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COHESION

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§ 1. INTRODUCTION: NEW IDEAS IN PHYSICS

THERE are in nature, as in politics, two opposing forces. One of these aims at a peaceful consolidation and the other at a more active and probably more spectacular disruptive process. In nature it is cohesion between atoms which tends to produce condensation and solidification, and temperature which tends to produce dissociation, first of solids into liquids and then into isolated molecules, then of molecules into atoms and finally into electrons and protons (as in the hotter stars).

Temperature is a manifestation of kinetic energy and cohesion of potential energy, and the interplay of these two forms of energy is responsible for many of the observed physical properties of matter. A knowledge of the nature of cohesion is thus a necessary step towards an understanding of these physical properties. In this lecture I propose to review some of the progress which the new wave mechanics has made possible in this direction and, by way of introduction, to refer to some of the new conceptions which have been introduced during the last few years.

First, there is the main idea of wave mechanics that it is impossible to follow the electron in all its ways. Instead of supposing that the electron of an hydrogen atom steadily pursues for all time a definite track or orbit, we are now content to know the probability that it will do this or do that. We represent the electron by continuous distributions—probability patterns. To each such pattern there corresponds a definite average energy and normally the electron stays in the pattern of lowest energy. The density of the pattern at any point of space is a measure of the probability that the electron shall be found there. The probabilities become infinitesimally small outside regions measuring one hundred-millionth of a centimetre, so that the electrons of an atom may be regarded as almost always within this small

region. This is the interpretation to be given to the "size" of an atom from the new point of view*.

The mathematical theory does not give these density patterns directly. The wave equation gives the possible energy levels and certain mathematical functions, usually called wave functions and denoted by ψ, associated with them. The quantity here denoted by ψ is a function of the three coordinates used to specify the position of the electron in space. When ψ is a real quantity, its square is interpreted as a measure of the density of the probability pattern, just as the square of the amplitude (and not the amplitude itself) is a measure of the intensity of a sound or light wave. When ψ contains the square root of -1, the square of the amplitude of ψ, viz. $|\psi|^2$, or the product of ψ with its conjugate complex function, viz. $\psi\bar{\psi}$, is taken to be the appropriate measure of the probability of a given configuration.

§ 2. PAULI EXCLUSION PRINCIPLE

The hydrogen is particularly simple to work out because there is only one electron. It is equally easy to work out the patterns for one electron alone in the presence of a nucleus of charge Ze. The patterns are similar to those of hydrogen, but are contracted in the ratio 1 to Z everywhere.

If electrons are added one at a time to a nucleus of charge Ze until the whole structure is neutral and thus complete, we must inquire what happens to the electrons after the first. There is nothing in the wave mechanics, as formulated at present, to prevent all the electrons taking up the same pattern. The density of the electrons might be regarded as identical and superimposed, except for the electrostatic repulsion between them which would tend to swell out the pattern again.

We know from experience, however, that all the electrons of an atom do not assume the same pattern, and we have had to invoke an entirely new principle, first enunciated by Pauli, and now generally referred to as the *exclusion principle*. This principle asserts that there are never more than two electrons in the same pattern; it goes further by asserting that it is not sufficient to describe patterns in terms of the three spatial coordinates of an electron, but that a fourth coordinate must be introduced. This fourth coordinate can take only two discrete values, so that the patterns we have described up to now are to have a further property added to them which will double their number. It is as though the patterns had colour as well as shape. Actually it is usual to attribute a spin to the electron, and to suppose that the axis of the spin can take up either of two quantized directions. The exclusion principle then asserts that there is only one electron, described by its four coordinates, in every pattern. In building up atoms by the addition of one electron at a time, the electrons arrange themselves in those patterns which respect

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* At this stage of the lecture, a number of diagrams of patterns of the excited states of the hydrogen atom were shown. It was intended to reproduce these, but since the lecture, a number of similar pictures have been published by H. E. White, *Phys. Rev.* **37**, 1416 (1931), to which reference may be made.

the exclusion principle, and at the same time take up the configuration of least energy. The application of this principle accounts in a very beautiful way for the main features of atoms and molecules.

§ 3. PRINCIPLE OF IDENTITY OF ELECTRONS

In this addition of electrons to an atom, we have tacitly assumed that each electron persists in one pattern. But so far as is known, electrons are identical, and a system in which two electrons are interchanged is indistinguishable from its original state. This principle of the *identity of electrons* has proved to be of great importance. A method must be found of introducing this fact into the mathematics, and this was first done about the same time by Dirac and Heisenberg.

If we suppose that there are N electrons in an atom and that the wave functions associated with the patterns which they occupy are $u_1, u_2, \ldots u_N$, these functions including spin as well as space coordinates, then the wave function of the whole system must be taken to be* N u_N

$$\Psi = \begin{vmatrix} u_1\,(1), & u_2\,(1), & \ldots & u_N\,(1) \\ u_1\,(2), & u_2\,(2), & \ldots & u_N\,(2) \\ \vdots & \vdots & \ldots & \vdots \\ u_1\,(N), & u_2\,(N), & \ldots & u_N\,(N) \end{vmatrix}$$

Ψ

In this determinant $u_N\,(1)$ indicates that the four coordinates of electron 1 are to be introduced into the Nth function, and so on. Now if two electrons 1 and 2 are interchanged, the effect on the determinant is to interchange rows 1 and 2, and this has the effect of changing only the sign of Ψ. Furthermore, if we suppose two wave functions u_1 and u_2 to be the same, two columns of the determinant become identical and the determinant vanishes. The mathematical expression of the Pauli exclusion principle is thus that no two of the wave functions $u_1, \ldots u_N$ may be the same. The determinantal form of Ψ thus takes into account the identity of the electrons and the exclusion principle at the same time. $u_N\,(1)$

Actually when the electrostatic repulsions between electrons in an atom are taken into account, we cannot regard the wave function as made up of N different functions $u_1 \ldots u_N$, each containing only the coordinates of one electron. All that we can be certain of is that the complete wave function, when found, must have the same properties as the determinant as regards the interchange of electrons and the exclusion principle. It has not been possible, however, as yet to deal mathematically with functions more complicated than the determinant.

The probability distribution of the N electrons is now given by $\Psi'\overline{\Psi}$, which

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* This is subject to the condition that there be not several functions of this type with the same energy. It is possible to write the wave function in the form given above for most atoms in their state of lowest energy.

is a generalization of the probability distribution for one electron. When the two determinants Ψ' and $\overline{\Psi}$ are multiplied together, we find

$$\Psi'\overline{\Psi} = \begin{vmatrix} \rho\,(1,\,1), & \rho\,(1,\,2), & \ldots & \rho\,(1,\,N) \\ \rho\,(2,\,1), & \rho\,(2,\,2), & \ldots & \rho\,(2,\,N) \\ \vdots & \vdots & \ldots & \vdots \\ \rho\,(N,\,1), & \rho\,(N,\,2), & \ldots & \rho\,(N,\,N) \end{vmatrix}$$

$\rho\,(1,\,2)$ where*

$$\rho\,(1,\,2) = \sum_{j} \bar{u}_{j}\,(1)\, u_{j}\,(2).$$

We note that $\rho\,(1,\,1)$ is the sum of terms like $\bar{u}_{j}\,(1)\,u_{j}\,(1)$ which are density functions of electron 1 in the different patterns; in fact, we have

$$\rho\,(1,\,1) = \sum_{j} \rho_{j}\,(1,\,1),$$

and we should be justified in superimposing the density patterns if it were not for the terms like $\rho\,(1,\,2)$. These indicate to us that we must no longer expect to express the charge density in three dimensions (or four, including spin), but we must use a six-dimensional function (or an eight-dimensional one if we include spin). This is not surprising. In the older theories, when electrons were assumed to be pursuing orbits, we needed a knowledge not only of space coordinates but also of the components of velocity of the electrons to specify their configuration completely. Now that we have given up the idea of attributing definite velocities and space coordinates to electrons simultaneously, we must not be surprised to find the six-dimensional character of the probability configuration appearing in another form.

§ 4. ELECTRON-DISTRIBUTIONS IN ATOMS

$d\tau$ The expression given above for $\Psi'\overline{\Psi}$, multiplied by elements of volume $d\tau_1, d\tau_2, \ldots d\tau_N$, in the configuration space of each electron, may be interpreted as the probability that an electron (we do not specify which one) shall be found in $d\tau_1$, another in $d\tau_2$, and so on simultaneously†. The probability that an electron shall be found in $d\tau_1$, irrespective of the position of the other electrons, is obtained by integrating $\Psi'\overline{\Psi}$ over the configuration space of electrons 2 to N. In the integration each electron configuration is to be counted only once, so that if $d\tau'$ indicates one specified element of volume and $d\tau''$ another, $d\tau_1'\,d\tau_2''$ is to be taken to be the same as $d\tau_1''\,d\tau_2'$. The result of the integration is $\rho\,(1,\,1)\,d\tau_1$ or $\sum_{j} \rho_j\,(1,\,1)\,d\tau_1$, and is thus the same as the superposition of the separate patterns ρ_1 to ρ_N‡. In this

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* This form of the function $\Psi'\overline{\Psi}$ has been given recently by Dirac, *Proc. Camb. Phil. Soc.* **27**, 240 (1931); cf. also Lennard-Jones, *Proc. Camb. Phil. Soc.* **27**, 469 (1931).

† P. A. M. Dirac, *loc. cit.*

‡ This result holds when the functions u_1 to u_N are normalized and orthogonal, that is, $\int \bar{u}_k u_l d\tau = \delta_{kl}$. For most atoms in their normal state, the wave functions can be adjusted to satisfy this condition.
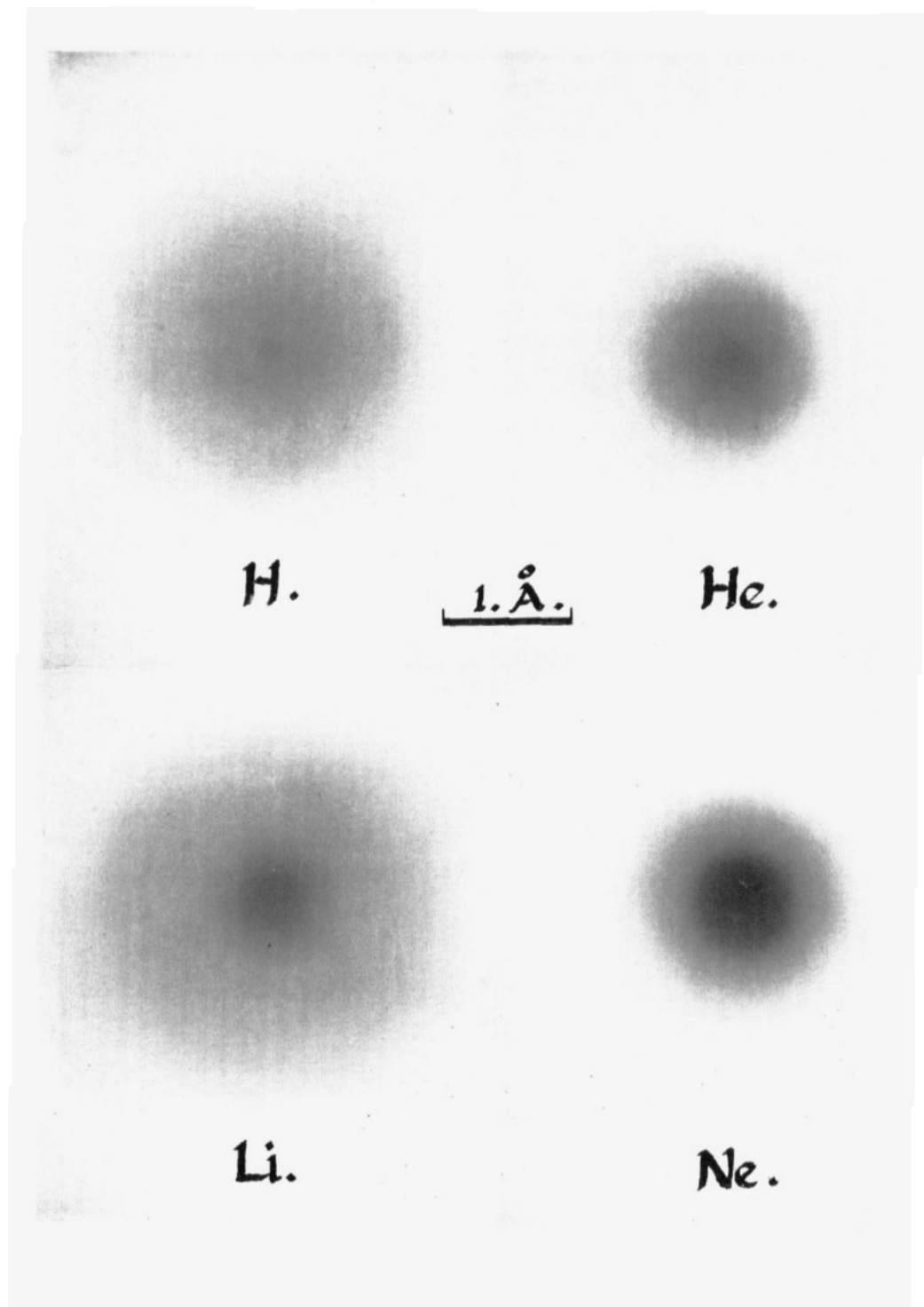
sense we may construct pictures of many-electron atoms, and these pictures represent the probability of finding *an* electron in any element of volume in ordinary space.

When the process is carried out, it appears that many atoms—more than were previously suspected—may be considered to be spherically symmetrical. Of the first ten atoms of the periodic table, six may be so regarded. They are hydrogen, helium, lithium, beryllium, nitrogen* and neon. Diagrammatic pictures of some of these atoms are given on the accompanying plate†. They have been calculated from some approximate wave functions given by Slater‡. The pictures cannot be regarded as accurate but they give a fair idea of the relative "spread" of the various atoms. The inert gas atoms, occurring at the end of a group of the periodic table, are usually the most compact atoms of that group.

The spread of these atoms may be gauged also from figure 1. The contours give the probability of finding an electron *outside* the contour. The first is 0·2—that is, the probability of finding an electron outside it is 1 in 5. The second, third... are 0·4, 0·6.... Outside the contour 1·0, there is a *certainty* of finding one electron; outside the contour 1·2 there is a probability of finding two electrons simultaneously. The spread of lithium, which combines with others in the solid state to form a metal, is in striking contrast to that of neon, although the latter contains many more electrons. Boron in its normal state has one electron in a 2p-state, or one with quantum numbers $n = 2$, $l = 1$, $m = 1$, 0 or − 1. The corresponding probability patterns are asymmetrical. The one with quantum numbers 2, 1, 0 consists of two blobs of electron charge situated symmetrically with respect to the nucleus. The plane of symmetry contains no charge, while a line through the nucleus perpendicular to this plane of symmetry passes through the centres of the blobs. Along this line the electron charge increases from zero to a maximum and then falls away to zero§. This line may be referred to as the axis of the pattern. Those with quantum numbers (2, 1, 1) and (2, 1, − 1) are like anchor rings. The concentration of charge in each is zero along the axis, and has a maximum along the core, from which it decreases to zero in each direction. The axis of the ring coincides with the axis of the (2, 1, 0) pattern so that the maximum concentration of the (2, 1, 1) pattern lies in the plane of zero concentration of the (2, 1, 0) pattern.

Carbon in its normal state may be regarded as having one of its two outer electrons in the (2, 1, 0) pattern and the other in either the (2, 1, 1) or the (2, 1, − 1) pattern, while the two electron spins are the same‖. The electron distribution thus consists of an anchor ring and two "balls" of charge on its axis above and below the nucleus, all of which is superimposed on a background due to the inner electrons, which is spherically symmetrical.

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* In its normal state, that is, in the ^4S state.

† I am greatly indebted to Mr H. H. M. Pike of the H. H. Wills Physical Laboratory, Bristol, for these pictures, as also for those in figure 1, and for the calculations involved in making them.

‡ J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

§ Cf. H. E. White, *loc. cit.*   ‖ The normal state of the carbon atom is a ^3P state.

Nitrogen has one outer electron in a (2, 1, 0) pattern, another in a (2, 1, 1) pattern and a third in a (2, 1, − 1) pattern. These three patterns when superimposed give a distribution which is spherically symmetrical. The spins of these three outer electrons in the normal state of the nitrogen atom are the same, for this configuration gives the lowest energy (the ^4S state).

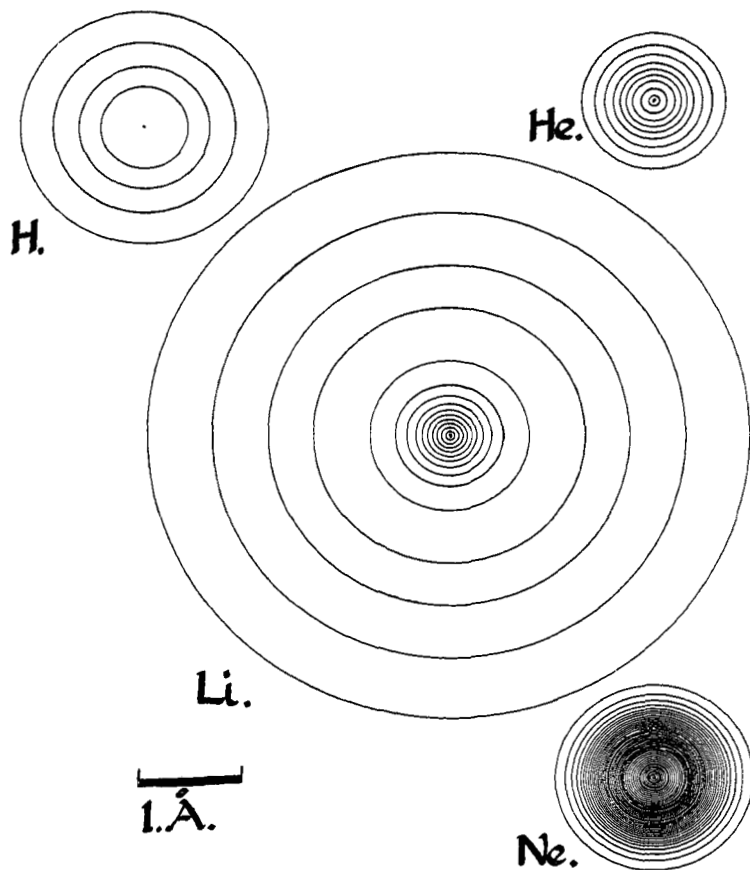

Fig. 1. The "spread" of the atoms hydrogen, helium, lithium and neon.

Neon, which has six electrons in the 2p-state, has two electrons, one of each spin, in each of the patterns (2, 1, 1), (2, 1, 0) and (2, 1, − 1). It also is spherically symmetrical. Flourine has one less electron than neon, and so we may regard it as an atom which requires one electron to complete its spherical symmetry*. It is an atom with a "hole" in it, and the "hole" is probably a (2, 1, 0) pattern†.

* This property is connected with the affinity which fluorine has for an electron.
† Cf. J. E. Lennard-Jones, *Trans. Faraday Soc.* 25, 668 (1929).

Oxygen has two "holes," one of which is probably a (2, 1, 0) and the other a (2, 11), or a (2, 1, − 1) pattern. Like divalent carbon, its normal state is a ^3P state, though now this state may be attributed to two *holes*, whereas in carbon it is due to the two *electrons*. In this sense oxygen may be regarded as the counterpart of divalent carbon.

These pictures of atoms throw considerable light on their chemical properties and elucidate the problem of molecular structure, to which we shall refer below.

§ 5. PRINCIPLE OF MINIMUM ENERGY

To the new principles already discussed, we must add an old one, viz., the principle of minimum energy; an atomic or molecular system tends to take up the state of lowest energy. This is of fundamental importance in the subject of cohesion.

§ 6. TYPES OF COHESIVE FORCES

The physical and chemical properties of matter show that cohesive forces fall into certain definite categories. Helium must be cooled down to − 269° C. before it begins to aggregate, whereas hydrogen exists in the diatomic form at ordinary temperatures. All the rare gases are similar to helium in exhibiting this weak cohesion. Neon liquifies at about − 240° C. and argon at − 186° C. The weak attractive fields of these gases is responsible for their small departure from the ideal gas laws, and as they were first investigated by van der Waals, they may conveniently and fittingly be referred to as *van der Waals attractive fields*. This type of attraction probably exists between all atoms and molecules, as will appear in the next paragraph, but it is usually masked by other large attractive fields of a different type.

The cohesive forces which hold together the atoms of a hydrogen or a nitrogen molecule are about a thousand times as great as those which two helium atoms exert on each other, even when they are neighbours in the solid form. These forces are the familiar *homopolar attractive fields* of the chemist. At the same time it should be pointed out that the *molecules* of hydrogen and nitrogen behave like the inert gases as regards liquefaction and solidification and it is almost certain that such molecules are held together in the condensed form by van der Waals forces. It requires only about 500 calories to evaporate one gram molecule of solid hydrogen, whereas 100,000 calories per gram molecule are required to dissociate 1 gram molecule of molecular hydrogen.

There is distinct evidence that in some solids, such as NaCl, there is a migration of an electron from one atom (such as an alkali) to another atom (such as a halogen). The atom which loses an electron becomes positively charged and the other negatively charged. There is thus a net electrostatic attraction between neighbouring atoms and this produces a very firm structure, which is difficult to disrupt. When

such solids are vaporized (usually at high temperatures) the vapour is diatomic. Such molecules may be said to be held by *ionic attractive fields*.

There are other solids which are also difficult to melt and to vaporize, but which stand in a different class from the ionic solids or salts. They have other properties not possessed by the salts in that they are good conductors of heat and electricity and, so far as is known, are monatomic in the vapour state. These solids, the metals, stand in a class by themselves and the forces holding them together may be called *metallic attractive fields*.

Intimately connected with the subject of cohesion is the question why atoms ever repel each other. The very existence of matter leads us to postulate that when atoms approach very near to one another they begin to repel. The resistance which solids offer to compression is evidence and indeed a measure of the repulsive forces between atoms. A theory which explains cohesion may be expected also to explain *intrinsic repulsive fields* and this proves to be the case.

§ 7. THE NATURE OF VAN DER WAALS FIELDS

Although it is sufficient for many purposes to represent electrons in atoms as continuous distributions, such representations are not, of course, accurate. It is only the average which is continuous, and there must be rapid fluctuations about this average, corresponding to the motion in a classical sense of the electrons within the atom. Without it, van der Waals fields, as we know them, would not exist. Two hydrogen atoms in their normal state, for example, are each represented by a spherically symmetrical distribution, and as each is neutral, the electrostatic potential of the one distribution on the other at a large distance apart is vanishingly small. Nor can van der Waals fields be interpreted in terms of a static disturbance of the continuous distribution. These fields have often been attributed vaguely to polarization. But this polarization cannot be a static one, for if it were, each atom so polarized could be represented by a small permanent dipole at its centre. As the interaction in the case of equal atoms is symmetrical, the dipoles produced must be symmetrical about a plane midway between them. They must therefore point either towards or away from each other. In either case they cause repulsion. Van der Waals fields, as we shall show, are due to a *dynamic* polarization. The motion of the electrons in one atom modifies that of the electrons in the other in such a way that *they tend on the average to move in phase*. An important consequence is that van der Waals fields to a close approximation are additive, even when one is surrounded symmetrically by several others. Although there was evidence from many sources that these fields were additive, this property could not be deduced from a theory of static polarization.

The nature of van der Waals fields may probably be brought out most clearly by means of a simple molecular model. Suppose that an atom is represented by a linear oscillator, that is, by an electron vibrating linearly about the nucleus. Such a

system requires only one coordinate z to specify it. The appropriate Schrödinger
equation is then

$$\frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} \left(E - \tfrac{1}{2}kz^2\right)\psi = 0,$$

where m is the mass of the electron, and $\tfrac{1}{2}kz^2$ is the potential energy of the electron.
On the classical theory, an oscillator of this type, subject as it is to a restoring force
of kz, would have a frequency given by

$$2\pi\nu_0 = \sqrt{k/m}.$$

The solution of the wave equation is well known. It consists of a set of discrete
values for E, viz., $E = (n + \tfrac{1}{2})h\nu_0$, where n is any integer. In the state of lowest
energy, the appropriate value of ψ is given by

$$\psi = (2\kappa\,\nu_0/\pi)^{\frac{1}{4}}\,e^{-\kappa\nu_0 z^2}$$

where $$\kappa^2 = 2\pi\,m/h.$$

The equation is written in such a form as to bring out the dependence of ψ on the
frequency ν_0 for a purpose which will be seen later.

The "smeared-out" pattern for the electron in this case is thus a Gaussian
error curve, symmetrical about the origin.

We suppose now the oscillator to be subject to a uniform electric field F, so
that the potential energy becomes $\tfrac{1}{2}kz^2 - eFz$ or $\tfrac{1}{2}k\,(z - eF/k)^2 - e^2F^2/2k$. The
appropriate wave equation can be written

$$\frac{\partial^2 \psi}{\partial \xi^2} + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2F^2}{2k} - \tfrac{1}{2}k\xi^2\right)\psi = 0,$$

which has the same form as the original equation, except that ξ, which $= z - eF/k$,
now takes the place of z.

The energy values are $E = (n + \tfrac{1}{2})h\nu_0 - e^2F^2/2k$. The last term gives the
change of energy due to the field—the so-called polarization energy.

$$Polarization\ energy = -\,e^2F^2/2k.$$

In terms of the coefficient of polarizability α, the polarization energy is $-\tfrac{1}{2}\alpha F^2$
by definition, so that $\alpha = e^2/k$.

The corresponding density pattern is proportional to $e^{-2\kappa\nu_0\,(z - eF/k)^2}$, which is the
same as the original one, except for a displacement of the maximum through an
amount eF/k in the direction of the field. This represents a static polarization.

We next suppose the oscillator to be subject to the field of a distant parallel
rigid dipole of strength μ at a distance R. The potential of the electron is then
$-2\mu ez/R^3$ and is like a parallel field except that the constant of proportionality
depends on R. The theory of the preceding paragraph applies if F is replaced by
$2\mu/R^3$, and so the energy of the oscillator, being proportional to the square of F,
is now proportional to $\mu^2 R^{-6}$.

$$Polarization\ energy = -\,2e^2\mu^2/kR^6.$$

Moreover, the energy being negative indicates attraction. The polarization of the oscillator is again a static one.

If now we suppose the dipole μ to fluctuate in value and to change in sign independently of the original oscillator (though this is an artificial assumption), the polarization of the oscillator is always such as to give an attraction proportional to R^{-6}; in fact, we have

$$\textit{Average polarization energy} = -\,2e^2\overline{\mu^2}/kR^6.$$

The polarization is now a fluctuating one and may be described as a *dynamic* one.

Actually the second dipole cannot be regarded as fluctuating independently of the first. It also will be subject to a dynamic polarization, and the two systems must be regarded as one complete coupled system. The method, however, prepares the way for a more accurate treatment* and suggests that two such oscillators will tend to move in phase.

The complete wave equation for two equal oscillators, each vibrating along the axis of z under each other's influence, is

$$\frac{\partial^2 \psi}{\partial z_1^2} + \frac{\partial^2 \psi}{\partial z_2^2} + \frac{8\pi^2 m}{h^2}\left(E - \tfrac{1}{2}kz_1^2 - \tfrac{1}{2}kz_2^2 + \frac{2e^2 z_1 z_2}{R^3}\right)\psi = 0,$$

and this can easily be transformed to new variables

$\xi_1,\ \xi_2$

$$\xi_1 = (z_1 + z_2)/\sqrt{2}, \quad \xi_2 = (z_1 - z_2)/\sqrt{2},$$

$$\frac{\partial^2 \psi}{\partial \xi_1^2} + \frac{\partial^2 \psi}{\partial \xi_2^2} + \frac{8\pi^2 m}{h^2}\left(E - \tfrac{1}{2}k_1\xi_1^2 - \tfrac{1}{2}k_2\xi_2^2\right)\psi = 0,$$

$k_1,\ k_2$ where $$k_1 = k - 2e^2/R^3, \quad k_2 = k + 2e^2/R^3.$$

The possible energy values of the equation are

$n_1,\ n_2$

$$E = (n_1 + \tfrac{1}{2})\,h\nu_1 + (n_2 + \tfrac{1}{2})\,h\nu_2,$$

where

$\nu_0,\ \nu_1,\ \nu_2$

$$\nu_1 = \frac{1}{2\pi}\,\sqrt{(k_1/m)} = \nu_0\,\sqrt{(1 - 2e^2/kR^3)}, \quad \nu_2 = \nu_0\,\sqrt{(1 + 2e^2/kR^3)}.$$

This transformation is accurate and valid as long as ν_1 is real, that is as long as $2e^2/kR^3 < 1$. This implies that R must be greater than $(2\alpha)^{\frac{1}{3}}$. For the state of lowest energy, we thus get

$$E = \tfrac{1}{2}h\,(\nu_1 + \nu_2)$$

$$= h\nu_0\,(1 - e^4/2k^2R^6),$$

if the square roots be expanded, as they can for large R. This indicates that the energy of interaction of the dipoles, or the

$$\textit{van der Waals polarization energy} = -\,h\nu_0 e^4/2k^2 R^6,$$

and that there is an attractive *force* proportional to the inverse seventh power of the distance.

* Cf. F. London, *Zeit. f. phys. Chem.* **11**, 222 (1930).

The wave function for the whole system for this lowest state is equal to the product of the appropriate functions in ξ_1 and ξ_2, viz.,

$$\psi = (4\kappa^2 \, \nu_1 \nu_2/\pi^2)^{\frac{1}{4}} \, e^{-\kappa \, (\nu_1 \xi_1{}^2 + \nu_2 \xi_2{}^2)}$$

$$= (2\kappa/\pi)^{\frac{1}{2}} \, (\nu_1 \nu_2)^{\frac{1}{4}} \, e^{-\kappa \nu_0 \, (z_1{}^2 + z_2{}^2)} \, e^{(\kappa \nu_0 e^2/k) \, (2z_1 z_2/R^3)}$$

$$= (\nu_1 \nu_2/\nu_0{}^2)^{\frac{1}{4}} \, \psi_0 \, e^{-(\kappa \nu_0/k)v},$$

where ψ_0 is the corresponding wave function before interaction, and v is the potential ψ_0, v
of interaction $(-\, 2e^2 \, z_1 z_2/R^3)$.

The probability of a specified configuration, that is, a specified z_1 and a specified z_2, is given by the square of ψ, and is thus proportional to $\psi_0{}^2 \, e^{-\beta v}$. When v is negative (indicating attraction between the dipoles), the probability is greater than $\psi_0{}^2$ and when v is positive (indicating repulsion between the dipoles), the probability is less than $\psi_0{}^2$.
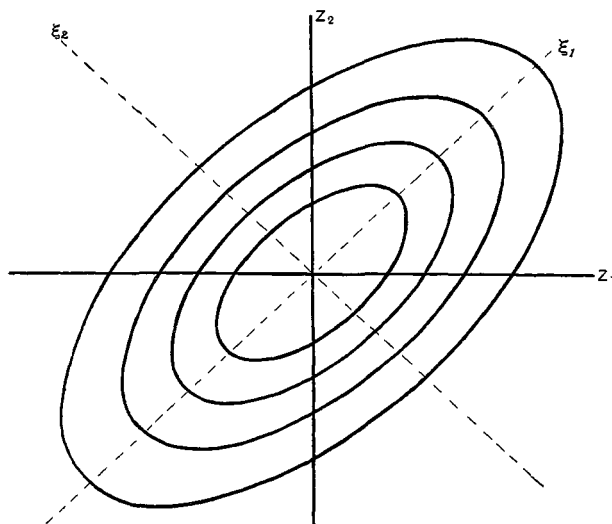

Fig. 2. The probability function for two interacting linear oscillators.

This result can be represented diagrammatically in a two-dimensional space, as shown in figure 2. The distribution function, being proportional to $e^{-2\kappa \, (\nu_1 \xi_1{}^2 + \nu_2 \xi_2{}^2)}$, is like a ridge with its maximum at the origin, and with elliptical contours. The major axes of the ellipses are $\xi_2 = 0$ or $z_1 = +\, z_2$, and the minor axes $z_1 = -\, z_2$. The corresponding distribution without interaction is a round-topped mountain with circular contours. The probability of finding z_1 and z_2 with the same sign has increased, while that of finding them with the opposite sign has decreased. In other words, the interacting dipoles tend on the average to move in phase.

A similar treatment can be given for two three-dimensional oscillators*. Let the line joining the centres of the oscillators be in each case the axis of z as before,

* F. London, *loc. cit.*

x, y   and let any convenient parallel sets of axes x and y be chosen in planes perpendicular to this axis through the respective centres. The mutual potential energy of the oscillators is then

$$V = e^2 \left(x_1 x_2 + y_1 y_2 - 2z_1 z_2 \right)/R^3.$$

The probability-distribution function can now be represented only in six-dimensional space. It appears that z_1 and z_2 tend to have the same sign (as before), while x_1 tends to be opposite to x_2, and y_1 opposite to y_2. These are just the configurations for which the oscillators attract. Hence we may say that two systems tend to interact in such a way that the attraction is a maximum. It is in the generalized sense that we use the expression "tend to move in phase," for actually in this example the x's and y's tend to be out of phase in the usual sense.

These simple examples, which can be worked out accurately, serve to bring out the essential nature of van der Waals fields, and we may presume that in other more complicated cases, where the mathematics is more difficult to interpret, the attraction is due to a *sympathetic* movement of the electric charge.

The mathematical calculations for actual atoms are not easy. Wang* was the first to attempt the calculation of the van der Waals fields of two hydrogen atoms. He showed that the asymptotic form of the interaction of two hydrogen atoms was like that of two dipoles, and used this additional potential as a perturbation of the wave equation of two normal atoms. He thus showed that the attractive force between them at large distances varied inversely as the seventh power of the distance. The numerical value has not, however, been confirmed by later investigations. Recently Eisenschitz and London† have given a method of calculating fields of this type for any atoms, which is based on the second approximation of the usual perturbation theory. (The first approximation of this theory vanishes at large interatomic distances). The wave function of the system is expressed in terms of certain selected unperturbed wave functions of the two atoms. The method is rather unwieldy and the authors themselves expressed the hope that some simpler method would be found. The problem has also been considered by Lennard-Jones‡, Hassé§, and Slater and Kirkwood∥. The first of these authors uses a modified form of the perturbation theory which considerably simplifies the calculation of the van der Waals fields of two hydrogen atoms, while the second two use specially adapted variation methods. In each case the *potential* of the attractive field is of the form $- \lambda R^{-6}$, and the values obtained for λ are as follows:

Eisenschitz and London	...	$6 \cdot 04 \cdot 10^{-60}$
Lennard-Jones	... ...	$6 \cdot 04 \cdot 10^{-60}$
Hassé	... ...	$6 \cdot 05 \cdot 10^{-60}$
Slater and Kirkwood ...	...	$6 \cdot 05 \cdot 10^{-60}$

These values of λ give the attraction in ergs when R is measured in centimetres.

* S. C. Wang, *Phys. Zeit.* **28**, 663 (1927).
† R. Eisenschitz and F. London, *Zeit. f. Phys.* **60**, 491 (1930).
‡ J. E. Lennard-Jones, *Proc. R.S.* A, **129**, 598 (1930).
§ H. R. Hassé, *Proc. Camb. Phil. Soc.* **27**, 66 (1931).
∥ J. C. Slater and Kirkwood, *Phys. Rev.* **37**, 682 (1931).

The calculations for hydrogen atoms are valid, of course, only at large interatomic distances. At smaller distances the exchange phenomenon, referred to below, comes into prominence, and leads eventually to the formation of the diatomic molecule. The exchange forces, however, fall off very rapidly (as e^{-ar}/r) and become small at distances at which the van der Waals fields are still important. It is unfortunate that in this case, where the theoretical calculations can be carried out with some accuracy, comparison with experiment is not possible.

An attempt has been made to extend the theory to more complicated atoms, but the main difficulty here is the lack of knowledge of the wave functions of these atoms. Even in the case of helium, the wave functions are only known approximately. London* has attempted to correlate the van der Waals fields of atoms with their coefficient of polarizability, but the correlation is only an approximate one, and only between certain rather wide limits can the magnitude of the fields be fixed by this method.

Hassé† has attempted the case of two helium atoms and has based his work on wave functions deduced by Hylleras‡ from a variation method. These wave functions are adjusted to make the energy of the helium electronic system a minimum and it does not follow that wave functions so deduced are valid over their whole range; in fact, it appears that they are probably fairly accurate near the nucleus (where the energy contributions are large) but less accurate in the outer parts of the atom. But it is just the outer parts of the atom which are most affected by outside fields, and so it is important that the wave function in those regions should be known accurately. Hassé finds that the Hylleras functions, which approximate best to the correct ionization potential of helium, do not give the best results for the polarization energy in a uniform electric field, which also is known experimentally. Similar calculations have been carried out for the van der Waals fields, but again there is a certain arbitrariness owing to the uncertainty of the Hylleras functions. The results obtained by Hassé are given below.

Slater and Kirkwood§ have given a further development of Hassé's method, also depending on the variation method. They work out the polarizability of helium and the van der Waals fields of two helium atoms by means of an approximate wave function, previously given by Slater‖. The results obtained so far for the attractive-force-constant of helium (λ in λR^{-7}) are as follows: λ

London	...	...	...	...	$7 \cdot 44 \cdot 10^{-60}$ ¶
Hassé	...	...	...	...	$(7 \cdot 91 - 8 \cdot 21) \, 10^{-60}$
Slater and Kirkwood		...	...	$8 \cdot 94 \cdot 10^{-60}$

Slater and Kirkwood give as well an expression for the field of two helium atoms at *close* distances. The potential curve obtained from their work is plotted in figure 3.

* F. London, *Zeit. f. phys. Chem.* **11**, 222 (1930).

† H. R. Hassé, *Proc. Camb. Phil. Soc.* **27**, 66 (1931).

‡ E. A. Hylleras, *Zeit. f. Phys.* **54**, 347 (1929).

§ J. C. Slater and Kirkwood, *Phys. Rev.* **37**, 682 (1931).

‖ J. C. Slater, *Phys. Rev.* **32**, 349 (1928).

¶ This figure is given as an upper limit, and is deduced from the formula given in the next paragraph, the observed value of the coefficient of polarizability being used.

Other inert gas atoms have been considered but the results can only be estimated roughly because the wave functions are not known sufficiently well. Both London and Slater-Kirkwood, unable to calculate the force-constants of these gases directly, attempt to correlate the force-constant with the coefficient of polarizability. Slater and Kirkwood give

$$\lambda = (\text{const.}) \, N^{\frac{1}{2}} \, \alpha^{\frac{3}{2}},$$

while London gives
$$\lambda = (\text{const.}) \, I \, \alpha^2.$$

λ, α
N
I
In each case λ is the constant of van der Waals field, and α is the coefficient of polarizability; in the first formula N is the number of electrons in the outer shell, and in the second I is the ionization potential. It is not known yet how far either formula is correct.

The attractive force constants of gases can also be determined from a study of the equation of state, as has been shown by the author*. A collected account of the methods used and the results obtained has already been published†, but some new results, which have been worked out recently on the assumption of an attractive force of the type λR^{-7}, may appropriately be given here‡. The repulsive field, which
$\lambda_{(\text{rep})}, n$
comes into play at short distances, is represented by a force of the type $\lambda_{(\text{rep.})} R^{-n}$. Theoretical calculations of the type discussed in the next paragraph show that the repulsive field is more complicated than this and contains terms of the form e^{-aR}, but it falls off very rapidly with distance and can (in the case of helium at any rate) be represented, over the range which is most effective in atomic collisions, by a term of the type $\lambda_{(\text{rep.})} R^{-n}$.

The equation of state alone does not determine the value of the index n in this repulsive field uniquely, but, for a given n, it determines the value of the
$\lambda_{(\text{att})}$
constant $\lambda_{(\text{rep.})}$, and the attractive constant $\lambda_{(\text{att.})}$. Other methods have to be employed to single out the right value of n from the array of possible ones thus determined. The crystal spacing of the solidified gas or its heat of sublimation may be used for this purpose. In the accompanying table the results are given for $n = 10$, 11 and 13. The experimental material from which these results are derived is cited elsewhere§, and later experimental results of Nijhoff‖, and of Gibby, Tanner and Masson¶ have been used as well. In table 1 are given calculated values of the closest distance of approach which these gases would have at absolute zero, if they set in the form of face-centred cubes. This is the form which would be expected theoretically for a force of the type $\lambda_{\text{rep.}} R^{-n} - \lambda_{\text{att.}} R^{-7}$,

* J. E. Lennard-Jones, *Proc. R.S.* A, **106**, 463 (1924), **107**, 157 (1925), **109**, 481 (1925), **112**, 214 (1926); J. E. Lennard-Jones and W. R. Cook, *Proc. R.S.* A, **115**, 334 (1927).

† J. E. Lennard-Jones, chap. x of *Statistical Mechanics*, by R. H. Fowler (Camb. Univ. Press, 1929).

‡ The author gratefully acknowledges the help of Miss M. J. Littleton (H. H. Wills, Physical Laboratory, Bristol) in the numerical calculations.

§ J. E. Lennard-Jones, chap. x of *Statistical Mechanics* by R. H. Fowler (Camb. Univ. Press, 1929).

‖ G. P. Nijhoff, *Dissert.* (Leiden, 1928).

¶ C. W. Gibby, C. C. Tanner and I. Masson, *Proc. R. S.* A, **122**, 283 (1929).

Table 1. Calculated force constants of gases from equation of state

		$\lambda_{(rep)}$	$\lambda_{(att.)}$	Calculated closest distance in crystal (A.U.)	Calculated heat of sublimation at abs. zero in cals/gm. mol.	Observed crystal spacing	Observed heat of sublimation*
Helium	$n = 10$	$4{\cdot}38.10^{-82}$	$13{\cdot}8.10^{-60}$	$3{\cdot}02$	106	—	—
	$n = 11$	$8{\cdot}94.10^{-90}$	$10{\cdot}3.10^{-60}$	$2{\cdot}93$	114	—	—
	$n = 13$	$4{\cdot}55.10^{-105}$	$7{\cdot}43.10^{-60}$	$2{\cdot}83$	126	—	—
Neon	$n = 10$	$2{\cdot}94.10^{-81}$	$8{\cdot}22.10^{-59}$	$3{\cdot}14$	499		
	$n = 11$	$6{\cdot}285.10^{-89}$	$6{\cdot}22.10^{-59}$	$3{\cdot}04$	542	$3{\cdot}20$†	590
	$n = 13$	$4{\cdot}36.10^{-104}$	$5{\cdot}07.10^{-59}$	$2{\cdot}99$	612		
Argon	$n = 10$	$7{\cdot}19.10^{-80}$	$10{\cdot}5.10^{-58}$	$3{\cdot}90$	1730		
	$n = 11$	$2{\cdot}10.10^{-87}$	$8{\cdot}32.10^{-58}$	$3{\cdot}83$	1847	3 84	2030
	$n = 13$	$2{\cdot}13.10^{-102}$	$6{\cdot}50.10^{-58}$	$3{\cdot}74$	2030		
Hydrogen	$n = 10$	$4{\cdot}59.10^{-81}$	$1{\cdot}07.10^{-58}$	$3{\cdot}33$	450	—	—
	$n = 11$	$1\ 16.10^{-88}$	$0{\cdot}85.10^{-58}$	$3{\cdot}28$	478	—	—
	$n = 13$	$7{\cdot}79.10^{-104}$	$0{\cdot}63.10^{-58}$	$3{\cdot}18$	529	—	—
Nitrogen	$n = 10$	$1{\cdot}19.10^{-79}$	$13{\cdot}6.10^{-58}$	$4{\cdot}23$	1380		
	$n = 11$	$3\ 93.10^{-87}$	$11{\cdot}1.10^{-58}$	$4{\cdot}17$	1460	$4{\cdot}0$‡	1860
	$n = 13$	$4{\cdot}44.10^{-102}$	$8{\cdot}38.10^{-58}$	$4{\cdot}06$	1640		

as it is the cubic form of least potential energy§. Argon|| and neon¶ have already been shown experimentally to exist in this form. The calculated values of the heat of sublimation at absolute zero from this crystal structure are also given. The force constants of neon are a little uncertain because the experimental results of Holborn and Otto and those of Cath and Kamerlingh Onnes are not very consistent. The figures given are obtained by taking both sets of experimental points and adjusting the theoretical curves to fit as well as possible. Figure 3 shows the curves of potential energy of pairs of inert gas atoms as a function of their distance apart for the model $n = 13$, $m = 7$.

It is probable that many other gases are held together in the liquid and solid state by van der Waals forces, for, as London** has pointed out, many cases are known where the heat of sublimation is of the same order of magnitude as those given in the above table. CH_4, HCl, HBr, CO may be quoted as examples. Forces of this type are probably responsible also in certain cases for the adsorption of

* For reference see F. London, *Zeit. f. phys. Chem.* 11, 240 (1930).
† J. de Smedt, W. H. Keesom and H. H. Mooy, *Proc Amst. Acad.* 33, 255–257 (1930).
‡ Vegard, *Nature*, 124, 267, 337 (1929), molecules being regarded as spheres.
§ J. E.. Lennard-Jones and A. E. Ingham, *Proc. R.S.* A, 107, 636 (1925).
|| F. Simon u. C. Simson, *Zeit. f. Phys.* 25, 160 (1924).
¶ J. de Smedt, W. H. Keesom and H. H. Mooy, *loc. cit.*
** F. London, *Zeit. f. phys. Chem. loc. cit.*

gases on solid surfaces. The author has shown that the order of magnitude of certain observed heats of adsorption can be explained in this way*. Other cases have been worked out recently by London†.
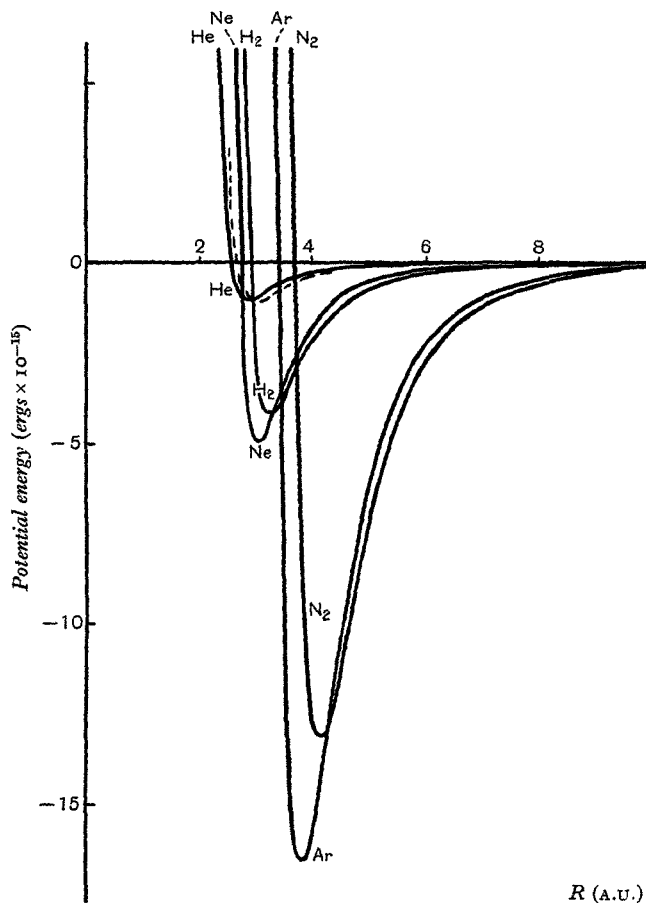

Fig. 3. The potential energy of pairs of inert gas atoms as a function of their distance apart in Å.‡

The experimental study of molecular spectra has established the existence of molecules such as HgAr, HgKr§, and lately it has been shown that a molecular form of K_2 exists quite other than the molecule formed by the usual homopolar forces‖. There is little doubt that these molecules are held together by van der Waals forces.

* J. E. Lennard-Jones and B. M. Dent, *Trans. Faraday Soc.* 24, 92 (1928).

† F. London, *Zeit. f. phys. Chem. loc. cit.*

‡ The continuous curves are obtained from the equation of state, hitherto unpublished, assuming a law of force $\lambda_{(rep)} R^{-13} - \lambda_{(att)} R^{-7}$. The dotted curve for helium is obtained by Slater and Kirkwood from its electronic structure.

§ O. Oldenburg, *Zeit. f. Phys.* 55, 1 (1929).   ‖ H. Kuhn, *Naturwissen.* 18, 332 (1930).

§ 8 HOMOPOLAR COHESION*

In an earlier paragraph we have seen that when there are several electrons in an atom, its configuration may in an approximate theory be specified by a number of wave functions $u_1, u_2 \ldots u_N$, each a function of the four coordinates of an electron, and that the probability of a specified configuration of the electrons is given by a certain determinant of N rows and columns. The importance of the new form for the probability function becomes evident when calculations are made of the *energy* of electronic systems. The average value of the electrostatic energy of the electrons can be calculated only when we know the probability that any pair of electrons will be at a specified distance apart. A detailed calculation of the energy of an atom or the interaction energy of two atoms depends then very closely on the probability function $\Psi\bar{\Psi}$.

The probability of finding two electrons in specified places $d\tau_1$ and $d\tau_2$, independently of the position of the other electrons, is obtained by integrating the probability function over the coordinates of all the electrons except two. The result proves to be

$$\{\rho\,(1,\,1)\,\rho\,(2,\,2) - \rho\,(1,\,2)\,\rho\,(2,\,1)\}\,d\tau_1\,d\tau_2,$$

with the definitions of $\rho\,(1,\,2)$, etc., given in § 3. The mutual potential of two electrons consists then of two terms; the first is the average of $(e^2/r_{12})\,\rho\,(1,\,1)\,\rho\,(2,\,2)$ integrated over the whole of space of electrons 1 and 2; the second is the average of $(e^2/r)\,\rho\,(1,\,2)\,\rho\,(2,\,1)$. Apart from certain terms of these expressions which cancel, the first represents the Coulomb interaction of the individual distributions of electric charge $u_1\,\bar{u}_1$, $u_2\,\bar{u}_2$, etc. This may be called the *Coulomb energy*. It is the mutual electrostatic potential energy of the superimposed patterns which go to make up atoms, as described in § 4.

The second term in the above expression is new. It is difficult to describe its physical nature. All that can be said of it is that it is the natural outcome of the introduction of two new physical concepts into the mathematical scheme, viz., the principle of the identity of electrons, and the exclusion principle of Pauli. It is sometimes described as the " exchange " term and the term in the energy expression arising from it as the *" exchange " energy*.

The " exchange " energy depends on the spin of the electrons, while the Coulomb energy does not. It is this property of the exchange term which has made it of so much importance in the theory of atoms and molecules. In a two-electron system, as in an excited helium atom, for instance, the electrons may have the same or opposite spins, and, owing to the exchange term, the energies of the states with the same spins are lower in every case than those of the corresponding states with opposite spin. The hydrogen molecule is another two-electron system, and here the energy is lowest when the electrons have opposite spin. This appears to

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* The account of homopolar forces given here is necessarily brief. A fuller account has been given recently by the author in a lecture to the London Mathematical Society on " The Quantum Mechanics of Atoms and Molecules." This is to be published in the *Journal of the London Mathematical Society* shortly.

be the case in the interaction of most atoms. For certain interatomic distances the energy is lowest, and, therefore, the cohesion greatest, when the electrons of one atom are "paired" with those of the other atom. The energy of two interacting nitrogen atoms is highest when the spins of the three outer electrons of the atoms are all of them the same, and lowest when the three electrons of one atom are paired with those of the other. This latter condition corresponds to the normal nitrogen molecule, held together—as the chemist describes it—with a triple bond.

The pairing of electrons is thus brought into close connexion with the valency rules of the chemist, and chemical homopolar forces are elucidated to this extent— that they are seen to be a consequence of the same mathematical and physical principles which have been formulated for other branches of physics. This result may conceivably come to be regarded as one of the greatest achievements of the present formulation of quantum mechanics.

The nature of these forces may be described in a simpler but less accurate way by an appeal to Pauli's exclusion principle. For one electron in the field of two nuclei, there is a set of patterns with different energies just as there is for an electron in the field of one nucleus. One electron in the presence of two hydrogen nuclei will take up the pattern of lowest energy. If a second electron is added to the system, it also can take up the same pattern provided that it has a spin, which is opposite from the first one. The two electrons now exist in the same *molecular* pattern and are paired. Provided the energy of the pattern, which depends on the internuclear distance, has a minimum, a stable molecule will be formed.

If, however, two helium atoms are brought together the electrons are paired already. When the nuclei are pushed together, two of the electrons must be "promoted" to a higher energy level if the exclusion principle is to be preserved. The act of promotion requires energy and this appears as repulsion. A similar argument may be used for other closed electron groups, which are brought into contact.

The more accurate method described above also shows that closed electron groups, like those of the inert gases, repel each other. The exchange term in this case becomes predominant and leads to an increase of energy as the two systems are brought near together. *Intrinsic repulsive* fields may be attributed to this new exchange term, which quantum mechanics has produced.

The exchange term is more important than the Coulomb term in the interaction of two hydrogen atoms, but the Coulomb term becomes relatively more and more important in the interaction of larger atoms. This is due not only to the increased spread of the atoms, but also to the form of the patterns which the outer electrons have to assume. The effect is found even in the interaction of two lithium atoms*. When the Coulomb part is important, the pictures of atoms given in an earlier paragraph are useful in constructing models of molecules and helpful in understanding their various shapes. We have, for instance, seen that an atom of fluorine, or indeed any halogen gas, has a "hole" in it. It follows that the nucleus is less screened in

* M. Delbrück, *Ann. d. Phys.* 5, 36 (1930).

some directions than others. If the hole in the F atom is like the (2, 1, 0) pattern, the atom is roughly like a spherical ball of electric charge with a double conical hole scooped out of it. It is then not difficult to understand why a hydrogen atom can combine with it to give a HF molecule. The hydrogen's electron cloud sinks as far as possible into the hole of the fluorine, for in this position it gets as near as possible to the fluorine nucleus. Of course, it must be stressed that this only provides a rough picture. In an accurate treatment, the wave function of the whole system must be considered.

§9. IONIC COHESION

The conception of a halogen atom as an inert gas atom with a hole in it is useful in many ways. It has an affinity for another electron, and when one has been secured the electron cloud becomes spherically symmetrical. Ionic salts, like NaCl, may be pictured as arrays of spherical distributions, each on the whole charged, either positively or negatively, and so held together by electrostatic forces. This brings us to the question of determining a criterion between homopolar cohesion and ionic cohesion. When are we to suppose that atoms become ionized in the process of binding? The criterion is one of energy. Suppose that in figure 4 the curve
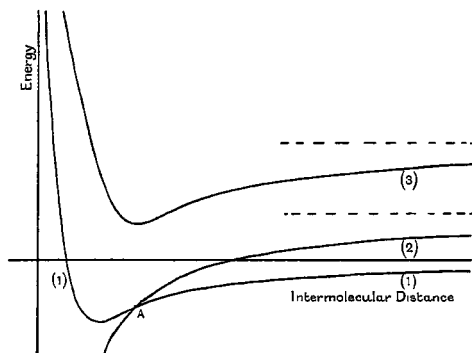

Fig. 4. Potential energy curves of atoms and ions.

(1) refers to the energy of two neutral atoms at various distances apart and that curve (2) refers to that of the corresponding ions. The difference between the energies (1) and (2) at infinite distance is equal to the difference of the ionization potential of one atom (say an alkali) and the electron affinity of the other (say a halogen). The curve (2) is then represented by $(a - b/R)$ because of the electrostatic attraction.

At the point of intersection A of the curves, the work put into the system at infinity has been recovered, and at interatomic distances less than this the ionic form has the less energy. If, however, the energy required for ionization is large, the interaction is of the type (3). Then the ions have to be brought to very close

distances before the ionic form has less energy than the atomic, but the close distances are not possible because of the intrinsic repulsion or the Pauli principle referred to in the preceding paragraph.

Table 2* shows how this condition is fulfilled in the case of some typical ionic compounds. The distance R refers to the value of the abscissa where the ionic curve cuts the axis; this is approximately the same as the place where it cuts the curve (1) when R is large.

Table 2.

	Ionization potential + electron affinity (volts)	(Å.u.)
KF	0·24	60
KCl	0·50	29
KBr	0·84	17
KI	1·23	11·8

It is likely that the terms *ionic* and *homopolar* refer to extreme cases, convenient for classification, but rarely existing in practice, actual cohesion being neither the one nor the other but partaking of both. The wave function of a perturbed system must be expressed in terms of all the wave functions of the unperturbed system and if there are two such wave functions of nearly the same energy, the wave function of the molecule is a linear function of both.

§ 10. METALLIC COHESION

From the point of view of wave mechanics, a metal must be regarded as an enormous molecule, with an enormous number of energy levels and electron patterns. The problem is to explain why a collection of atoms in the form of a metal has less energy than the isolated atoms of which it is composed. Is the cohesion due to ordinary electrostatic forces or to the exchange phenomenon or both? The problem has been considered recently in a qualitative way by J. C. Slater[†], who has shown that it is likely that atoms of one spin are surrounded by others of opposite spin[‡]. In those metals, which are of the body-centred-cubic type of structure, each atom is at the centre of eight others of opposite electron spin.

In the bringing of the atoms together in this way the patterns of the individual atoms have been made to overlap. An electron which formerly belonged to one nucleus is now brought under the influence of several. This has the effect of increasing the electrostatic attraction, and even in the absence of any other cohesive force the metal would hold together. The metal is like a sea of electric fluid, in which the nuclei float like buoys.

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* This method of illustration is due to F. London, *Zeit. f. Phys.* 46, 475 (1928).

† J. C. Slater, *Phys. Rev.* 35, 509 (1930).

‡ This is not true, of course, for the ferromagnetic bodies.

Now we inquire how the exchange phenomenon affects the cohesion. It is not difficult to show that the state of a crystal, in which all the electron spins are perfectly paired, combines only with the states in which two of the spins are interchanged. Thus, to use a linear example, the electron spins being denoted by α and β, the state $\alpha\beta\ \alpha\beta\ \alpha\beta\ldots$ combines only with $\alpha\beta\ \beta\alpha\ \alpha\beta\ldots$ and similar arrays. In the body-centred-cubic lattice the effect of such an interchange is to surround two electrons with seven neighbours of the same spin. The resulting structure has then considerably higher energy, because the contiguity of like spins causes a repulsion. It is thus highly improbable. The electron seems to know what will be the result of an interchange and decides that it simply is not done—or at any rate only with moderation. The net result is that the exchange effect is not as important in metals as it is in diatomic molecules, whereas the electrostatic attraction is relatively more important. An accurate quantitative treatment of the problem is, however, still required.

There are some metals, such as zinc and cadmium, in which the exchange term probably makes little or no contribution to the cohesion. The atoms of which they are composed have paired electron spins even when widely separated, and may be expected on that account to repel like inert-gas atoms when brought into contact. The fact that the metals are diamagnetic is further evidence that the metals consist of perfectly paired electron spins and are formed from normal unexcited atoms. Now the diatomic molecules Zn_2, Cd_2, are known to exist and the order of magnitude of their heats of dissociation, which is known from molecular spectra, suggests that these molecules are held together by van der Waals fields. The cohesion of the corresponding metals is several times greater, but this is probably due to the larger number of immediate neighbours and the additive property of van der Waals fields. Thus it seems likely that van der Waals fields make a greater contribution to the cohesion of some metals than has yet been realized.

Metallic cohesion cannot therefore be classified in any simple way. It is probably due partly to the electrostatic interaction of space-charge distributions, partly to the exchange phenomenon, and partly to van der Waals fields. The relative extents to which these various factors contribute to the cohesion of a metal must vary from case to case and is still a matter for investigation.

§ 11. CONCLUSION

In conclusion we may summarize the contributions of the new quantum mechanics to this branch of physics under four headings:

(1) It has provided density pictures of atoms which have permitted the evaluation of the electrostatic interaction of atoms in a way quite impossible in an orbital theory.

(2) It has led to the introduction of a new concept—an exchange force, which is responsible for the homopolar bonds of the chemist.

(3) It has provided pictures of asymmetrical atoms like the halogens and thrown light on the nature of electron affinity. This affinity is responsible for ionic structures of the NaCl type.

(4) It has provided an explanation of van der Waals fields, which formerly were not understood.

The general principles seem to be established. What is now required is a mathematical technique capable of applying them to particular cases.