

which is our final result as it is given by Eq. (30).

We finally wish to calculate the contribution from the pole. Here we write

$$R_p(\omega) = 16\pi \frac{1}{\omega} \int dq q^2 \frac{\mathcal{E}_i(q\omega)}{[\mathcal{E}_r(q\omega)]^2 + [\mathcal{E}_i(q\omega)]^2}$$

$$= -16\pi^2 \frac{1}{\omega} \int dq q^2 \delta[\mathcal{E}_r(q\omega)]. \quad (A9)$$

In order to evaluate the integral in Eq. (A9), we shall

approximate \mathcal{E}_r by

$$\mathcal{E}_r(q\omega) = 1 - \frac{\omega_p^2}{\omega^2} - \frac{12}{5} \left(\frac{\omega_F}{\omega_p} \right)^2 q^2. \quad (A10)$$

The integration in Eq. (A9) is straightforward and we obtain

$$R_p(\omega) = 4\pi^2 \left(\frac{5}{12} \right)^{3/2} \frac{1}{\omega_F} \left(\frac{\omega_p}{2\omega_F} \right)^2 \frac{[(\omega/\omega_p)^2 - 1]^{1/2}}{(\omega/\omega_p)^2}$$

$$= \frac{16\pi}{3} \left(\frac{5}{12} \right)^{3/2} \frac{1}{\omega_F} \frac{[(\omega/\omega_p)^2 - 1]^{1/2}}{(\omega/\omega_p)^2}, \quad (A11)$$

which is our final result given in Eq. (32).

Many-Electron Perturbation Theory for Nonmetallic Low-Density Systems

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(Received 10 April 1963)

A perturbation theory is developed to second order for the energy of a system of weakly interacting atoms. For a large uniform system the expression is correctly proportional to the number of atoms N . The result is given as the sum of electrostatic and Van der Waals terms plus exchange effects. The exchange energy is described first in the pair approximation, followed by corrections due to electron exchange among three or more atoms in both the first and second orders of the perturbation series. The second-order exchange term is due to the effect on exchange produced by the first-order perturbation on the wave function caused by Van der Waals forces.

The zeroth-order term is the energy of the isolated atoms so that in the ground state all other terms are successive corrections to the smaller binding energy.

In the case where the unperturbed atoms have an angular momentum, use of degenerate perturbation theory leads to a spin-wave type of solution, with coupling between the atoms.

ALTHOUGH the perturbation treatment developed here has some general features, the specific formulation is for the case of electrons in a nonmetallic solid, where the solid is not dense and the individual atoms are well separated. This case does not lend itself well to treatment with the usual many-body theory based in zeroth order upon noninteracting electrons.

In the limit of zero density the electrons on different atoms are distinguishable, being associated with the various atomic sites, and the problem is to calculate the binding energy as the density is increased and interatomic exchange of electrons begins to occur.

One obvious choice for an unperturbed Hamiltonian is

$$H_0 = \sum_{i=1}^N h_i(\mathbf{R}_i), \quad (1)$$

which describes a collection of N , noninteracting atoms, with $h_i(\mathbf{R}_i)$ the Hamiltonian of the i th atom having

nuclear coordinates \mathbf{R}_i . The eigenfunctions of H_0 are

$$\psi_J = \psi_{j_1}(\mathbf{R}_1) \cdots \psi_{j_N}(\mathbf{R}_N) \quad (2)$$

and the eigenvalues

$$\epsilon_J = \epsilon_{j_1} + \epsilon_{j_2} + \cdots + \epsilon_{j_N}, \quad (3)$$

where $\psi_{j_i}(\mathbf{R}_i)$ is centered about \mathbf{R}_i and is an eigenfunction of $h_i(\mathbf{R}_i)$ (antisymmetric in the space and spin coordinates of those electrons about \mathbf{R}_i) with eigenvalue ϵ_{j_i} . Here we have arbitrarily assigned particular electrons to particular atoms and $\psi(\mathbf{R}_1)$ indicates $\psi(\mathbf{R}_1; 1, 2, \dots)$ where the electrons 1, 2, \dots are assigned to the atom at \mathbf{R}_1 .

The Ψ_J form a complete orthogonal set and, therefore, it might seem that the set $\alpha\Psi_J$ would be convenient for the expansion of an antisymmetric function of all electrons, where

$$\alpha = \sum_{\nu} (\pm) P_{\nu}, \quad (4)$$

the sum being over all permutations P_{ν} of electronic space and spin coordinates, and the sign being given by the parity. However, the $\alpha\Psi_J$ are no longer eigen-

* Most of the work reported here was done while the author was at the Atomic Energy Research Establishment (Theoretical Physics Division) Harwell, England.

functions of H_0 , since H_0 is not symmetric in the electron coordinates. As a consequence, the antisymmetrized functions are nonorthogonal and linearly dependent, and cannot serve as a basis for a straightforward perturbation expansion. The use in some sense of H_0 as the unperturbed Hamiltonian, therefore, requires a special treatment, independent of a configuration expansion. However, it is not difficult to formulate the problem so that iteration procedures can be used. Particular attention is required for the case of large N where a central part of the problem is in obtaining expressions which are proportional to the number of atoms in the system.

DEVELOPMENT OF THE PERTURBATION THEORY

We seek a solution of the Schrödinger equation

$$(H-E)\Phi=0, \quad (5)$$

subject to the requirement that Φ is an antisymmetric function, a requirement which may be satisfied by setting Φ equal to $a\psi$, where a is an antisymmetrizing operator, or more properly, a reduced antisymmetrizing operator defined for later convenience by

$$a = \alpha / \langle \alpha \rangle. \quad (6)$$

The angular brackets $\langle \rangle$ in (6) indicate a mean with respect to ψ_0 , which serves as the zeroth-order approximation to ψ , and is one of the set of unperturbed functions given by (2) (assumed for the present to be nondegenerate), having the eigenvalue ϵ_0 . Thus, the value of $\langle a \rangle$ is unity.

The Hamiltonian of the system is

$$H = H_0 + H', \quad (7)$$

where H' is the interaction among the atoms, and with this and the above substitution, Eq. (5) becomes

$$(H_0 - \epsilon_0 + H' - \langle H' \rangle - \Delta E)a\psi = 0, \quad (8)$$

with ΔE defined by $E - \langle H \rangle$.

It is important to remember that a commutes with the complete Hamiltonian, but not with H_0 and H' separately.

By multiplying on the left in Eq. (8) by ψ_0 and integrating, the result is obtained that

$$\Delta E = \langle \psi_0 | H' - \langle H' \rangle | a\psi \rangle, \quad (9)$$

providing ψ is normalized so that $\langle \psi_0 | a | \psi \rangle = 1$.

It also follows since ΔE is real that

$$\Delta E = \frac{1}{2} [\langle \psi_0 | H' - \langle H' \rangle | a\psi \rangle + \text{c.c.}]. \quad (10)$$

Now if ψ is written as $\psi_0 + \Delta\psi$, then

$$\Delta E = \langle (H' - \langle H' \rangle) a \rangle + \frac{1}{2} [\langle \psi_0 | (H' - \langle H' \rangle) | a\Delta\psi \rangle + \text{c.c.}], \quad (11)$$

since $\langle (H' - \langle H' \rangle) a \rangle$ is obviously real, as it is equal to $\langle (H - \langle H \rangle) a \rangle$ or to $\langle a(H - \langle H \rangle) \rangle$.

Returning to the Schrödinger Eq. (5) we substitute

$a(\psi_0 + \Delta\psi)$ for Φ and obtain

$$a(H-E)\psi_0 + (H-E)a\Delta\psi = 0, \quad (12)$$

which may be written in this manner because of the commutivity of H and a .

If $H-E$ is written as in (8), then (12) becomes

$$a(H' - \langle H' \rangle - \Delta E)\psi_0 + (H_0 - \epsilon_0 + H' - \langle H' \rangle - \Delta E)a\Delta\psi = 0. \quad (13)$$

Consider now the projection operator \mathcal{P}_0 defined by

$$\mathcal{P}_0 f = \psi_0 (\psi_0 | f). \quad (14)$$

Since $\mathcal{P}_0(H_0 - \epsilon_0)$ is null, we may obtain, by transposing some terms in (13) and operating on both sides of the equation by the same factor, the result that

$$(H_0 - \epsilon_0)a\Delta\psi = -[1 - \mathcal{P}_0] \quad (15)$$

$$[a(H' - \langle H' \rangle - \Delta E)\psi_0 + (H' - \langle H' \rangle - \Delta E)a\Delta\psi].$$

Following the notation of Brueckner,¹ we define

$$\frac{1}{b} = \frac{1}{\epsilon_0 - H_0} [1 - \mathcal{P}_0]. \quad (16)$$

Then, from (15), the expression for $a\Delta\psi$ which properly normalizes $a\psi$ is given by

$$a\Delta\psi = \frac{1}{b} a(H' - \langle H' \rangle)\psi_0 + \frac{1}{b} (H' - \langle H' \rangle)a\Delta\psi - \Delta E \frac{1}{b} a\psi. \quad (17)$$

Because $\langle 1/b \rangle$ vanishes, $\langle \psi_0 | a | \Delta\psi \rangle = 0$ and $\langle \psi_0 | a | \psi \rangle = 1$.

Substitution of the relation (17) into (11) leads to the result

$$\Delta E = \langle (H' - \langle H' \rangle) a \rangle + \frac{1}{2} \left[\left\langle \frac{1}{b} a(H' - \langle H' \rangle) \right\rangle + \left(\psi_0 | \frac{1}{b} (H' - \langle H' \rangle) | a\Delta\psi \right) - \Delta E \left(\psi_0 | \frac{1}{b} a\psi \right) + \text{c.c.} \right], \quad (18)$$

where use again has been made of the fact that $\langle 1/b \rangle$ vanishes.

To shorten the notation and to give physical interpretation to the results, we define $a-1$ as the exchange operator and define a non-Hermitian exchange Hamiltonian by

$$H_{\text{ex}}' = (H' - \langle H' \rangle)(a-1), \quad (19)$$

where

$$H_{\text{ex}}'^{\dagger} = (a-1)(H' - \langle H' \rangle). \quad (20)$$

¹ K. A. Brueckner in *The Many Body Problem*, edited by C. deWitt (John Wiley & Sons, Inc., New York, 1959), p. 47.

Then from (18)

$$\begin{aligned} \Delta E = & \langle H_{\text{ex}}' \rangle + \left\langle \frac{1}{b} H' - H' \right\rangle + \frac{1}{2} \left[\left\langle \frac{1}{b} H' - H_{\text{ex}}'^{\dagger} \right\rangle \right. \\ & \left. + \left\langle \frac{1}{b} H_{\text{ex}}' - H' \right\rangle \right] + \frac{1}{2} \left[\left(\psi_0 \left| \frac{1}{b} H' - \langle H' \rangle \right| a \Delta \psi \right) \right. \\ & \left. - \Delta E \left(\psi_0 \left| \frac{1}{b} H' \right| a \psi \right) + \text{c.c.} \right]. \quad (21) \end{aligned}$$

Continuing the iteration by the use of (17) in (21) would lead to a formal series expansion for the energy. However, we consider here only the second-order terms in (21), under the assumption that the last bracketed expression on the right-hand side is small at low density.² The second-order term $\langle H'(1/b)H' \rangle$ is, for large internuclear separation, just the Van der Waals energy; while the second-order exchange term

$$\frac{1}{2} [\langle H_{\text{ex}}'(1/b)H' \rangle + \text{c.c.}]$$

shows itself to be the change in exchange energy due to the first-order change $(1/b)H'\psi_0$ in the wave function, caused by the Van der Waals polarization. At very large atomic separations the second-order terms dominate the first-order terms, since it is well known that $\langle H'(1/b)H' \rangle$ becomes larger than $\langle H' \rangle$, and it can be shown, at least in some cases, that $\frac{1}{2} [\langle H_{\text{ex}}'(1/b)H' \rangle + \text{c.c.}]$ likewise becomes larger than $\langle H_{\text{ex}}' \rangle$. The reason for the latter result is that the exchange energy in very low density, depends largely upon the wave function in the region between the atoms, a region where it is very small and easily perturbed by the Van der Waals forces.³ The basis for the expectation that (21) may to good approximation be cut off at second order is the assumption that the aggregate of terms beyond second order does not introduce new qualitative features but only higher Van der Waals corrections.

Thus, if ΔE in (21) is replaced by $E - \langle H \rangle$ or $E - \epsilon_0 - \langle H' \rangle$, we have

$$\begin{aligned} E \simeq \epsilon_0 + \langle H' \rangle + \left\langle \frac{1}{b} H' - H' \right\rangle + \langle H_{\text{ex}}' \rangle \\ + \frac{1}{2} \left[\left\langle \frac{1}{b} H_{\text{ex}}' - H' \right\rangle + \text{c.c.} \right]. \quad (22) \end{aligned}$$

For a large uniform system it can be shown that all terms in (22) are proportional to the number of atoms N , providing a is interpreted as a series expansion discussed in the following sections.

² The difficulty of treating the complete series, apart from convergence questions, is one of demonstrating that "unlinked" parts leading to spurious powers of N cancel.

³ This point has been emphasized by T. Holstein and C. Herring; see Conyers Herring, *Rev. Mod. Phys.* **34**, 631 (1962).

Since ϵ_0 is exactly the energy of the isolated atoms, $E - \epsilon_0$ for the ground state is the binding energy. Therefore, it is necessary to evaluate the terms beyond ϵ_0 only to the accuracy needed for the binding energy itself.

The magnitude of $\langle H' \rangle + \langle H_{\text{ex}}' \rangle$ (with $\langle H' \rangle + \langle H_{\text{ex}}' \rangle$ assumed negative) is a lower limit on the magnitude of the binding energy, since the sum of the zeroth- and first-order terms is

$$\epsilon_0 + \langle H' \rangle + \langle H_{\text{ex}}' \rangle = \langle Ha \rangle = \langle H\alpha \rangle / \langle \alpha \rangle, \quad (23)$$

as can be demonstrated by expanding the right-hand side. The expression $\langle H\alpha \rangle / \langle \alpha \rangle$ is just the mean value of the true Hamiltonian with respect to an antisymmetrized wave function $\alpha\psi_0$ and, therefore, it is an upper bound on the ground-state energy.

In evaluating the terms in (22), the products in the angular brackets may, of course, be expanded in terms of intermediate states ψ_J from (2). However, the exact summation is difficult to perform. In diatomic molecular calculations it is known that in the term $\langle H'(1/b)H' \rangle$ a good approximation is obtained⁴ by replacing $(1/b)$ with $(1/\epsilon)(1 - \mathcal{O}_0)$, where ϵ is the unperturbed energy of the pair of atoms. Since $\langle H'(1/b)H' \rangle$ here can be reduced to a sum over pairs of atoms, a similar approximation can be made; however, some caution must be used in making such an approximation for the exchange terms.

The form of the exchange energy as written in (22) is most appropriate for the case of only moderately large atomic separation, where $\langle H_{\text{ex}}' \rangle$ is expected to be the dominant exchange term and the second-order part is a smaller perturbation. However in the limit of very large separation $\langle H_{\text{ex}}' \rangle$ is known in some cases to give nonsensical results.³ In this situation the second-order term can dominate as may be shown by the following transformation. Since $\langle H_{\text{ex}}' \rangle = \langle (H' - \langle H' \rangle)(a-1) \rangle$ which, in turn, can be written as $\langle (H - \langle H \rangle)(a-1) \rangle$ or as $\langle (a-1)(H - \langle H \rangle) \rangle$, it follows that

$$\begin{aligned} \left\langle \frac{1}{b} H_{\text{ex}}' - H' \right\rangle = \left\langle (a-1)(H' - \langle H' \rangle) \frac{1}{b} H' \right\rangle \\ - \langle (a-1)(H' - \langle H' \rangle) \rangle \quad (24) \end{aligned}$$

and, therefore, since the second term on the right-hand side is $\langle H_{\text{ex}}' \rangle$,

$$\begin{aligned} \langle H_{\text{ex}}' \rangle + \frac{1}{2} \left[\left\langle \frac{1}{b} H_{\text{ex}}' - H' \right\rangle + \text{c.c.} \right] \\ = \frac{1}{2} \left[\left\langle (a-1)(H' - \langle H' \rangle) \frac{1}{b} H' \right\rangle + \text{c.c.} \right]. \quad (25) \end{aligned}$$

The same transformation applies to any individual term in a . As the matrix elements of $(1/b)$ are negative

⁴ H. Margenau, *Phys. Rev.* **38**, 747 (1931).

if ϵ_0 is the unperturbed ground state, the right-hand side of (25) can have a sign opposite to that of $\langle H_{ex} \rangle$.

Various approximations may be made for $(1/b)$ in either (22) or (25), depending on the interatomic distance. However, a precise evaluation of the second-order exchange terms, apart from direct summation over the intermediate states, requires a solution for $(1/b)H'\psi_0$. If this function is called ψ_1 , then the equation which ψ_1 satisfies is

$$(\epsilon_0 - H_0)\psi_1 = (H' - \langle H' \rangle)\psi_0, \quad (26)$$

obtained by multiplying the expression for ψ_1 by $\epsilon_0 - H_0$.

FACTORIZATION OF α

For the case of more than one electron per atom, the antisymmetrizing operator can be simplified due to the use of the wave functions (2) which are already antisymmetric in electrons on the same atom. For any arbitrary permutation operator $\pm P$, (taken with its proper sign) which operates on ψ_J , there are M equivalent permutations obtained by following P , with all the M ways of permuting electrons on the same atom or atoms. Thus, in (6), the substitution $\mathcal{A} \rightarrow A$ can be made, where A contains all permutations such that no two can be made equal to one another by intra-atomic exchange of electrons.

In general, \mathcal{A} can be written as

$$\mathcal{A} = 1 + \sum_{n=2}^N \mathcal{A}_n, \quad (27)$$

where \mathcal{A}_n includes all permutations involving n electrons, with the explicit expressions given in Appendix I.

Likewise,

$$A = 1 + \sum_{n=2}^N A_n, \quad (28)$$

where A_n includes only the permutations of n electrons in which all n are exchanged to atoms different from those to which they were assigned in ψ_J ; for any permutation which leaves one or more of the permuted electrons on its original atomic site must be ignored, since by an intra-atomic exchange it can be made equal to a lower order permutation.

It is easy to write A_2 and A_3 . From Appendix I they are given by

$$A_2 = -\frac{1}{2} \sum_i' \sum_j P_{ij} \quad (29)$$

and

$$A_3 = \frac{1}{3} \sum_k'' \sum_i' \sum_j P_{ki} P_{ij}, \quad (30)$$

where the prime on the i summation indicates that the sum is over all electrons assigned to atomic sites different from that of j , and the double prime indicates that k must be on a site different from both i and j .

The terms beyond A_3 , as seen in Appendix I, are more complex, containing both "linked" permutations as in (30) and "unlinked" terms, which in A_4 involve

four sums over $P_{ij}P_{kl}$, where k and l are different from i and j . Matrix elements of the linked terms, particularly with respect to bound states, are small unless all electrons are in the same locality; but such is not the case for the unlinked terms, and it is necessary to show that in the energy expression cancellation occurs among the unlinked parts.

MATRIX ELEMENTS OF A AND CANCELLATION OF UNLINKED PERMUTATIONS

Because of the unlinked permutations, matrix elements of A , with respect to the set of states ψ_J of (2), are given by a series in ascending powers of N . However, we may expect the ratio A_{IJ}/A_{00} to be independent of N , where 0 is again the unperturbed ground state, or the state taken for zeroth order in the perturbation series ($\langle A \rangle = A_{00}$).

From Eqs. (6) and (28) for an infinite system

$$a_{IJ} = \frac{\delta_{IJ} + \sum_{n=2}^{\infty} \langle A_n \rangle_{IJ}}{1 + \sum_{n=2}^{\infty} \langle A_n \rangle} = \delta_{IJ} + \frac{\sum_{n=2}^{\infty} [\langle A_n \rangle_{IJ} - \langle A_n \rangle \delta_{IJ}]}{1 + \sum_{n=2}^{\infty} \langle A_n \rangle}. \quad (31)$$

By adding and subtracting terms in the numerator, the A_2 terms may next be divided out and a repetition of this procedure leads to a series expansion for a_{IJ} . The general expression is obtained by writing

$$A = 1 + \sum_{n=2}^{\infty} \lambda^n A_n \quad (32)$$

and

$$a_{IJ} = \delta_{IJ} + \sum_{n=2}^{\infty} \lambda^n a_{IJ}^{(n)} \quad (33)$$

($\lambda = 1$), and equating powers of λ in the expression

$$A_{IJ} = \langle A \rangle a_{IJ}. \quad (34)$$

We find

$$a_{IJ}^{(2)} = (A_2)_{IJ} - \langle A_2 \rangle \delta_{IJ}, \quad (35)$$

$$a_{IJ}^{(3)} = (A_3)_{IJ} - \langle A_3 \rangle \delta_{IJ}, \quad (36)$$

$$a_{IJ}^{(4)} = (A_4)_{IJ} - \langle A_4 \rangle \delta_{IJ} - \langle A_2 \rangle a_{IJ}^{(2)}, \quad (37)$$

etc.

It is easily established (Appendix II) that the matrix elements of $a^{(2)}$ and $a^{(3)}$ in a large system are independent of N .

In $a^{(4)}$ a product of second-order terms appears as well as the fourth-order permutations. It is this product which nearly cancels the unlinked permutations of

fourth order, leaving again a term independent of N , as is shown explicitly in Appendix II. There is no reason to suppose the same is not true in all orders since we are calculating the ratio of two matrix elements of the same quantity. Thus, if I and J are bound states, higher orders of a_{IJ} contain proportionately more products of overlap integrals and the expansion for a tends to converge at sufficiently low density.⁵

DIRECT AND INDIRECT EXCHANGE COUPLING

By substituting (33) into (19) an expansion

$$H_{\text{ex}}' = (H' - \langle H' \rangle) a^{(2)} + (H' - \langle H' \rangle) a^{(3)} + \dots \quad (38)$$

is obtained, where the first term on the right-hand side is the sum of the direct exchange interactions, i.e., the exchange in the pair approximation,⁶ and the next term gives the correction to the pair approximation due to exchange among groups of three atoms, etc.

Because exchange couplings are usually expressed as an effective interaction between pairs, the terms beyond $a^{(2)}$ are "indirect" couplings, in that the interaction between a given pair of atoms is obtained via one or more other atoms.

If ψ_0 is approximated by a product of one-electron orbital and spin functions, then $\langle H_{\text{ex}}' \rangle$, evaluated by the use of (38), is just an expression previously given by the author for exchange energy.⁷ However, we have in (38) a generalization to use in calculating exchange in higher order (off-diagonal) terms as well.

PROOF THAT THE ENERGY IS PROPORTIONAL TO N

The proof that the expression (22) for the energy gives a result proportional to the number of atoms, when the expansion (38) for H_{ex}' is substituted into it, is obtained by expressing H' and P , as a sum over pairs and groups of atoms and noting that unlinked terms tend to cancel. For terms not involving the exchange operator, the proof follows directly from the work of Brueckner.¹ Also from previous work⁷ (see also the more recent calculations of Arai⁸), it is obvious that $\langle H_{\text{ex}}' \rangle$ is correctly proportional to N . We may infer that the second-order exchange energy is also proportional to N from the fact that off-diagonal matrix elements of H_{ex}' are independent of N ,⁹ and from the fact

⁵ A different dependence on internuclear distance may occur when unbounded levels (which are necessary for completeness) appear in ψ_J . However, we assume the expansion may be used, in general, for low-lying states, where most of the atoms are in bound states.

⁶ In which the denominator in the pair interaction is also expanded, see W. J. Carr, Jr., J. Phys. Soc. Japan 17, Suppl. B-1, 36 (1962).

⁷ W. J. Carr, Jr., Phys. Rev. 92, 28 (1953); J. Phys. Soc. Japan 17, Suppl. B-1, 36 (1962). In the first reference the results are given with H_{ex}' replaced by $H_{\text{ex}} = (H - \langle H \rangle)(a - 1)$.

⁸ T. Arai, Phys. Rev. 126, 471 (1962).

⁹ Because the difference $H' - \langle H' \rangle$ appears in the expression rather than H' alone, $(H'a)_{IJ}$ by itself is proportional to N as can be established by writing it as $H_{I1}'a_{1J} + \sum_{K \neq 1} H_{IK}'a_{KJ}$, where the first term involves a factor of N because of H_{I1}' . However, $H_{I1}' - H_{00}'$ depends only on the number of excited atoms in I relative to 0.

that in a pure lattice the sum over intermediate states introduces a factor of N . The latter comes about, if ψ_0 describes all noninteracting atoms in their ground states, because each intermediate excited state ψ_J has an N -fold degeneracy (obtained by making a translation of all the excited atoms), all degenerate functions having the same matrix elements with ψ_0 .

By making use of the translational degeneracy of the lattice and the fact H_{0J}' vanishes except for single atom excitations and for two atom excitations, the energy of a pure lattice, as given by (22), may be reduced to a problem of about the same complexity as a molecular problem.

TREATMENT OF DEGENERACY

The unperturbed states possessing angular momentum have a degeneracy corresponding to the various possible atomic orientations. If this or other degeneracy exists then in (22) it is necessary to replace ψ_0 by a proper linear combination of the degenerate functions. In order to bring contact with the usual way of treating this problem, we write the sum of the zeroth- and first-order terms in (22) as $\langle HA \rangle$ or $\langle HA \rangle / \langle A \rangle$, according to (23), and demand that ψ_0 be that combination of degenerate functions for which

$$\delta \langle HA \rangle / \langle A \rangle = 0, \quad (39)$$

the variation being made on the coefficients of the linear combination. If the degeneracy is removed by this procedure, i.e., if the first-order terms in the energy which are given by the solution of (39) are nondegenerate, then it is easily shown that both A and HA (and consequently $H'A$) have been diagonalized in the subspace of the degenerate functions. Thus, $H' + H_{\text{ex}}'$ will be diagonal, and we may immediately calculate the second-order terms in (22) by ignoring the degenerate levels in the sum over intermediate states; or what amounts to the same thing, we may replace $[1 - \mathcal{O}_0]$ in the definition of $(1/b)$ in (16) by $[1 - \sum \mathcal{O}_{0n}]$, the sum being over all the degenerate unperturbed states (assumed to be taken as orthogonal).

In case the solutions of (39) only partially remove the degeneracy, then a further diagonalization in this restricted degenerate subspace is necessary before the higher order terms are calculated.

When the degeneracy involved is due to spin, Eq. (39) will be recognized as leading to a typical spin wave problem with the addition that it is the spins of the atoms (rather than individual electrons) which are coupled together and with the additional advantage that the "exchange integrals" which arise have a precise definition. If H is independent of spin then a spin Hamiltonian may be constructed in the usual way, for example, as in Ref. 7.

Presumably, cases including orbital angular momentum may be treated in a similar manner, and in general, the exchange and nonexchange parts in (22) become

interrelated by spin-orbit coupling and through the solution of the degeneracy problem.

THE CHOICE OF H_0

The choice of H_0 and ψ_0 determines which state is being "followed" by the perturbation procedure and it is necessary to note that different types of states require different unperturbed Hamiltonians. For example, the ground state of the system may go over into a collection of neutral atoms as the density approaches zero, whereas "polar" states will go over into a set of atoms some of which are ionized and others possessing an extra electron. We must obviously start with different H_0 's to describe these two situations. There is some question, however, about treating the case where the ionized states have translational degeneracy as in a pure lattice.

In some problems it may be desirable to choose for H_0 a Hamiltonian which only approximately represents the noninteracting atoms. An example here is the description of a system where the angular momentum has been quenched by the inclusion in H_0 of a crystalline field, or the use of a fictitious potential in exchange problems.³

ACKNOWLEDGMENTS

The author is indebted to Dr. Walter Marshall for the opportunity of visiting Harwell during the summer of 1962, and to Dr. John Hubbard for some useful discussions.

APPENDIX I

α_2 is given by $-\sum \sum_{i>j} P_{ij}$, the sum being over all pairs of electrons. The term α_3 is

$$\sum \sum \sum_{i>j>k} (P_{ijk,jki} + P_{ijk,kij}),$$

with $P_{ijk,jki}$ meaning $i \rightarrow j, j \rightarrow k, k \rightarrow i$; and, in general, α_n is given by the total of all the ways of permuting a given n electrons, summed over all groups of n .

α_4 , which contains terms with different parity, is

$$\begin{aligned} \alpha_4 = & -\sum \sum \sum_{i>j>k>l} [P_{ijkl,jkli} + P_{ijkl,jlik} + P_{ijkl,klji} \\ & + P_{ijkl,kljl} + P_{ijkl,lijk} + P_{ijkl,lkij}] \\ & + \sum \sum \sum_{i>j>k>l} [P_{ijkl,jilk} + P_{ijkl,klil} + P_{ijkl,lkji}]. \end{aligned} \quad (40)$$

These terms may be expressed in a more compact notation by

$$\alpha_2 = -\frac{1}{2!} \sum \sum_{i \neq j} P_{ij}, \quad (41)$$

$$\alpha_3 = -\frac{2}{3!} \sum \sum \sum_{i \neq j \neq k} P_{ijk,jki} = -\frac{1}{3} \sum \sum \sum_{i \neq j \neq k} P_{ki} P_{ij}, \quad (42)$$

$$\begin{aligned} \alpha_4 = & -\frac{6}{4!} \sum \sum \sum \sum_{i \neq j \neq k \neq l} P_{ijkl,jkli} + \frac{3}{4!} \sum \sum \sum \sum_{i \neq j \neq k \neq l} P_{ijkl,jilk} \\ = & -\frac{1}{4} \sum \sum \sum \sum_{i \neq j \neq k \neq l} P_{jk} P_{kl} P_{li} + \frac{1}{8} \sum \sum \sum \sum_{i \neq j \neq k \neq l} P_{ij} P_{kl}. \end{aligned} \quad (43)$$

In α_4 the first group of terms on the right-hand side of (43) are "linked" and the second group "unlinked." Matrix elements of the latter are generally a factor of N larger than for the former so that in an energy expression the unlinked terms must enter in such a way that they largely cancel.

APPENDIX II

It is obvious that off-diagonal elements $a_{IJ}^{(2)}$ are independent of N , because in the double sum over P_{ij} in A_2 , the j th electron must be near the site of the i th for an appreciable matrix element, and the position of the i th, for example, is determined by the excitations of J relative to I . The diagonal elements of $a^{(2)}$ are likewise independent of N , for although $(A_2)_{JJ}$ is proportional to N the difference $(A_2)_{JJ} - \langle A_2 \rangle$ depends only on the excitations of J relative to I .

Similar considerations apply for $a^{(3)}$ and for the linked terms on the right-hand side of Eq. (37), defining $a^{(4)}$. The unlinked terms in (37) are, from A_4 , Eq. (43) in Appendix I:

$$\frac{1}{8} \sum' \sum \sum' \sum [(P_{ij} P_{kl})_{IJ} - \langle P_{ij} P_{kl} \rangle \delta_{IJ}] \quad (44)$$

and from these is subtracted

$$\langle A_2 \rangle a_{IJ}^{(2)} = \frac{1}{4} \sum' \sum \sum' \sum \langle P_{ij} \rangle [(P_{kl})_{IJ} - \langle P_{kl} \rangle \delta_{IJ}]. \quad (45)$$

Assume that the state I has excited atoms with respect to 0 at $\mathbf{R}_1, \mathbf{R}_2, \dots$ and J at $\mathbf{R}_3, \mathbf{R}_4, \dots$. If neither electron in the pair ij and in the pair kl is on an excited atom, then $(P_{ij} P_{kl})_{IJ} = \langle P_{ij} P_{kl} \rangle \delta_{IJ}$ and $(P_{kl})_{IJ} = \langle P_{kl} \rangle \delta_{IJ}$ and both (44) and (45) vanish. If the pair kl involves an excited atom but the pair ij does not, the bracketed part of (44) becomes

$$\langle P_{ij} \rangle [(P_{kl})_{IJ} - \langle P_{kl} \rangle \delta_{IJ}],$$

since $\langle P_{ij} P_{kl} \rangle = \langle P_{ij} \rangle \langle P_{kl} \rangle$. This result is (except for a term independent of N) one-half the corresponding result in (45). Cancellation between (44) and (45) occurs when the case is considered where the pair ij involves an excited atom and kl does not, for then (44) is the same as before and (45) vanishes. The case where both ij and kl involve excited atoms causes no difficulty.