REVIEWS OF MODERN PHYSICS VOLUME 35, NUMBER 3 JULY 1963

A Method for the Analysis of Many-Electron Wave Functions*

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THIS article gives a method by which: (a) a given trial function $\tilde{\psi}$ of arbitrary form of a many electron system can be analyzed into various correlation effects, if the Hartree–Fock wave function (ϕ_0) of that system is also available. One can then compare this new form in which various effects are explicit with the form of the exact many electron wave function given and discussed before.[1] By taking out the spurious terms which the comparison would reveal and by putting in the effects inadequately represented in $\tilde{\psi}$ the trial function can be improved. (b) If one has a good many electron trial function $\tilde{\psi}$, but not the Hartree–Fock wave function ϕ_0 of that system, the Hartree–Fock ϕ_0 can be obtained directly from $\tilde{\psi}$ without necessitating a separate variational calculation.

The method involves only partial integrations.

Many computations on atoms and molecules using computers have yielded wave functions containing arbitrary forms and variational parameters. The method described allows one to sort out of such functions the various correlation effects such as intershell, intrashell, and those involving different numbers of electrons. This not only shows the reason for the success or failure or a trial function in yielding a good energy, but also, by separating the various physically and chemically meaningful terms contained in it, makes it suitable for semiempirical use. One isolates for instance the portions that would be about the same in related ions or molecules.

Many such trial functions aim at getting a good energy. Sometimes they "bypass" a Hartree–Fock calculation. But Hartree–Fock orbitals are useful in themselves. They provide the basis for the simple "orbital picture" so useful in discussing the spectra and structure of molecules.[1a,c] It is desirable therefore to have both ϕ_0 and an energy $\tilde{E}[\tilde{\psi}]$ corrected for correlation. Fortunately, the one and the same $\tilde{\psi}$ yields both, without two separate variational calculations.

THE METHOD OF "SUCCESSIVE PARTIAL ORTHOGONALIZATIONS"

The form of the exact many electron wave function of a closed-shell system was given before.[1] This form is derived most simply by what may be called the method of successive partial orthogonalizations.

Consider an N-electron system with the *exact* wave function ψ. Suppose there is an orbital approximation ϕ_0^0 to this. ϕ_0^0 is a Slater determinant[2] of N spin-orbitals i^0 for this closed-shell case.

$$\phi_0^0 = \mathcal{A}(1^0 2^0 3^0 \cdots N^0)\ . \tag{1}$$

The best orbital function[3] representing ψ will be the Hartree–Fock one.

$$\phi_0 = \mathcal{A}(123\cdots N)\ . \tag{2}$$

Let us find the detailed form of ψ in terms of what would be left over were it approximated by ϕ_0^0. To simplify the notation let us do this with ϕ_0 with the understanding that formally the same results apply with i^0 as with i.

Schmidt-orthogonalize ψ to ϕ_0. This gives all that remains in ψ after ϕ_0 is taken out. If ϕ_0 is the H. F. wave function, then the remainder is the correlation wave function.

$$\chi \equiv \psi - \langle\psi,\phi_0\rangle\phi_0 = \psi - \phi_0\ . \tag{3}$$

The arbitrary normalization of ψ has been chosen such that

$$\langle\psi,\phi_0\rangle = 1\ ;\quad \text{i.e.,}\quad \langle\psi,\psi\rangle = 1 + \langle\chi,\chi\rangle \tag{4}$$

with $\langle\phi_0,\phi_0\rangle = 1$.

Next "orthogonalize"[1] χ to spin-orbital products obtained from ϕ_0 by dropping one of the spin-orbitals each time, e.g., to $(23\cdots N)$, $(134\cdots N)$, etc. The resulting χ' is a smaller portion of χ:

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* This work was supported by a grant from the National Science Foundation.

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[1] (a) O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962) (I); (b) **36**, 3198 (1962); (c) O. Sinanoğlu and D. Fu-tai Tuan, *ibid.* **38**, 1740 (1963).

[2] For notation see ref. 1(a).

[3] In Eqs. (1) and (2) we assume the usual closed-shell determinant with each orbital doubly occupied. One could also let the spatial part of say *1* and *2* be different (e.g., $1s\alpha 1s'\beta$) and then use a projection operator more general than $[\mathcal{A}/(N!)^{1/2}]$ to pick out say the ^1S component ϕ. ["Split Shell" method, see e.g., P. O. Löwdin, in *Advances in Chemical Physics*, edited by O. Prigogine (Interscience Publishers, Inc., 1959) Vol. II, pp. 207 ff.]. Such a ϕ however may be considered a trial function $\tilde{\psi}$ which "by-passes" the usual Hartree–Fock ϕ_0. The analysis described in text then applies to it and splits its ϕ_0 and "correlation" parts.

$$\chi' = \chi - \sum_{i=1}^{N} \det \left\{ \left\langle \chi, \frac{(123\cdots N)}{(i)} \right\rangle' \left\langle \frac{(123\cdots N)}{(i)} \right\} \right.$$

where

$$\det \equiv (N!)^{\frac{1}{2}} \mathcal{A} , \tag{5}$$

and $\langle \chi, (123\cdots N)/(i) \rangle'$ means integration over all coordinates except $\mathbf{x}_i$, the one missing from the orbital product along with spin-orbital i.

Each integral $\langle\ \rangle'$ in Eq. (5) gives a function of $\mathbf{x}_i$ only and defines

$$\hat{f}_i(\mathbf{x}_i) \equiv (N!)^{\frac{1}{2}} \langle \chi, [123\cdots(i-1)(i+1)\cdots N] \rangle' . \tag{6}$$

The "det" in Eq. (5) antisymmetrizes this with the remaining orbitals, $(123\cdots N)/(i)$.

So far we get

$$\psi = \phi_0 + \sum_{i=1}^{N} \mathcal{A} \left\{ (123\cdots N) \frac{\hat{f}_i}{(i)} \right\} + \chi' . \tag{7}$$

From Eq. (6) and $\langle \phi_0, \chi \rangle = 0$, it also follows[4] that

$$\langle \hat{f}_i, k \rangle = 0 \qquad (k = 1,2,3,\cdots i, \cdots N) . \tag{8}$$

Equation (7) is continued each time giving a new part of ψ, by the Schmidt "orthogonalization" of the remainders χ', χ'', $\cdots$ to the products of fewer and fewer spin-orbitals out of ϕ_0. Thus

$$\chi'' = \chi' - \sum_{i>j}^{N} \times \det \left\{ \left\langle \chi', \frac{(123\cdots N)}{(ij)} \right\rangle' \left\langle \frac{(123\cdots N)}{(ij)} \right\} \right. , \tag{9}$$

and[2]

$$\hat{U}'_{ij} \equiv \left(\frac{N!}{2!} \right)^{\frac{1}{2}} \langle \chi', [123\cdots(i-1)(i+1)\cdots(j-1)(j+1)\cdots N] \rangle , \tag{10}$$

$$\langle \hat{U}_{ij}, k \rangle = 0 \qquad (k = 1,2,\cdots i, \cdots j, \cdots N) . \tag{11}$$

In this way one derives the complete ψ.

$$\psi = \phi_0 + \sum_{i=1}^{N} \{\hat{f}_i\} + \sum_{i>j}^{N} \{\hat{U}'_{ij}\} + \sum_{ijk}^{N} \{\hat{U}'_{ijk}\} + \cdots + \{\hat{U}'_{123\cdots N}\} , \tag{12}$$

where, e.g.,

$$\{\hat{U}'_{ijk}\} \equiv \frac{\mathcal{A}}{(3!)^{\frac{1}{2}}} \left\{ (123\cdots N) \frac{\hat{U}'_{ijk}}{ijk} \right\} . \tag{13}$$

Each $\hat{U}'$ is antisymmetric and satisfies equations similar to (11)

$$\langle \hat{U}_{ijk\cdots n}, k \rangle = 0 \quad (k = 1,2,\cdots i,j,k \cdots n, \cdots N) . \tag{14}$$

The form Eq. (12) was arrived at in different ways before.[1] The method just presented shows in addition that

$$\hat{U}'_{\underbrace{ijk\cdots n}_{q}} = \left(\frac{N!}{q!} \right)^{\frac{1}{2}} \left\langle \chi^{(q-1)}, \frac{(123\cdots N)}{(ijk\cdots n)} \right\rangle' ; \tag{15}$$

a q-electron "cluster"[1] function is obtained from the $(q-1)$th remainder $\chi^{(q-1)}$.

These results, Eqs. (12) and (15), formally apply not just with the Hartree–Fock orbitals of ϕ_0 but with any ϕ_0^0, Eq. (1). The magnitudes and meanings of each term however differ depending on what the initial orbitals are. It was shown previously[1] that in the particular case when ϕ_0 is the Hartree–Fock wave function the remaining terms are particularly simple and most of them are of negligible magnitude. The main terms that remain are the pair functions $\hat{U}'_{ij}$.

The derivation above is for a closed-shell case. A similar derivation can be carried out for a nonclosed shell system too using a projection operator $\mathcal{O}$ that turns an orbital product into the desired symmetry function instead of $[\mathcal{A}/(N!)^{\frac{1}{2}}]$ in Eq. (1). The derivation of this general case, however, will not be attempted here.

APPLICATION TO THE ANALYSIS AND IMPROVEMENT OF TRIAL FUNCTIONS

Above derivation has been given for an exact many-electron function ψ. The same type of analysis can be carried out on any many electron function. The results of many computations on many electron atoms and molecules are trial functions $\tilde{\psi}$ which do not show the various correlation effects as in Eq. (12) but instead contain various convenient functional forms and variational parameters. The method described above can be used to analyze such a $\tilde{\psi}$ and write it in the form of Eq. (12). Then it becomes possible to see what effects are represented by $\tilde{\psi}$ and to gain much more information from it.

In addition to such detailed interpretation this method also gives a means for the improvement of trial functions. Consider the case of a many electron atom or molecule for which in addition to a trial function $\tilde{\psi}$ the Hartree–Fock wave function ϕ_0 is known. Suppose that using Eqs. (15) various terms $\hat{f}_i$, $\hat{U}'_{ij}$, $\hat{U}'_{ijk}, \cdots$ have been obtained from these. Now according to the general many electron theory[1] certain terms such as $\hat{f}_i$, $\hat{U}'_{ijk}$, etc. are expected to be small in well-defined cases[1a,c]. Suppose however the trial

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[4] Equation (6) is simply a partial integral over $(N-1)$ spin-electron coordinates. One could evaluate $\langle \phi_0, \chi \rangle$ by doing these $(N-1)$ partial integrations first; integration over the remaining χ_i would then give $\langle \phi_0, \chi \rangle = 0$. Thus different partial integrations out of $\langle \phi_0, \chi \rangle$ define the various terms of ψ.

function $\tilde{\psi}$ comes out with one of these terms large. Then if the general conclusions of the theory are correct, it must mean that such a term has been introduced as a spurious effect just because of the poorness of the trial function. But then, removal of spurious terms must yield a better trial function as judged by an improved variational energy.

Such a procedure has in fact been applied to several systems in examining whether $\hat{f}_i$ are indeed small.[1c] The same procedure applies to terms like $\hat{U}_{ijk}$.

If the trial function comes out not to contain enough of the terms which are expected to be large then a similar improvement should result by modifying just those terms.

It would be interesting to analyze for example the "alternant orbital" wave functions[5] on conjugated systems, also the wave functions of Harris and Taylor[6] on small diatomic molecules like LiH, in the way described above.

APPLICATION TO OBTAINING HARTREE-FOCK WAVE FUNCTIONS DIRECTLY FROM MANY ELECTRON TRIAL FUNCTIONS

Consider now an atom or molecule for which a good trial function $\tilde{\psi}$ has been obtained directly by a method which "by-passes" the Hartree–Fock calculation. It is still desirable to have the Hartree–Fock orbitals both for the interpretation of $\tilde{\psi}$ and because they are of intrinsic interest.[1a,c]

The H.F. ϕ_0 can be obtained directly by the above method without a separate variational calculation, if $\tilde{\psi}$ is close to ψ. One starts with some very simple orbitals i^0 which in general will be available. For instance in molecules these could be simple LCAO–MO's, in atoms single Slater orbitals.

Taking these as the ϕ_0^0, Eq. (1), one calculates according to Eq. (6) and in the way demonstrated by some examples[1c] the corrections $\hat{f}_i^0$ to these orbitals i^o. Now if the $\hat{f}_i$ [corrections to the H.F. orbitals i] that would have appeared in the exact wave function Eq. (12) starting with the Hartree–Fock ϕ_0 are indeed negligible then the new $\hat{f}_i^0$ obtained will be only the corrections to i^0 which try to turn them into the Hartree–Fock orbitals i. In fact a good approximation to a Hartree–Fock orbital i in this case would be obtained just by

$$i \cong \frac{i^o + \hat{f}_i^o}{(1 + \langle \hat{f}_i^o, \hat{f}_i^o \rangle)^{\frac{1}{2}}} \tag{16a}$$

$$\hat{f}_i^o(\mathbf{x}_i) = (N!)^{\frac{1}{2}} \langle \chi^o, 1^o 2^o \cdots [i-1]^o [i+1]^o \cdots N^o \rangle' \tag{16b}$$

$$\chi^o = \tilde{\psi} - \langle \tilde{\psi}, \phi_0^0 \rangle \phi_0^0 \,. \tag{16c}$$

The new orbital has been renormalized to unity. Note also that the normalization of $\tilde{\psi}$ changes depending on what ϕ_0^0 is [Eq.(4)].

Kestner[7] did such a calculation on helium atom. His trial $\tilde{\psi}$ was a three term Hylleraas function containing r_{12} and his starting orbital i^o a single Slater 1*s*. Then with just one integration [$\langle U_{12}, i^o \rangle$] he obtained a Hartree–Fock 1*s* orbital very close to the analytic Hartree–Fock function of Clementi and Roothaan.[8] Orbitals thus obtained could be further improved by more iterations corresponding to the repeated use of Eq. (16) each time using a better i^0.

In this way one avoids two separate variational problems, one for the Hartree–Fock ϕ_0 another for the total $\tilde{\psi}$ for methods which "by-pass" Hartree–Fock calculations. Again the alternant orbital wave functions and the small molecule calculations mentioned above,[5,6] would be other interesting cases on which to try this procedure.

DISCUSSION

The method described above shows also how one could obtain the orbitals of various generalized SCF methods, such as Brueckner's.[9–11] In fact orbitals obtained at each iteration of Eqs. (16), after approaching the H.F. orbital, would, if iterations are continued, approach the generalized SCF one [see Eq. (17) below]. In general there will not be any need to calculate the $\hat{f}_i$ beyond H.F. however, since it has been shown[1,12] that the difference between the generalized SCF and H.F. orbitals should be negligible in closed shells. There are cases on the other hand intermediate between closed and nonclosed shells[1c] for which one needs to go beyond the appropriate H.F. ϕ_0 and get the additional $\hat{f}_i$.

It is desirable to use Hartree–Fock orbitals as the basis of an orbital picture as much as possible instead of generalized ones. Hartree–Fock orbitals can be obtained either by the usual independent variational method or from the given trial $\tilde{\psi}$ in the way described above. For the generalized SCF orbitals on

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[5] R. Pauncz, J. De Heer and P. O. Löwdin, J. Chem. Phys. **36**, 2242, 2257 (1962); J. DeHeer, J. Chem. Phys. **37**, 2078 (1962); R. Pauncz, J. Chem. Phys. **37**, 2739 (1962).

[6] F. E. Harris and H. S. Taylor, J. Chem. Phys. (to be published).

[7] N. R. Kestner, J. Chem. Phys. (to be published).

[8] We are indebted to C. C. J. Roothaan and to E. Clementi for making their analytic Hartree–Fock programs available to us.

[9] K. A. Brueckner, in *The Many-Body Problem*, edited by C. DeWitt and P. Nozieres (John Wiley & Sons, Inc., New York, 1959).

[10] P. O. Löwdin, J. Math. Phys. **3**, 1171 (1962).

[11] J. C. Slater, Phys. Rev. **91**, 528 (1953).

[12] E. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 2966 (1962).

the other hand there is no independent way; to get them one must have essentially the exact many electron function ψ to start with.

The orbitals obtained by adding the further $\hat{f}_i$ to the H.F. orbitals approach the generalized SCF orbitals i_G. They are also close to the first natural spin orbitals $i_{\rm nso}$ as shown by Davidson and Jones.[11]

$$i_G \cong \frac{i_{\rm H.F.} + \hat{f}_i}{(1 + \langle \hat{f}_i, \hat{f}_i \rangle)^{\frac{1}{2}}} \cong i_{\rm nso} \,. \qquad (17)$$

Their calculations on the ground state of H_2 at the equilibrium distance showed the first natural orbital to be very close to the Hartree–Fock orbital.

CONCLUSION

A method has been given which shows how a many electron trial function $\tilde{\psi}$ of arbitrary functional form and many parameters can be analyzed into physically and chemically meaningful terms and improved by the examination of these terms. It is also shown how from a trial $\tilde{\psi}$ which bypasses the Hartree–Fock method, the Hartree–Fock orbitals can be obtained just by partial integrations without requiring a separate variational calculation.

Discussion on Atomic Spectra

J. C. Slater, *Chairman*

Murrell: Can anything further be deduced from Rydberg defects for molecules concerning the effects of penetration or polarization?

Mack: Edlén's forthcoming *Handbuch der Physik* monograph has a pertinent discussion.

Horak: Some years ago, I made calculations of x-ray states like $1s(2s)^2(2p)^6\ {}^2S$ using the Morse–Young–Haurwitz analytical wave functions (Z. Horak, Czech. J. Phys. **8**, 271, 1958). In connection with this research an interesting problem arose.

The question is: If you apply the variational principle, you have to orthogonalize—as everybody suggests—to lower lying states of the same symmetry. But what to do here? Let's analyze what we do in practice. We forget about our "orthogonality catastrophe" and look simply for the extremum of the variational functional, $\delta \int \psi^* H \psi d\tau$. No doubt, such extremes exist; this means also that the extremization should be useful even for ordinary excited states like $(1s2s)\ {}^1S$, which was actually the case. Evidently in the case of extremization the advantage of the variation principle $E \geqslant E_{\rm exact}$ is now lost.

The question is: why don't we substitute in atoms the variation principle by the Z perturbation expansion? Especially in x spectra, everybody knows that the Moseley-like formulas of the type $1/n^2\ (Z - S)^2$ or simply three-term formulas $aZ^2 + bZ + c$ fit the experimental data very well. The problem is in the calculation of c, but if we start with the second-order perturbation formula $\sum_j [|H_{ij}|^2/(E_i - E_j)]$ (including the continuum), we can calculate energy differences directly. We thus avoid taking small differences between two big quantities as the HF-method does (a particularly outstanding feature in x-ray spectra) a procedure which Professor Coulson characterized as "weighing of the captain of the ship by weighing the ship when he is or is not on board."

Löwdin: Just a word of warning from the mathematical side: orthogonality $\langle \varphi_k | \varphi_l \rangle = 0$ is not sufficient to ensure the existence of an upper bound to the energy; one needs also the noninteraction property $\langle \varphi_k | H | \varphi_l \rangle = 0$.

McWeeny: In some recent work [R. McWeeny and Y. Öhrn, Technical Report, No. 60, 15 Feb. 1961, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden (unpublished)], Yngve Öhrn and I investigated systems with a single-series electron, using an approximate wave function

$$\Psi(1,2,\cdots N) = \mathcal{A}[\Phi(1,2,\cdots N-1)\varphi(N)] \,.$$

Here Φ is an arbitrary wave function (possibly an exact wave function for the positive ion), φ describes the series electron, and $\mathcal{A}$ is an antisymmetrizer. It is then possible to formulate a one-body eigenvalue equation to determine φ, all core penetration effects (including nonorthogonality) being absorbed into an effective one-body Hamiltonian, containing certain pseudopotentials which ensure that a variational φ will not "collapse" into the core. The energy of the whole system is then $E = E_{\rm core} + E_{\rm series}$ and if $E_{\rm core}$ is sensibly constant for different series electron states