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Suggested Calculations Using Transition Density Matrices

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It is suggested that certain transition density matrices, N-representable in a limit, be used in a variational calculation. It is noted that such trial matrices should yield reasonable values for the ground state energies of small atoms or molecules provided a set of overlap integrals is maximised.

Es wird vorgeschlagen, bestimmte Übergangsdichtematrizen, die im Limit N-darstellbar sind, in einer Variationsrechnung zu benutzen. Es wird festgestellt, daß solche Näherungsmatrizen gute Werte für die Energie des Grundzustandes kleiner Atome oder Moleküle geben sollten, falls im Satz von Überlappungsintegralen maximiert wird.

On propose d'utiliser dans un calcul variationnel certaines matrices densité de transition, N représentables à la limite. Ces matrices d'essai devraient fournir des valeurs raissonnables pour l'énergie de l'état fondamental dans les petits atomes et les petites molécules à condition de maximiser un ensemble d'intégrales de recouvrement.

Introduction

Quantum chemistry has met with considerable success in calculating the ground state energies of atoms and atomic ions and more recently in computing molecular binding energies.

These calculations are normally performed on a computer by varying the different parameters which define a trial wave function, according to a minimisation procedure. Such minimisation procedures rely upon the Variation Theorem and hence upon totally antisymmetric trial functions.

Since full N-representability conditions have not been found for density matrices, any numerical work has been done in trivial cases or using density matrices formed by integration of an antisymmetric function. This compromise is motivated from fear of violating the Variation Principal during a minimisation procedure and may account for the lack of success of the density matrix in the field of quantum chemistry. For example although the density matrix was introduced seventeen years ago [1], no theory of valency has been advanced which has a basis in density matrix theory or uses the notation of geminals.

A resolution of the dilemma would be to adopt a perturbation approach to add corrections to the density matrix. The question of perturbation corrections and their relation to N-representability has never been properly discussed and there is no reason why a systematic approach along these lines should not be adopted.

It has also been suggested [2—4] that density matrices which are "approximately N-representable" may be used to obtain bounds upon the energy. It would not seem unreasonable therefore to relate such bounds to the particular order of the perturbation corrections. In this paper a scheme is outlined which uses transition density matrices which do not fulfill all the N-representability conditions.

The Transition Matrix

The discussion below is restricted to a system containing four electrons but may be extended to more general cases.

A totally antisymmetric wave function $\Psi(1234)$ may be expanded in terms of the eigenfunctions $\{\Phi_n(12)\}$ to the reduced two electron Hamiltonian $\boldsymbol{h}(12)$; that is

$$\Psi(1234) = \sum_n \Phi_n(12) f_n(34), \tag{1}$$

where

$$f_n(34) = \int_{34} \Phi_n^*(12)\, \Psi(1234). \tag{2}$$

The reduced Hamiltonian is related to the N-particle Hamiltonian $\boldsymbol{H}(1234)$ by [5]

$$\boldsymbol{H}(1234) = \frac{1}{2} N \boldsymbol{Q} \boldsymbol{h}(12), \tag{3}$$

where $\boldsymbol{Q}$ is a projection operator formed from all even permutations $\boldsymbol{P}$ of the N-particles, that is

$$\boldsymbol{Q} = \frac{2}{N!} \sum_{\text{even}} \boldsymbol{P}. \tag{4}$$

In the $\{\Phi_n\}$ representation the second order reduced density matrix is written

$$\boldsymbol{D}^{(2)}(12:1'2') = \sum_{nm} B_{nm} \Phi_n(12)\, \Phi_m^*(1'2'), \tag{5}$$

where

$$B_{nm} = \int_{12} f_n(34) f_m^*(34). \tag{6}$$

The advantage of the density matrix formalism lies in the possibility of working with this function directly rather than with the wave function which becomes more difficult to define numerically with an increasing member of electrons. The drawback to this approach is that one does know how to choose the $\{f_n\}$ or $\{B_{nm}\}$ in order that the density matrix be N-representable [6]. (An N-representable density matrix is one derivable from an N-particle antisymmetric function or an ensemble of such functions.)

Grimley and Peat [5] suggested that as a first approximation to (5) the $\{f_n\}$ be projected from a zero order determinantal wave function $\Psi^0(1234)$ by zero order geminals $\{\Phi_n^{(0)}\}$ expanded in the same basis set. These zero order functions are Slater Determinants or linear combinations of such determinants with simple coefficients. That is

$$f_n^{(0)}(34) = \int_{34} \Phi_n^{*(0)}(12)\, \Psi^{(0)}(1234). \tag{7}$$

The approximate $\{B_{nm}^{(0)}\}$

$$B_{nm}^{(0)} = \int_{34} f_n^{(0)}(34)\, f_m^{(0)*}(34) \tag{8}$$

are inserted into (5), the correlated basis $\{\Phi_n\}$ being retained, and therefore define a trial density matrix $\boldsymbol{D}_T^{(2)}(12:1'2')$,

$$\boldsymbol{D}_T^{(2)}(12:1'2') = \sum_{nm} B_{nm}^{(0)} \Phi_n(12)\, \Phi_m^*(1'2')\,. \tag{9}$$

The energy computed using this trial density matrix generally falls below the true energy since the wave function

$$\Psi_T(1234) = \sum_n \Phi_n(12)\, f_n^{(0)}(34) \tag{10}$$

is not antisymmetric under the permutation (2, 3). (It can not, however, be proved that the calculated energies form a lower bound.) Since the $\{\Phi_n\}$ are orthonormal the energy calculated using $\boldsymbol{D}_T'^{(2)}(34:3'4')$, where

$$\boldsymbol{D}_T'^{(2)}(34:3'4') = \int_{12} \Psi_T(1234)\, \Psi_T^*(123'4')\,, \tag{11}$$

lies above the true energy. If $\Psi_T^0(1234)$ is chosen to be the Hartree-Fock wave function then the energy calculated using (11) is the Hartree-Fock energy.

The preceding discussion suggests that one may be able to improve upon the Grimley-Peat result employing the transition matrix defined by using the non antisymmetric wave functions;

$$\bar{\boldsymbol{D}}_T^{(2)}(34:12) = \int_{1'2'} \Psi_T^*(1'2'34)\, \Psi_T(121'2') \tag{12}$$

$$= \Sigma\, \bar{B}_{nm} f_n^{*(0)}(34)\, \Phi_m(12)\,, \tag{13}$$

where

$$\bar{B}_{nm} = \int_{1'2'} \Phi_n^*(1'2')\, f_m^{(0)}(1'2')\,. \tag{14}$$

The energy calculated using this matrix is

$$\bar{E} = \frac{N}{2} \operatorname{Trace} \boldsymbol{h}(1'2')\, \boldsymbol{D}_T^{(2)}(12:1'2') + \operatorname{Trace} \bar{\boldsymbol{D}}_T^{(2)} \tag{15}$$

$$= \frac{N}{2} \bar{B}_{nm}^2 \varepsilon_m + \sum_n \bar{B}_{nm}^2\,, \tag{16}$$

where the ε_m are eigenvalues to $\boldsymbol{h}(12)$ associated with the eigenfunctions Φ_n. The lower bound to $\bar{E}$ occurs if the overlaps $\{\bar{B}_{nm}\}$ are maximized with respect to the $\{f_m^{(0)}\}$, in such a limit $\bar{E}$ approaches the Grimley-Peat result. This limit is unobtainable of course since the zero order $\{f_m^{(0)}\}$ can never overlap completely with correlated $\{\Phi_n\}$. The expression (16) will therefore give an improvement over the Grimley-Peat result. Conversely the meaning of maximizing the $\{\bar{B}_{nm}\}$ with respect to the $\{\Phi_n\}$ may be investigated. Such a maximization could only be achieved if the $\{\Phi_n\}$ were limited to determinantal wave functions, with a corresponding increase in the energy; for example in the case of Hartree-Fock geminals, an upper bound $\bar{E}$ would be given by the Hartree-Fock energy. Therefore this transition matrix gives a calculated energy bracketed between the Grimley-Peat and Hartree-Fock results.

The example of anzats (12) suggests therefore that a more general transition matrix

$$D^{(2)}_{AB}(12:1'2') = \int_{34} \Psi^*_A(1234)\,\Psi_B(1'2'34) \tag{17}$$

could be used in calculations. Ψ_A is a Hartree-Fock or configurational interaction wave function while Ψ_B is a trial function built up from correlated geminals, possibly the eigenfunctions to $\boldsymbol{h}(12)$, and may not be totally antisymmetric. Given the form $D^{(2)}_{AB}$ one would work directly with this density matrix rather than with the wave functions. An attempt would be made to maximize the overlap by varying Ψ_A and by selecting the geminals from the set $\{\Phi_n\}$ which are to be inserted in Ψ_B. For example in the case of the ground state to a four electron ion the dominant configuration in Ψ_A will be $(1S^2\,2S^2)$ indicating that the overlap may be maximised if the $\Phi(2S^2)$ geminal is included in Ψ_B. Since the energy corresponding to this geminal is quite large it would not have been included in Ψ_B on the grounds of energy minimisation alone.

No calculations have been performed using this program, however a simple argument gives an order of magnitude estimate of the success of the method. Consider Ψ_A to be the Hartree-Fock solution and Ψ_B to be composed of six eigenfunctions $\Phi(1s^2:{}^1S)$; $\Phi(1s\,2s:{}^1S)$; $\Phi(1s\,2s:{}^3S)$; $\Phi(2s^2;{}^1S)$ to $\boldsymbol{h}(12)$. The energy calculated using $D^{(2)}_{AB}$ with these functions is

$$E_{AB} = \Sigma\, B^{(0)}_{nm}\Delta^2_{nm}\varepsilon_n \div \Sigma\, B^{(0)}_{nm}\Delta^2_{nm}\,, \tag{18}$$

where Δ_{nm} is the overlap between Φ_n and the relevant geminal projected out of Ψ_A, $B^{(0)}_{nm}$ is defined through (8) and the ε_n are the eigenvalues to $\boldsymbol{h}(12)$. The overlap between the exact ground state of Beryllium and the Hartree-Fock result is 0.985 [7]. The significant deviations from an overlap of unity occur for the highly correlated $1S^2$ and $2S^2$ geminals [8] and it will be supposed that these overlaps occurring in equal proportion [8] give rise to the deficiency of 0.015 in the overlap of Ψ_A with the ground state.

Unfortunately the eigenvalues to $\boldsymbol{h}(12)$ are not known in the case of Berryllium but they are known [5] for the ion C^{2+}. Since it is reasonable to suppose that the Δ_{nm} do not change rapidly with the nuclear charge in an isoelectronic series, the values for the Δ_{nm} obtained for Berryllium are inserted into (18). The ground state energy of C^{2+} is calculated to be 7981893 cm^{-1} and is 0.5% above the "experimental" non-relativistic energy of 8020746 cm^{-1} [9]. If a calculation were made using this technique it would be possible to improve upon this energy by maximizing the overlap integrals with respect to some configurational Ψ_A.

The method suggested above is essentially that of taking the expectation value of the Hamiltonian over two different wave functions then passing to the reduced transition density matrix formation for convenience in performing the calculations. This approach is a special case of the problem of determining the eigenvalues to an operator $\boldsymbol{H}$. In general the matrix elements

$$H_{nm} = \langle \Phi_n | \boldsymbol{H} | X_m \rangle \tag{19}$$

over two basis sets $\{\Phi_n\}$ and $\{X_m\}$ are computed and the eigenvalue equation

$$\sum_n (H_{nm} - E\Delta_{nm})\, a_m = 0 \tag{20}$$

solved. The Δ_{nm} are overlap integrals between the two bases

$$\Delta_{nm} = \langle \Phi_n | X_m \rangle \tag{21}$$

and the a_m define an eigenfunction Ψ_E to $\boldsymbol{H}$ associated with the eigenvalue E, that is

$$a_m = \langle \Psi_E | X_m \rangle\,. \tag{22}$$

Use of different basis sets may give an advantage [10] over the calculation of matrix elements with a single basis. For example the $\{X_n\}$ may be expected to provide an excellent approximation to the eigenfunctions to $\boldsymbol{H}$, however any integrals involved may be difficult to compute and the introduction of a set $\{\Phi_n\}$ which simplifies the integration without a significant reduction in accuracy would therefore be advisable. Recently use has been made of this convenience in making accurate calculations of the correlation energy of atoms [11].

Conclusion

If it is decided to work with wave functions which are not totally antisymmetric or density matrices which are not completely N-representable then it may be possible to develop successful computational procedures which would yield bounds upon the eigenvalues to the operators of interest. The particular anzats suggested in this paper enables one to work with a reduced density matrix directly rather than referring back to the wave function during any variation of the density matrix. Since the N-representability problem appears at present to be rather intractable investigations involving "almost N-representable" density matrices may prove to be profitable.

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