The curve of $QE$ as a function of $\ln E$ (see Fig. 18), is not really applicable to this process since the Born approximation predicts an $E^{-6}$ dependence of cross section for charge exchange. The curve does, however, show that the energy decreases less rapidly than the prediction of the Born approximation. The energy dependence of the cross section is approximately $E^{-1.6}$.

The change in the slope of the curve of cross section as a function of energy, for hydrogen-atom impact (Fig. 12), implies that more than one process contributes to the excitation of the $2p$ state. One possibility is a process $A$, for which the cross section decreases very rapidly with energy, dominating at the low energies, and a process $B$ for which the cross section is nearly independent of energy, dominating at the high energies.

Experimental data for basic atom-molecule inelastic cross sections are not adequate for making a quantitative analysis of the processes involved in producing Lyman-$\alpha$ emission. On the basis of this work some observations can be made, however. For energies above 45 keV the cross section for Lyman-$\alpha$ emission due to hydrogen-atom impact is almost independent of energy. This behavior is very similar to the stripping cross section in Fig. 13, where the electron is removed from the atom instead of remaining in an excited state. Further, the energy dependence of the cross-section curve plotted in terms of $QE$ as a function of $\ln E$ shown in Fig. 18 seems to be approaching the prediction of the Born approximation for a simple dipole excitation. Process $B$ could, therefore, be identified with a simple excitation of the hydrogen atom without specifying the final state of the nitrogen molecule. Below 45 keV the rapid decrease of cross section with energy is indicative of an electron-exchange mechanism. Process $A$, therefore, could be thought of as involving electron exchange.

Comparing the Lyman-$\alpha$ results for hydrogen-atom impact with the emission cross section for the second positive system of $N_2$ due to hydrogen-atom impact, one notes shapes that are similar for energies less than 45 keV. From Figs. 15 and 18, it is also noted that the breaks in the two hydrogen-atom curves occur at about the same energy. One possible explanation for the break in the cross section for excitation by hydrogen atoms of the $N_2$ second positive system (Fig. 18) is the conservation of probability. One supposes that this excitation process is coupled via a charge-exchange mechanism to the excitation of Lyman-$\alpha$ in the projectile. At an energy of 45 keV, process $B$ begins to dominate the Lyman-$\alpha$ channel, which in turn affects the $N_2$ channel. The effect is rather small because of the great number of alternate inelastic channels in the collision.

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# Theory of Weak Atomic and Molecular Interactions*

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A new perturbation procedure for calculating interatomic interaction energies in which the wave function is expanded in terms of product functions is presented. The method is used to discuss various difficulties which can arise in such calculations and these are illustrated by considering the problem of the interaction of two hydrogen atoms. It is found that (a) the inclusion of continuum states in the basis set of functions is of vital importance; (b) the inclusion of charge-transfer states or of antisymmetrical product functions in the basis set can lead to ambiguous results; (c) in general, exchange integrals cannot be neglected relative to Coulomb integrals; and (d) only when the basis functions are products of the individual atomic wave functions is it possible to make *a priori* estimates of the magnitudes of the higher-order terms in the perturbation expansion.

## I. INTRODUCTION

THE energy of interaction between atoms, molecules, and magnetic ions has long been of interest, since it provides the cohesive energy of rare-gas atomic and molecular crystals, the spin-dependent energy between sublattices in insulators containing magnetic ions, the mechanism for enhancing forbidden optical transitions, etc. Nevertheless, since the classic paper of Eisenschitz and London,[1] there have been few attempts to treat the problem in a more or less rigorous fashion, most authors having restricted their discussions to the

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situation in which "exchange" is neglected.[2] As one of us discussed previously,[3] in certain special cases, among which is that of two interacting ground-state hydrogen atoms, it is not exchange which is neglected in the usual calculation of the London-van der Waals energy; the "approximation" made is rather the expansion of the perturbation potential in inverse powers of $R$, which is at best valid in some asymptotic sense.[4]

The present paper develops a theory of weak interatomic and intermolecular interactions—both from a secular equation and a perturbation-theoretic viewpoint—based on the expansion of the system wave function in the complete set of simple products of wave functions of the noninteracting components.[5] The formal result can be related to that of Eisenschitz and London, who expanded in an over-complete set of antisymmetrized product functions and whose expansion coefficients are not unique, as discussed recently by van der Avoird.[6] The procedure employed is essentially different from that of the several authors who have recently revived interest in the problem of interatomic and intermolecular "forces."[7–14] It differs from the work of Murrell, Salem, and Musher and co-workers in that it obtains an antisymmetric wave function without requiring the complete set of functions to be themselves antisymmetric, a requirement which in the past has led to the use of an overcomplete set and an energy expression which is incorrect, order by order, to powers of a numerical factor. It differs from the very interesting studies of Herring and Hirschfelder and Silbey in that it solves for the eigenfunctions directly rather than the sums and differences of eigenfunctions belonging to a single "configuration" and hence does not run the risk of losing information when a perturbation-theoretic procedure is applied.

In order to illustrate explicitly certain important implications of the formal procedure for calculations on weakly interacting atoms and molecules, we treat the classic problem of two interacting hydrogen atoms in some detail. When the magnitudes of the various terms are examined critically, we find, among other things, that the principal contribution to the second-order energy is the sum of Coulomb and exchange contributions with the contribution of the latter, contrary to much earlier expectation, *equal* to that of the former. We also are able to show that many generally accepted procedures[14] of quantum chemistry and solid-state physics which employ wave functions which are not all eigenfunctions of the same Hamiltonian such as ion-pair (or charge transfer) configurations often required to be antisymmetrized, are inherently dangerous, and the results obtained using those procedures are likely to be misleading and deceptive. To our knowledge, the brief discussion we present here is the first serious indication in the literature of the potential weaknesses of these procedures, and we hope in the future to examine one of the many explicit calculations in an attempt to justify the assumptions on which it is based.

In Sec. II the formal description is sketched, a suitable complete set of wave functions is constructed, and the error introduced by the use of overcomplete sets is discussed. The dependence of the individual terms in the perturbationlike expansion on the basis set employed is pointed out and its significance and the convergence of the different expansions are discussed. The simple system of two interacting hydrogen atoms is discussed in Sec. III using as $\Psi_0$ the Heitler-London functions of correct symmetry and as the complete set of wave functions the remaining simple product functions. The second-order "spin-independent" energy correction, which gives the London-van der Waals energy plus a sum of polynomials times exponentials, is examined and the effect of the latter is shown to be extremely important. The second-order "spin-dependent" energy correction, contributing to the so-called exchange splitting, is examined and a differential equation from which it can be obtained directly is derived. While no computation is carried out, an argument is given to indicate the likelihood that this term dominates the first-order term at large interatomic separation, which would serve to correct the erroneous behavior of the Heitler-London zeroth-order solution that places the singlet below the triplet.[7] In Sec. IV, the use of several types of approximate functions is examined critically and in Sec. V an equivalent perturbation-theoretic procedure for evaluating the interaction energy from the direct solution of partial differential equations is developed, and com-

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[14] See, e.g., P. W. Anderson, Solid State Phys. **14**, 99 (1963); R. N. Stuart and W. Marshall, Proc. Phys. Soc. (London) **87**, 749 (1966); J. Hubbard, D. E. Rimmer, and F. R. A. Hopgood, Proc. Phys. Soc. (London) **88**, 13 (1966); N. L. Huang and R. Orbach, Phys. Rev. **154**, 487 (1967); R. Silbey, J. Jortner, M. T. Vala, and S. A. Rice, J. Chem. Phys. **42**, 2948 (1965); R. Silbey, S. A. Rice, and J. Jortner, *ibid.* **43**, 3336 (1965); and Ref. 8.

parison is made to the recent theory of Hirschfelder and Silbey.[13]

## II. GENERAL THEORY

### A. The Expansion Procedure

Consider a system built up of $N$ weakly interacting elements which may be atoms, molecules, ions, etc., but which we will henceforth refer to as atoms.

The wave functions for the interacting system can be expressed as a linear sum of any complete set of functions $\{\Psi_n\}$ and the energy eigenvalues of the interacting systems can be found by diagonalizing the secular determinant

$$\det|H_{mn}-ES_{mn}|=0, \tag{1}$$

where $H_{mn}=\langle m|H|n\rangle$ and $S_{mn}=\langle m|n\rangle$, with $H$ the total Hamiltonian for the entire system. Because this procedure is not in general tractable, it is desirable to take advantage of the fact that the atoms are weakly coupled, so that the interaction changes the energy levels only slightly from those of the noninteracting system. For example, if the ground state is to be considered, a good approximation to the lowest root of (1) will be

$$E_A{}^0+E_B{}^0+\cdots+E_N{}^0, \tag{2}$$

the sum of the energies of the ground states of the individual atoms. It is thus sutiable to take as the ground-state wave function

$$\Psi_0=N\mathcal{A}\{A_0B_0\cdots\}, \tag{3}$$

where $A_0$, $B_0$, etc., are the exact ground-state wave functions for the individual atoms containing disjoint sets of electrons, $N$ is a normalization constant, and $\mathcal{A}$ is the antisymmetrizing operator which normalizes $\Psi_0$ in the limit of infinite interatomic separations (and if necessary projects out the eigenfunction of desired spin). Since in this limit $H_{00}$ is exactly Eq. (2), it might have been thought that instead of the $\Psi_0$ of (3) we could have taken the simple product wave function

$$\Psi_0=A_0B_0\cdots. \tag{4}$$

This, however, is not possible, except when (1) is solved directly, since in a perturbative procedure there is no guarantee that an antisymmetrized total wave function, and hence an allowed approximate energy eigenvalue, will result unless $\Psi_0$ itself is antisymmetric. Note, however, that since $H$ is totally symmetric, the complete set of states $\Psi_n$ need not be antisymmetric; the only contributions to the matrix elements $\langle 0|H|n\rangle$ arise from the antisymmetric part of $\Psi_n$.

Adopting this $\Psi_0$, the energy in the vicinity of $H_{00}$ is given by the well-known expansion of the secular determinant (1) as

$$\mathcal{E}=H_{00}+\sum_{n\neq0}\frac{|H_{0n}-S_{0n}H_{00}|^2}{H_{00}-H_{nn}}+\sum_{m,n\neq0}\frac{(H_{0m}-S_{0m}H_{00})(H_{nm}-S_{nm}H_{00})(H_{0n}-S_{0n}H_{00})}{(H_{00}-H_{nn})(H_{00}-H_{mm})}, \tag{5}$$

which is formally exact but whose convergence properties depend greatly on the particular choice of the expansion functions $\Psi_n$, $n\neq0$, where the set $\{\Psi_n\}$ is not necessarily orthogonal. Different, and generally greater, rates of convergence can be obtained by the selective summation[10] of the terms on the right side of (5), such as in the Feenberg[15] iteration procedure, which approaches the Fredholm solution, and the partitioning technique used by Hirschfelder and Löwdin.[16] An example of such a selective summation would be obtained by making a linear transformation among the $\Psi_n$, so that the $\Psi_n'$ are all orthogonal, with $\Psi_0'=\Psi_0$, for which there would be no overlap terms in (5) when the matrix elements were written in terms of the new functions. Notice that in the special case for which all the $\Psi_n$ are eigenfunctions of some $H_0$, Eq. (5) reduces to the usual perturbation-theory expansion. This, however, almost never occurs, as discussed elsewhere,[2c] because of the fact that a legitimate $\Psi_0$ must contain all the electrons equivalently and so must be an eigenfunction of a Hamiltonian which includes the interatomic interactions, just the type of problem we had considered intractable at the start. The term $H_{00}$ will be referred to as the zeroth-order energy, the first summation as the second-order energy, $\mathcal{E}_2$, etc. The concept of order will, however, be applied loosely since any of the selective summation procedures just referred to will change the absolute value of a term of given order. Thus, for example, we will generally refer to any expression for $\mathcal{E}_2$ which differs from that of (5) only by small terms, i.e., of the order of the higher-order terms of (5), as being the second-order energy. We will emphasize, however, that while order in this sense may be only a theoretical construct, there is generally justifiable ordering in absolute size of contributing terms which enables cutting off the expansion when the desired accuracy has been reached.

It remains to define the choice of the functions $\Psi_n$, $n\neq0$, which together with $\Psi_0$ are to form a complete set. Each of the $N$ interacting systems has associated with it a complete set of states which we denote by $\{A_i\}$, $\{B_i\}$, etc. These may or may not be the eigenstates for the isolated system although, as we show below, we prefer $A_0$, $B_0$, $\cdots$, $N_0$ to be the exact ground states. A complete (and not overcomplete) set of functions for the

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[15] E. Feenberg, Phys. Rev. 74, 206 (1948).

[16] J. O. Hirschfelder and P. O. Löwdin, Mol. Phys. 2, 229 (1959).

$N$-atom system is obtained by taking products of these functions, i.e.,

$$\Psi_n = A_i B_j C_k \cdots \equiv |ijk\cdots\rangle \equiv |n\rangle, \qquad (6)$$

where the single index $n$ replaces the ordered set of indices $i, j, \cdots$. [The ordering here is most important. If the atom $A$ contributes $\alpha$ electrons, $B$ contributes $\beta$ electrons, etc., and the coordinates of the electrons are $x_1 \cdots x_{\alpha+\beta+\gamma+\cdots}$, then by the product $|n\rangle$ we mean

$$A_i(x_1\cdots x_\alpha)B_j(x_{\alpha+1}\cdots x_{\alpha+\beta})C_k(X_{\alpha+\beta+1}\cdots x_{\alpha+\beta+\gamma})\cdots$$

This is, of course, to be distinguished from, for example,

$$B_j(x_1\cdots x_\beta)A_i(x_{\beta+1}\cdots x_{\beta+\alpha})\cdots.]$$

This set does not contain $\Psi_0$ as a member but we can replace $|000\cdots\rangle$, i.e., the product $A_0B_0\cdots$, by $\Psi_0$ of (3) without changing the completeness of the set or making it overcomplete.

Since the final wave function must be antisymmetric, it has generally been thought appropriate to choose the $\Psi_n$ as being totally antisymmetric themselves.[1,3–9] However, aside from the fact that antisymmetry of the $n\neq 0$ is not at all necessary, as noted above, the particular set of antisymmetrized wave functions generally employed

$$\Psi_n{}^a = N_n \mathcal{A}\{A_iB_jC_k\cdots\}, \qquad (7)$$

obtained by antisymmetrizing the functions of (6), are in fact, overcomplete. This set is $Q=(\alpha+\beta+\gamma+\cdots)!/\alpha!\beta!\gamma!\cdots$-fold redundant or contains $Q$ independent complete sets, as first noted by Eisenschitz and London,[1] who showed how to correct for the redundancy in their pseudoperturbation expansion, although the importance of this has been, in general, neglected by subsequent authors.

This argument of Eisenschitz and London[1] can be applied exactly to our Eq. (5), giving

$$\mathcal{E} = H_{00} + Q^{-1}\sum_{n\neq 0}\frac{|H_{0n}-S_{0n}H_{00}|^2}{H_{00}-H_{nn}} + \cdots \qquad (8)$$

for the set $\Psi_n{}^a$ of redundancy $Q$. It can be seen that the energies obtained order by order in (5) and (8) will be equal up to higher-order terms, and thus as long as $Q$ is included correctly either basis set can be used. The 1:1 correspondence between the states $\Psi_n$ and $\Psi_n{}^a$ of (6) and (7), respectively, is probably what has led to the general confusion on this point.[8–12] However, it is easy to see that by symmetry all the permutations of $\Psi_n$ will contribute equally, and hence the set of $\Psi_n{}^a$ is equivalent to a $Q$-fold redundant set of functions. The relationships between the explicit expressions for the first-order coefficients and second-order energies are given in our previous paper.[5]

### B. Various Expansion Functions

Since the rate of convergence of (5) is critically dependent on the choice of expansion functions $\Psi_n$, the various possible choices should be examined carefully. The choice of products of exact eigenfunctions of the isolated system Hamiltonians, although rarely obtainable in practice, is particularly desirable since it is the only choice for which the degree of convergence of (5) can be estimated *a priori.*

Denoting the isolated system Hamiltonians by $H_A$, $H_B$, etc., and the eigenfunctions by $A_i$, $B_j$, we find that

$$\begin{aligned} H_AA_i &= E_i{}^AA_i, \\ H_BB_j &= E_j{}^BB_j, \qquad (9) \\ &\text{etc.} \end{aligned}$$

The product functions $|ijk\cdots\rangle$ are eigenfunctions of the noninteracting Hamiltonian

$$H_0 = H_A(r_A) + H_B(r_B) + \cdots + H_N(r_N), \qquad (10)$$

with eigenvalues $E_{ijk\cdots}\equiv E_n$. In addition, since the functions $A_i$, $B_j$, etc., are orthonormal, so are the product functions $\Psi_n$, $n\neq 0$. However, the functions $\Psi_n$ are not orthogonal to $\Psi_0$.

If the total Hamiltonian of the interacting system is written as

$$H = H_0 + V, \qquad (11)$$

then the matrix elements can be written

$$\begin{aligned} \langle m|H|n\rangle &= \langle m|V|n\rangle, \quad m, n\neq 0; \\ \langle n|H|0\rangle &= E_n\langle n|0\rangle + \langle n|V|0\rangle \\ &= E_0\langle n|0\rangle + N\langle n|\mathcal{A}V|000\rangle, \qquad (12) \end{aligned}$$

while $\langle 0|H|0\rangle$, which is the first term in (5), is

$$E_0 + N\langle 0|\mathcal{A}V|00\cdots\rangle = E_0{}^A + \cdots + E_0{}^N + N\langle 0|\mathcal{A}V|00\cdots\rangle,$$

so that using the eigenfunctions $A_i$, $B_j$, etc., leads to an explicit expression for the interaction energy as a correction to the sum of the isolated atom energies.

The rate of convergence of the expansion (5) depends on the ratio of terms of the form $(H_{nm}-S_{nm}H_{00})$ to the energy denominator. From (12) we have

$$H_{nm} - S_{nm}H_{00} = \langle m|V|n\rangle, \qquad (13)$$

which has simply the form of an interatomic potential. Thus, for example, the third-order term in (5) is of third order in the interaction potential and should be small, and will be vanishingly small in the limit as the atoms cease to interact.

In practice, however, one rarely obtains exact eigenfunctions of the isolated system Hamiltonian, so that (a) $H_{00}$ does not approach the exact energy in the limit of noninteracting atoms, and (b) the expansion of (5) is not only in terms of the interaction between the atoms but also in terms of the difference between the exact Hamiltonians and the Hamiltonians of which the product functions are eigenfunctions. In other words, we have a multiple perturbationlike expansion, and we have no clear argument for the rate of convergence, as has been emphasized previously[2c,10,17] Thus if instead of the functions (9) we use, say, the Hartree-Fock functions $A_i^{\mathrm{HF}}$, $B_j^{\mathrm{HF}}$, which are eigenfunctions of

$$H_A{}^{\mathrm{HF}}A_i=E_i{}^{A,\mathrm{HF}}A_i\,,\qquad H_B{}^{\mathrm{HF}}B_j=E_j{}^{B,\mathrm{HF}}B_j,\cdots, \tag{14}$$

then

$$H_0{}^{\mathrm{HF}}=H_A{}^{\mathrm{HF}}+H_B{}^{\mathrm{HF}}+\cdots \tag{15}$$

and

$$H=H_0{}^{\mathrm{HF}}+H_1{}^{\mathrm{HF}}+V\,, \tag{16}$$

where $H_1{}^{\mathrm{HF}}$ is the sum of the correlation Hamiltonians for each of the isolated atoms, $A$, $B$, etc. The expansion of (5) then involves terms analogous to (13);

$$H_{nm}-S_{nm}H_{00}=\langle m|\,V+H_1{}^{\mathrm{HF}}|n\rangle\,, \tag{17}$$

and hence mixes the interatomic interaction $V$ with the intra-atomic $H_1{}^{\mathrm{HF}}$ in every order. Because the correlation Hamiltonian $H_1{}^{\mathrm{HF}}$ is likely to give terms at least as large as the interatomic potential $V$, this makes it impossible to obtain even the leading part of the second-order interaction energy without having to deal with $H_1{}^{\mathrm{HF}}$ explicitly. One can improve on this situation, through at least second order, if the states $A_0$, $B_0$, etc., although not $A_i$, $B_j$, etc., $i$, $j\neq0$, are known exactly, since the argument of Eq. (9) still applies for matrix elements connecting $\Psi_0$ to the other states. This is equivalent to partially summing to infinite order a set of terms of (5) involving these matrix elements, but there still remain intra-atomic effects in the third- and higher-order terms. An example of this type of error is given below for the case of two hydrogen atoms, in which the Löwdin-Shull orbitals are used instead of the hydrogenic orbitals.

It has been standard practice[14] to calculate perturbation-theory energies by adding a finite number of configurations which are chosen because of their physical significance, as in charge transfer wave functions, because of their symmetry, as in antisymmetrized product wave functions, or for convenience, as in *ad hoc d* orbitals in magnetic ions due to the unavailability of real eigenfunctions. It turns out, as can be seen by the above discussion and the illustration to follow in the next section, that all of these procedures are fraught with difficulties, or more generally stated, any procedure which does not deal with the set of functions (9) in the expression (5) must be subjected to serious analysis before its conclusions can be accpeted. In Sec. IV we give a brief but explicit indication of the kinds of errors involved in three types of calculations—where the use of Löwdin-Shull orbitals is demonstrated as an analog to pseudo-eigenfunctions in the magnetic-ion case. This is not meant to imply at all a necessary invalidity of many common procedures, but merely to illustrate the kind of errors that can appear when such calculations are performed uncritically.

## III. INTERACTION OF TWO HYDROGEN ATOMS

### A. Energy Expression

To illustrate the points made in the previous section and to serve as a prototype study for more complicated systems, we consider the interaction between two hydrogen atoms $A$ and $B$ separated by a distance $R$. For this problem, the complete sets of functions for the individual atoms will be one-electron functions which are products of a space function and a spin factor $\alpha$ or $\beta$. For the ground state there are, therefore, two possible choices for each of the functions $A_0$ and $B_0$, which are degenerate;

$$A_0(i)=a_0(i)\alpha(i)\quad\text{or}\quad a_0(i)\beta(i)\,,$$
$$B_0(j)=b_0(j)\alpha(j)\quad\text{or}\quad b_0(j)\beta(j)\,.$$

When the antisymmetrized products (1) of these are formed there are four possibilities for the zero-order wave function $\Psi_0$, the proper choice of which must be made according to the prescription of perturbation theory for degenerate states. This amounts, in practice, to choosing the four zero-order wave functions which are eigenfunctions of the total spin, giving one singlet state and three triplet states. The singlet and one of the triplet states, $\Psi_0{}^S$ and $\Psi_0{}^T$, can be written

$$\Psi_0{}^{S,T}=(2\pm2S_{00}{}^2)^{-1/2}\times[a_0(1)b_0(2)\pm b_0(1)a_0(2)]\sigma_{1,3}(1,2)\,, \tag{18}$$

with

$$S_{ij}=\int a_i(1)b_j(1)d\tau\,,$$

where $\sigma_1(1,2)$ and $\sigma_3(1,2)$ indicate the normalized spin eigenfunctions of $S=0$ and $S=1$, $S_z=0$, respectively, the $S_z$ value of the latter being chosen arbitrarily.

The remaining members of the complete sets for the triplet functions will be

$$\Psi_n{}^S=a_i(1)b_j(2)\sigma_1(1,2) \tag{19}$$

and

$$\Psi_n{}^T=a_i(1)b_j(2)\sigma_3(1,2)$$

for $i$ and $j$ not both equal to zero. Note that the $\{\Psi_n{}^S\}$ and $\{\Psi_n{}^T\}$ are normalized and orthogonal except with respect to $\Psi_0{}^S$ and $\Psi_0{}^T$.

The total Hamiltonian for the problem is

$$\begin{aligned}H&=-\tfrac{1}{2}(\nabla_1{}^2+\nabla_2{}^2)-\left(\frac{1}{r_{1A}}+\frac{1}{r_{1B}}+\frac{1}{r_{2A}}+\frac{1}{r_{2B}}\right)+\frac{1}{r_{12}}+\frac{1}{R}\\&=H_A(1)+H_B(2)-(1/r_{2A}+1/r_{1B})+1/r_{12}+1/R\\&=H_A(1)+H_B(2)+V\end{aligned} \tag{20}$$

with the obvious notation. Since the total energy of the interacting atoms will differ little from that of the two noninteracting atoms at values of $R$ greater than the singlet state minimum, i.e., $R>1.4a_0$, the perturbation

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[17] J. I. Musher, Opt. i Spektroskopiya [English transl.: Opt. Spectry. **20**, 442 (USSR)] **20**, 793 (1966).

expansion can be used with the basis functions $\Psi_0{}^{S,T}$, $\Psi_n{}^{S,T}$.

The first term in (5), $H_{00}{}^1$ and $H_{00}{}^3$ are the Heitler-London energies for the singlet and triplet levels which we do not write out explicitly. The second-order terms can be written as

$$\mathcal{E}_2{}^{S,T}=\tfrac{1}{2}\sum_{ij}{}'\frac{[J_{00ij}\pm K_{00ij}\mp S_{0i}S_{0j}H_{00}]^2}{J_{0000}\pm K_{0000}-J_{ijij}(1\pm S_{00}{}^2)},\qquad(21)$$

where the prime refers to the exclusion of $i=j=0$ and

$$\begin{aligned}J_{00ij}&=\int a_0(1)b_0(2)Ha_i(1)b_j(2)d\tau_{12},\\K_{00ij}&=\int a_0(1)b_0(2)Hb_j(1)a_i(2)d\tau_{12}.\end{aligned}\qquad(22)$$

The expression (21) which differs by the factor of $\frac{1}{2}$ from that of Ref. 11 contains two types of terms, those which contribute equally to both singlet and triplet states and those which have different signs for the two states. The contributions to the average energy, which can be shown to dominate for all $i$, $j$, give the London-van der Waals energy in $R^{-6}$ (at all values of $R$) and the contributions to the energy difference give rise to the exchange splitting. The relative sizes of these terms can be seen from a comparison of the best calculated potential curves,[18] which show the error in the Heitler-London estimate of the singlet-triplet splitting to be generally an order of magnitude less than the error in the respective energies at usual values of $R$. Thus, for example, at $R=8$, the zeroth-order calculated splitting is

$$H_{00}{}^3-H_{00}{}^1=3.12\times10^{-5},$$

which is in error by $0.20\times10^{-5}$ from the exact

$$\mathcal{E}^3-\mathcal{E}^1=3.32\times10^{-5},$$

as compared with the error in the zeroth-order calculated singlet energy

$$H_{00}{}^1-\mathcal{E}^1=3.54\times10^{-5}$$

and that in the triplet energy

$$H_{00}{}^3-\mathcal{E}^3=3.38\times10^{-5}$$

### B. Average Second-Order Energy

It is convenient to examine separately the average of the singlet and triplet second-order energies, $\mathcal{E}_2$, and the difference of the two second-order energies $\Delta\mathcal{E}_2$. From Eq. (21) and using the interaction potential $V$ defined by (20), the average second-order energy may be written, when small terms are neglected, as

$$\begin{aligned}\mathcal{E}_2&=\tfrac{1}{2}(\mathcal{E}_2{}^S+\mathcal{E}_2{}^T)\\&=\tfrac{1}{2}\sum_{ij}{}'\frac{|\langle a_0b_0|V|a_ib_j\rangle|^2+|\langle a_0b_0|V|b_ia_j\rangle|^2}{2E_0-E_i-E_j},\end{aligned}\qquad(23)$$

which is the sum of Coulomb and exchange terms. While it has often been argued that the exchange integrals may be neglected relative to the Coulomb integrals, it can, in fact, be shown that both of these terms are of equal size, up to terms of higher order, so that (23) can be written as

$$\mathcal{E}_2=\sum_{ij}{}'\frac{|\langle a_0b_0|V|a_ib_j\rangle|^2}{2E_0-E_i-E_j}.\qquad(24)$$

This is demonstrated as follows. Since the set of product functions $a_i(1)\ b_j(2)$ is complete we can write

$$b_i(1)a_j(2)=\sum_{kl}S_{ik}S_{jl}a_k(1)b_l(2),$$

where the symbol $\sum$ includes an integration over the continuous index of the positive-energy states and the sum is over all $k$ and $l$. The sum over the exchange terms can be written as

$$\tfrac{1}{2}\sum_{ijklmn}{}'\frac{\langle a_0b_0|V|a_kb_l\rangle\langle a_mb_n|V|a_0b_0\rangle}{2E_0-E_i-E_j}S_{ik}S_{jl}S_{im}S_{jn},\qquad(25)$$

where the prime still refers to the exclusion of $i=j=0$ in the sum. By expanding $(2E_0-E_i-E_j)^{-1}$ as a series in $(2E_0-E_k-E_l)^{-1}$ for $k$, $l\neq0$ along the lines developed by Musher[19] in another context and noting that $\sum_i S_{ik}S_{il}=\delta_{kl}$, the leading term in (25) is found to be exactly

$$\tfrac{1}{2}\sum_{kl}{}'\frac{|\langle a_0b_0|V|a_kb_l\rangle|^2}{2E_0-E_k-E_l},$$

with the remaining terms (including the term of $k=l=0$) being of the same form as higher-order terms in the perturbationlike expansion.

The nonsymmetrical singlet wave function[3]

$$\Psi_0=a_0(1)b_0(2)\sigma_1(1,2)\qquad(26)$$

can also be used to demonstrate this equality. When the first-order correction to $\Psi_0$ is expanded in the complete set $a_i(1)b_j(2)\sigma_1(1,2)$, ordinary perturbation theory gives the second-order energy as

$$\mathcal{E}_2'=\sum_{ij}{}'\frac{|\langle a_0b_0|V|a_ib_j\rangle|^2}{2E_0-E_i-E_j},\qquad(27)$$

where the $V$ is the same as in (20). If instead one had used the complete set $\{a_0(1)b_0(2);\,b_i(1)a_j(2)\}$ ($i$ and $j$ not both equal to zero) in the expansion, the second-

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[18] W. Kolos and L. Wolniewicz, J. Chem. Phys. 43, 2429 (1965).

[19] See, for example, H. Silverstone. J. Chem. Phys. 45, 4337 (1966).

order energy becomes

$$\mathcal{E}_2''=\sum_{ij}{}'\frac{|\langle a_0b_0|V|b_ia_j\rangle|^2}{2E_0-E_i-E_j}\tag{28}$$

plus terms of third and higher order. As the third- and higher-order terms are neglected in both procedures it is consistent to neglect them here, and because the matrix elements $H_{mn}$ are the same and small in both basis sets, all such terms will be truly higher order, so that $\mathcal{E}_2'$ must equal $\mathcal{E}_2''$ with an error of only higher-order terms.

Energy upper bounds on the magnitude of these integrals are also equal up to terms which decay exponentially. Thus, using (27), or equivalently twice the Coulomb term of (23),

$$|\mathcal{E}_2'|\leqslant\min|2E_0-E_i-E_j|^{-1}\times\{\langle a_0b_0|V^2|a_0b_0\rangle-\langle a_0b_0|V|a_0b_0\rangle^2\},$$

while, using (28) or twice the exchange term of (23),

$$|\mathcal{E}_2''|\leqslant\min|2E_0-E_i-E_j|^{-1}\times\{\langle a_0b_0|V^2|a_0b_0\rangle-\langle a_0b_0|V|b_0a_0\rangle^2\},$$

where the complete set for the summation of the latter is chosen to be the orthogonal one $b_i(1)a_j(2)$, all $i,j$.

This discussion does not mean to suggest that term by term the Coulomb and exchange integrals are the same, but that the sums of these integrals divided by the energy denominators will be. It is known that the major contribution to the Coulomb integral sum arises from the discrete states while the contribution from the lowest discrete states to the exchange integral sum is relatively small. Thus it is surmised that the greatest contribution to the latter comes from the continuum states, a natural consequence of the fact that when a function centered on one atom is expanded about another the major terms arise from the continuum states. (It should be possible to demonstrate this behavior by taking the asymptotic forms of $b_i$ and $a_j$ for $i$ and $j$ in the continuum and integrating over the indices $i$ and $j$ before integrating over the electron coordinates.) One can see, therefore, that neglect of continuum states in the expansion is likely to lead to an $\mathcal{E}_2$ which is too small by a factor of 2 since only the first term of (23) will give an important contribution. On the other hand, the inclusion of the continuum—or equivalently the use of Löwdin-Shull orbitals and higher-order energy corrections[16]—in the calculation of Alexander and Salem[11] only leads to the correct result for $\mathcal{E}_2$ because the neglect of all the exchange terms of (23) exactly offsets the neglect of $Q^{-1}=\frac{1}{2}$ in their Eq. (9).

The expression (24) for $\mathcal{E}_2$ can be written in terms of single-and double-excitations as

$$\mathcal{E}_2=\sum_{i,j\neq0}\frac{|\langle a_0b_0|1/r_{12}|a_ib_j\rangle|^2}{2E_0-E_i-E_j}+2\sum_{i\neq0}\frac{|\langle a_0b_0|V|a_ib_0\rangle|^2}{E_0-E_i}.\tag{29}$$

It is easy to show[19] that for the discrete states

$$\langle a_0b_0|1/r_{12}|a_ib_j\rangle=c/R^m-P(R)\exp-qR$$

and

$$\langle a_0b_0|V|a_ib_0\rangle=\sum_\gamma P_\gamma(R)\exp-\gamma R,$$

where $m=l_i+l_j+1$, $q=1+n_i^{-1}+n_j^{-1}$, with $n_i$, $l_i$ and $n_j$, $l_j$ the respective quantum numbers of states $i$ and $j$, the various $P(R)$ are finite polynomials in increasing powers of $R$, and $c=0$ if either or both of the states $a_i$, $b_j$ is an $s$ state. Since similar expressions can be obtained for the integrals over continuum functions and the energy denominators of (29) are independent of $R$, the $\mathcal{E}_2$ is thus of the form

$$\mathcal{E}_2=\sum_{l,l'\neq0}[k_{ll'}R^{-2(l+l'+1)}+\sum_\alpha p_\alpha{}^{ll'}(R)\exp-\alpha_{ll'}R]+\sum_\beta p_\beta(R)\exp-\beta R,\tag{30}$$

where the individual terms in the first summation arise from summing all the terms of (29) of given $l$ and $l'\neq0$, while the second summation is simply the collection of terms arising from either $l$ or $l'$ or both equal zero, including the single excitations.

Note that the terms in $R^{-2(l+l'+1)}$ are precisely the terms which arise when the potential $V$ is expanded in inverse powers of $R$, on the assumption that $r_{1A}$ and $r_{1B}$ are both less than $R$, and the London-van der Waals energy is, in fact,

$$E_L=\sum_{l,l'\neq0}k_{ll'}R^{-2(l+l'+1)}.\tag{31}$$

The leading term of this expression was calculated by Eisenschitz and London using the summation method, the result being $-6.47R^{-6}$. Of this, $-4.0R^{-6}$ arises from both $i$ and $j$ in the discrete spectrum $-2.2R^{-6}$ from one state discrete and one in the continuum, and $-0.3R^{-6}$ from both states in the continuum. This term has been calculated by numerous researchers and most accurately by Hirschfelder and Löwdin,[16] who obtained $-6.499026R^{-6}$. The first eight terms in the expansion have been given by Bell,[20] the first few terms of which are

$$E_L=-6.50R^{-6}-124R^{-8}-3290R^{-10}-122000R^{-12}.\tag{32}$$

Since it is impossible to express the coefficients $k_{ll'}$ in closed form it is not possible to prove whether or not the series for $E_L$ converges for $R$ greater than some $R_0$. However, when particular numerical values of $R$ are used in the series (32), the contributions of the various terms rather than decreasing eventually become almost equal in size,[21] which, together with the fact that the

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[20] R. J. Bell, Proc. Phys. Soc. (London) **87**, 594 (1966).

[21] See, e.g., the tables given by Dalgarno and Lewis (Ref. 22).

upper bounds to these terms form a divergent series,[22] suggest that $E_L$ is, in fact, infinite at all $R$. The expression $E_L$ is sometimes a useful approximation to $\mathcal{E}_2$ since it has the appearance of being the asymptotic expansion for $\mathcal{E}_2$, though this cannot be proven without knowing $\mathcal{E}_2$ itself analytically. In any case, the difference between $\mathcal{E}_2$ and $E_L$, the terms of the form $p(R)e^{-\alpha R}$, are not at all negligible despite their "exponential decay" and their sum is, in all probability, infinite. This is so, since $\mathcal{E}_2$ itself is finite as we now prove, and although we do not agree with Brooks' argument[4] that $\mathcal{E}_2$ is asymptotically equal to $E_L$ we agree that the likely divergence of $E_L$ is due to the expansion of $V$, and we do not agree with the criticism of Dalgarno and Lewis,[22] which claimed that this divergence was due to the neglect of exchange. In fact, their discussion of the asymptotic behavior of the energy bound in $H_2{}^+$ can be said to prove the argument of Brooks for this case.

That the expansion of $\mathcal{E}_2$ is indeed convergent is easily demonstrated by determining the upper bound to $|\mathcal{E}_2|$ which is obtained by a procedure analogous to that of Eisenschitz and London.[1] Thus,

$$
\begin{aligned}
|\mathcal{E}_2| &= \sum_{kl}{}' (E_k+E_l-2E_0)^{-1}|\langle a_0b_0|V|a_kb_l\rangle|^2 \leqslant \min(E_k+E_l-2E_0)^{-1}[\langle a_0b_0|V^2|a_0b_0\rangle - \langle a_0b_0|V|a_0b_0\rangle^2] \\
&= \min(E_k+E_l-2E_0)^{-1}\{-7/12+1/R^2+e^{-2R}[\overline{Ei}(2R)][-11/16R-11/8+\tfrac{1}{2}R+\tfrac{1}{6}R^2] \\
&\qquad +e^{2R}[Ei(-2R)][11/16R-11/8-\tfrac{1}{2}R+\tfrac{1}{6}R^2]\}, \qquad (33)
\end{aligned}
$$

(neglecting bounded terms dominated by $\exp-2R$) and the bound is finite everywhere except at $R=0$, so that $|\mathcal{E}_2|$ is bounded at all finite $R$. A bound to the leading term in the asymptotic expansion of $\mathcal{E}_2$ is obtained by using the asymptotic expansions

$$Ei(x)=\overline{Ei}(x)=\frac{e^x}{x}\sum_{n=0}^{\infty}\frac{n!}{x^n}$$

to give as a leading term

$$(6/R^6)\min(E_k+E_l-2E_0)^{-1}=16/R^6 \qquad (34)$$

as compared with the exact value of $6.50R^{-6}$. Eisenschitz and London, who had a slightly different[1,6] expression for $\mathcal{E}_2$, obtained the same leading term in the bound except that they took the minimum energy denominator to be that of the double excitation and hence obtained $8R^{-6}$. This is not legitimate, as can be seen from the fact that if only double excitations are included—let us say on the grounds that the single excitations give contributions proportional to $\exp(-\alpha R)$—then $V$ in Eq. (33) can be replaced by $r_{12}{}^{-1}$, so that the single excitations are consistently neglected and the leading terms of the bound are

$$\tfrac{3}{4}^{-1}[2R^{-4}+15R^{-6}],$$

in which the term in $R^{-4}$ is spurious and would be cancelled out by the bound to the single excitations which is also in $R^{-4}$ despite the exponential behavior of the exact solution.

It is important, however, to note that the asymptotic expansion of (33) cannot be applied through terms of $R^{-8}$, as necessary to give $\mathcal{E}_2\propto R^{-6}$ unless $R$ is large enough that

$$R\gg 9$$

is satisfied. Hence the energy bound for the values of $R$ of physical interest *cannot* be expressed by (34), and is, in fact, the value obtained by direct substitution into (33), several of orders of magnitude larger. This is perhaps surprising since at $R=8$, $\mathcal{E}_2$ is very well approximated by the term in $R^{-6}$ alone—it gives $2.7\times10^{-5}$ as compared with the best value of $3.54\times10^{-5}$ of the total correction—but it illustrates well the fact that energy bounds are not necessarily good approximations to the energies themselves.

When the potential $V$ is expanded in inverse powers of $R$ as

$$V=R^{-3}(x_1x_2+y_1y_2-2z_1z_2)+O(R^{-4}),$$

the bound to London's result is

$$|E_L(R^{-6})|\leq\min(E_k+E_l-2E_0)^{-1}6R^{-6}=8R^{-6},$$

since here the single excitations give a zero contribution to the sum and can be neglected in determining the minimum-energy denominator. The bound therefore differs by a factor of 2 from that determined by (34) and is closer to the correct solution, a fact merely due to the vagaries of the crude bounding procedure.

The labor involved in obtaining $\mathcal{E}_2$ explicitly using the summation of (30) is clearly prohibitive and a more satisfactory procedure is to rewrite (29) in terms of the solution to a partial differential equation. We do not do this here because this is equivalent to the perturbation-theoretic procedure of Sec. V, and in any case, the detailed calculation of $\mathcal{E}_2{}^{S,T}$ is not properly part of the present study.

### C. The Exchange Energy

The difference in the triplet and the singlet energies

$$\Delta\mathcal{E}=\mathcal{E}^T-\mathcal{E}^S \qquad (35)$$

is often called the exchange energy, although this usually refers only to the Heitler-London or zeroth-order energy

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[22] A. Dalgarno and J. T. Lewis, Proc. Phys. Soc. (London) **69**, 57 (1956). Notice that A. Dalgarno and N. Lynn [Proc. Phys. Soc. (London) **70**, 223 (1957)] have demonstrated that the inverse power series in $R$ is the asymptotic expansion for the $\mathcal{E}_2$ of the rather different problem of a proton interacting with a hydrogen atom.

differences. This was first calculated by Sugiura[23] to be

$$H_{00}{}^3-H_{00}{}^1=\{56/45-(4/15)(\gamma+\ln R)\}R^{-3}\times e^{-2R}+\text{terms of order } R^2e^{-2R}. \quad (36)$$

This expression becomes negative[7] for $R>50$ a.u., a physically impossible result, so that the second-order contribution to the exchange splitting should be positive to correct for this. When certain small integrals are neglected, the second-order splitting becomes[11]

$$\Delta\mathcal{E}_2=-\tfrac{1}{2}\sum_{ij}{}'\,(2E_0-E_i-E_j)^{-1}J_{00ij}\times[4K_{00ij}-8S_{0i}S_{0j}E_0-2L_{00ij}S_{00}{}^2], \quad (37)$$

where $L_{00ij}=J_{00ij}J_{ijij}(E_i+E_j-2E_0)^{-1}$. Unfortunately, the terms in square brackets have different signs, so that it is difficult to make an *a priori* estimate of the sign of their sum. However, the Mulliken approximation for exchange integrals and the work of Murrell *et al.*[12] suggest that the first two terms for $i$ and $j$ belonging to the discrete spectrum are roughly proportional to $S_{0i}S_{0j}R^{-1}$. If this is correct then at large $R$ this term will dominate and

$$\Delta\mathcal{E}_2=\sum_{ij}\frac{c_{ij}S_{0i}S_{0j}}{R^{l_i+l_j+2}}. \quad (38)$$

If the value at $R=8$ for $i$ and $j$ being $2p\sigma$ states is examined, the term corresponding to $2p\sigma$ states will be positive and vary as $R^{-2}e^{-R}$. This will clearly be sufficient to dominate the logarithmic term in (36) and to insure that $\Delta\mathcal{E}$ is positive in the limit of large $R$. However, the terms arising from states of higher principal quantum number decrease even less rapidly, $S_{0i}$ going as $\exp(-R/n_i)$, so that unless all the terms are of like sign this argument breaks down. Furthermore, the size of the continuum-state contributions, although here likely to be small, appears even more problematical. Notice that the argument which showed the total exchange and Coulomb contributions to $\mathcal{E}_2$ to be equal cannot be applied here since the transformation coefficients $S_{0i}$ do not appear quadratically. In fact, $\Delta\mathcal{E}_2$ can be argued to be small relatively to $\mathcal{E}_2$ precisely because these $S_{0i}$ appear linearly. We intend to investigate this problem explicitly in the future.

At the present the best that can be done with the present formalism is to use the Unsold "approximation" to obtain an arbitrary estimate of $\Delta\mathcal{E}_2$, giving a leading term proportional to

$$(4/15)R^3\ln R\exp(-2R)\times\min|2E_0-E_i-E_j|^{-1}=(32/45)R^3\ln R\exp(-2R), \quad (39)$$

but this cannot be considered as a very convincing result.[7] Herring has devoted a considerable effort to obtain an estimate to the true exchange energy using an ingenious perturbative method which is quite different than the one given here but which does manage to correct the erroneous behavior at large $R$. We have not succeeded in finding an appropriate way to relate the work of Herring to our own but this should be, in principle, possible. There is however, we believe, a legitimate question, arising from our discussion of the effect of the continuum wave function and exchange integrals, concerning the physical arguments Herring used to justify his approximations, but this is a subject for further study.

$\Delta\mathcal{E}_2$ can, however, be evaluated explicitly by writing (37) in terms of $G(1,2)$, the solution to a partial differential equation, which gives the same result as the perturbation-theoretic procedure of Sec. V when the term in $S_{00}{}^2$ is neglected. Thus, neglecting the latter term for simplicity—it is in fact, important and is easily included—

$$\begin{aligned}\Delta\mathcal{E}_2=2\sum_{ij\neq 0}&\langle G(1,2)|a_i(1)b_j(2)\rangle\\&\times\langle a_i(1)b_j(2)|H-2E_0|b_0(1)a_0(2)\rangle\\&=2[\langle G(1,2)|V'|b_0(1)a_0(2)\rangle\\&\quad-\langle G(1,2)|a_0(1)b_0(2)\rangle\\&\qquad\times\langle a_0(1)b_0(2)|V|b_0(1)a_0(2)\rangle], \quad (40)\end{aligned}$$

where $G(1,2)$ is the solution to the partial differential equation

$$(H_0-2E_0)G(1,2)=(\mathcal{E}_1-V)a_0(1)b_0(2), \quad (41)$$

with

$$\mathcal{E}_1=\langle a_0(1)b_0(2)|V|a_0(1)b_0(2)\rangle,$$

and with $V'=P_{12}V$. The two electron-equation (41) is the same equation that has to be solved in order to determine the average second-order energy $\mathcal{E}_2$, if the explicit expansion in $\Psi_n$ is to be avoided. Thus when an approximate solution for this $G(1,2)$ is found, it can be applied to the problems of both $\mathcal{E}_2$ and $\Delta\mathcal{E}_2$.

## IV. OTHER BASIC FUNCTIONS

The difficulties of convergence encountered when eigenfunctions of the exact Hamiltonians of the noninteracting systems are not employed as the expansion functions were discussed in Sec. II. These can be illustrated very well by examining the two-hydrogen-atom problem of the preceding section when Löwdin-Shull oribitals and charge transfer functions are employed.

### A. Löwdin-Shull Orbitals

Consider the complete set of radial atomic orbitals

$$R(r)=C_{n,l}(2r)^lL^{2l+2}{}_{n+l+1}(2r)\exp-r,$$

which differ from the hydrogenic functions in that the exponential factor is always $\exp-r$ instead of $\exp-(r/n)$. These functions are eigenfunctions of an opera-

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[23] Y. Sugiura, Z. Physik, **45**, 484 (1927).

tor which differs from the hydrogen-atom Hamiltonian, although the lowest states $a_0'$, $b_0'$, etc., in this basis are identical with that in the hydrogen basis, $a_0$, $b_0$, etc., and thus $H_{00}$ is the same for both sets of expansion functions. The second-order energy correction, however, differs, since only the states composed of $2p\sigma'$ and $2p\pi'$ atomic states have nonvanishing matrix elements[16] $\langle a_0b_0|1/r_{12}|\times a_ib_i\rangle$ contributing a total of

$$-6/R^6+P(R)e^{-2R}$$

to the energy when the denominator is expanded. The exact leading term $-6.50R^{-6}$, which arises from the second-order term in the hydrogen basis set, is only approximated by the second-order term when the Löwdin-Shull set is employed, the remaining contribution arising from what have been labelled higher-order terms, which illustrates the arbitrary and dangerous nature of the terminology. Hirschfelder and Löwdin have obtained this exact result by using Löwdin's partitioning techinique, for which

$$\mathcal{E}=H_{00}+\sum_{m,n\neq 0}(H_{0n}-H_{00}S_{0n})\times(H_{00}\mathbf{S}_1-\mathbf{H}_1)^{-1}{}_{nm}(H_{0m}-H_{00}S_{0m}),$$

where $\mathbf{S}_1$ and $\mathbf{H}_1$ are those parts of the $\mathbf{S}$ and $\mathbf{H}$ matrices which remain when the rows and columns connected to the state $\Psi_0$ are removed, a procedure which is precisely equivalent to summing all the higher-order terms of (5) which are bilinear in $(H_{0n}-H_{00}S_{0n})$ and $(H_{0m}-H_{00}S_{0m})$. It can easily be seen that both of these terms will give leading contributions proportional to $R^{-3}$, so that higher-order terms in $R^{-6}$ can only arise if a basis set is used which has matrix elements $H_{mn}-S_{mn}H_{00}$ containing terms independent of $R$. By Eq. (11) this clearly does not occur for hydrogenic functions, but does indeed occur for Löwdin-Shull functions for which the leading term of $H_{mn}$, $\langle a_i'b_j',|H_A+H_B|a_k'b_l'\rangle$, is independent of $R$ and can be appreciably large. When the coefficients of $R^{-6}$, $R^{-8}$ are considered for the second-order contribution of (5) using this basis set, and comparison is made with the best known values of these coefficients, it appears that in this particular case the agreement for the several coefficients is quite good. This is, in a way, heartening since these results are much easier to obtain than the solution of Sec. III. This would indicate that if a single atomic excited state is to be added perturbatively to describe the interaction between atoms or magnetic ions it might be better to *increase* the effective charge on the nuclei rather than screen it as is usually done, i.e., the $2p\sigma'$ states are $2p\sigma$ states in the field of a nucleus for which $Z=2$. Unfortunately, however, there is no way to ascertain *a priori* the goodness of a particular screening or antiscreening parameter and thus there appears to be little justification for the procedure of adding a single configuration perturbatively, so often used in solid-state physics, because the results obtained depend critically on an arbitrary and capricious parameter.

### B. Charge-Transfer States

The use of charge-transfer or ion-pair states which supposedly are of importance in the interpretation of molecular spectra,[24] as well as in the theories of antiferromagnetism,[14] should now be considered of skeptical validity in view of the contribution of the matrix elements $H_{mn}$ analogous to the case of the Löwdin-Shull orbitals. There is also the additional problem that when charge-transfer states are included in the set of functions the set becomes overcomplete, with the resulting arbitrariness and instability of the final answer we have referred to earlier. The overcompleteness can, in fact, be dealt with by removing from the set $\Psi_n$ one function for each charge-transfer state, thus giving a mixed set of product functions and charge-transfer states. Provided that each charge-transfer state overlaps the product state it replaces, the mixed set will be complete and not overcomplete. However, the almost unlimited choice of which product functions to disregard in such a procedure, and the accompanying variability of $\mathcal{E}_2$, must be considered a demonstration of its arbitrariness. As different choices are made, the value of $\mathcal{E}_2$ will change, and this implies that there will be large correcting terms from $\mathcal{E}_3$, $\mathcal{E}_4$, etc. These terms actually arise from the charge-transfer states and the product functions which will be, for example,

$$\langle a_ib_j|a_ia_i\rangle=S_{ij},$$

whereas the overlap between product functions is zero, and they can be estimated by orthogonalizing the charge-transfer states to the product functions which has the effect of bringing the overlap terms into $\mathcal{E}_2$. For example, suppose we consider a three-member basis set $\Psi_0$, $\Psi_1$, $\Psi_2$ where $\Psi_0$, $\Psi_1$ are members of the set (2) and $\Psi_2$ is a charge-transfer state, with $\langle 0|1\rangle=\langle 0|2\rangle=0$ but $\langle 1|2\rangle=S$. The second-order terms in (5) will be

$$H_{01}^2/(H_{00}-H_{11})+H_{02}^2/(H_{00}-H_{22}). \qquad (42)$$

Suppose we now define a new function

$$\Psi_2'=\Psi_2-S\Psi_1,$$

so that $\langle 2'|1\rangle=0$. In terms of $\Psi_0$, $\Psi_1$, $\Psi_2'$, the second-order terms are

$$H_{01}^2/(H_{00}-H_{11})+|H_{02}-SH_{01}|^2/(H_{00}-H_{2'2'}). \qquad (43)$$

So long as $S\neq 0$ the two expressions will be different, with (43) including the higher-order terms in $S$ in the expansion of which (42) is the second-order term. For the expansion implicit in substituting the more accurate expression (43) by (42) to be valid, the inequality

$$|SH_{01}|\ll|H_{02}|$$

must hold. Since $S$ for charge-transfer states can be quite large it is difficult for this condition to be satisfied.

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[24] J. N. Murrell and J. Tanaka, Mol. Phys. 7, 363 (1964).

Presumably it would be argued that the choice of which product functions to replace by which charge-transfer states will be made so that $\mathcal{E}_3$ and $\mathcal{E}_4$ are small and the total energy will be just $\mathcal{E}_0+\mathcal{E}_2$. However, there seems to be no way of making such a choice *a priori.*

Alexander and Salem[11] calculated the contribution of the charge-transfer $2p\sigma_A'2p\sigma_A'$ state to the energy of singlet $H_2$ at $R=8$ to be $2.26\times10^{-6}$. They also observed that the significant third-order term was just that arising from the overlap with the isolated-system state $2p\sigma_A'2p\sigma_B'$ as in the case above, and that inclusion of this term reduced the contribution to $1.42\times10^{-6}$. We suspect that by including fourth-order terms, the energy contribution is reduced even more.[25] Thus, a large majority of the second-order effect of charge-transfer states is cancelled out by the higher-order terms and it is difficult to escape the conclusion that results obtained based on the use of charge-transfer states are likely to be extremely deceptive and misleading.

### C. Antisymmetrized Functions

Almost exactly the same criticism made against the inclusion of a limited number of charge-transfer states among the basis functions can be made if antisymmetrized functions are included. We have already pointed to the fact that when the full set of antisymmetrized functions $\Psi_n^a$ replaces the product set $\Psi_n$ the second-order term must be divided by $Q$ (in the case of $H_2$, $Q=2$) to correct for the overcompleteness. But exactly as for charge-transfer states, it is possible to use a mixed set in which each of a *finite* number of the product functions is replaced by an antisymmetrized component. Such a set will *not* be overcomplete, and so the Eisenschitz-London argument for dividing by $Q$ will not hold. On the other hand, it is quite easy, by judicious choice of which product functions to replace, to change the value of considerably. For example, if the $2p\sigma_A2p\sigma_B$ hydrogenic product function is replaced by the antisymmetrical product $\mathcal{A}2p\sigma_A2p\sigma_B$, then the contribution of these states to the $\mathcal{E}_2$ term to the London-van der Waals energy is doubled while the overlap terms, which will only appear in higher order, will eventually subtract off this extra factor of 2. Thus as in the case of charge-transfer states, results obtained by the inclusion of a limited number of antisymmetric functions and the truncation of the perturbation expansion after two terms cannot be accepted as satisfactory.

A procedure for simulating the continuum functions which appear in nonsymmetrical formulations of the electron-hydrogen scattering problems—and the removal of an awkward singularity—by using such antisymmetrized products has been given by Castillejo *et al.*,[26] who have noted the nonunique expansion coefficients, and has been discussed further by Burke and Schey[27] among others. The difficulties with such expansions have also been discussed by Herring in Sec. V of Ref. 7c, who points out, among other things, the interesting apparent ambiguities one obtains when the wave functions are expanded about a third point in space at which there is no nucleus whatsoever.

## V. PERTURBATION EQUATIONS

Ever since the early work of Eisenschitz and London,[1] it has been of interest[2c,3,16,17] to obtain a hierarchy of perturbation-theoretic equations which can treat the problem of weakly interacting atoms; it was the inability to find such a set of equations that led to the expansion method of Sec. II and its predecessors[8–10]. Recall that most of the calculations on cohesive energies of solids were restricted to determining the expectation value of $H$ over the zeroth-order antisymmetrized wave function.[2c]

In actual fact one can write down such a procedure with little difficulty once one realizes that the perturbation corrections to the wave functions need not be explicitly antisymmetric as in the London-Eisenschitz-van der Avoird expansion. Thus, if we use the notation of Sec. II, with $\Psi_0$ defined by (3) and $H_0$ and $V$ defined by (10) and (11), we can write

$$N\mathcal{A}(H_0+\lambda V)A_0B_0\cdots+(H_0+\lambda V)(\lambda\Psi_1+\lambda^2\Psi_2+\cdots)$$
$$=(\epsilon_0+\lambda\epsilon_1+\cdots)(\Psi_0+\lambda\Psi_1+\cdots), \quad (44)$$

which coincides with the Schrödinger equation for our problem when the smallness parameter $\lambda=1$ for which $\Psi$ and $\epsilon$ are given by the power-series expansions in $\lambda$. The equations, order by order in $\lambda$, are

$$H_0A_0B_0\cdots=\epsilon_0A_0B_0\cdots, \quad (45a)$$

$$(H_0-\epsilon_0)\Psi_1=N\mathcal{A}(\epsilon_1-V)A_0B_0\cdots, \quad (45b)$$

$$(H_0-\epsilon_0)\Psi_2=\epsilon_2\Psi_0+(\epsilon_1-V)\Psi_1,\ \text{etc.}, \quad (45c)$$

where the constants $\epsilon_1$, $\epsilon_2$, etc., are determined by multiplying the respective equations on the left by $A_0B_0\cdots$. Note that whereas $\Psi_0$ is antisymmetric in an obvious way, the fact that $\Psi_1$ and $\Psi_2$ are actually antisymmetric must be demonstrated, since the Eisenschitz-London expansion of

$$\Psi_1=\sum c_n\mathcal{A}\Psi_n \quad (46)$$

is not possible due to the presence of the nonsymmetric operator $H_0$.

To illustrate the behavior of Eqs. (45) we write out the first-order equation for two hydrogen atoms with

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[25] By orthogonalizing the charge-transfer state to the non-charge-transfer state along the lines of the example given in this section, the energy contribution is reduced to about 20% of the original value. Note, however, that in this example the states are antisymmetrized functions, and not product functions as assumed in the text.

[26] L. Castillejo, I. C. Percival, and M. J. Seaton, Proc. Roy. Soc. (London) **A254**, 259 (1959).

[27] P. G. Burke and H. M. Schey, Phys. Rev. **126**, 147 (1962).

$\Psi_0^{S,T}$ of (18) and $\epsilon_0 = 2E_0$. Thus we have

$$(H_0-\epsilon_0)\Psi_1^{S,T}=(1\pm P)(\epsilon_1-V)\times(2\pm 2S_{00}^2)^{-1/2}a_0(1)b_0(2)\,, \tag{47}$$

with $P\equiv P_{12}$ and

$$\epsilon_1^{S,T}=(1\pm S_{00}^2)^{-1}[\langle a_0b_0|V|a_0b_0\rangle \pm\langle a_0b_0|V|b_0a_0\rangle] \tag{48}$$

as in the Heitler-London case. While $\Psi_1^{S,T}$ can be solved for directly or variationally,[28] the expansion in the set of eigenfunctions (19) of $H_0$ enables examination of the symmetry of $\Psi_1^{S,T}$. Thus we write

$$\psi_1^{S,T}=\sum_{ij}{}' c_{ij}^{S,T}a_i(1)b_j(2)\,, \tag{49a}$$

whence

$$c_{ij}^{S,T}=(2\pm 2S_{00}^2)^{-1/2}\langle a_ib_j|(1\pm P)(V-\epsilon_1)|a_0b_0\rangle \times(2E_0-E_i-E_j)^{-1}. \tag{49b}$$

Now, the argument (although none was given by London and Eisenschitz) for expanding in terms of antisymmetrized functions (46) is apt to have been based on the supposition that these $\Psi_1^{S,T}$ do not have the proper symmetry since electron 1 seems to be located on $A$ and electron 2 on $B$. This supposition is false, however, and in fact $\Psi_1^S$ and $\Psi_1^T$ are, respectively, symmetric and antisymmetric spatial functions up to terms of higher order, as can be proven immediately by the same argument that showed Coulomb terms to equal exchange terms. This is done by writing

$$\begin{aligned}\pm P_{12}\Psi_1^{S,T}&=\pm(2\pm 2S_{00}^2)^{-1/2}\sum_{ij}{}' c_{ij}b_j(1)a_i(2)\\&=\pm(2\pm 2S_{00}^2)^{-1/2}\sum_{ij\neq 0}\;\sum_{klmn} S_{jk}S_{il}S_{jm}S_{in}(2E_0-E_i-E_j)^{-1}\\&\qquad\times\langle b_na_m|(1\pm P)(V-\epsilon_1)|a_0b_0\rangle a_k(1)b_l(2)\\&=(2\pm 2S_{00}^2)^{-1/2}\sum_{kl\neq 0}\langle a_kb_l|(1\pm P)(V-\epsilon_1)|a_0b_0\rangle\\&\qquad\times(2E_0-E_k-E_l)^{-1}a_k(1)b_l(2)+\text{higher order terms}=\Psi_1^{S,T}.\end{aligned} \tag{50}$$

The perturbation theory is therefore seen to lead to no inconsistencies and the hierarchy of equations can be used to find the singlet and triplet wave functions and energies to any desired degree of accuracy. For example, the second-order energies are given by an expression which differs from (21) only by terms of higher order (which are partially summed in the secular-equation procedure) and the exchange energy can be determined by an expression similar to (37) or (40). When the equations are solved variationally the Löwdin-Shull expansion can, of course, be used without the ambiguities referred to in Sec. IV.

It is interesting to note the resemblance between these equations and the equations of the nonsymmetrical perturbation procedure of Hirschfelder and Silbey. For the example of $H_2$, these authors would try to solve for functions $A^*$ and $B^*$, respectively, the sum and the difference of the non-normalized $\Psi^S$ and $\Psi^T$, in a perturbation expansion with

$$A_0^*=a_0(1)b_0(2)$$

and

$$B_0^*=b_0(1)a_0(2)=PA_0^*.$$

They then obtain an equation for $A_1^*$,

$$(H_0-\epsilon_0)A_1^*=(\tfrac{1}{2}\epsilon_1^+-V)A_0^*+\tfrac{1}{2}\epsilon_1^-B_0^* \tag{51}$$

where $\epsilon_1^+$, $\epsilon_1^-$ are the sum and difference of $\epsilon_1^S$ and $\epsilon_1^T$ and a similar equation for $B_1^*\equiv PA_1^*$ which can be obtained by multiplying (51) on the left by $P$. The function $A_1^*$ is then essentially the same as the sum of $\Psi_1^S$ and $\Psi_1^T$ of (47), but $B_1^*$ is not the same as the difference in these functions as $PH_0\neq H_0$. In other words,

$$\Psi_1^S-\Psi_1^T\neq P(\Psi_1^S+\Psi_1^T).$$

Since the two equations for $A_1^*$ and $B_1^*=PA_1^*$ are not sufficient to define $\epsilon_1^S$ and $\epsilon_1^T$—the determinant of the coefficients vanishes—Hirschfelder and Silbey have argued that an additional condition,

$$\langle B_0^*|H_0-\epsilon_0|A_1^*\rangle=0\,, \tag{52}$$

must be satisfied. We find it extremely suggestive that in our expansion this condition (52) is automatically satisfied, and we wonder whether, in fact, the expansion procedure defined by (44) and (45) when the perturbation equations are added and subtracted order by order is not the one sought after by these authors rather than the one they have actually used.

It was hoped that the comparison of the explicit expression for the second-order energy[24] of the nonsymmetrical wave function with that of the singlet energy in the scheme discussed here would shed some light on the ability of the expansion of the former to converge to the correct singlet or triplet energies. Similarly, it was hoped that the comparison of the corresponding wave functions would show the possibility of the convergence to a function of one symmetry or the other. However, the examinations of the symmetry of (50) show that when higher-order terms can be neglected the nonsymmetrical first-order wave function will only be the sum of the singlet and the triplet function and will not possess the proper symmetry. In other words, only for values of $R$ at which the second-order wave function is of importance can the perturbation expansion of the

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[28] J. I. Musher, Ann. Phys. (N. Y.) 32, 416 (1965).

nonsymmetrical wave function converge to a solution of a particular symmetry. This is, of course, what was in some sense expected, because at large $R$ the lowest singlet and triplet are virtually degenerate, so that the perturbation procedure has no way to pick out either of the two solutions. What we have still not succeeded in demonstrating explicitly is that at sufficiently small $R$ the procedure will converge correctly, even though it seems most reasonable to assume that will be the case. Of course, a direct solution of the secular equations using the compete set $\{a_i(1)b_j(2)\}$ ,all $i$, $j$, must pick out automatically the solutions of correct symmetry.

## VI. SUMMARY

The major portion of this paper has been devoted to a development leading to Eqs. (24) and (37) and their perturbative analogs of Sec. V for the interaction energy between weakly interacting systems. Although our interest has been for the most part directed toward this rather academic problem, whose solution has apparently eluded previous workers in the field, there are several places at which our discussion has touched upon points of real practical importance. We would like to summarize here the implications of our research for practical theoretical problems in molecular and solid-state physics without expanding the discussion to a comparison of literature calculations.

1. The inclusion of continuum states in a basis set—or linear combinations thereof—is of utmost importance since without them the interaction energy will be incorrect by a factor of 2. Thus, the use of a finite number of basis functions can lead to misleading results, e.g., convergence of a perturbation-theory sum in such a basis set can be deceptive.

2. The inclusion of charge-transfer states, or other states which are not good approximate eigenstates of the isolated system Hamiltonians, in a basis set will only lead to unambiguous results if the entire secular determinant is diagonalized, and not if it is to be solved merely to lowest order in a perturbation expansion.

3. If antisymmetrized functions are used for a finite number of elements of a basis set in a perturbation expansion, care must be exercised to orthogonalize the continuum functions to these functions, since otherwise there will be a large continuum contribution to the second-order energy which will be cancelled out by higher-order terms. It is probably better, therefore, to use this finite number of antisymmetrized states and leave out the continuum.

4. In general, exchange integrals cannot be neglected relative to Coulomb integrals since, in fact, the totality of the two contributions are equal.

5. The perturbation correction to the exchange energy, because of the fact that it is considerably smaller than the average energy correction to the same order, is particularly sensitive to the choice of basis functions and the type of perturbation procedure used. Before conclusions are made as to ferromagnetism or antiferromagnetism of a particular ionic configuration, the effect of the limited basis set, the use of pseudo-eigenfunctions and the other approximations generally made should be thoroughly investigated using an expression such as given by Eq. (40).

6. Since unambiguous second-order results in terms of an interatomic potential obtain only for an expansion in exact atomic wave functions, it is not meaningful to assume an orbital approximation for the atomic wave functions and describe the interaction between atoms as sums of Coulomb and exchange interatomic contributions.

7. The results of the present study indicate that repulsive exponential terms, as in Eq. (30), occur in the exact expansion for the van der Waals attractive energy and are of importance at all values of $R$, contrary to common belief. Thus when attempts are made to fit experimental interatomic interaction curves, in the attractive region, with paramaterized expressions going beyond the $R^{-6}$ term, exponential terms should be included as well as the higher inverse powers of $R$. This shows that corrections to the simple $R^{-6}$ law are apt to be exceedingly complex.