TABLE IV (*continued*)

	Pr III	Pr III	Pr III	Nd^{3+} in $LaCl_3$	Er^{3+} in $LaCl_3$
a_{11}		317 ±105	340 ± 95	355 ±240	[0]
a_c		-1.0 ± 0.7	-1.1 ± 0.7	[0]	[0]
σ	31 cm^{-1}	11 cm^{-1}	11 cm^{-1}	7 cm^{-1}	18 cm^{-1}
No. of levels	40	40	40	22	20
No. of parameters	14	27	25	17	14
Largest deviation	74 cm^{-1}	17 cm^{-1}	18 cm^{-1}	9 cm^{-1}	23 cm^{-1}

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Accurate Atomic and Molecular Wave Functions Without Exchange

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A perturbation-theoretic procedure is developed for obtaining the spatial function Φ_0 for the many-electron problem, from which the total wave function can be projected by the relation $\Psi = \sum_i \tilde{D}_{i0}(r) D_{i0}(\sigma) \Phi_0(r) \chi_0(\sigma)$. This function is expanded in a perturbation series in which the $\Phi_0{}^0$ contains a sufficient set of pair symmetries of Φ_0 itself, such as in the Hartree nonantisymmetrized wave function for closed-shell atoms. When the expansion converges, the remaining symmetries are introduced exactly. The energy eigenvalue does not contain the usual "exchange" terms, since the zeroth-order Hamiltonian, unlike the Hartree-Fock H_0, has no degeneracies. Applications to interaction energies in molecular crystals and asymmetric wave functions are discussed briefly.

I. INTRODUCTION

The exact wave function for a many-electron system can be written as the sum of products of spatial functions with spin functions.[1] In this paper a perturbation expansion for a single one of these spatial functions is derived. The remaining spatial functions and hence the exact wave function can be obtained directly from this single function by utilizing the symmetry properties of these functions under the operations of the permutation group for the N electrons.[1,2] The spatial function solved for here possesses complicated symmetry properties except with respect to a small number of permutations under which, for closed-shell systems, it is symmetric. It is argued that the procedure can only be applied when the zeroth-order spatial wave function is a nondegenerate eigenfunction of the zeroth-order Hamiltonian. This requires that the zeroth-order Hamiltonian possess *only* the simple symmetries of the spatial function, i.e., for closed-shell systems it is symmetric under a certain set of permutations but *not* symmetric under any others. Such a condition is satisfied, for example, by the Hartree Hamiltonian, in which each electron "sees" the effective field of all other electrons, but is not satisfied by the Hartree-Fock Hamiltonian in which all electrons formally "see" the *same* field even though the self-interaction is subtracted off by the exchange term. The present procedure has all the usual problems of convergence; and in addition, it has the problem that the higher-order corrections to the spatial function have to correct for the fact that the zeroth-order function does not have *all* the necessary transformation properties, although it does have *sufficient* symmetry so that there are no other functions belonging to the same representation to which it can converge. Thus the likelihood of convergence to an undesired solution, which must belong to a different representation and hence will give a null antisymmetric wave function, is actually minimal. For example, since Hartree orbitals are close to Hartree-Fock orbitals, the first-order energies and zeroth-order charge distributions are similar; and the present Hartree procedure should have convergence properties similar to those of Hartree-Fock perturbation theory.[3-5] The formulas which are derived from the present theory are rather simple, and we believe that the higher-order contributions are easier to calculate than the corresponding terms for Hartree-Fock and other many-electron perturbation theories.[3-6]

The idea of calculating "spin-free" parts of the wave function has been dealt with at length by Matsen and co-workers,[7] and these studies, along with recent work of Goddard,[8] Hirschfelder and Silbey,[9] Claverie,[10] and Musher[11] can be considered as precedents for the discussion given here.

In the next section we present the general argument and describe the application to two types of problems: the calculation of atomic (and molecular) wave functions and the calculation of interatomic interaction energies. In Sec. III we discuss briefly the possibility of using a zeroth-order wave function which does not have the sufficient pair symmetry of the total spatial wave function; and in the two appendices we present some details of the group theory and the explicit application to the lithium atom.

II. THEORY

The total Hamiltonian H of a many-electron system must be symmetric under the permutation of all pairs of electron indices, i.e.,

$$[H, P_{ij}] = 0 \quad \text{all } i, j, \tag{1}$$

where P_{ij} permutes the indices of electrons i and j. If H is also independent of spin so that

$$[H, S_i] = 0 \quad \text{all } i, \tag{2}$$

then it is well known that each eigenfunction Ψ of the Schrödinger equation

$$(H-E)\Psi(r,\sigma) = 0, \tag{3}$$

which is antisymmetric under the permutations P_{ij}, can be written in terms of a set of orthonormal spin functions $\chi_i(\sigma)$ as

$$\Psi(r,\sigma) = \textstyle\sum_i \Phi_i(r)\chi_i(\sigma). \tag{4}$$

The set of spin functions $\chi_i(\sigma)$ make up the manifold of eigenfunctions of total S^2 of appropriate eigenvalues S and S_z; and as they provide a basis for an irreducible representation of the permutation group, there is an operation D_{ji} which takes the function χ_i into the function χ_j. Similarly, the set of spatial functions $\Phi_i(r)$ provide a basis for the conjugate irreducible representation of the permutation group, and there is an operator $\tilde{D}_{ij}$ which takes the function Φ_i into Φ_j, so that each totally antisymmetric $\Psi(r,\sigma)$ can be written as[2]

$$\Psi(r,\sigma) = \textstyle\sum_i \tilde{D}_{i0}(r) D_{i0}(\sigma)\Phi_0(r)\chi_0(\sigma). \tag{5}$$

Because the D's assure that Ψ is an antisymmetric function of all the electrons, this expression can also be written as (unnormalized)

$$\Psi(r,\sigma) = \mathcal{A}\Phi_0(r)\chi_0(\sigma), \tag{6}$$

where $\mathcal{A}$ is the usual antisymmetrizing operator.

From this argument it is easy to see (and is perhaps well-known) that each Φ_i, and hence Φ_0, is an eigenfunction of H, satisfying

$$(H-E)\Phi_0 = 0, \tag{7}$$

so that this single function contains *all* the necessary information about the wave function. Thus not only is the energy determined by the solution to (7), but the expectation value of any symmetric operator A, which commutes with S^2, reduces to

$$\frac{\langle\Psi|A|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\sum_i\langle\Phi_i|A|\Phi_i\rangle}{\sum_i\langle\Phi_i|\Phi_i\rangle} = \langle\Phi_0|A|\Phi_0\rangle; \tag{8}$$

and the second-order spin-independent properties, such as the electric polarizability, can be obtained from a calculation of Φ_0 as

$$E_2 = \frac{\langle\Psi|H_1|\Psi_1\rangle}{\langle\Psi|\Psi\rangle} = \frac{\sum_i\langle\Phi_i|H_1|\Phi_i^{(1)}\rangle}{\sum_i\langle\Phi_i|\Phi_i\rangle}$$

$$= \langle\Phi_0|H_1|\Phi_0^{(1)}\rangle. \tag{9}$$

Here H_1 is the perturbation due to the electric field, and $\Phi_0^{(1)}$ is the first-order perturbed function, the solution to

$$(H-E)\Phi_0^{(1)} = -H_1\Phi_0, \tag{10}$$

assuming for simplicity that $E_1 = 0$.

For each problem of interest, it is only necessary to choose a χ_0 suitable for the problem to determine the symmetries of the Φ_0 and then to choose an approximation Φ_0^0 to act as the first term in a perturbation expansion

$$\Phi_0(\lambda) = \Phi_0^0 + \lambda\Phi_0^1 + \cdots, \tag{11}$$

which should converge to Φ_0 for $\lambda = 1$, and its eigenvalue E_0 such that

$$E(\lambda) = E_0 + \lambda E_1 + \cdots, \tag{12}$$

which should converge to E for $\lambda=1$. The $\Phi_0{}^0$ must be a *nondegenerate* eigenfunction of some H_0, so that the perturbation theory equations for Φ_0 are

$$(H_0-E_0)\Phi_0{}^0=0, \tag{13a}$$

$$(H_0-E_0)\Phi_0{}^1=(E_1-H_1)\Phi_0. \tag{13b}$$

Here $H(\lambda)$, which coincides with the true H at $\lambda=1$, is given by

$$H(\lambda)=H_0+\lambda H_1. \tag{14}$$

The fact that $\Phi_0{}^0$ must be nondegenerate in the present treatment places an important restriction on H_0, and in particular excludes the Hartree-Fock or any separable[6] H_0 with

$$H_0=\sum h_0(i) \tag{15}$$

from being used in this scheme. At the same time it virtually obliges the H_0 to be something like the Hartree Hamiltonian—having a different operator for each orbital in an independent-particle scheme. All of this will be further discussed below.

A. Atoms

Consider now an atom (or molecule) containing N electrons of total spin $S=0$. It can be seen that the spin function

$$\chi_0=[\alpha(1)\beta(2)-\beta(1)\alpha(2)][\alpha(3)\beta(4)-\beta(3)\alpha(4)] \cdots [\alpha(N-1)\beta(N)-\beta(N-1)\alpha(N)], \tag{16}$$

which is pairwise-antisymmetric, satisfying

$$P_{n,n+1}\chi_0=-\chi_0, \quad n \text{ odd}, \tag{17}$$

is an eigenfunction of S^2 and an allowed χ_0, since the remaining orthogonal χ_i can be generated by the operations D_{i0}. The corresponding Φ_0 must have the symmetries

$$P_{n,n+1}\Phi_0=\Phi_0, \quad n \text{ odd}, \tag{18}$$

and in addition, must have the other, more complex symmetries, which enable it to transform as the appropriate row of the irreducible representation of the permutation group. Note that there will be several eigenfunctions of H having the symmetry of (18), only one of which has the desired remaining symmetry. The judicious choice of $\Phi_0{}^0$ will insure convergence to the desired Φ_0, since the other solutions, belonging to Young tableaux of more than two columns, will be avoided by an application of the noncrossing rule and a generalization of Hund's rule.

Generally, however, we have an idea of the type of solution desired. Thus in a ground-state singlet atom or molecule we know that the wave function can be approximately described as containing pairs of electrons in individual atomic or molecular orbitals. Thus a zeroth-order function for a perturbative solution to Φ_0 can be taken as

$$\Phi_0{}^0=a(1)a(2)b(3)b(4)\cdots v(N-1)v(N). \tag{19}$$

Although this $\Phi_0{}^0$ possesses the symmetries of (18), it does not possess the remaining symmetries as indicated in Appendix A. If, however, the perturbation expansion for Φ_0 converges, then it converges to an exact solution which possesses all the symmetries or transformation properties and for which, of necessity, the Φ_i also possess the appropriate symmetries and are solutions to the Schrödinger equation. Perturbation theory, if it converges, must converge to an exact solution, since there are (from the rules for constructing Young tableaux), in general, no degenerate solutions possessing all the same pair symmetry. Notice that, of course, the symmetries of $\Phi_0{}^0$ can never be lost in this perturbation scheme, which requires that the solution to which $\Phi_0{}^0$ converges possess one of a limited number of symmetries. The solution obtained actually possesses the symmetry necessary to give a wave function by (4), as discussed below.

The approximate energy of $\Phi_0{}^0$ is given schematically, in terms of the total Hamiltonian H and its one- and two-electron parts, f and g, by

$$E_0+E_1=\langle\Phi_0{}^0|H|\Phi_0{}^0\rangle =\sum_i\langle i|f|i\rangle+\sum_{i<j}\langle ij|g|ij\rangle \tag{20}$$

using notation parallel to Slater's.[12] Thus the usual "exchange energy" does not appear explicitly in the expectation value of H, and will not appear linearly in higher orders of perturbation theory, so that the present procedure provides accurate wave functions and energies without "exchange" effects. Notice, however, that it is not consistent with the present procedure to calculate a Ψ_0 by antisymmetrizing $\Phi_0{}^0\chi_0$ and then take the expectation value of H, which would introduce exchange integrals. In fact, the only reason $\langle\Phi_0{}^0|H|\Phi_0{}^0\rangle$ differ from $\langle\Psi_0|H|\Psi_0\rangle$ is that the $\Phi_i{}^0$ do not have the correct symmetry of Φ_i itself. This is discussed explicitly in Appendix B for the case of the Li atom so that the behavior of these approximate functions can be better appreciated.

The function $\Phi_0{}^0$ can be guessed at, and the appropriate H_0 constructed from it, for example, by using the Sternheimer procedure,[13] or conversely one can choose H_0 and compute the functions $\Phi_0{}^0$. In either case, the operator H_0 must possess the symmetry

$$P_{n,n+1}H_0=H_0, \quad n \text{ odd}; \tag{21}$$

and it is allowed no other—such as, for example, exists in the totally symmetric Hartree-Fock Hamiltonian, for which

$$P_{n,m}H_0{}^{\mathrm{HF}}=H_0{}^{\mathrm{HF}}, \text{ all } n, m. \tag{22}$$

This is so because, if H_0 were totally symmetric, then there would be an eigenfunction of H_0 degenerate with $\Phi_0{}^0$, such as

$$a(1)b(2)a(3)b(4)\cdots v(N-1)v(N),$$

which would mix with $\Phi_0{}^0$ in zeroth order so that the perturbation theoretic procedure (13) could not be applied without modification. If the $\Phi_0{}^0$ are chosen first—the orbitals could even be the Hartree-Fock orbitals—and the resulting H_0 assumed to contain no integral operators, then such a condition is automatically satisfied except for states of different m_l that are exact eigenfunctions of l_z, which can be taken care of in a variety of ways, including actually symmetrizing them. On the other hand, the unrestricted Hartree Hamiltonian, i.e., that is not restricted to be centrosymmetric for atoms, and for which each orbital is an eigenfunction of a different Hamiltonian, is ideally suited for this procedure. Although the Hartree Hamiltonian is by no means the unique Hamiltonian that can be utilized in the present scheme, it is sufficiently well-known to prompt us to give the specific example of the Be atom, based on the Hartree function $\Phi_0{}^0$, and then compare it with the Hartree-Fock solution.

Let $\Phi_0{}^0$ be

$$\Phi_0{}^0 = a(1)a(2)b(1)b(2), \tag{23}$$

where the orbital a and b are the lowest and second-lowest normalized eigenfunctions, respectively, ($a \equiv a_1$ or $1s$, and $b \equiv b_2$ or $2s$) of the equations

$$h_a(i)a_k(i) = \epsilon_k{}^a a_k(i) \tag{24a}$$

and $$h_b(i)b_k(i) = \epsilon_k{}^b b_k(i) \tag{24b}$$

with the operators defined by[14]

$$h_a = -\tfrac{1}{2}\nabla^2 - \frac{4}{r} + 2[-b\,|\,-b] + [-a\,|\,-a] \tag{25a}$$

and

$$h_b = -\tfrac{1}{2}\nabla^2 - \frac{4}{r} + 2[-a\,|\,-a] + [-b\,|\,-b]. \tag{25b}$$

Thus $\Phi_0{}^0$ is the Hartree or wave function (self-consistent field without exchange), and is an eigenfunction of the zeroth-order Hamiltonian

$$H_0 = h_a(1) + h_a(2) + h_b(3) + h_b(4) \tag{26}$$

which possesses the symmetry of (21) above and no other. The zeroth-order energy eigenvalue is

$$E_0 = 2\epsilon_1{}^a + 2\epsilon_2{}^b; \tag{27}$$

and the first-order correction to the energy, E_1, is given by

$$\begin{aligned} E_1 = \langle \Phi_0{}^0 | H_1 | \Phi_0{}^0 \rangle &= \langle \Phi_0{}^0 | \sum_{i<j} \frac{1}{r_{ij}} - \sum_i V(i) | \Phi_0{}^0 \rangle \\ &\equiv \langle \Phi_0{}^0 | \sum g(ij) | \Phi_0{}^0 \rangle. \end{aligned} \tag{28}$$

This expression contains no exchange integrals. The $V(i)$, which are divided up symmetrically to give the

$$g(ij) = 1/r_{ij} - \tfrac{1}{3}[V(i) + V(j)] \tag{29a}$$

different for each (i,j), are defined as

$$V(i) = 2[-b\,|\,-b] + [-a\,|\,-a] \quad i = 1, 2 \tag{30a}$$

and

$$V(i) = 2[-a\,|\,-a] + [-b\,|\,-b] \quad i = 3, 4. \tag{30b}$$

A definition of a pair function $g'(ij)$ more closely analogous to the pair functions in the usual Hartree-Fock description[3] is

$$g'(ij) = 1/r_{ij} - V_j(i) - V_i(j), \tag{29b}$$

where $$V_j(i) = [-a\,|\,-a] \quad j = 1, 2, \tag{30c}$$

$$V_j(i) = [-b\,|\,-b] \quad j = 3, 4. \tag{30d}$$

The solution $\Phi_0{}^1$ of (13b) can be written as

$$\Phi_0{}^1 = \sum_{i<j} u_{ij}(ij)m(m)n(n), \tag{31}$$

where the orbitals m and n are the orbitals of $\Phi_0{}^0$ which are not i and j; the sum runs over the six distinct ij pairs, and each $u_{ij}(ij)$ is the solution to a two-electron inhomogeneous partial differential equation. Thus, e.g.

$$\begin{aligned} [h_a(1) + h_b(3) - \epsilon_1{}^a - \epsilon_2{}^b]u_{ab}(13) \\ = [k - g(13)]a(1)b(3) \end{aligned} \tag{32a}$$

with

$$k = \langle a(1)b(3)\,|\,g(13)\,|\,a(1)b(3)\rangle. \tag{32b}$$

The solution to this equation is unique, since the right-hand side is orthogonal to the single solution of the homogeneous equation $a(1)b(3)$ [there being no other degenerate eigenfunctions of the operator $h_a(1) + h_b(3)$], and the second-order energy is given by the relatively simple expression

$$E_2 = \langle \Phi_0{}^0 | [\sum g(ij) - E_1] | \sum u_{ij}(ij)m(m)n(n) \rangle, \tag{33}$$

in which again there are no exchange integrals of the usual type, but only sums and products of two- and three-electron terms.

It can be demonstrated that there are no contributions to E_2 due to single excitations, the analog of the Brillouin-Møller-Plesset theorem.[15] While the u_{ij} calculated from (32) with the $g(ij)$ of (29a) contain single excitations, their net effect vanishes identically. If the $g'(ij)$ of (29b) is used, the corresponding $u_{ij}{}'$ does not contain single excitations.

An "exact pair" in the sense of Sinanoğlu[3b] can be calculated from the implicit equation of the form

$$\begin{aligned} [h_a(1) + h_b(3) - \epsilon_1{}^a - \epsilon_2{}^b]u_{ab}{}^{(\infty)}(13) \\ = [k_\infty - g(13)][a(1)b(3) + u_{ab}{}^{(\infty)}(13)], \end{aligned} \tag{34a}$$

where

$$\begin{aligned} k_\infty = \langle a(1)b(3)\,|\,g(13)\,|\,a(1)b(3) + u_{ab}{}^{(\infty)}(13)\rangle \\ \times \{1 + \langle a(1)b(3)\,|\,u_{ab}{}^{(\infty)}(13)\rangle\}^{-1} \end{aligned} \tag{34b}$$

if higher-order corrections are desired.

The perturbation-theoretic expansion can be expected to converge, since the "Hartree energy"[16] $E_0 + E_1$ is a good approximation to the total energy — a recent calculation shows this to give 99% of the experimental nonrelativistic energy for the argon atom[16] — and since the orbitals and the orbital energies are very close to the Hartree-Fock orbitals and energies.[16] These latter are generally accepted as being the "best possible" orbitals, although the convergence of the Hartree-Fock perturbation procedure has only recently been considered for the first time.[3-6]

In order to appreciate this point further, the similarity of the Hartree perturbation-theoretic procedure to the Hartree-Fock procedure should be noted. The Hartree-Fock orbitals a_{HF} and b_{HF} are both eigenfunctions of[14]

$$h_{\mathrm{HF}} = -\tfrac{1}{2}\nabla^2 - 4/r + 2\{[-a_{\mathrm{HF}} \,|\, -a_{\mathrm{HF}}] + [-b_{\mathrm{HF}} \,|\, -b_{\mathrm{HF}}]\} - \{[-a_{\mathrm{HF}} \,|\, a_{\mathrm{HF}}-] + [-b_{\mathrm{HF}} \,|\, b_{\mathrm{HF}}-]\} \tag{35}$$

with energies $\epsilon_{\mathrm{HF}}{}^{a}$ and $\epsilon_{\mathrm{HF}}{}^{b}$, respectively. The first-order Hartree-Fock wave function is given by[3-6]

$$\Psi_1{}^{\mathrm{HF}} = \mathfrak{A} \sum_{i<j} u_{ij}{}^{\mathrm{HF}}(ij)m(m)n(n)\xi(ijmn), \tag{36}$$

where $\xi(ijmn)$ is a spin function. The second-order energy is given by

$$E_2 = \langle \Psi_0 \,|\, [\sum g_{\mathrm{HF}}(ij) - E_1] \,|\, \mathfrak{A} \sum u_{ij}{}^{\mathrm{HF}} mn\xi \rangle \tag{37}$$

with the pair functions the solutions to pair-equations such as

$$[h_{\mathrm{HF}}(1) + h_{\mathrm{HF}}(3) - \epsilon_{\mathrm{HF}}{}^{a} - \epsilon_{\mathrm{HF}}{}^{b}]u_{ab}{}^{\mathrm{HF}}(13) = [k - g(13)]a_{\mathrm{HF}}(1)b_{\mathrm{HF}}(3) + k'b_{\mathrm{HF}}(1)a_{\mathrm{HF}}(3), \tag{38}$$

with k a Coulomb integral as in (32) and k' an exchange integral.[6] It can thus be seen that since the orbitals are similar, the pair functions $u_{ab}{}^{\mathrm{HF}}$ and u_{ab} will also be similar, the principal difference between Eqs. (38) and (32) being in the term $k'b_{\mathrm{HF}}(1)a_{\mathrm{HF}}(3)$ on the right-hand side of (38), which term is necessary because of the existence of two degenerate solutions of the inhomogeneous equation. It is precisely this degeneracy which serves to complicate the Hartree-Fock description and requires a perturbation treatment based on the total Ψ_0 instead of on the spatial function Φ_0 treated here. Furthermore, it is only because of this degeneracy that exchange integrals appear in the Hartree-Fock procedure—not only complicating the algebra, but being given a physical interpretation—whereas by (28) and (34) they never appear linearly in the strict Hartree procedure for closed-shell atoms and should therefore probably not be interpreted physically.

It is interesting to note also that the leading contributions to second-order properties, such as the electric polarizability, are given by the identical expressions[17] in both procedures

$$E_{02} = \sum_i \langle i \,|\, z \,|\, i_1 \rangle. \tag{39}$$

Here the perturbed orbitals i_1 for the Hartree-Fock and Hartree cases are solutions to the two equations

$$(h - \epsilon_i)i_1 = -zi, \tag{40}$$

where the h, ϵ_i, and i refer to the Hartree-Fock and Hartree orbitals, energies, and Hamiltonians, respectively. Thus despite most of the literature —which gives a term in the Hartree-Fock E_{02}

$$-\sum_{ij} \langle i \,|\, z \,|\, j \rangle \langle j \,|\, i_1 \rangle \tag{41}$$

which can be seen to vanish identically—there is no "orthogonalization" or "exchange effect" in the leading term in the Hartree-Fock polarizability, and both the Hartree and Hartree-Fock polarizabilities are given as sums over independently perturbed orbitals.

There is, however, one condition for convergence of the perturbation procedure for Φ_0, which, although it is usually satisfied and the Hamiltonian can probably always be modified to assure that it is satisfied, must nevertheless be noted. In the equation for $u_{ab}(13)$, the presence of a solution to the homogeneous equation which is nearly degenerate with $a(1)b(3)$ could make the series

$$a(1)b(3) + \lambda u_{ab}(13) + \lambda^2 u_{ab}{}^{(2)}(13) + \cdots \tag{42}$$

diverge. The major possibility for such a near degeneracy is the state $a_2(1)b_1(3)$ or the product of the 2*s* function calculated in the effective potential for determining the 1*s* function and the 1*s* function calculated in the effective potential for the 2*s* function. Substituting

$$u_{ab}(13) = \sum_{kl} \alpha_{kl} a_k(1) b_l(3) \tag{43}$$

into (32), we get the coefficient

$$\alpha_{21} = (\epsilon_1{}^{a} + \epsilon_2{}^{b} - \epsilon_2{}^{a} - \epsilon_1{}^{b})^{-1} \times \langle a_2(1)b_1(3) \,|\, 1/r_{13} \,|\, a_1(1)b_2(3) \rangle, \tag{44}$$

which must be less than 1 for the perturbation theory to converge. Since the Hartree and Hartree-Fock orbitals are very similar, we can assume that the differences between the operators h_a and h_b can be treated perturbatively, so that the orbitals a_2 and b_1 can be expanded as series whose leading terms are b_2 and a_1, respectively, i.e.,

$$a_2 = b_2 + c_2{}^{(1)} + \cdots \tag{45a}$$

and $b_1 = a_1 + b_1{}^{(1)} + \cdots$. (45b)

Thus it is found that the leading term of α_{21} is given by

$$\alpha_{21} = \{[aa \,|\, aa] + [bb \,|\, bb] - 2[ab \,|\, ab]\}^{-1}[ba \,|\, ab]; \tag{46}$$

and because of the typical magnitudes of the integrals involved, it can be seen that, except in unusual cases of accidental cancellation, α_{21} should indeed be small. Since any exact solution implicitly includes such functions as $a_2(1)b_1(3)$, and any limited variational solution will explicitly include them, these "exchange" integrals will appear in the total energy, although only quadratically in second order. It is precisely such terms which will make the appropriate Φ_0 have all the requisite symmetry [i.e., transform properly under the D's and not only satisfy (18)] even though $\Phi_0{}^0$ does not.

Finally it should be noted that, as with any perturbative scheme, this one is not guaranteed to converge to the particular state desired, the actual convergence being to some extent governed by the closeness of $E_0 + E_1$ to the eigenvalue of any state of the same symmetry. Here there is the further problem that H_0 and hence $\Phi_0{}^0$ does not have all the symmetry of H itself but only of the subset defined by (18) and (21). Thus there will be more than one eigenfunction of H possessing the symmetries of (18) with eigenvalue close to E_0+E_1. However, all such eigenfunctions other than the desired one, are degenerate with solutions containing "higher" pair symmetry, such as the one which is symmetric under all P_{nm}. By a generalization of Hund's rule, the spatial eigenfunctions of higher symmetry will be of higher energy than the one of interest, so that a noncrossing rule assures that we obtain the desired Φ_0. There will be cases in which this argument fails. However, the undesired solutions are easily detected since the function $\mathcal{A}\Phi_0\chi_0$ will then vanish. For example, in Be if the orbital b had significant overlap with the orbital a, then the $\Phi_0{}^0$ is not a good enough approximation to Φ_0 for a perturbative scheme to work, and must be modified appropriately. It should be noted that such convergence to an undesired state is also possible in the Hartree-Fock perturbation scheme of Eqs. (35)–(38), in which case the total Ψ obtained goes to zero.

The discussion so far has dealt with systems of N electrons of total spin $S=0$ which can be described in terms of a spatial function Φ_0 for which all electrons are paired, in the sense of there being two electrons per atomic orbital in the zeroth-order function $\Phi_0{}^0$. Such is, of course, not the only possible singlet function; the next simplest is one in which all but two electrons are paired, the remaining two being in different spatial orbitals; and the zeroth-order function $\Phi_0{}^0$ can be given by

$$\Phi_0{}^0=a(1)a(2)b(3)b(4)\cdots[v(N-1)w(N)+w(N-1)v(N)], \tag{47}$$

with the perturbation procedure being the same as for closed shells. Other singlet systems can be constructed analogously.

Consider now the simplest doublet $S=S_z=\frac{1}{2}$, in which all but one of the electrons are paired. For this doublet, suitable χ_0 and $\Phi_0{}^0$ are

$$\chi_0=[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\times[\alpha(3)\beta(4)-\beta(3)\alpha(4)]\cdots\alpha(N), \tag{48}$$

and

$$\Phi_0{}^0=a(1)a(2)b(3)b(4)\cdots v(N). \tag{49}$$

An example of such a state is the ground state of Li which is discussed in Appendix B.

As a last example, consider the simplest triplet $S=1$, $S_z=0$ of an N-electron system for which all but two electrons are paired. The functions χ_0 and $\Phi_0{}^0$ can be written as

$$\chi_0=[\alpha(1)\beta(2)-\beta(1)\alpha(2)][\alpha(3)\beta(4)-\beta(3)\alpha(4)]\cdots[\alpha(N-1)\beta(N)+\beta(N-1)\alpha(N)] \tag{50}$$

and

$$\Phi_0{}^0=a(1)a(2)b(3)b(4)\cdots[v(N-1)w(N)-w(N-1)v(N)]. \tag{51}$$

Notice that if the orbitals v and w are eigenfunctions of the same one-electron operator, this $\Phi_0{}^0$ and the spatial singlet given by (19) have equal zeroth-order energies whose degeneracy is only split in first order. This corresponds to the well-known fact that two electrons both in open shells form nearly degenerate singlets and triplets as in the various ${}^1S$ and ${}^3S$ of ($1sns$) excited helium atoms.

B. Molecular Crystals

The theoretical description of weakly interacting atoms and molecules has been beset with problems and complications, the most famous of which is the orthogonality catastrophe.[18] These have been reviewed to some extent by Musher[11a] and have been dealt with in part recently by Musher and Amos.[19] The arguments presented here provide a simple and immediate resolution of an important problem in the treatment of intermolecular interaction: how to take into account the indistinguishability of the electrons while preserving the isolated molecule wave function in zeroth order.

Consider, for example, a system consisting of a number of ground-state singlet atoms I, II, ⋯ whose Φ_0's are denoted by $\Phi_0(\text{I})$, $\Phi_0(\text{II})$, ..., and whose $\Phi_0{}^0$'s are of the form

$$\Phi_0{}^0(\text{I})=a_{\text{I}}(1)a_{\text{I}}(2)b_{\text{I}}(3)b_{\text{I}}(4)\ldots, \tag{52}$$

where electrons 1 through N are associated with I, electrons $N+1$ through $2N$ with II, etc., and where χ_0's are as in (16). Thus the total wave function for the problem can be written as

$$\Psi_0(\text{I},\text{II},\ldots)=\textstyle\sum_i\Phi_i(\text{I},\text{II},\ldots)\chi_i(\text{I},\text{II},\ldots), \tag{53}$$

with

$$\chi_0(\text{I},\text{II},\ldots)=\chi_0(\text{I})\chi_0(\text{II})\cdots, \tag{54a}$$

$$\chi_0(\text{I},\text{II},\ldots)=\Phi_0{}^0+\Phi_0{}^1+\cdots, \tag{54b}$$

and with $\Phi_0{}^0$ given by either the product of *exact* atomic functions

$$\Phi_0{}^0=\Phi_0(\text{I})\Phi_0(\text{II})\cdots \tag{55a}$$

or the product of approximate atomic functions

$$\Phi_0{}^0=\Phi_0{}^0(\text{I})\Phi_0{}^0(\text{II})\cdots. \tag{55b}$$

Using the latter choice, the total energy can be found by performing perturbation theory with

$$H_0=H_{\text{I}}(1,\ldots,N)+H_{\text{II}}(N+1,\ldots,2N)+\cdots, \tag{56}$$

and

$$\begin{aligned}H_1&=V_{\text{I}}(1,\ldots,N)+V_{\text{II}}(N+1,\ldots,2N)+\cdots\\&\quad+V_{\text{I, II}}(1,\ldots,2N)\\&\quad+V_{\text{I, III}}(1,\ldots,N,2N+1,\ldots,3N)+\cdots\\&\equiv H_1(\text{atomic})+H_1(\text{interatomic}).\end{aligned} \tag{57}$$

This operation is similar to a previous description by Musher,[20] in which the respective $\sum\Phi_i(\text{I})\chi_i(\text{I})$ were written as determinantal functions, and the exact nature of the result was not fully appreciated. As H_1 is divided into atomic and interatomic parts, the energy corrections can be classified as atomic and interatomic, the latter arising from mixed interatomic and atomic interactions.

A good approximation to the energy of spherical atoms in a crystal will thus be of the form[20]

$$E=(E_{\mathrm{I}}+E_{\mathrm{I}}^{1}+\cdots)+(E_{\mathrm{II}}^{0}+E_{\mathrm{II}}^{1}+\cdots)$$
$$+E_{\mathrm{I,II}}^{2}+E_{\mathrm{I,III}}^{2}+\cdots. \qquad (58)$$

with the $E_{\mathrm{I,II}}^{2}$ the London-van der Waals energy, roughly proportional to $R_{\mathrm{I,II}}^{-6}$. Since the Born-Oppenheimer Hamiltonians H_{I}, H_{II}, etc., are completely different from each other (the atoms being located in different parts of space), there is likely to be no problem about the convergence of the interatomic energy expansion. It is significant to note that there are no orthogonality integrals and no antisymmetrizing or exchange effects contributing to the interaction energy. Thus, as is eminently reasonable, the addition of an atom to a many-atom system makes *no* contribution to the interaction energy in zeroth order, where, by lack of degeneracy in the individual atoms, the possibility of collective behavior must be considered negligible. The present argument also serves to justify the usual treatment of single excitations in crystals (excitons), for which, however, it is not correct to say that exchange is neglected, since it is completely correct within a perturbation-theoretic framework to take as the energy the expectation of the Hamiltonian over the usual nonantisymmetrized exciton wave function.

Notice that when the interacting atoms or molecules are not closed-shell systems, in order for this procedure to hold, the unpaired electrons must be combined into spin eigenfunctions, and the methods of Musher and Amos[19] may be applied to these electrons, although not to the inner-shell electrons. In the next section it will be pointed out that in certain circumstances one might obtain useful results using a truly nonsymmetric Φ_0^0, i.e., one which does not satisfy (18) or its analogs, so that the procedure of Ref. 19 can be avoided.

III. NONSYMMETRIC Φ_0^0

In the discussion of the previous section it was always assumed that the zeroth-order approximate function Φ_0^0 had the sufficient pair symmetry of the exact function Φ_0, such as given by (18). This, of course, is not necessary and it is certainly, in principle, possible to expand Φ_0 in terms of a perturbation expansion which does not have the sufficient pair symmetry, although it is not possible to ascertain beforehand whether the expansion converges and whether it converges to the desired solution.

As a first example, consider a singlet-state atom with two electrons in open shells whose Φ_0 has the symmetry of (18). Instead of taking Φ_0^0 as (19), we take it as

$$\Phi_0^0=a(1)a(2)b(3)b(4)\cdots v(N-1)w(N), \qquad (59)$$

which does not possess any symmetry under $P_{N-1,N}$. The zeroth-order Hamiltonian H_0 can also not be symmetric under $P_{N-1,N}$, for otherwise there would be another degenerate function which would mix to zeroth order. If the perturbation expansion of (11), using this H_0 and Φ_0^0, converges to a solution of the spinless Schrödinger equation, then it must converge to a solution which either is symmetric or antisymmetric under $P_{N-1,N}$ or belongs to a Young tableau with more than two columns. This is so because all spatial eigenfunctions of H possess certain symmetries; and since Φ_0^0 is restricted to be symmetric under $P_{n,n+1}$ (odd $n<N-1$) the only remaining choice in pair symmetry for Φ_0^0 is that under $P_{N-1,N}$. There is no definite indication, however, as to which of these solutions the perturbation expansion will converge, if it actually converges. If, however, it converges to a solution which is antisymmetric or belongs to one of the more complex symmetries, the wave function defined by $\Psi=\mathcal{A}\Phi_0\chi_0$ vanishes, so that one can determine whether the desired function has been indeed obtained. While the utility of this procedure is not evident, the point made here is merely that there is no explicit objection to using such nonsymmetric functions in a perturbation expansion. When both solutions are required, then the methods of the previous section, in which a true exchange integral appears, are best used.

Notice, of course, that because of the symmetry of both H_0 and Φ_0^0 under all the remaining $P_{n,n+1}$ (n odd), the perturbation expansion *cannot* change the symmetry behavior under these permutations; but because of the lack of symmetry with respect to $P_{N-1,N}$, the perturbation expansion *can* produce the correct symmetry that was not included in Φ_0^0. This method can be considered the inverse of symmetry breaking, in that one starts with a broken symmetry in order to approach the exact symmetry perturbatively.

As a second example, and one whose two-electron analog, the hydrogen molecule, has been given previously,[11b] consider a closed-shell singlet, diatomic molecule whose Φ_0^0 would ordinarily be given by (19). If, however, for some reason it proved desirable to take Φ_0^0 as

$$\Phi_0^0=a(1)a(2)b(1)b(2)\cdots A(N-1)B(N), \qquad (60)$$

where A and B are the valence "bonding" atomic orbitals of the two atoms, respectively, molecular orbital description would have taken $v=A+B$ in (19), and the valence-bond description would have taken the sum $A(N-1)B(N)+B(N-1)A(N)$ as in (47). If perturbation theory converges, however, and $\mathcal{A}\Phi_0\chi_0\neq 0$, it will converge to the symmetric solution that one would have obtained from both the molecular-orbital (MO) and the valence-bond (VB) Φ_0^0—assuming their convergence. If, of course, there is essentially no bonding (for example, if the atoms are very far apart), then the symmetric and antisymmetric solutions will be very nearly degenerate, and the perturbation expansion will not be able to pick out either of them,[9,20] and can oscillate rather than converge. This, however, will not occur in chemical bonds where the "bonding" states are always several eV away from the "nonbonding" (MO) and "antibonding" (VB) states of opposite symmetry, as well as any other states of the same symmetry. Notice that such a procedure would not be useful if one conceived of the two pair functions as being built from the same atomic orbitals, as implied in simple MO theories. Thus for example, in the He$_2$ molecule both $1s_a(1)1s_b(2)$ and $1s_a(3)1s_b(4)$ would converge to the same state and not to two different ones; this result is necessary for Ψ not to vanish. Actually electrons 3 and 4 should be placed in a nonsymmetric linear combination, such as

$1s_a(3)2s_b(4)-2s_a(3)1s_b(4)$, in order to correspond to the doubly occupied antibonding state of He_2^{++} if the other electrons were absent.

The utility of these nonsymmetric wave functions, other than for the hydrogen molecule, is probably negligible, so that the point made here is a rather academic one. An example where a chemist might claim an advantage in using a nonsymmetric wave function is in benzene where the π electrons in $\Phi_0{}^0$ could be written as

$$\Phi_0{}^0(\pi)=A(1)B(2)C(3)D(4)E(5)F(6), \tag{61a}$$

although it is difficult to assess in advance what symmetry this will converge to and which χ_0 would be most suitable. It would be interesting to compare the expansion for benzene based on the usual molecular orbitals Φ_i,

$$\Phi_0{}^0(\pi)=\varphi_1(1)\varphi_1(2)\varphi_2(3)\varphi_2(4)\varphi_3(5)\varphi_3(6), \tag{61b}$$

with that based on electrons in diatomic molecular orbitals, i.e.,

$$\Phi_0{}^0(\pi)=(A+B)(1)(A+B)(2)(C+D)(3)\times(C+D)(4)(E+F)(5)(E+F)(6). \tag{61c}$$

As a last point it should be noted that the calculations of the magnetic susceptibility of the benzene molecule in the MO approximation follow in a straightforward way from the arguments given here (for pair-wise symmetric $\Phi_0{}^0$'s) and our previous discussion,[21] since the one-electron Sternheimer Hamiltonians can be constructed for each orbital independently.

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APPENDIX A: GROUP-THEORETICAL ARGUMENTS

The solutions of the N-electron Schrödinger equation which satisfy the Pauli principle for the case when the Hamiltonian is independent of spin may be written as[2]

$$\Psi=\sum_i\Phi_{[\alpha i]}(r)\chi_{[\tilde{\alpha}\tilde{i}]}(\sigma), \tag{A1}$$

where the $\Phi_{[\alpha i]}(r)$ is a function of the spatial coordinates of the N electrons and transforms like the ith row of the αth irreducible representation of the permutation group, S_N. The $\chi_{[\tilde{\alpha}\tilde{i}]}(\sigma)$ is a function of the spins of the N electrons which transforms like the conjugate row of the conjugate irreducible representation. In terms of standard Young diagrams (which label the rows of the irreducible representations) we have, for example, in S_3, that if the spatial part transforms like Fig. 1(a), then the spin part must transform like Fig. 1(b). The latter is symmetric under all permutations, while the former is antisymmetric under transpositions P_{ij}. It can be shown that for spins of $\frac{1}{2}$, the spin functions must transform like a Young diagram with at most two rows. This then implies that the spatial parts of the wave function must transform like a Young diagram with at most two columns in order to be an allowed eigenfunction, i.e., one which can satisfy the Pauli principle when put into a form such as (A1).

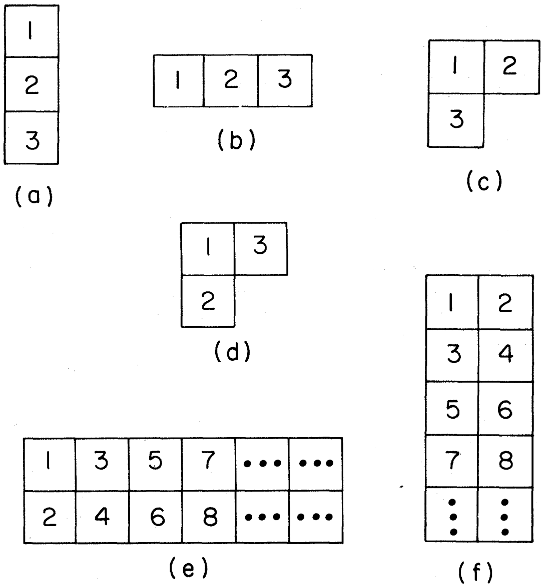

FIG. 1. Various Young tableaux used in the analysis.

The $\Phi_{[\alpha i]}(r)$ [or $\chi_{[\tilde{\alpha}\tilde{i}]}(\sigma)$] for different i are related to each other by projection operators[22] which take a function belonging to the ith row into one belonging to the jth row. Let us consider as an example the case of three electrons. The group S_3 has two one-dimensional representations and one two-dimensional representation. The one-dimensional representations are the totally symmetric (A_1) and the antisymmetric (A_2) representations whose projection operators are the symmetrizer and the antisymmetrizer, respectively. The two-dimensional representation (E) has the following projection operators associated with it:

$$D_{11}{}^{(E)}=\tfrac{1}{3}(I+P_{12}-\tfrac{1}{2}P_{23}-\tfrac{1}{2}P_{13}-\tfrac{1}{2}P_{132}-\tfrac{1}{2}P_{123}), \tag{A2}$$

$$D_{22}{}^{(E)}=\tfrac{1}{3}(I-P_{12}+\tfrac{1}{2}P_{23}+\tfrac{1}{2}P_{13}-\tfrac{1}{2}P_{132}-\tfrac{1}{2}P_{123}), \tag{A3}$$

$$D_{12}{}^{(E)}=(1/2\sqrt{3})(P_{23}-P_{13}+P_{132}-P_{123}), \tag{A4}$$

$$D_{21}{}^{(E)}=(1/2\sqrt{3})(P_{23}-P_{13}-P_{132}+P_{123}). \tag{A5}$$

If one operates on a function of the three electron coordinates with $D_{ii}{}^E$, a function transforming like the ith row is formed. If one operates on a function transforming like the ith row with $D_{ij}{}^E$, one produces a function transforming like the jth row. The projection operators have the following properties[22]:

$$D_{ij}{}^{(\alpha)}D_{kl}{}^{(\beta)}=\delta_{\alpha\beta}\delta_{il}D_{kj}{}^{(\alpha)}, \tag{A6}$$

$$\{D_{ij}{}^{(\alpha)}\}^{\dagger}=D_{ji}{}^{(\alpha)}. \tag{A7}$$

Starting with the spin function $\chi = \alpha(1)\beta(2)\alpha(3)$, we may form (unnormalized)

$$\chi_{22} = D_{22}^{(E)}\chi = \tfrac{1}{2}\{(\alpha_1\beta_2 - \beta_1\alpha_2)\alpha_3\}, \tag{A8}$$

$$\chi_{11} = D_{11}^{(E)}\chi = \tfrac{1}{6}\{\alpha_1\beta_2\alpha_3 + \beta_1\alpha_2\alpha_3 - 2\alpha_1\alpha_2\beta_3\}. \tag{A9}$$

One can easily verify that

$$D_{12}^{(E)}\chi_{11} = (1/2\sqrt{3})\{(\beta_1\alpha_2 - \alpha_1\beta_2)\alpha_3\}, \tag{A10}$$

that is, operating on a function transforming like the first row with D_{12}^{E} has produced a function transforming like the second row. The function χ_{11} transforms like the standard Young diagram in Fig. 1c, while the function χ_{22} transforms like Fig. 1d.

It can be shown, from the rules for constructing the matrix representation of the permutation groups, that if the numbers n and $n+1$ are in the same row (column) of a standard Young tableau, then the function transforming like this tableau is symmetric (antisymmetric) with respect to the permutation $P_{n,n+1}$. Hence, if a spin function transforms like the standard tableau in Fig. 1e, then the function is antisymmetric under the permutations $P_{12}, P_{34}, \cdots, P_{2n+1,2n+2}\cdots$. If this spin function were to be used in an expression such as (A1), then the orbital function which multiplies it would transform like Fig. 1f, that is, be symmetric under $P_{12}, P_{34}, \cdots, P_{2n+1,2n+2}$. The transformation properties under other permutations are more complicated. Operating on this function by another permutation produces a linear combination of partner functions (derived from the original function by projection operators of the form D_{ij}^{α}), with the particular linear combination given by the matrix representation of the particular permutation in question. For example, in the case of S_3 (see above):

$$P_{13}\chi_{11} = -\tfrac{1}{2}\chi_{11} - \tfrac{1}{2}\sqrt{3}\chi_{12}. \tag{A11}$$

In general, of course, we have for a function $\chi_{ij}^{\alpha} = D_{ij}^{\alpha}\chi$, transforming like the jth row,

$$P\chi_{ij}^{\alpha} = \textstyle\sum_k \chi_{ik}^{\alpha}\Gamma_{kj}^{(\alpha)}(P), \tag{A12}$$

where $\Gamma_{kj}^{(\alpha)}(P)$ is the kjth matrix element in the matrix representing the permutation P for the αth irreducible representation.

In the perturbation-theoretic treatment of this paper, we start with a zeroth-order function Φ_0^0 which has some of the requisite symmetry (i.e., that under the transpositions $P_{2n+1,2n+2}$) but does not have the property exemplified by (A12). As there is no other Young tableau which belongs to the same irreducible representation and which possesses these pair symmetries, there is no degenerate Φ_i, $i \neq 0$ which can mix with Φ_0^0. Thus the specified pair symmetries are sufficient to ensure that if the perturbation expansion converges to a function belonging to this irreducible representation, it must converge to Φ_0.

APPENDIX B: LITHIUM ATOM

The total wave function for the ground state of Li can be simply given by

$$\Psi = \sum_{i=0}^{1} \Phi_i(r)\chi_i(\sigma) \tag{B1}$$

with the *normalized* χ_i

$$\chi_0 = 2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\alpha(3) = -P_{12}\chi_0, \tag{B2a}$$

$$\begin{aligned}\chi_1 &= 6^{-1/2}[2\alpha(1)\alpha(2)\beta(3) - \alpha(1)\beta(2)\alpha(3) \\ &\qquad - \beta(1)\alpha(2)\alpha(3)] \\ &= (1/2\sqrt{3})(P_{23} - P_{13} - P_{132} + P_{123})\chi_0 = P_{12}\chi_1,\end{aligned} \tag{B2b}$$

and with Φ_1 related to

$$\Phi_0 = P_{12}\Phi_0 \tag{B3a}$$

by
$$\begin{aligned}\Phi_1 &= (1/2\sqrt{2})(P_{23} - P_{13} + P_{132} - P_{123})\Phi_0 \\ &= -P_{12}\Phi_1.\end{aligned} \tag{B3b}$$

If Φ_0^0 is taken as the simple orbital product

$$\Phi_0^0 = a(1)a(2)b(3), \tag{B4}$$

then Φ_1^0 is given from (B3b) by

$$\Phi_1^0 = 2^{-1/2}[a(1)b(2) - b(1)a(2)]a(3), \tag{B5}$$

which clearly is antisymmetric under P_{12} as required for Φ_1. In fact Φ_1^0 transforms as a row of the two-dimensional irreducible representations of the permutation group, whereas Φ_0^0 does not. Therefore it is possible to construct from this Φ_1^0 a function

$$\begin{aligned}\Phi'^0_0 = 6^{-1/2}[&2a(1)a(2)b(3) - b(1)a(2)a(3) \\ &- a(1)b(2)a(3)]\end{aligned} \tag{B6}$$

which possess all the correct symmetry. Such a function is, however, not amenable to the perturbative treatment of the paper. Notice that, if a and b are Hartree-Fock orbitals, then Φ'^0_0 and Φ_1^0 are degenerate eigenfunctions of the Hartree-Fock Hamiltonians, whereas if they are Hartree-like orbitals then Φ_0^0 and Φ_1^0 are *not* degenerate eigenfunctions of the same H_0. As discussed in the text, once the perturbation theory corrections to Φ_0^0 are included, the resultant Φ_0 will have all the correct symmetry and one need not be concerned about the nonsymmetric nature of Φ_0^0 itself. In principle, the expansion could converge to the nearly degenerate solution transforming like A_1 instead of the desired solution (E_1). This can be checked by looking at the antisymmetric projection when spin is included.

The approximation to Ψ which is

$$\Psi_0 = \sum_{i=0}^{1} \Phi_i^0\chi_i^0 \tag{B7}$$

is, however, not antisymmetric under all permutations, although an antisymmetric wave function can be simply constructed by

$$\Psi'_0 = \mathfrak{A}\Phi_0^0\chi_0 \tag{B8}$$

which is, in fact, the Slater determinant

$$\Psi'_0 = \mathfrak{A}\, a(1)a(2)b(3)\alpha(1)\beta(2)\alpha(3) \tag{B9}$$

and an eigenfunction of S^2.

It is important to note, however, that the expectation value

$$\langle\Psi'_0|H|\Psi'_0\rangle$$

includes exchange integrals explicitly even though

$$\langle \Phi_0^0 | H | \Phi_0^0 \rangle$$

does not. Therefore the two energies differ from each other. Similarly, while the expectation values of H over the exact Φ_0 and Φ_1 must be equal, the one over Φ_0^0 has no exchange integrals while the one over Φ_1^0 has. All of this is due to the fact that the exact functions Φ_0 and Φ_1 have not been used, and in fact, the difference of these expectation values is a measure of the goodness of the various approximate functions.

In the procedure of this paper, the perturbation expansion is for the Φ_0 and its energy eigenvalue. Thus it is of no real importance how the expectation value of H over Ψ'_0 differs from that over Φ_0^0. The perturbative procedure for Φ_0 is well-defined and such that, when it has converged, the expectation values of H over Φ_0 and over

$$\Psi = \mathfrak{a}\Phi_0\chi_0 = \sum \Phi_i \chi_i$$

are equal and there is no reason whatsoever to consider Ψ or its approximations. That is, in fact, the advantage of the present procedure; the problem of solving for Ψ has been reduced to solving for Φ_0, and it only confuses the issue to switch back to Ψ in midstream.

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