static attraction between oppositely charged groups in neighbouring molecules is an important factor in the strength of the gluten network.

The upward bend of the reloading curve up to the point where flow (i.e. the rupture of further links) occurs is probably mainly due to the irregularity of assembly of the elastic members, but may also indicate that individual chains are approaching the limit to which they can be extended.

Evidence has been obtained that the starch paste penetrating the gluten network has a "yield value", in consequence of which there is elastic hysteresis even when the cycle is carried out slowly enough to avoid elastic after-effect.

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The Quantum Theory of Atomic Polarization
I—Polarization by a Uniform Field

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1—Introduction

Two problems of atomic energy, the energy of polarization of an atom in a plane electrostatic field and the energy of interaction, or van der Waals energy, of two distant atoms, are particularly suited to attack by approximate methods. In each, the disturbing field, whether that of the static field or of the distant atom, is small in comparison with the internal fields acting on the electrons of the atomic system, and so the standard methods by which quantum mechanics deal with small disturbances, namely the perturbation and variation methods, can be and have been successfully applied to these problems. Though the perturbation method, strictly applied, is the more accurate, since it takes into account the possible excited states of the system, its usefulness is restricted to atoms of simple structure, and having relatively simple wave functions. Generally speaking the variation methods, which require a knowledge of the unperturbed state of the system only, are more suitable for larger atoms; ignorance of the excited states is largely compensated for by expressing the perturbed wave functions in terms of parameters, which are then chosen to make the total energy a minimum.

As one would expect, the atoms of hydrogen and helium have been studied most fully, the perturbation theory being used by Wang, Eisenschitz and London, and Lennard-Jones, and variation methods by Atanasoff, Hassé, Slater and Kirkwood, Pauling and Beach.† Owing to the first order Stark effect, the calculated polarizability of the hydrogen atom cannot be compared with experiment, but the calculated value for helium agrees well in most cases with that observed. The van der Waals energy of two hydrogen atoms given by Pauling and Beach includes accurate values not only of the usual dipole-dipole term, which varies as $1/R^6$, but also of the dipole-quadripole and quadripole-quadripole terms, varying as $1/R^8$, $1/R^{10}$ respectively.

The most accurate calculation of the dipole-dipole term for two helium atoms is probably that of Hassé (1930, 1931), and the higher order terms have been estimated by Margenau (1931).

The treatment of larger atoms has been largely devoted to obtaining a relation between the dipole-dipole constant c (the van der Waals energy being $-c/R^6$) and the polarizability α. It was started by London (1930), who deduced that for two similar atoms

$$c = (\text{const.})\, I\alpha^2,$$

where I is the ionization potential. The use of the variation method by Slater and Kirkwood (1931) suggested that

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

where N is the number of electrons in the outer shell, and though their work was restricted mainly to hydrogenic wave functions and functions without nodes, the method was later modified by Kirkwood (1932) to include any type of wave function. A different line of approach was followed by Vinti (1932), who used the Kuhn-Reiche sum rule to simplify the second order terms of the perturbation theory (the first order terms vanish in these problems), showing at the same time that the assumptions made were

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† For the treatment of H: Wang (1927); Eisenschitz and London (1930); Lennard-Jones (1930*a*); Pauling and Beach (1935). For H and He: Hassé (1930, 1931); Slater and Kirkwood (1931). For He: Atanasoff (1930).

implied also in Kirkwood's variation method. Using the same idea, Hellmann (1935) was able to extend the results of Vinti and Kirkwood, by treating the electrons of each atom not as a single group but as a number of shells, which in the variation method corresponds to the use of several parameters instead of one, and by including the Pauli Principle.

In this paper, Kirkwood's variation method is used throughout, with one or more parameters and with inclusion of electron exchange, and formulae derived for the polarizability of atoms with any number of electrons. The results are somewhat more general than those of Hellmann. Calculations are then made with the available wave functions of the rare gas atoms and alkali ions, and the results compared with experiment as far as possible. In a second paper, the van der Waals energy of atoms will be considered.

2—ENERGY OF PERTURBATION

We shall begin by deriving an expression for the increase in energy of an atom containing N electrons when subject to a small perturbing field. We shall assume that the electronic system is in a non-degenerate state which can be adequately represented by a wave function involving the space and spin co-ordinates of the electrons only. Thus if the unperturbed wave function is Ψ, and its complex conjugate is Ψ^*, the energy of the system is given by

$$E = \int \Psi^* H \Psi \, d\tau \Big/ \int \Psi^* \Psi \, d\tau, \qquad (2\cdot1)$$

where $$H = \sum_{p=1}^{N} \{-\tfrac{1}{2}\nabla_p^2 + V_p\},$$

V_p being the potential energy of the pth electron, expressed as a function of the space co-ordinates of the pth electron only, and ∇_p^2 the Laplacian operator for the same electron. The integration is carried out over the coordinate space of every electron.

When an external field is applied to the system, let us suppose V_p to be increased by a small amount v_p to $V_p + v_p$. H is therefore increased to $H + v$, where $v = \Sigma v_p$, and at the same time the function Ψ is changed to $\Psi + \Phi$, where $\Phi^*\Phi$ is of the order of magnitude of v^2. The energy of the perturbed state is then

$$E + \bar{h} = \frac{\int (\Psi^* + \Phi^*)(H + v)(\Psi + \Phi)\, d\tau}{\int (\Psi^* + \Phi^*)(\Psi + \Phi)\, d\tau}, \qquad (2\cdot2)$$

$\bar{h}$ being the energy of perturbation we wish to evaluate. Now in the problems to be discussed later, v and $\Psi^*\Phi$ are odd functions† of the electron co-ordinates, and a number of integrals in (2·2) vanish, including

$$\int \Psi^* v \Psi \, d\tau, \quad \int \Phi^* v \Phi \, d\tau, \quad \int \Psi^* \Phi \, d\tau, \quad \int \Phi^* \Psi \, d\tau.$$

Hence

$$E + \bar{h} = \frac{1}{a+b}\left[\int (\Psi^*\Phi + \Phi^*\Psi)\, v \, d\tau + \int (\Psi^* + \Phi^*)\, H(\Psi + \Phi)\, d\tau\right], \tag{2·3}$$

where

$$a = \int \Psi^*\Psi \, d\tau, \quad b = \int \Phi^*\Phi \, d\tau.$$

By transforming the integral containing ∇_p^2 by Green's Theorem, so that the surface integral vanishes over the infinite boundary, and by neglecting terms in v^4 and higher powers of v, and also terms of the form

$$a\int \Phi^* V_p \Phi \, d\tau - b\int \Psi^* V_p \Psi \, d\tau, \tag{2·4}$$

we find that

$$\bar{h} = \frac{1}{a}\int (\Psi^*\Phi + \Phi^*\Psi)\, v \, d\tau$$
$$+ \frac{1}{2a}\sum_p \left[\int \operatorname{grad}_p \Phi^* . \operatorname{grad}_p \Phi \, d\tau - \frac{b}{a}\int \operatorname{grad}_p \Psi^* . \operatorname{grad}_p \Psi \, d\tau\right]. \tag{2·5}$$

The expression for $\bar{h}$ given by Kirkwood and Hellmann is slightly different from (2·5), but follows immediately from it when Φ is replaced by Ψu, provided that we can neglect terms of the type

$$\int \operatorname{grad}_p \Psi^* . \operatorname{grad}_p u^2 \Psi \, d\tau - \frac{1}{a}\int \Psi^* u^2 \Psi \, d\tau \int \operatorname{grad}_p \Psi^* . \operatorname{grad}_p \Psi \, d\tau. \tag{2·6}$$

We then obtain

$$\bar{h} = \frac{1}{a}\int \Psi^* \{2uv + \tfrac{1}{2}\sum_p (\operatorname{grad}_p u^2)\}\, \Psi \, d\tau. \tag{2·7}$$

Both (2·5) and (2·7) will be used in the applications which follow, and we shall assume that the terms of which (2·4) and (2·6) are typical are small‡ in comparison with other terms of the order of v^2.

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† The sign of the function is changed if the co-ordinates of any electron are reversed in sign.

‡ It can be shown that, when Ψ is real and satisfies the Schrödinger equation for the atom exactly, Kirkwood's result (2·7) holds without approximation. This suggests that when Φ cannot be written in the form Ψu, the neglect of the terms corresponding to (2·4) and (2·6) is in fact justified. It is intended to examine these terms in a later paper.

3—Polarization by a Uniform Field

The results of § 2 will first be applied to the increase in energy of an atom in a uniform plane electrostatic field. Let us assume that the wave function of the atom when the electrostatic field is absent, is the determinant

$$\Psi = \begin{vmatrix} \psi_{\alpha 1}\,\psi_{\alpha 2} & \cdots\cdots & \psi_{\alpha N} \\ \psi_{\beta 1}\,\psi_{\beta 2} & \cdots\cdots & \psi_{\beta N} \\ \vdots & & \\ \psi_{\nu 1}\,\psi_{\nu 2} & \cdots\cdots & \psi_{NN} \end{vmatrix}, \tag{3·1}$$

where $\psi_{\alpha p}, \psi_{\beta p}, \ldots, \psi_{\nu p}$ are the wave functions of the occupied electronic states of the atom, the Greek suffix being an abbreviation for the four quantum numbers n, l, m, s, of the state, and the italic suffix indicating the electron whose co-ordinates are inserted. The ψ's are assumed to include the spin function as a factor, to be orthogonal and each to be normalized to unity. If Ψ^* is the conjugate complex of Ψ then

$$a = \int \Psi^* \Psi \, d\tau = N!$$

if the integration is carried out over the co-ordinate space of every electron. Ψ also satisfies the Pauli Exclusion Principle and permits any pair of electrons to exchange places freely.

When the atom is subjected to an external field the ψ's are changed. It is convenient to express the perturbed function corresponding to $\psi_{\rho p}$ which contains the co-ordinates of the pth electron, in the form

$$\psi_{\rho p}\,(1 + f(r_p)\,v_p)$$

where v_p is the increase in the potential energy of the pth electron and $f(r_p)$ is a polynomial function of its radial co-ordinate. As a first approximation we shall take $f(r_p) = \lambda$, a constant for all values of ρ and p. The perturbed wave function of the whole atom is then obtained by replacing $\psi_{\rho p}$ in the determinant Ψ by $\psi_{\rho p}(1 + \lambda v_p)$ and therefore, if only linear terms in v_p are retained, it is

$$\Psi(1 + \lambda v),$$

where $v = \Sigma v_p$. This function is likewise antisymmetrical in the electron co-ordinates, and so satisfies the Pauli Principle.

The energy of perturbation is now given by (2·7); inserting $a = N!$, $u = \lambda v$, we have

$$\bar{h} = \frac{1}{N!} \int \Psi^* \{2\lambda v^2 + \tfrac{1}{2}\lambda^2 \sum_p (\mathrm{grad}_p v)^2\} \, \Psi \, d\tau. \tag{3·2}$$

Let $\mathbf{r}_p$ be the position vector of the pth electron, and $\mathbf{F}$ a constant vector representing the electrostatic field. Then in atomic units, the field perturbing the pth electron is $v_p = -\mathbf{F}.\mathbf{r}_p$ and so

$$v = -\sum_{p=1}^{N} (\mathbf{F}.\mathbf{r}_p). \tag{3·3}$$

With this expression for v, (3·2) can easily be reduced to a sum of simple integrals involving one electron wave functions only. As this part of the process is long it is omitted here, though further details of this and similar reductions which arise later will be found in an appendix. We find that, after averaging for all orientations of the atom relative to the direction of the external field,

$$\bar{h} = F^2(\tfrac{2}{3}\lambda \bar{R}^2 + \tfrac{1}{2}N\lambda^2), \tag{3·4}$$

where $$\bar{R}^2 = \sum_{\rho} (R^2)_\rho$$

and $$(R^2)_\rho = (r^2)_{\rho\rho} - \sum_{\sigma \neq \rho} \{(x)_{\sigma\rho}(x)_{\rho\sigma} + (y)_{\sigma\rho}(y)_{\rho\sigma} + (z)_{\sigma\rho}(z)_{\rho\sigma}\}.$$

The quantity $(r^2)_{\rho\rho}$ is the average value of r^2 with respect to the charge density $\psi_\rho^* \psi_\rho$, i.e.

$$(r^2)_{\rho\rho} = \int \psi_\rho^* r^2 \psi_\rho \, d\tau.$$

It is independent of the electron considered and so the electronic suffix is omitted. The other terms in $(R^2)_\rho$ are exchange integrals, of which

$$(x)_{\sigma\rho} = \int \psi_\sigma^* x \psi_\rho \, d\tau,$$

is typical. These integrals are discussed in detail in § 3*a*.

We see that expression (3·4) for $\bar{h}$ contains the unknown parameter λ, which must be chosen to make the energy a minimum. Accordingly we introduce the condition $d\bar{h}/d\lambda = 0$ which gives $\lambda = -2\bar{R}^2/3N$ and

$$\bar{h}_{\text{min.}} = -\frac{2}{9}\frac{F^2}{N}(\bar{R}^2)^2.$$

The quantity of practical importance is the atomic polarizability α defined by $\bar{h}_{\text{min.}} = -\frac{1}{2}\alpha F^2$ and therefore given by

$$\alpha = \frac{4}{9N}(\bar{R}^2)^2 \tag{3·5}$$

in atomic units.

In deriving (3·5) it was assumed that each wave function $\psi_{\rho p}$ is perturbed in the same degree, determined by the parameter λ. This is unlikely to be accurate, if only because electrons in the inner shells are shielded by those in the outer from a perturbing field acting from without, and so we will consider the effect of using a different parameter for each electronic wave function. Thus let us now assume the perturbed form of $\psi_{\rho p}$ to be $\psi_{\rho p}(1+\lambda_\rho v_p)$ where λ_ρ is a different constant for each state ρ from α to ν. The perturbed wave function of the atom, obtained by replacing $\psi_{\rho p}$ in Ψ (3·1) by $\Psi_{\rho p}(1+\lambda_\rho v_p)$ now becomes, when only linear terms in v_p are retained,

$$\Psi+\Phi,$$

where $\Phi=\sum_\rho \lambda_p \sum_\rho \psi_{\rho p} D_{\rho p} v_p$, $D_{\rho p}$ being the first minor of $\psi_{\rho p}$ in the determinant Ψ. Φ is no longer a simple multiple of Ψ, and so equation (2·5) for the energy of perturbation must be used instead of (2·7). However, this does not affect the accuracy of the final result, as in the course of reduction to simple integrals we neglect certain terms comparable with (2·6). After averaging for all orientations of the atom as before, we obtain in place of (3·4)

$$\bar{h} = F^2 \sum_\rho \{\tfrac{2}{3}\lambda_\rho (R^2)_\rho + \tfrac{1}{2}\lambda_\rho^2\}, \tag{3·6}$$

and when the parameters are chosen to make $\bar{h}$ a minimum,

$$\bar{h}_{\text{min.}} = -\tfrac{2}{9}F^2 \sum_\rho (R^2)_\rho^2,$$

and

$$\alpha = \tfrac{4}{9}\sum_\rho (R^2)_\rho^2, \tag{3·7}$$

where the summation for ρ includes all the occupied electronic states.†

As a further refinement we shall take the perturbed form of $\psi_{\rho p}$ to be‡

$$\psi_{\rho p}\{1+\lambda_\rho v_p(1+\mu_\rho r_p)\},$$

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† By applying the Kuhn-Reiche sum rule to the second order terms of the perturbation theory, Hellmann (1935) obtains the following expressions for α:

$$\alpha = 4\sum_i (z^2)_{ii}\{(z^2)_{ii} - \sum_{k\neq i} |(z)_{ik}|^2\}.$$

Different orientations of the atom relative to the external field are not considered. When written in the same way (3·7) becomes

$$\alpha = 4\sum_i \{(z^2)_{ii} - \sum_{k\neq i} |(z)_{ik}|^2\}^2.$$

It is not clear why the two results should differ.

‡ In dealing with He, Hassé (1930) showed that for the introduction of the linear term of the polynomial $f(r_p)$ improved the calculated value of the polarizability considerably. The higher powers of r_p were found to have a negligible effect.

where μ_ρ, like λ_ρ, is a different constant for each wave function. The analysis is scarcely affected and yields the result

$$\bar{h} = F^2 \sum_\rho [\tfrac{2}{3}\lambda_\rho\{(R^2)_\rho + \mu_\rho (R^3)_\rho\} + \tfrac{1}{2}\lambda_\rho^2\{1 + \tfrac{8}{3}\mu_\rho (r)_{\rho\rho} + 2\mu_\rho^2 (r^2)_{\rho\rho}\}], \tag{3·8}$$

where $$(R^3)_\rho = (r^3)_{\rho\rho} - \sum_{\sigma \neq \rho} \{(rx)_{\sigma\rho}(x)_{\rho\sigma} + (ry)_{\sigma\rho}(y)_{\rho\sigma} + (rz)_{\sigma\rho}(z)_{\rho\sigma}\}$$

and $(R^2)_\rho$ is the same as in (3·4). The minimum value of $\bar{h}$ gives for the polarizability

$$\alpha = \frac{4}{9}\sum_\rho (R^2)_\rho^2 (1 + \Delta_\rho), \tag{3·9}$$

$$1 + \Delta_\rho = \frac{1 + \dfrac{(R^3)_\rho^2}{2(r^2)_{\rho\rho}(R^2)_\rho^2} - \dfrac{4}{3}\dfrac{(r)_{\rho\rho}(R^3)_\rho}{(r^2)_{\rho\rho}(R^2)_\rho}}{1 - \dfrac{8}{9}\dfrac{(r)_{\rho\rho}^2}{(r^2)_{\rho\rho}}}. \tag{3·10}$$

The quantity Δ_ρ, which may be regarded as a correction to the much simpler formula (3·7), is shown in § 4*b* to be important for the lighter atoms.

3*a*—*Evaluation of Integrals*

The functions $(R^2)_\rho$ and $(R^3)_\rho$ which occur in formulae (3·5), (3·7) and (3·10) for the atomic polarizability can easily be evaluated once the electronic wave functions are known. We have defined

$$(R^2)_\rho = (r^2)_{\rho\rho} - \sum_{\rho' \neq \rho} \{(x)_{\rho'\rho}(x)_{\rho\rho'} + (y)_{\rho'\rho}(y)_{\rho\rho'} + (z)_{\rho'\rho}(z)_{\rho\rho'}\},$$

in which ρ, ρ' are written shortly for the quantum numbers n, l, m, s, and n', l', m', s', respectively and

$$(r^2)_{\rho\rho} = \int \psi_\rho^* r^2 \psi_\rho \, d\tau, \quad (x)_{\rho\rho'} = \int \Psi_\rho^* x \psi_{\rho'} \, d\tau, \text{ etc.}$$

ψ_ρ is usually expressed in spherical polar co-ordinates in the form $(2\pi)^{-\frac{1}{2}} R(nl \mid r) P_l^{|m|}(\cos\theta) e^{im\phi} \times$ spin function, where $R(nl \mid r)$ is the radial wave function, normalized to unity, and $P_l^{|m|}(\cos\theta)$ the associated Legendre function. The angular and spin factors of $(r^2)_{\rho\rho}$, $(x)_{\rho\rho'}$, $(y)_{\rho\rho'}$ and $(z)_{\rho\rho'}$ can be integrated at once, and incidentally $(z)_{\rho\rho'}$ vanishes unless the quantum numbers of ψ_ρ and $\psi_{\rho'}$ satisfy

$$|l' - l| = 1, \quad m' = m, \quad s' = s;$$

likewise $(x)_{\rho\rho'}$, $(y)_{\rho\rho'}$ vanish unless

$$|l' - l| = 1, \quad |m' - m| = 1, \quad s' = s.$$

The integration for r introduces integrals of the types

$$(r^2)_{nl,\,nl} = \int_0^\infty r^2[P(nl\,|\,r)]^2\,dr, \quad (r)_{nl,\,n'l'} = \int_0^\infty rP(nl\,|\,r)\,P(n'l'\,|\,r)\,dr,$$

where $P(nl\,|\,r) = r\,.\,R(nl\,|\,r)$ and we find eventually that for an atom containing complete $(n,\,l)$ subgroups,

$$(R^2)_{nlms} = (r^2)_{nl,\,nl} - \frac{1}{2(2l+1)}\sigma_{nl}, \tag{3·11}$$

where σ_{nl} is a function whose form depends upon the azimuthal quantum number l, but is independent of the magnetic and spin quantum numbers. Thus, for an atom containing complete s, p, d and f shells:

$$\left.\begin{aligned}\sigma_{n0} &= 2\sum_{n'}(r)^2_{n'1,\,n0},\\ \sigma_{n1} &= 2\sum_{n'}\{(r)^2_{n'0,\,n1} + 2(r)^2_{n'2,\,n1}\},\\ \sigma_{n2} &= 2\sum_{n'}\{2(r)^2_{n'1,\,n2} + 3(r)^2_{n'3,\,n2}\},\\ \sigma_{n3} &= 6\sum_{n'}(r)^2_{n'2,\,n3}.\end{aligned}\right\} \tag{3·12}$$

The range of n' in these sums depends upon the value of l' (either 0, 1, 2, or 3) associated with n', but it includes every occupied subgroup having the quantum numbers n', l'.

The terms $(R^3)_\rho$ are treated similarly, and we find

$$(R^3)_{nlms} = (r^3)_{nl,\,nl} - \frac{1}{2(2l+1)}\tau_{nl}, \tag{3·13}$$

where τ_{nl} is simply related to σ_{nl}, as it is only necessary to replace $(r)^2_{n'l',\,nl}$ where it occurs in σ_{nl} by the product $(r^2)_{n'l',\,nl}(r)_{n'l',\,nl}$. For example

$$\tau_{n1} = 2\sum_{n'}\{(r^2)_{n'0,\,n1}(r)_{n'0,\,n1} + 2(r^2)_{n'2,\,n1}(r)_{n'2,\,n1}\}.$$

When the atom contains incomplete subgroups, it is necessary first to consider whether the electronic configuration is degenerate and, if so, whether the previous argument needs to be modified. However, if an s shell is incomplete, as in the alkali atoms, no modification is required other than that the contribution of that shell to the σ and τ terms, as defined by (3·12), shall be halved.

The self-consistent atomic fields calculated by Hartree and others provide suitable functions $P(nl\,|\,r)$ from which to evaluate $(r^2)_{nl,\,nl}$, $(r)_{n'l',\,nl}$ etc., by numerical integration, and we can therefore calculate the polarizability of any atom or ion for which the self-consistent field is known, provided proper care is taken when there is an incomplete subgroup. It is true that the Hartree functions for the same l but different n are not exactly orthogonal, but the error is found to be too small to make it necessary to derive an orthogonal set. A more important disadvantage is that they neglect electron exchange entirely, and although the self-consistent field equations have been modified by Fock to include exchange, Fock wave functions have as yet been calculated for very few atoms. A comparison of Hartree and Fock functions is made below.

3*b*—*Numerical Results and Discussion*

In § 3, three different expressions for the polarizability of an atom were obtained by progressive application of the variation method. We shall now discuss the following points which arise in comparing the polarizabilities calculated from these formulae with each other and with experimental values: the effect of exchange on the calculated polarizabilities; the effect of introducing exchange in the electronic wave functions; the effect of the more accurate variation function leading to (3·9); and Kirkwood's relation between polarizability and magnetic susceptibility. These points will be illustrated with the help of available wave functions for atoms and ions with complete subgroups.

It was shown above that the functions $(R^2)_\rho$ occurring in (3·5) and (3·7) depend only on the quantum numbers n and l and hence the summation within each (n, l) subgroup can be carried out at once. If this is done and (3·11) substituted for $(R^2)_\rho$, then (3·5) and (3·7) rewritten in c.g.s. units are respectively

$$\alpha = \frac{4a_0^3}{9N}\Big[\sum_{nl}\{\nu_l(r^2)_{nl,\,nl}-\sigma_{nl}\}\Big]^2, \qquad \mathrm{I}$$

$$\alpha = \frac{4a_0^3}{9}\sum_{nl}\frac{1}{\nu_l}\{\nu_l(r^2)_{nl,\,nl}-\sigma_{nl}\}^2, \qquad \mathrm{II}$$

where a_0 is the radius of the first Bohr orbit in the hydrogen atom ($4a_0^3/9 = 0{\cdot}654\times10^{-25}$ cm.^{3}); the terms $(r^2)_{nl,\,nl}$ and σ_{nl} are still expressed in atomic units. The summations are for all occupied subgroups, and

$$\nu_l = 2(2l+1).$$

Of these results, *I* was derived from one parameter only, and should be compared with that found by Kirkwood, using for the atomic wave function the simple product

$$\Psi = \psi_{\alpha 1}\psi_{\beta 2}\cdots\psi_{\nu N},$$

which takes no account of electron exchange; likewise with II we may compare the result obtained by Hellmann, also neglecting exchange but using a different parameter for each subgroup of electrons. The formulae of Kirkwood and Hellmann, which we will denote by I A, II A respectively, are

$$\alpha = \frac{4a_0^3}{9N}\{\sum_{nl} \nu_l (r^2)_{nl,\,nl}\}^2, \qquad \text{I A}$$

$$\alpha = \frac{4a_0^3}{9}\sum_{nl} \nu_l (r^2)^2_{nl,\,nl}, \qquad \text{II A}$$

in the same units and notation. It will be seen that the only difference is in the absence of the terms σ_{nl}.

These four expressions for α exemplify two general principles; first, that the inclusion of electron exchange, which is similar to the removal of a constraint on the system, decreases the energy of perturbation and therefore the polarizability. Thus the values obtained from I and II are respectively less than those obtained from I A and II A, since σ_{nl} is always positive. Secondly, it is generally true in applications of the variation method with a given form for the perturbed wave function that, as more parameters are introduced, the calculated energy approaches the exact value as a lower limit. The energy of polarization being negative, we should expect the calculated polarizability to increase *in magnitude* as the number of parameters is increased; and, in fact, the values given by II and II A are respectively greater than those given by I and I A. To illustrate these remarks, the known Hartree† fields of Ne, A, Rb^+ and Cs^+ have been applied, as suggested in § 3*a*, to calculate values of α, which are shown in Table I.

TABLE I—CALCULATED ATOMIC POLARIZABILITIES: $\alpha \times 10^{24}$

Method			Ne	A	Rb^+	Cs^+
I	With exchange	One parameter	0·348	1·49	1·09	1·43
I A	Without exchange		0·774	3·38	2·54	4·32
II	With exchange	Parameter for each subgroup	0·517	4·09	4·35	8·44
II A	Without exchange		0·969	7·16	7·47	16·9

Table I shows that the inclusion of exchange terms in the formula for α may reduce the calculated value by as much as 50 %. Before making any comparison with experiment we must also consider the effect of exchange on the electron wave functions, as shown by the difference between Hartree

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† I am indebted to Dr J. McDougall for the use of unpublished wave functions for Ne. Other Hartree fields have been used as follows: A, a field calculated by J. McDougall and R. A. Buckingham; Cs^+ (and also K^+) from D. R. Hartree (1934); Rb^+, analytical wave functions derived from the Hartree function by J. C. Slater (1932).

and Fock functions. The few Fock functions which are known indicate the change to be expected; thus D. R. and W. Hartree (1935)† have already pointed out that in normal Be the term $(r^2)_{20,\,20}$ is about 12 % less, and in Na^+ $(r^2)_{21,\,21}$ is about 13 % less for the Fock field than for the Hartree field. In Cl^-, the decrease in $(r^2)_{31,\,31}$ is as much as 30 %. The effect of exchange on the σ_{nl} terms can be examined in Na^+, Cl^-, and it is found that these terms are practically the same for the Fock and Hartree fields. The corresponding values of $\alpha\,.\,10^{24}$ calculated from II are as follows:

	Hartree	Fock
Be	12·0	9·28
Na^+	0·183	0·134
Cl^-	16·2	6·9

The use of Fock functions thus leads to a further decrease in the calculated polarizabilities, and therefore to better agreement with experiment, since Hartree functions are found to give values which are too high. There is, however, one important exception to this general statement: the Hartree field for Na^+ gives $\alpha = 0{\cdot}183\times10^{-24}$, which is slightly larger than the $0{\cdot}17\times10^{-24}$ deduced by Mayer (1933) from spectroscopic data, but less than the $0{\cdot}245\times10^{-24}$ given by Heydweiller's (1925) measurements of the refractivities of alkali halides in solution. We are therefore led to consider the more accurate formula (3·9) which, when written in c.g.s. units, is

$$\alpha = \frac{4a_0^3}{9}\sum_{nl}\frac{1}{\nu_l}\{\nu_l(r^2)_{nl,\,nl}-\sigma_{nl}\}^2\,(1+\Delta_{nl}). \tag{III}$$

This represents the closest approximation to the actual atomic system which has been considered, as the assumed system satisfies the Pauli Principle and allows two independent parameters for each subgroup. The difficulty in applying it arises from the calculation of the Δ_{nl} terms for which accurate wave functions are necessary.

Nevertheless, the available functions indicate the relative importance of these terms in different atoms. In Table II are given the values of $1+\Delta_{nl}$, those in the first column being derived by numerical integration from self-consistent functions (Hartree functions, with the exception of Be and Na^+, for which Fock functions were used), and those in the second column from analytical functions (Slater 1930) of the type $r^{n^*-1}\exp(-n^*r/Z-S)$, in which n^* is an effective quantum number and S a screening constant. Since the inner groups of electrons make a very small contribution to α,

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† The Fock field for Na^+ was calculated by V. Fock and M. Petrashen (1934). I am indebted to Professor Hartree for information about the Fock field of Cl^- before it was published (Hartree, D. R. and W. 1936).

only the outer group in each atom has been considered, although a calculation for Na^+ shows that the contribution of an inner *S*-group may be doubled. The large discrepancy between the two values for the $2p$ group of neon may be understood by comparing the theoretical values of the magnetic susceptibility χ given by the same wave functions: thus the Slater function underestimates the extension of the $2p$ charge distribution from the nucleus and gives a susceptibility less than that observed, whereas the Hartree function does the opposite. Hence the proper value of $1+\Delta(2p)$ probably lies between those given. For Na^+, however, both the Slater and Fock functions† appear to underestimate χ, so that the correct value of $1+\Delta(2p)$ may be greater than 1·15. But the general conclusion is that the value of $1+\Delta_{nl}$ for an outer group differs appreciably from unity only for the lighter atoms such as He, Ne, and Na^+. Its effect is then to increase the calculated polarizability, and for Na^+ the agreement with experiment is thereby slightly improved.

TABLE II

		Self-consistent functions	Slater
He	$1+\Delta(1s)$	—	1·125
Be	$1+\Delta(2s)$	1·00	1·01
Ne	$1+\Delta(2p)$	1·40	1·03
A	$1+\Delta(3p)$	$1{\cdot}00_5$	1·00
Kr	$1+\Delta(4p)$	—	$1{\cdot}00_5$
Xe	$1+\Delta(5p)$	—	1·01
Na^+	$1+\Delta(2s)$	2·03	2·83
	$1+\Delta(2p)$	1·15	1·03
K^+	$1+\Delta(3p)$	1·03	1·00

It is perhaps worth mentioning an empirical method of estimating these correction terms. It was pointed out by Kirkwood that polarizability and magnetic susceptibility are related quantities and using his result for α (formula I A) he suggested the relation

$$-\chi = \frac{Le^2a_0^{\frac{1}{2}}}{4mc^2}\sqrt{N\alpha}.$$

Further developments by the variation method show that this is hardly justified, though as an empirical relation it is more successful than one would expect (Brindley 1933). However, we may make use of the result that the main part of α comes from an outer group of electrons, say ν_0 in

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† The Slater and Fock functions give $\chi = -4{\cdot}17,\ 5{\cdot}0\times10^{-6}$ respectively. The experimental value for ions in solution is about $-5{\cdot}7\times10^{-6}$, and for crystal ions about $-6{\cdot}1\times10^{-6}$.

number; then if $(r^2)_0$ and σ_0 are the values of $(r^2)_{nl,\,nl}$ and σ_{nl} for this group, its contribution to χ is

$$\chi_0 = -\frac{Le^2a_0^2}{6mc^2}\nu_0(r^2)_0. \tag{3·14}$$

By comparing (3·14) and III, we find that approximately

$$\left\{\frac{9\nu_0\alpha}{4a_0^3(1+\Delta_0')}\right\}^{\frac{1}{2}} + \sigma_0 = -\frac{6mc^2}{Le^2a_0^2}\chi_0. \tag{3·15}$$

Now suppose α and χ are known experimentally, and that χ_0 can be estimated from χ, as when the relative importance of the different electron groups is known from the self-consistent field. If in addition σ_0, which is usually much smaller than the other terms, is given its theoretical value, then the relation (3·15) can be applied to find $1+\Delta_0'$. The results in Table III have been derived in this way.

TABLE III†

	$\alpha \times 10^{24}$	$-\chi \times 10^6$	$-\chi_0 \times 10^6$	σ_0	$1+\Delta_0'$
Ne	0·392	6·75	5·37	1·79	1·43
Na^+	0·280	6·1	4·56	1·23	1·23
Cl^-	3·01	24·2	18·9	5·74	0·84
A	1·63	19·54	14·7	4·77	0·79
K^+	1·09	14·6	10·7	3·67	1·03
Kr	$2{\cdot}46_5$	28·0	17·4	6·5‡	0·95
Cs^+	2·72	35·1	19·3	8·37	0·96

† For the rare gases, the experimental values of α are taken from C. and M. Cuthbertson (1911) and of χ from Mann (1936). The data for the ions refer to ions in the crystalline state; the values of χ are those given by Brindley and Hoare (1935), and the values of α are derived from the refractivities of the alkali halide crystals, measured by Spangenberg (1923).

‡ The value of σ_0 for Kr is calculated from approximate self-consistent wave functions for the 4*s* and 4*p* electrons, kindly sent to me by Professor D. R. Hartree.

Direct comparison of the values of $1+\Delta_0'$ with the theoretical values $1+\Delta_0$ is hardly justified, since the error of approximation involved in (3·15) is not known. Further errors may be introduced by inaccuracy in the wave functions, affecting σ_0 and the ratio χ_0/χ, and in the experimental data, which for the ions are especially uncertain. But although the values in Table III must be accepted with caution, they do confirm the theoretical result that the Δ terms are important for the lighter atoms Ne and Na^+. It is, however, rather surprising that the Δ_0' value for argon should be so large and negative.

APPENDIX

Much of the integration required in § 3 is applicable to other problems, and so we shall give a separate account of the methods used, beginning with the integrals, such as those in (3·2), which contain the density function $\Psi^*\Psi$. This is replaced by the determinant A obtained by multiplication of the determinants Ψ^* and Ψ, defined by (3·1). A has the form

$$A = \begin{vmatrix} a_{11}\,a_{12} & \cdots\cdots & a_{1N} \\ a_{21}\,a_{22} & \cdots\cdots & a_{2N} \\ \vdots & & \\ a_{N1}\,a_{N2} & \cdots\cdots & a_{NN} \end{vmatrix}, \tag{1}$$

where $a_{pq} = \sum_\rho \psi^*_{\rho p}\psi_{\rho q}$, the summation including all occupied states from α to ν, and A has the property that it can easily be integrated over the co-ordinate space of any electron (see Lennard-Jones 1930*b*). For instance, if $f(p)$ is a function of the co-ordinates of the pth electron only, then by completing the integration for all electrons except the pth, it is easily proved that

$$\frac{1}{N!}\int \Psi^* f(p)\Psi\,d\tau = \frac{1}{N}\int f(p)\,a_{pp}\,d\tau_p,$$

a result which is independent of the choice of p. We can therefore drop the electron suffix, and remove the factor $1/N$ by summing for p from 1 to N; thus

$$\frac{1}{N!}\sum_p \int \Psi^* f(p)\Psi\,d\tau = \sum_\rho \int \psi^*_\rho f \psi_\rho\,d\tau. \tag{2}$$

Similarly if $g(p)$, $g'(q)$ are respectively functions of the co-ordinates of the pth and qth electrons only, then by integrating for all electrons except the pth and qth

$$\frac{1}{N!}\int \Psi^* g(p)\,g'(q)\,\Psi\,d\tau = \frac{1}{N(N-1)}\iint g(p)\,g'(q)\begin{vmatrix} a_{pp} & a_{pq} \\ a_{qp} & a_{qq} \end{vmatrix} d\tau_p\,d\tau_q$$

$$= \frac{1}{N(N-1)}\sum_\rho\sum_\sigma \iint g(p)\,g'(q)\,\{\psi^*_{\rho p}\psi_{\rho p}\psi^*_{\sigma q}\psi_{\sigma q}$$

$$-\psi^*_{\rho p}\psi_{\rho q}\psi^*_{\sigma q}\psi_{\sigma p}\}\,d\tau_p\,d\tau_q.$$

This is likewise independent of the choice of p and q, and hence, dropping the electron suffices,

$$\frac{1}{N!}\sum_{p}\sum_{q\neq p}\int \Psi^* g(p)\,g'(q)\,\Psi\,d\tau$$
$$=\sum_{\rho}\sum_{\sigma}\left[\int\psi_\rho^* g\,\psi_\rho\,d\tau\int\psi_\sigma^* g'\,\psi_\sigma\,d\tau'-\int\psi_\rho^* g\,\psi_\sigma\,d\tau\int\psi_\sigma^* g'\,\psi_\rho\,d\tau'\right]. \qquad (3)$$

Turning now to (3·2), we require the integral of v^2 where $v=-\sum_{p}(\mathbf{r}_p\,.\,\mathbf{F})$. v^2 may be written

$$\sum_{p}\{(\mathbf{r}_p\,.\,\mathbf{F})^2+\sum_{q\neq p}(\mathbf{r}_p\,.\,\mathbf{F})\,(\mathbf{r}_q\,.\,\mathbf{F})\}$$

and so from (2) and (3) we get at once

$$\frac{1}{N!}\int\Psi^* v^2\,\Psi\,d\tau=\sum_{\rho}\Bigg[\int(\mathbf{r}\,.\,\mathbf{F})^2\,\psi_\rho^*\,\psi_\rho\,d\tau$$
$$+\sum_{\sigma\neq\rho}\left\{\int(\mathbf{r}\,.\,\mathbf{F})\,\psi_\rho^*\,\psi_\rho\,d\tau\int(\mathbf{r}'\,.\,\mathbf{F})\,\psi_\sigma^*\,\psi_\sigma\,d\tau'\right.$$
$$\left.-\int(\mathbf{r}\,.\,\mathbf{F})\,\psi_\rho^*\,\psi_\sigma\,d\tau\int(\mathbf{r}'\,.\,\mathbf{F})\,\psi_\sigma^*\,\psi_\rho\,d'\tau\right\}\Bigg].$$

Let us introduce a system of rectangular axes in which $\mathbf{r}$ has direction cosines l, m, n, and $\mathbf{F}$ has direction-cosines α, β, γ. Then if r, F are the magnitudes of $\mathbf{r}$ and $\mathbf{F}$

$$\int\psi_\rho^*\,(\mathbf{r}\,.\,\mathbf{F})^2\,\psi_\rho\,d\tau=F^2\int\psi_\rho^*\,r^2\,(l\alpha+m\beta+n\gamma)^2\,\psi_\rho\,d\tau,$$

and when we average for all values of l, m, n, i.e. for all orientations of the atom relative to the direction of $\mathbf{F}$, this integral reduces to

$$\tfrac{1}{3}F^2(r^2)_{\rho\rho}.$$

Now $(\mathbf{r}\,.\,\mathbf{F})$ is an odd function of r and so its average value with respect to the charge density $\psi_\rho^*\,\psi_\rho$ is zero; the second term in (4) therefore vanishes. The remaining integrals can be treated like the first, and finally

$$\frac{1}{N!}\int\Psi^*\,v^2\,\Psi\,d\tau=\tfrac{1}{3}F^2\sum_{\rho}[(r^2)_{\rho\rho}-\sum_{\sigma\neq\rho}\{(x)_{\sigma\rho}\,(x)_{\rho\sigma}+(y)_{\sigma\rho}\,(y)_{\rho\sigma}+(z)_{\sigma\rho}\,(z)_{\rho\sigma}\}].$$

We also require the integral of $(\mathrm{grad}_p\,v^2)$, in which $\mathrm{grad}_p\,v=-\mathrm{grad}_p(\mathbf{r}_p\,.\,\mathbf{F})$. From (2) it follows that

$$\frac{1}{N!}\sum_{p}\int\Psi^*\,(\mathrm{grad}_p\,v)^2\,\Psi\,d\tau=\sum_{\rho}\int\psi_\rho^*\{\mathrm{grad}(\mathbf{r}\,.\,\mathbf{F})\}^2\,\psi_\rho\,d\tau,$$

and the right-hand side is easily shown to be equal to N. These results lead at once to equation (3·4).

When it is necessary to use equation (2·5) for the perturbation energy, rather more complicated integrals occur but they can be reduced in essentially the same way. Instead of the charge density $\Psi^*\Psi$ we usually have $\psi^*_{\rho q} D^*_{\rho q} D_{\rho p} \psi_{\rho p}$, in which $D_{\rho p}$ is the first minor of $\psi_{\rho p}$ in the determinant Ψ. $D^*_{\rho q}$ and $D_{\rho p}$ are therefore determinants with $(N-1)$ rows and columns and their product is likewise a determinant $(N-1)$ rows and columns, having the form

$$D^*_{\rho q} D_{\rho p} = (-)^{p+q} \begin{vmatrix} a'_{11} & \cdots\cdots & a'_{1,p-1} & a'_{1,p+1} & \cdots\cdots & a'_{1N} \\ \vdots & & & & & \vdots \\ a'_{q-1,1} & & & & & a'_{q-1,N} \\ a'_{q+1,1} & & & & & a'_{q+1,N} \\ \vdots & & & & & \vdots \\ a'_{N1} & \cdots\cdots & a'_{N,p-1} & a'_{N,p+1} & \cdots\cdots & a'_{NN} \end{vmatrix},$$

where $a'_{pq} = \sum\limits_{\sigma \neq \rho} \psi^*_{\sigma p} \psi_{\sigma q}$, the summation including all states from α to ν except ρ. The product of this determinant with $\psi^*_{\rho q} \psi_{\rho q}$ is, like (1), easily integrated over the co-ordinate space of any electron, and we obtain the following useful results:

$$\left.\begin{aligned} \sum_p \int \psi^*_{\rho q} D^*_{\rho q} D_{\rho p} \psi_{\rho p} f(p)\, d\tau &= 0, \quad \text{when } q \neq p, \\ &= N! \int \psi^*_\rho f \psi_\rho\, d\tau, \quad \text{when } q = p, \\ \sum_p \sum_{q \neq p} \int \psi^*_{\rho q} D^*_{\rho q} D_{\rho p} \psi_{\rho p} g(p) g'(t)\, d\tau &= 0, \quad \text{when } t \neq q, \\ = N! \sum_{\sigma \neq \rho} \left\{ \int \psi^*_\rho g \psi_\rho\, d\tau \int \psi^*_\sigma g' \psi_\sigma\, d\tau' \right. &- \left. \int \psi^*_\rho g \psi_\sigma\, d\tau \int \psi^*_\sigma g' \psi_\rho\, d\tau' \right\}, \\ &\quad \text{when } t = q. \end{aligned}\right\} \quad (4)$$

Integrals which involve $\psi^*_{\rho q} D^*_{\rho q} D_{\sigma p} \psi_{\sigma p}$ $(\sigma \neq \rho)$ can also be reduced by the same method, and we find that

$$\left.\begin{aligned} \int \psi^*_{\rho p} D^*_{\rho p} D_{\sigma p} \psi_{\sigma p}\, d\tau &= 0, \\ \int \psi^*_{\rho q} D^*_{\rho q} D_{\sigma p} \psi_{\sigma p} f(p)\, d\tau &= 0, \\ \int \psi^*_{\rho q} D^*_{\rho q} D_{\sigma p} \psi_{\sigma p} g(p) g'(q)\, d\tau &= 0. \end{aligned}\right\} \quad (5)$$

Let us now consider the integral of $\Psi^* v \Phi$, where $v = \sum_p v_p$ as above, and $\Phi = \sum_\rho \lambda_\rho \sum_p \psi_{\rho p} D_{\rho p} v_p$. We write

$$\Psi^* v \Phi = \Psi^* (\sum_t v_t) \sum_\rho \lambda_\rho \sum_p \psi_{\rho p} D_{\rho p} v_p,$$

in which the coefficient of λ_ρ is

$$\Psi^* \sum_p \psi_{\rho p} D_{\rho p} v_p (\sum_t v_t).$$

If Ψ^* in this expression is replaced by its expansion in terms of the elements of the ρth row, i.e. by $\sum_q \psi^*_{\rho q} D^*_{\rho q}$, then

$$\Psi^* v \Phi = \sum_\rho \lambda_\rho \{\sum_p \sum_q \psi^*_{\rho q} D^*_{\rho q} D_{\rho p} \psi_{\rho p} (v_p^2 + \sum_{t \neq p} v_p v_t)\}.$$

When we apply equations (4) and insert $v_p = -(\mathbf{r}_p . \mathbf{F})$ the terms which do not vanish on integration give

$$\frac{1}{N!} \int \Psi^* v \Phi \, d\tau = \sum_\rho \lambda_\rho \left[\int \psi^*_\rho (\mathbf{r} . \mathbf{F})^2 \psi_\rho \, d\tau \right.$$
$$\left. - \sum_{\sigma \neq \rho} \int \psi^*_\rho (\mathbf{r} . \mathbf{F}) \psi_\sigma \, d\tau \int \psi^*_\sigma (\mathbf{r}' . \mathbf{F}) \psi_\rho \, d\tau' \right],$$

which by our previous results

$$= \tfrac{1}{3} F^2 \sum_\rho \lambda_\rho (R^2)_\rho.$$

From (2·5) we have also the following term involving grad_p:

$$\int \text{grad}_p \Phi^* . \text{grad}_p \Phi \, d\tau - \frac{1}{N!} \int \Phi^* \Phi \, d\tau \int \text{grad}_p \Psi^* . \text{grad}_p \Psi \, d\tau.$$

Since $\Phi = \sum_\rho \lambda_\rho \sum_p \psi_{\rho p} D_{\rho p} v_p$ and $D_{\rho p}$ contains the co-ordinates of all electrons *except* the pth,

$$\text{grad}_p \Phi = \sum_\rho \lambda_\rho \{D_{\rho p} (\psi_{\rho p} \text{grad}_p v_p + v_p \text{grad}_p \psi_{\rho p}) + \sum_{q \neq p} \psi_{\rho q} v_q \text{grad}_p D_{\rho q}\}.$$

On integration, we neglect all terms except that in $(\text{grad}_p v_p)^2$ assuming that the remainder, which with the integral of $\text{grad}_p \Psi^* . \text{grad}_p \Psi$ are analogous to (2·6), are small. Approximately therefore

$$\frac{1}{N!} \sum_p \left\{ \int \text{grad}_p \Phi^* . \text{grad}_p \Phi \, d\tau - \frac{1}{N!} \int \Phi^* \Phi \, d\tau \int \text{grad}_p \Psi^* . \text{grad}_p \Psi \, d\tau \right\}$$
$$= \frac{1}{N!} \sum_p \int \sum_\rho \lambda_\rho D^*_{\rho p} \psi^*_{\rho p} \{\sum_\sigma \lambda_\sigma D_{\sigma p} \psi_{\sigma p}\} (\text{grad}_p v_p)^2 \, d\tau$$
$$= \frac{1}{N!} \sum_p \sum_\rho \lambda_\rho^2 \int \psi^*_{\rho p} D^*_{\rho p} D_{\rho p} \psi_{\rho p} (\text{grad}_p v_p)^2 \, d\tau \qquad \text{by (5)}$$
$$= \sum_\rho \lambda_\rho^2 \int \psi^*_\rho \{\text{grad}(\mathbf{r} . \mathbf{F})\}^2 \psi_\rho \, d\tau \qquad \text{by (4)}$$
$$= F^2 \sum_\rho \lambda_\rho^2.$$

Equation (3·6) for the energy of polarization follows at once from these results.

The integrals which arise when we introduce the more accurate perturbed functions described in § 3 do not require any extension of the method outlined above, and we shall therefore not give further details.

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SUMMARY

The theory of the polarization of an atom by a uniform electric field is developed, using a variation method introduced by Kirkwood, and the atomic polarizabilities of several atoms containing closed electron groups calculated from their self-consistent fields. It is verified that an antisymmetrical wave function for the atom gives better results than a symmetrical function. Higher approximations, in which more parameters are introduced in the perturbed wave functions, are considered. Calculations with the Fock fields of the atoms of Be, Na^+, and Cl^- show that the inclusion of exchange in the electron wave functions has considerable effect on the calculated polarizabilities.

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The Quantum Theory of Atomic Polarization

II—The van der Waals Energy of Two Atoms

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In a previous paper (p. 94) (which will be referred to as Paper I), the polarizability of an atom in a uniform electric field was calculated by a method of varying parameters. The same method can equally well be applied to find the energy of interaction of two atoms a large distance apart, by treating their interaction as a perturbation of the system in which the atoms are separated by an infinite distance. The mutual energy, other than that arising from the ionic charges, if they exist, of the atoms, is usually called the van der Waals energy.

We shall suppose that one atom contains N_1 electrons, and is represented in its unperturbed state by a determinantal wave function Ψ_1 (as in equation (3·1) of Paper I), containing electronic functions of the type $\psi_{\rho_1 p}$, where ρ_1 may be any one of the N_1 occupied states $\alpha_1, \beta_1, \ldots, \nu_1$ of this atom, and p denotes that the spatial and spin co-ordinates of the pth electron are inserted in $\psi_{\rho_1 p}$. Similarly the second atom contains N_2 electrons, and is represented in its unperturbed state by a determinant Ψ_2, containing functions $\psi_{\rho_2 r}$, where ρ_2 may be one of the N_2 occupied states $\alpha_2, \beta_2, \ldots, \nu_2$, and r refers to the co-ordinates of the rth electron. Then if we neglect any exchange of electrons between the atoms, the wave function of the unperturbed system of two atoms is

$$\Psi = \Psi_1 \Psi_2$$

and

$$\int \Psi^* \Psi \, d\tau = N_1! \, N_2!,$$