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The Use of Explicitly Correlated, Partially Antisymmetric Wave Functions in Atomic and Molecular Calculations

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Abstracts

Trial wave functions, written as the sum of a configuration interaction expansion and an explicitly correlated term which is *not* antisymmetric, are proposed for use in calculating the electronic properties of atoms and molecules. A variational principle, modified to allow the use for such partially antisymmetric wave functions, is developed. It is shown that the consequences of partial antisymmetry on calculated expectation values can be estimated. The method avoids difficult three-electron integrals which arise in other theories.

On propose des fonctions d'onde d'essai, écrites comme la somme d'un développement d'interaction de configurations et d'un terme correlé explicite, qui n'est pas antisymmétrique, pour le calcul des properiétés électroniques des atomes et des molécules. Un principe de variation a été développé qui permet l'emploi de fonctions d'onde partiellement antisymmétriques. On démontre que les conséquences de cette antisymmétrie partielle pour les valeurs moyennes calculées peuvent être estimées. Avec la méthode développée ici on évite les intégrales difficiles à trois électrons.

Es wird vorgeschlagen für die Berechnung der elektronischen Eigenschaften von Atomen und Molekülen Versuchsfunktionen zu verwenden, die als die Summe einer CI-Entwicklung und eines explizit korrelierten Glieds geschriben werden können. Dieses Glied ist nicht antisymmetrisch. Ein Variationsprinzip wird beschrieben, das den Gebrauch solcher teilweise antisymmetrischenFunktionen erlaubt. Es wird gezeigt, dass die Wirkungen dieser partiellen Antisymmetrie auf die berechneten Erwartungswerte abgeschätzt werden können. Mit dieser Methode können die schwierigen Dreielektronenintegrale vermieden werden.

1. Introduction

The success of explicitly correlated wave functions‡ in predicting the electronic properties of atoms containing a few electrons [1–6] has inspired considerable research aimed at using wave functions in variational calculations on larger atoms and molecules [7–9]. Many of the complications which arose in attempts

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‡ Explicitly correlated wave functions depend explicitly on the interelectronic coordinates r_{ij}.

to incorporate relative coordinates (r_{ij}) into a trial wave function (ψ) can be traced to the requirement that ψ be antisymmetric under permutation of particle coordinates (space and spin). For example, in the many-electron-theory of Sinanoğlu [7] the particle exchange operator P_{ij}, whose presence is due to the antisymmetry of ψ, introduces into the effective two-electron Hamiltonian difficult three-electron integrals involving r_{12}, r_{13}, and r_{23}. Even for simple molecular systems, e.g., LiH, the necessary two-center, three-electron integrals containing r_{12}, r_{13}, and r_{23} cannot presently be easily evaluated [10].†

Because of the computational difficulties in using explicitly correlated wave functions, the method of configuration interaction (CI) remains the most commonly accepted technique for going beyond Hartree–Fock in predicting electronic properties of atoms and molecules. The principal weakness of the CI method is the rather slow convergence of such an expansion of ψ in Slater determinants.‡ Pseudonatural orbitals [11] can be extracted from small CI calculations and then used to form Slater determinants for a larger CI expansion, but even in this optimum case [12] convergence may be very slow. In some instances a small CI expansion provides a significant improvement over the Hartree–Fock wave function (e.g., in the Beryllium atom, where the configurations $1s^22s^2$ and $1s^22p^2$ are important), but further increases in quality require the addition of many more Slater determinants. Generally, the correlations between loosely-bound outer electrons, which arise from the near degeneracy of the higher "occupied" Hartree–Fock orbitals with the lower "unoccupied" orbitals,§ are accurately described by these small CI expansions. However, the dynamical correlations,‖ which dominate the core-electron interactions and which are also present to a lesser extant in intershell correlations, can only be correctly described by an extensive CI expansion or by the use of r_{ij} in the trial wave function.

To include both dynamical and non-dynamical correlations in ψ we consider in Section 2 a mixed expansion in terms of both Slater determinants and explicitly correlated functions. The difficulties which arise from the antisymmetry requirement are overcome by writing the trial wave function as the sum of a CI expansion, which is properly antisymmetric, and a correlated expansion which is *not* antisymmetric. Although the resulting trial function is not necessarily antisymmetric (this is the price of eliminating such problems as three-electron integrals), we show in Section 3 that it can be used in variational calculations of the electronic energy levels and that the consequences of this partial antisymmetry can be estimated.

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† Although three-electron, one-center integrals have been calculated, their presence is a significant complication, cf. [10].

‡ Using natural orbitals to form the Slater determinants leads to the most rapidly convergent series, cf. [12].

§ By occupied (unoccupied) orbitals we mean those orbitals which do (do not) occur in the Hartree–Fock wave function.

‖ For a good discussion of the various types of correlation which appear in atoms, see the papers in Bibliography [8].

The approach taken here is closely related to that of Peat [13] and coworkers. In Peat's notation, we restrict our trial wave function to lie within the space spanned by the symmetric eigenvectors of the **Q**-matrix having eigenvalues -1 and $-\binom{N}{2}^{-1}$. However, we do not expand the wave function in a basis consisting of products of correlated geminals as Peat has done.

2. The Partially Antisymmetric Wave Function

We choose to expand the trial wave function $\psi(1, 2, 3, \cdots, N)$ in the following form:

$$\begin{aligned}\psi(1, 2, \cdots, N) &= X_0\Phi(1, 2, \cdots, N)\\ &+ \sum_{\varepsilon<\theta=1}^{N} \sum_{r<s=N+1}^{R} X^{rs}_{\varepsilon\theta}\Phi^{rs}_{\varepsilon\theta}(1, 2, \cdots, N) + \sum_{i=1}^{M} \sum_{\varepsilon<\theta}^{N} X^{i}_{\varepsilon\theta}\xi_i(1, 2)\Phi_{\varepsilon\theta}(3, 4, \cdots, N)\end{aligned} \tag{1}$$

where Φ is a Slater determinant† composed of the N "occupied" Hartree–Fock spin orbitals‡

$$\Phi(1, 2, \cdots N) = \mathscr{A}_N[\phi_1(1) \cdots \phi_N(N)] \tag{2}$$

$\Phi^{rs}_{\varepsilon\theta}$ is a double excitation§ function in which the "occupied" ϕ_ε‖ and ϕ_θ are replaced by the "unoccupied" ϕ_r and ϕ_s respectively

$$\Phi^{rs}_{\varepsilon\theta}(1, 2, \cdots, N) = \mathscr{A}_N[\phi_1(1) \cdots \phi_r(\varepsilon) \cdots \phi_s(\theta) \cdots \phi_N(N)] \tag{3}$$

and $\Phi_{\varepsilon\theta}$ is the $(N-2)$-electron minor of Φ formed by removing the first two rows and the εth and θth columns of Φ

$$\begin{aligned}\Phi_{\varepsilon\theta}(3, 4, \cdots, N) &= (-1)^{\varepsilon+\theta+1+2}\mathscr{A}_{N-2}\\ &\times [\phi_1(3) \cdots \phi_{\varepsilon-1}(\varepsilon+1)\phi_{\varepsilon+1}(\varepsilon+2) \cdots \phi_{\theta-1}(\theta)\phi_{\theta+1}(\theta+1) \cdots \phi_N(N)]\end{aligned} \tag{4}$$

The N-electron antisymmetrizer $\mathscr{A}_N$ is defined by

$$\mathscr{A}_N = (N!)^{-1/2} \sum_{P\in S_N} (-1)^p P \tag{5}$$

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† The approach is easily generalized to treat a linear combination of Slater determinants in case more than one determinant is required for symmetry reasons, e.g. to make ψ an eigenfunction of $\mathscr{S}^2$.

‡ It is not necessary that Hartree–Fock orbitals be used; if other functions are used then one would probably want to add single—and higher—excitations to the expansion of ψ given in Equation (1).

§ The generalization to include single excitations is straightforward and is probably necessary if the ϕ_i are *not* unrestricted Hartree–Fock spin orbitals. We will include only double excitations because this is the most common case.

‖ Greek indices ε, θ, α, and β are used to indicate "occupied" spin orbitals while r, s, t, and v are reserved for "unoccupied" spin orbitals.

and is proportional the (idempotent) antisymmetric projection operator O_N

$$O_N = (N!)^{-1/2}\mathscr{A}_N \tag{6}$$

The ξ_i are explicitly correlated two-electron functions (spin geminals) which are chosen before the calculation is begun. They are chosen so as to accurately describe the dynamical correlations between various electron pairs in the system of interest.† The only restrictions on the ξ_i are the orthogonality conditions given below:‡

$$\int \xi_i^*(1, 2)\mathscr{A}_2\phi_\varepsilon(1)\phi_\theta(2)\, d\tau_1\, d\tau_2 = 0 \tag{7a}$$

$$\int \xi_i^*(1, 2)\mathscr{A}_2\phi_\varepsilon(1)\phi_r(2)\, d\tau_1\, d\tau_2 = 0 \tag{7b}$$

$$\int \xi_i^*(1, 2)\mathscr{A}_2\phi_r(1)\phi_s(2)\, d\tau_1\, d\tau_2 = 0 \tag{7c}$$

$$\int \xi_i^*(1, 2)\xi_j(1, 2)\, d\tau_1\, d\tau_2 = \delta_{ij} \tag{7d}$$

for $\varepsilon, \theta = 1, 2, \cdots N$; $i, j = 1, 2, \cdots M$; $r, s = N + 1 \cdots R$. In the above expressions M is the number of correlated spin geminals which we choose to use in the calculation, R–N is the number of "unoccupied" spin orbitals appearing in the CI part of ψ,§ and N is the number of electrons.

The variational parameters X_0, $X_{\varepsilon\theta}^{rs}$, $X_{\varepsilon\theta}^{i}$ are to be determined in two steps. For a specific system we first decide which of the coefficients $X_{\varepsilon\theta}^{rs}$ and $X_{\varepsilon\theta}^{i}$ are to be taken as non-zero. This choice is made according to which spin orbital pairs (ε, θ) interact (virtually) with which "unoccupied" spin orbital pairs (r, s) to yield non-dynamical correlation, and which spin orbital pairs (ε, θ) are best described as dynamically correlated. For example in the Beryllium atom we would certainly want $X_{2s,2s}^{2p,2p}$ to be non-zero, whereas the dynamically correlated $1s^2$ core would require at least one non-zero $X_{1s,1s}^{i}$. The intershell $(1s2s)$ correlation, which is usually quite small due to the localization of the two orbitals in different regions of space, can probably be treated by including either non-zero

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† Some experimentation is clearly needed to find a set of rules for constructing reasonable $\{\xi_i\}$ for specific molecular problems. The experience of researchers who have used theories such as Sinanoğlu's many-electron theory would undoubtedly be very valuable in these regards.

‡ These constraints force one to orthogonalize the chosen $\{\xi_i\}$ to one another and to the Slater spin geminals $\mathscr{A}_2[\phi_i(1)\phi_j(2)]$. This can be done using any of the standard techniques (Schmidt orthogonalization, symmetric orthogonalization, etc.). They are much weaker constraints than the strong orthogonality which arises in Sinanoğlu's many-electron theory [7].

§ We have in mind a rather limited CI expansion whose purpose is to include non-dynamical correlations. Thus, R will probably be much less than the total number of Hartree–Fock spin orbitals (occupied and unoccupied) which is determined by the size of the atomic-orbital basis set.

$X_{1s,2s}^{r,s}$ or $X_{1s,2s}^{i}$. Once the above decisions have been made, the non-zero variational parameters are chosen so as to minimize the energy functional defined in Section 3. Because the trial wave function given in Equation (1) is not necessarily antisymmetric, the usual definition of the energy as the expectation value of the N-electron Hamiltonian is somewhat modified.

3. The Variational Problem

If the trial wave function ψ were totally antisymmetric, we could define the electronic energy E in either of the following two equivalent ways (ψ is taken to be normalized to unity):

$$E \equiv \int \psi^*(1, 2, \cdots, N) H_N \psi(1, 2, \cdots, N)\, d\tau_1 \cdots d\tau_N \tag{8a}$$

or

$$E \equiv \int \psi^*(1, 2, \cdots, N) K(1, 2) \psi(1, 2, \cdots, N)\, d\tau_1 \cdots d\tau_N \tag{8b}$$

where the N-electron Hamiltonian H_N is assumed to consist of a symmetric sum of one-electron operators $f(i)$ and two-electron operators $g(i,j)$

$$H_N = \sum_{i=1}^{N} f(i) + \sum_{i<j=1}^{N} g(i,j) \tag{9}$$

and the reduced Hamiltonian K is given by

$$K(1, 2) = \binom{N}{2} \{g(1, 2) + (N-1)^{-1}[f(1) + f(2)]\} \tag{10}$$

The equivalence of the above two definitions of E can easily be verified by using the identity of the electrons and the antisymmetry of ψ.

However, the trial wave function given in Equation (1) is not necessarily antisymmetric, and so the energies defined by Equations (8a) and (8b) are, in this case, not identical. We arbitrarily choose to define an energy functional E by Equation (8b). There are two principal reasons for this choice. Firstly, the energy functional given in Equation (8b) is, as shown later, bounded from below by a number which depends on how nearly antisymmetric our wave function is. The existence of this lower bound is taken as justification for the variational calculation of the energy. Secondly, the problem of minimizing E to find the optimum values of the variational parameters X_0, $X_{\varepsilon\theta}^{rs}$, $X_{\varepsilon\theta}^{i}$ is computationally tractable; only one- and two-electron integrals arise, there are no three-electron integrals involved.

Before we proceed with the development of a variational method, we first introduce the concept of a measure of antisymmetry μ [14], defined as the square of the norm of the antisymmetric component of ψ

$$\mu \equiv \int O_N\psi^*(1, 2, \cdots, N) O_N\psi(1, 2, \cdots, N)\, d\tau_1 \cdots d\tau_N \tag{11}$$

Because $\mathcal{O}_N$ is a projection operator [see Equation (6)] μ is bounded by $0 \leqq \mu \leqq 1$, and the value $\mu = 1$ implies a totally antisymmetric wave function. For the trial function in Equation (1) the calculation of μ is easily performed by using Equations (7a)–(7d) and the orthonormality of the spin orbitals $\{\phi_i\}$. The result is

$$\mu = |X_0|^2 + \sum_{\varepsilon<\theta=1}^{N} \sum_{r<s=N+1}^{R} |X_{\varepsilon\theta}^{rs}|^2 + \binom{N}{2}^{-1} \sum_{i=1}^{M} \sum_{\varepsilon<\theta=1}^{N} |X_{\varepsilon\theta}^{i}|^2 \tag{12}$$

Because ψ is normalized to unity we also have

$$1 = |X_0|^2 + \sum_{\varepsilon<\theta=1}^{N} \sum_{r<s=N+1}^{R} |X_{\varepsilon\theta}^{rs}|^2 + \sum_{i=1}^{M} \sum_{\varepsilon<\theta=1}^{N} |X_{\varepsilon\theta}^{i}|^2 \tag{13}$$

Notice that a non-zero $X_{\varepsilon\theta}^{i}$ contributes an amount $|X_{\varepsilon\theta}^{i}|^2$ to the normalization constraint [Equation (13)] but only $\binom{N}{2}^{-1} |X_{\varepsilon\theta}^{i}|^2$ to the value of μ [Equation (12)]; clearly this must render μ less than its maximum value of 1. The result $\mu = 1$ can only be obtained if all of the $X_{\varepsilon\theta}^{i}$ vanish; i.e., in the case of a pure CI wave function (not necessarily exact).

Let us now consider the relationship between the energy functional defined by Equation (8b) and the following expectation value of the N-electron Hamiltonian:

$$\hat{E} \equiv \int O_N\psi^* H_N O_N\psi\, d\tau \Big/ \int O_N\psi^* O_N\psi\, d\tau \tag{14}$$

Because the function $\mathcal{O}_N\psi$ is totally antisymmetric, $\hat{E}$ must be an upper bound to the true ground-state energy of the system E_0

$$\hat{E} \geqq E_0 \tag{15}$$

but it is not necessarily true that $E \geqq E_0$. Making use of the definitions of E, $\hat{E}$, and μ, as well as the Schwarz and triangle inequalities, one can derive† the important inequality shown below‡:

$$|\hat{E} - \mu E| \leqq (1 - \mu)\, |K|_{\max} + 2\left[\mu(1 - \mu) \int \psi^* K^2(1, 2) \psi\, d\tau\right]^{1/2} \tag{16}$$

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† See pages 1039–1040 of Bibliography [14] for details.

‡ Any other symmetric two-electron operator can be substituted for the Hamiltonian if an appropriate reduced operator is defined.

where $|K|_{\max}$ is the eigenvalue of maximum absolute value associated with the operator $K(1, 2)$ in the space spanned by the two-electron functions

$$\{\mathscr{A}_2[\phi_i(1)\phi_j(2)],\ i, j = 1, 2, \cdots R;\ \ \xi_i(1, 2),\ i = 1, 2, \cdots M\}$$

It should be noted that $K^2(1, 2)$ ($\equiv K(1, 2)\, K(1, 2)$) is the square of a two-electron operator, and thus is itself a two-electron operator. Therefore the integral appearing in Equation (16) involves only one- and two-electron integrals.

The above inequality is easily rearranged to give the following lower bound to the energy functional E:

$$(17) \qquad E \geqq E_0 - \Delta$$

where Δ is defined as

$$(18) \quad \Delta \equiv -(\mu^{-1} - 1)E_0 + (\mu^{-1} - 1)\, |K|_{\max} + 2\left[(\mu^{-1} - 1)\int \psi^* K^2(1, 2)\psi\, d\tau\right]^{1/2}$$

If the ground-state energy E_0 is negative, as is the case for bound systems, Δ is a non-negative quantity which approaches zero as μ approaches unity. Thus the bound $E \geqq E_0 - \Delta$ approaches the usual variational bound $E \geqq E_0$ as μ approaches one.

The inequality of Equation (17) can now be seen to justify the use of the functional E for variational calculations, in the following sense. If the parameters X_0, $X_{\varepsilon\theta}^{rs}$, and $X_{\varepsilon\theta}^{i}$ are chosen so as to minimize E (call the minimum value E^*), then Equation (17), together with the definitions of μ [Equation (12)] and Δ [Equation (18)], tells us that E^* can fall no more than Δ below the true ground-state energy E_0.† Thus, evaluating μ and Δ at the optimum values of X_0, $X_{\varepsilon\theta}^{rs}$, and $X_{\varepsilon\theta}^{i}$ affords us a measure of the consequences of the partial antisymmetry of ψ.

The problem of minimizing E subject to the constraint that ψ remain normalized is a linear variational problem. To obtain the optimum values of the variational parameters and the minimum value (E^*) of E we must calculate the lowest eigenvalue (and its associated eigenvector) of the matrix $\mathbf{K}$ whose entries are the matrix elements of $K(1, 2)$ between pairs of the basis functions Φ, $\Phi_{\varepsilon\theta}^{rs}$, and $\xi_i\Phi_{\varepsilon\theta}$. The evaluation of $\langle\Phi|\, K\, |\Phi\rangle$, $\langle\Phi|\, K\, |\Phi_{\varepsilon\theta}^{rs}\rangle$, and $\langle\Phi_{\varepsilon\theta}^{rs}|\, K\, |\Phi_{\alpha\beta}^{tv}\rangle$ can be

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† Bounding $\int \psi^* K^2 \psi\, d\tau$ by $|K|_{\max}^2$ and using $0 \leqq \mu \leqq 1$, we can generalize the right side of Equation (16) so that $|\hat{E} - \mu E| \leqq \Delta'$, where Δ' is independent of μ. However, this is not necessary for justifying the minimization of E. The philosophy of our modified variational approach is as follows: the values of X_0, $X_{\varepsilon\theta}^{rs}$, and $X_{\varepsilon\theta}^{i}$ which minimize E result in a value of μ given by Equation (12). If we judge μ to be not sufficiently close to unity, then the calculation is fruitless; new spin geminals $\{\xi_i\}$ must be chosen for a new calculation. However, if the resulting value of μ is reasonably close to one, then Equations (16)–(18) can be used to estimate the consequences of partial antisymmetry. Thus, for a *fixed* set of spin geminals, we minimize E and then calculate μ. The resulting value of μ, when substituted into Equation (17), allows us to state with confidence that the minimum value of $E(E^*)$ has not fallen more than Δ below the true ground-state energy E_0.

accomplished by using the well-known rules for calculating matrix elements of the Hamiltonian between Slater determinants [15]. Using Equations (7a)–(7d) and the orthonormality of the $\{\phi_i\}$ one can derive expressions for the remaining elements of $\mathbf{K}$:

$$\text{(19a)} \qquad \langle\Phi|\, K\,|\xi_i\Phi_{\varepsilon\theta}\rangle = \binom{N}{2}^{-1/2} \int \mathscr{A}_2[\phi_\varepsilon(1)\phi_\theta(2)]^* K(1,2)\xi_i(1,2)\, d\tau_1\, d\tau_2$$

$$\text{(19b)} \qquad \langle\Phi^{rs}_{\varepsilon\theta}|\, K\,|\xi_i\Phi_{\alpha\beta}\rangle = \delta_{\alpha\varepsilon}\delta_{\beta\theta}\binom{N}{2}^{-1/2} \int \mathscr{A}_2[\phi_r(1)\phi_s(2)]^* K(1,2)\xi_i(1,2)\, d\tau_1\, d\tau_2$$

$$\text{(19c)} \qquad \langle\xi_i\Phi_{\varepsilon\theta}|\, K\,|\xi_j\Phi_{\alpha\beta}\rangle = \delta_{\alpha\varepsilon}\delta_{\beta\theta}\int \xi_i^*(1,2)\, K(1,2)\xi_j(1,2)\, d\tau_1\, d\tau_2 \dagger$$

The practical details of the method proposed here are clearly very similar to those of the CI approach. One is faced with evaluating various one- and two-electron integrals which are then used to construct the matrix $\mathbf{K}$ whose lowest eigenvalue is E^*. The eigenvector of $\mathbf{K}$ belonging to the eigenvalue E^* then gives the optimum values of X_0, $X^{rs}_{\varepsilon\theta}$, and $X^i_{\varepsilon\theta}$. The principal computational difficulty of the method, beyond that occurring in a CI calculation, is the evaluation of the two-electron integrals appearing in Equations (19a)–(19c). This added complexity must be balanced against the advantages mentioned earlier (no need for an extensive CI expansion, explicit correlation, no three-electron integrals, etc.) in deciding whether this approach represents a useful tool for calculating electronic properties of molecules. Results of using such partially antisymmetric wave functions in specific molecular calculations are, of course, also essential in making this decision. We plan to carry out some calculations in the near future which, hopefully, will shed some light on the value of the proposed method.

4. Concluding Remarks

In this paper we have proposed the use of explicitly correlated, partially antisymmetric wave functions for calculating the electronic properties of atoms and molecules. Such trial functions can simultaneously treat both dynamical and non-dynamical correlations, while avoiding the difficult three-electron integrals which arise in other theories. A modified variational method, based on minimizing the energy functional E of Equation (8b), was developed, and a bound was placed on the amount E could fall below the true ground-state energy E_0. The measure of antisymmetry μ, which determines this bound on E, also allows us to

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† These formulas can be used to calculate the expectation value of any two-electron operator (by defining a corresponding reduced operator), once the optimum values of X_0, $X^{rs}_{\varepsilon\theta}$, and $X^i_{\varepsilon\theta}$ are known. That is, in calculating $\int \psi^* J(1,2)\psi\, d\tau$ with ψ given by Equation (1), one need only know the X_0, $X^{rs}_{\varepsilon\theta}$, $X^i_{\varepsilon\theta}$, those integrals involving the reduced operator $J(1,2)$ which are analogous to the integrals in Equations (19a)–(19c), and the standard two-electron integrals $\langle\phi_i\phi_j|\, J\,|\phi_k\phi_l\rangle$ which arise in CI calculations.

estimate the consequences of partial antisymmetry on other calculated expectation values by using Equation (16).

The necessary steps in applying this method are as follows:

(*1*) Decide which of the $X_{\varepsilon\theta}^{rs}$ and $X_{\varepsilon\theta}^{i}$ are to be non-zero (see page 442).

(*2*) Choose a set of explicitly correlated spin geminals and orthogonalize them to one another and to the Slater geminals $\{\mathscr{A}_2[\phi_l(1)\phi_m(2)]\}$ to form the $\{\xi_i\}$.

(*3*) Calculate the integrals in Equations (19a)–(19c) and the integrals needed to form the CI part of the **K**-matrix.

(*4*) Form the **K**-matrix.

(*5*) Find the lowest eigenvalue of **K** and its associated eigenvector. The eigenvalue is E^*; the eigenvector gives the optimum values of X_0, $X_{\varepsilon\theta}^{rs}$, and $X_{\varepsilon\theta}^{i}$.

(*6*) Calculate the expectation values of any one- or two-electron operator (J) of interest ($\int \psi^* J(1, 2)\psi \, d\tau$, see footnote, page 446).

(*7*) Use Equation (12) to evaluate the measure of antisymmetry μ. If the value of μ calculated in step (*7*) is not reasonably close to unity, the resulting wave function cannot be used with much confidence. In this case, the remaining four steps need not even be carried out; one should choose new $\{\xi_i\}$ and return to step (*2*).

(*8*) Calculate $|K|_{\max}$ of Equation (16) by finding the largest (in absolute value) eigenvalue of $K(1, 2)$ in the basis of the Slater geminals and the ξ_i.

(*9*) Using the optimum variational parameters calculate $\int \psi^* K^2 \psi \, d\tau$.

(*10*) Evaluate Δ by using Equation (18).

(*11*) Use Equation (16) to estimate the consequences of partial antisymmetry on the expectation values of any other one- or two-electron operators.

Although we have presented formal justification for using explicitly correlated, partially antisymmetric wave functions in molecular calculations, the real test of the theory lies in its application to particular problems. It might prove very difficult to choose a set of correlated spin geminals $\{\xi_i\}$ which gives good antisymmetry ($\mu \approx 1$) and, at the same time, accurately describes the dynamical correlations of electrons in the molecule. It may also be that spin geminals which prove acceptable in describing correlation and yielding good antisymmetry lead to very large values of $|K|_{\max}$, so that the value of Δ given in Equation (18) is too large. The results of Löwdin and Lim [16] indicate that the value of $|K|_{\max}$ can be expected to increase fairly rapidly as the number of electrons is increased. Thus, for a given value of μ, the bounding function Δ cannot be assumed to increase slowly (if at all) with N. However, it is possible that the maximum *relative* error in the energy Δ/E_0 does vary rather slowly as a function of N. Therefore, it may be possible to maintain maximum errors of a few per cent over a wide range of N. The data of Löwdin and Lim and the results of Peat and coworkers on Li, He_2, and Li_2 (see Bibliography 13) seem to substantiate the slow variation† of Δ/E_0 for

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† For example, Löwdin and Lim [16] find that $|K|_{\max}/E_0$ changes from 1.0 to 2.2 as N is varied from 0 to 8.

N in the range 0 to 8. To evaluate more realistically the advantages and disadvantages of this theory, we plan to carry out more test calculations in the future.

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Thanks are due to the referee for raising an interesting question concerning the virial theorem in calculations such as we have proposed here. We plan to investigate this problem in the near future.

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