, *Advan. Phys.*, **2**, 103 (1953).
67. H. A. Bethe, *Proc. Roy. Soc. (London)*, **A150**, 552 (1935).
68. F. Bloch, *Z. Physik*, **52**, 555 (1928); **53**, 216 (1929); **59**, 208 (1930).
69. K. F. Bonhoeffer and L. Farkas, *Z. Physik*, **A134**, 337 (1927)
70. M. Born, Die Gültigkeitsgrenze der Theorie der Idealen Kristalle und ihre Ueberwindung, *Nachr. Akad. Wiss. Goettingen, II. Math.-Physik Kl.*, **1951**, 1.
71. M. Born, Kopplung der Elektronen und Kernbewegung in Moleküle und Kristallen," *Nachr. Akad. Wiss. Goettingen, II. Math.-Physik Kl.*, **1951**, 1.
72. M. Born and G. H. Begie, *Proc. Roy. Soc. (London)*, **A188**, 179 (1947).
73. M. Born and E. Brody, *Z. Physik*, **11**, 327 (1922).
74. M. Born and T. v. Karman, *Phys. Z.*, **13**, 297 (1912).
75. S. N. Bose, *Z. Physik*, **26**, 178 (1924).
76. A. Bravais, "Abhandlung über die Systeme von Regelmässig auf einer Ebene oder im Raum verteilten Punkten," *Ostwald's Klassiker*, **No. 90**, 1848.
77. C. J. Brester, *Kristallsymmetrie und Reststrahlen*, Dissertation monograph, J. VanDruten, Utrecht, 1923.
78. P. J. W. Debye, *Ann. Physik*, **39**, 789 (1912).
79. P. J. W. Debye and P. Scherrer, *Nachr. Akad. Wiss. Goettingen, II. Math.-Physik Kl.*, **1915**; **1916**; *Phys. Z.*, **18**, 291 (1917).
80. D. M. Dennison, *Proc. Roy. Soc. (London)*, **A115**, 483 (1927).
81. P. A. M. Dirac, *Proc. Roy. Soc. (London)*, **A112**, 660 (1926).

82. P. A. M. Dirac, *Proc. Roy. Soc.* (*London*), **A114,** 243 (1927); **A114,** 710 (1927).
83. A. Einstein, *Ann. Physik*, **22,** 180 (1907).
84. A. Einstein, *Phys. Z.*, **18,** 121 (1917).
85. A. Einstein, *Berl. Sitz.*, **1924,** 261; **1925,** 3.
86. O. Emersleben, *Phys. Z.*, **24,** 97 (1923).
87. A. Eucken, Der Nernstsche Wärmesatz, *Ergeb. Exakt. Naturw.*, **1,** 120 (1922).
88. E. Fermi, *Z. Physik*, **36,** 902 (1926).
89. E. Fermi, *Z. Physik*, **48,** 73; **49,** 550 (1928).
90. E. Fermi, "The Statistical Atom," *Leipziger Vorträge*, (1928); compare also some notes of the same author in *Atti Acad. Naz. Lincei, Rend. Classe Sci. Fis. Mat. Nat.*, 1927, 1928.
91. E. Fermi and L. Marshall, Interference Phenomena of Slow Neutrons, *Phys. Rev.*, **71,** 666 (1947).
92. E. Fermi and F. Rasetti, *Z. Physik*, **71,** 689 (1931).
93. W. Gerlach, *Z. Physik*, **38,** 828 (1926).
94. M. C. Goldberger and F. Seitz, Theory of Refraction and Diffraction of Neutrons by Crystals, *Phys. Rev.*, **71,** 294 (1947).
95. D. R. Hartree, *Proc. Cambridge Phil. Soc.*, **24,** 89 (1928).
96. A. E. V. Haschemeyer and H. M. Sobell, *Proc. Natl. Acad. Sci. U.S.*, **50,** 872 (1963).
97. Abbé Haüy, Essai d'une Theorie sur la structure des crystaux, *Acad. Roy. Sci.*, **1784.**
98. W. Heitler and F. London, *Z. Physik*, **44,** 455 (1927).
99. V. Henri, *Compt. Rend.*, **177,** 1037 (1923).
100. A. Herpin, *Ann. Phys.*, **7,** 91 (1952).
101. G. Herzberg, Die Prädissoziation und verwandte Erscheinungen, *Ergeb. Exakt. Naturw.*, **10,** 207 (1931).
102. H. M. James and A. S. Coolidge, *J. Chem. Phys.*, **1,** 825 (1933).
103. H. M. James and A. S. Coolidge, *Phys. Rev.*, **55.** 184 (1939).
104. P. Klemens, *Proc. Roy. Soc.* (*London*), **A208,** 108 (1951).
105. W. Kossel, *Ann. Phys.*, **49,** 229 (1916).
106. H. A. Kramers and W. Heisenberg, *Z. Physik*, **31,** 681 (1925).
107. H. A. Kramers and G. P. Ittmann, *Z. Physik*, **53,** 553 (1929); **58,** 217 (1929); **60,** 663 (1930).
108. R. de L. Kronig, *Z. Physik*, **50,** 347 (1928); **62,** 300 (1930); *Physica*, **1,** 617 (1934).
109. W. E. Lamb, Jr., *Phys. Rev.*, **55,** 190 (1939).
110. W. Friedrich, P. Knipping, and M. Laue, Interferenz-Erscheinungen in Röntgenstrahlen, *Sitz. Math.-Physik, Kl., München Akad. Wiss.*, **1912.**
111. P. Langevin, *Ann. Chem. Phys.*, **5,** (8), 70 (1905).
112. F. London and R. Eisenschitz, *Z. Physik*, **60,** 491 (1930).

113. A. A. Maradudin, Absorption of γ-Rays by Nuclei in a Crystal, *Proc. 3rd Intern. Conf. Mössbauer Effect, Rev. Mod. Phys.*, **36**, 417 (1964).
114. R. L. Mössbauer, *Z. Physik*, **151**, 124 (1958).
115. R. L. Mössbauer, Kernresonanz Absorption von Gammastrahlung in Ir^{191}, *Naturwiss.*, **45**, 538 (1958).
116. R. L. Mössbauer and D. H. Sharp, Resonance Scattering of γ-Rays by Nuclei Bound in Crystals, *Rev. Mod. Phys.*, **36**, 410 (1964).
117. R. S. Mulliken, *Phys. Rev.*, **32**, 880 (1928).
118. T. Nagamiya, *Proc. Phys. Math. Soc. Japan*, **18**, 497 (1936).
119. L. Nordheim, Die Theorie der Elektronenemission der Metalle, *Phys. Z.*, **30**, 177 (1929).
120. R. E. Peierls, *Ann. Phys.*, **3**, 1055 (1929) (thermal conduction).
121. R. E. Peierls, *Proc. Natl. Inst. Sci. India*, **20**, 121 (1954); **96**, 780 (1936).
122. G. Placzek and L. Van Hove, Crystal Dynamics and Inelastic Scattering of Neutrons, *Phys. Rev.*, **93**, 1207 (1954).
123. C. V. Raman and K. S. Krishnan, *Nature*, **121**, 501 (1928).
124. F. Rasetti, *Nuovo Cimento*, **6**, 356 (1929).
125. F. Rasetti, *Phys. Rev.*, **34**, 367 (1929).
126. F. Rasetti, *Z. Physik*, **61**, 598 (1930).
127. R. S. Richardson, *Publ. Astron. Soc. Pacific*, **44**, 250 (1932).
128. W. Ritz, *Reine Angew. Math.*, **135**, 1 (1909).
129. O. Sackur, *Nernst Festschrift, Knapp, Halle*, **1912**, 405; *Ann. Physik*, **40**, 67 (1913).
130. M. N. Saha, *Phil. Mag.* **40**, 472, 809 (1920); *Proc. Roy. Soc. (London)*, **A99**, 136 (1921).
A131. A. Sommerfeld, *Naturwiss.*, **15**, 824 (1927); **16**, 374 (1928); *Z. Physik*, **47**, 1 (1928).
132. O. Stern, *Phys. Z.*, **14**, 629 (1913).
133. Y. Sugiura, *Z. Physik*, **44**, 484 (1927).
134. H. Tetrode, *Ann. Phys.* **38**, 434 (1912); **39**, 255 (1912).
135. L. H. Thomas, *Proc. Cambridge Phil. Soc.*, **23**, 542 (1927).
136. J. H. Van Vleck, *Phys. Rev.*, **33**, 467 (1929); **37**, 733 (1929).
137. S. Wang, *Phys. Rev.*, **31**, 579 (1928).
138. S. Wang, *Phys. Rev.*, **34**, 243 (1929).
139. J. D. Watson and F. H. C. Crick, *Nature*, **171**, 373 (1953).

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