

Solution of the Hartree-Fock Problem by Expansion onto Nested Bases*

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Abstracts

A method for solving the Hartree-Fock problem in a finite basis set is derived, which permits each orbital to be expanded in a different basis. If the basis set for each orbital ϕ_i contains the basis functions for the preceding orbitals, ϕ_{i-1} , ϕ_{i-2} , \dots , ϕ_1 , then the ϕ_i form an orthonormal set. One advantage over the standard Hartree-Fock method is that a different long range behavior for each orbital, as for example is required in the Hartree-Fock-Slater method, can be forced. A calculation on the ground state of beryllium is performed using the nested procedure. Very little energy is lost because of nesting, and the node in the $1s$ orbital disappears.

On décrit une méthode pour résoudre les équations de Hartree-Fock avec une base finie, et qui permet un développement dans une base différente pour chaque orbitale. Si la base pour chaque orbitale ϕ_i contient les fonctions de base des orbitales précédentes, ϕ_{i-1} , ϕ_{i-2} , \dots , ϕ_1 , les orbitales ϕ_i forment un système orthonormal. Un avantage sur la méthode Hartree-Fock ordinaire, est qu'un comportement à longue portée différent pour chaque orbitale peut être imposé, ce qui est nécessaire par exemple dans la méthode de Hartree-Fock-Slater. Un calcul de l'état normal de l'atome de béryllium a été fait avec la méthode proposée ici. Très peu d'énergie a été perdue et le noeud de l'orbitale $1s$ disparaît.

Es wird eine Methode für die Lösung des Hartree-Fock'schen Problems mit einem endlichen Basissatz hergeleitet, was die Entwicklung jedes Orbitals in einem verschiedenen Basissatz ermöglicht. Wenn der Basissatz jedes Orbitals ϕ_i die Basisfunktionen der früheren Orbitale ϕ_{i-1} , ϕ_{i-2} , \dots , ϕ_1 enthält, bilden die Orbitale ϕ_i ein Orthogonalsystem. Ein Vorteil über der gewöhnlichen Hartree-Fock-Methode ist dass ein verschiedenes Verhalten für grosse Argumente für jedes Orbital erzwungen werden kann, was z.B. in der Hartree-Fock-Slaterschen Methode erfordert ist. Eine Berechnung wird mit der vorgeschlagenen Methode ausgeführt. Sehr wenig Energie wird verloren, und der Knoten in dem $1s$ -Orbitale verschwindet.

1. Introduction

A most successful approach to solving the Hartree-Fock problem for atoms and molecules involves expansion of the Hartree-Fock (H-F) orbitals as linear

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combinations of basis functions [1, 2]. The coefficients of the basis functions are determined by minimizing the energy. In the standard approach, all basis functions of a given symmetry contribute to each H-F orbital; there is no way to use different basis sets for different orbitals of the same symmetry without destroying the orthogonality which is essential to the method.

There are situations, however, in which certain basis functions definitely should be excluded from certain H-F orbitals. In an atomic configuration consisting only of s orbitals and in any atomic or molecular configuration whenever a Slater-type average exchange potential [3] is used, the orbitals behave asymptotically like [4]

$$(1) \quad \phi_i \sim \exp(-r\sqrt{-2\varepsilon_i}),$$

where ε_i is the orbital energy of ϕ_i . Clearly, Slater-type orbital basis functions with orbital exponents less than $\sqrt{-2\varepsilon_i}$ should be excluded from ϕ_i . Often in an actual calculation one finds that certain basis functions play a crucial role in one or two orbitals, but only clutter up the representation of the other orbitals. One would like to be able to exclude such "unnecessary" basis functions from H-F orbitals.

It is the purpose of the present paper to derive an "analytical-basis-set expansion" method for solving the Hartree-Fock problem, which permits the use of different bases for different orbitals. The limiting wavefunction in this new method, in the limit of a complete basis, is the Hartree-Fock wavefunction. Only the *approach to the limit*, not the limit itself, differs from the standard [1, 2] expansion method.

In this method the total energy remains a minimum (for determinantal wavefunctions satisfying the basis set restriction), and the resultant orbitals are automatically orthogonal (even though they are not all expressed as linear combinations of the same basis functions). A sample calculation on the beryllium ground state is given which displays an additional feature: when orbital exponents less than $\sqrt{-2\varepsilon_{1s}}$ are excluded from ϕ_{1s} , the node [5] formerly found in ϕ_{1s} disappears.

2. Statement of the Nested Basis Hartree-Fock Problem

The problem is to find the single determinant,

$$(2) \quad \Psi = A\{\phi_1^2 \phi_2^2 \cdots \phi_N^2\}$$

which minimizes the energy of an atom or molecule. We later treat the general case that each orbital be expanded on its own, independent basis, but first we discuss a more restricted case which permits the usual requirement that the ϕ_i be orthonormal. Let the basis set for the last orbital ϕ_N be $\{\chi_1, \chi_2, \cdots, \chi_M \mid M > N\}$.

Require that the next-to-last orbital ϕ_{N-1} be composed from a subset of this basis, that ϕ_{N-2} be from a subset of this subset, and so on. We thus require,

$$(3) \quad \phi_i = \sum_{j=1}^{n_i} c_{ij} \chi_j,$$

where

$$(4) \quad n_1 \leq n_2 \leq \dots \leq n_N = M.$$

From the first orbital on, each ϕ_i is expanded on a larger basis than the preceding ϕ_{i-1} , and all the bases are nested.

We treat only the closed shell case with no considerations of symmetry, but both symmetry and open-shells can be included with simple changes.

3. Brillouin-Type Conditions

The Ψ of the form of Equation (2) which minimizes the energy satisfies the Brillouin-type condition,

$$(5) \quad \langle \delta\phi_{i\perp} | h + \sum_{j=1}^N (2J_j - K_j) | \phi_i \rangle = 0, \quad (i = 1, 2, \dots, N),$$

where h is the Hamiltonian for an electron moving in the field of the bare nuclei, and J_j and K_j are the usual Coulomb and exchange operators for orbital ϕ_j . The quantity $\delta\phi_{i\perp}$ is a change in orbital ϕ_i , subject to the restriction that only basis functions χ_j with $j \leq n_i$ are allowed to occur in $\delta\phi_i$,

$$(6) \quad \delta\phi_i = \sum_{j=1}^{n_i} \delta c_{ij} \chi_j,$$

which has then been orthogonalized to all N orbitals ϕ_k ,

$$(7) \quad \delta\phi_{i\perp} = \left(1 - \sum_{k=1}^N |\phi_k\rangle\langle\phi_k| \right) \delta\phi_i.$$

Let

$$(8) \quad P = \sum_{k=1}^N |\phi_k\rangle\langle\phi_k|,$$

and

$$(9) \quad F = h + \sum_{j=1}^N (2J_j - K_j).$$

Then Equation (5) can be written

$$(10) \quad \langle \delta\phi_i | (1 - P) F | \phi_i \rangle = 0,$$

where the only restriction on $\delta\phi_i$ is Equation (6). For Equations (5)–(10) to be valid, the ϕ_i 's must be orthonormal.

4. Pseudo-Eigenvalue Equation and Iterative Computational Procedure

Equation (10) leads directly to an eigenvalue equation for ϕ_i . Let $P_{<i}$ and $P_{>i}$ denote:

$$(11) \quad P_{<i} \equiv \sum_{k=1}^{i-1} |\phi_k\rangle\langle\phi_k|$$

$$(12) \quad P_{>i} \equiv \sum_{k=i+1}^N |\phi_k\rangle\langle\phi_k|$$

Then Equations (6) and (10) imply that ϕ_i is an eigenfunction of the operator F_i , defined by

$$(13) \quad F_i \equiv (1 - P_{<i} - P_{>i})F(1 - P_{<i} - P_{>i}),$$

$$(14) \quad = (1 - P_{<i})(1 - P_{>i})F(1 - P_{>i})(1 - P_{<i}),$$

within the basis $\{\chi_1, \chi_2, \dots, \chi_{n_i}\}$. Define the $n_i \times n_i$ matrices \mathbf{F}_i and \mathbf{S}_i by

$$(15) \quad (\mathbf{F}_i)_{ab} \equiv \langle\chi_a| F_i |\chi_b\rangle, \quad (a, b \leq n_i),$$

$$(16) \quad (\mathbf{S}_i)_{ab} \equiv \langle\chi_a | \chi_b\rangle, \quad (a, b \leq n_i),$$

and let

$$(17) \quad \mathbf{c}_i \equiv \begin{bmatrix} c_{i1} \\ c_{i2} \\ \vdots \\ c_{in_i} \end{bmatrix}.$$

Then the \mathbf{c}_i are determined by the pseudo-eigenvalue equations,

$$(18) \quad \mathbf{F}_i \cdot \mathbf{c}_i = \varepsilon_i \mathbf{S}_i \cdot \mathbf{c}_i, \quad (i = 1, 2, \dots, N),$$

which are the analogue of the standard [1] Hartree–Fock equations in the finite analytical basis-set approach. Note that the functions ϕ_i are orthogonal because they are all eigenfunctions of the same Hermitian operator, F_N . An expression for F_i in matrix notation is given in the Appendix.

One may construct the following iterative procedure for calculating the ϕ_i .

(1) Make an initial guess of (orthonormal) $\phi_i : \phi_i^{(0)}$. The $\phi_i^{(0)}$ determine an initial $F^{(0)}$ and $P_{>1}^{(0)}$.

(2) Diagonalize $\mathbf{F}_1^{(0)}$,

$$(19) \quad (\mathbf{F}_1^{(0)})_{ab} = \langle \chi_a | (1 - P_{>1}^{(0)}) F^{(0)} (1 - P_{>1}^{(0)}) | \chi_b \rangle, \quad (a, b \leq n_1),$$

and select the eigenfunction which represents the first iteration for $\phi_1, \phi_1^{(1)}$. If the ϕ_i are numbered in order of increasing orbital energy, then $\phi_1^{(1)}$ corresponds to the lowest eigenvalue of $\mathbf{F}_1^{(0)}$.

(3) To obtain $\phi_2^{(1)}$, construct $\mathbf{F}_2^{(0)}$ so that its solutions are orthogonal to $\phi_1^{(1)}$, not $\phi_1^{(0)}$. Thus, define

$$(20) \quad P_{<2}^{(0)} \equiv |\phi_1^{(1)}\rangle\langle\phi_1^{(1)}|$$

and

$$(21) \quad (\mathbf{F}_2^{(0)})_{ab} = \langle \chi_a | (1 - P_{<2}^{(0)}) (1 - P_{>2}^{(0)}) F^{(0)} (1 - P_{>2}^{(0)}) (1 - P_{<2}^{(0)}) | \chi_b \rangle, \quad (a, b \leq n_2).$$

Diagonalize $\mathbf{F}_2^{(0)}$ and select the first iteration for $\phi_2, \phi_2^{(1)}$. Note that $\phi_1^{(1)}$ is an eigenfunction of $\mathbf{F}_2^{(0)}$ with eigenvalue 0.

(4) In the i th step of the m th iteration, $\phi_i^{(m)}$ is determined as an eigenfunction of $F_i^{(m-1)}$ within the basis $\{\chi_1, \chi_2, \dots, \chi_{n_i}\}$, where

$$(22) \quad P_{>i}^{(m-1)} = \sum_{k=i+1}^N |\phi_k^{(m-1)}\rangle\langle\phi_k^{(m-1)}|,$$

$$(23) \quad P_{<i}^{(m-1)} = \sum_{k=1}^{i-1} |\phi_k^{(m)}\rangle\langle\phi_k^{(m)}|,$$

$$(24) \quad F^{(m-1)} = h + \sum_{j=1}^N (2J_j^{(m-1)} - K_j^{(m-1)}),$$

in which $J_j^{(m-1)}$ and $K_j^{(m-1)}$ are computed with $\phi_j^{(m-1)}$, and

$$(25) \quad F_i^{(m-1)} = (1 - P_{<i}^{(m-1)}) (1 - P_{>i}^{(m-1)}) F^{(m-1)} (1 - P_{>i}^{(m-1)}) (1 - P_{<i}^{(m-1)}).$$

(5) Continue until self consistency is achieved.

A variant of the above procedure is to iterate without changing $F^{(m-1)}$ until self-consistency has been reached among the $\phi_i^{(m)}$, $P_{<i}^{(m-1)}$, and $P_{>i}^{(m-1)}$, and then to compute $F^{(m)}$. The $P_{<i}^{(m-1)}$ and $P_{>i}^{(m-1)}$ must always refer to the most recently obtained ϕ_j , ($j \neq i$).

5. Remarks

Note that in contrast to the Hartree-Fock method, in general,

$$(26) \quad \langle \phi_i | F | \phi_j \rangle \neq 0.$$

If, however, the bases were complete for the Hartree-Fock orbitals, the ϕ_i would be equivalent to *the* Hartree-Fock orbitals, i.e., connected by a unitary transformation which would diagonalize F . The unitary transformation would not in general leave the "nestedness" of the bases invariant. It is to be emphasized, however, that in practice the finite-basis-set ϕ_i can of course be made to approximate closely the Hartree-Fock orbitals by suitable choice and arrangement of the basis functions.

In the nested basis procedure, the total energy will be greater than the energy found by the standard Hartree-Fock finite-expansion procedure with the same number of basis functions. If the basis is good enough, the energy difference should be negligible.

For the exact Hartree-Fock orbitals, Equation (26) is an equality, and Equation (1) holds for the states under consideration. Approximate orbitals which are determined by the standard Hartree-Fock procedure will satisfy Equation (26) as an equality, but they will not satisfy Equation (1) with a finite basis set. Moreover, in general, it is not possible to make these approximate orbitals satisfy Equation (1) by a unitary transformation. In the present method, the approximate orbitals satisfy Equation (1), but Equation (26) becomes an inequality.

In the case that two or more orbitals, say ϕ_i and ϕ_{i+1} , share the same basis set (i.e., $n_i = n_{i+1}$), the procedure outlined above can be used, but ϕ_i and ϕ_{i+1} will not be uniquely determined. Note however that since Ψ is unchanged by a unitary transformation on $[\phi_i, \phi_{i+1}]$, Ψ is uniquely determined. A way to select ϕ_i and ϕ_{i+1} in this case, agreeing in spirit with the Hartree-Fock method, is to diagonalize

$$(27) \quad (1 - P_{<i})(1 - P_{>i+1})F(1 - P_{>i+1})(1 - P_{<i})$$

over the basis $\{\chi_1, \chi_2, \dots, \chi_{n_{i+1}}\}$ and to select the two corresponding orbitals ϕ_i and ϕ_{i+1} . In this case,

$$(28) \quad \langle \phi_i | F | \phi_{i+1} \rangle = 0.$$

We now consider the general case that the bases are not nested and the orbitals are not orthogonal. For clarity, we denote the nonorthogonal orbitals by ω_i :

$$(29) \quad \Psi = A\{\omega_1^2 \omega_2^2 \cdots \omega_N^2\},$$

$$(30) \quad \langle \omega_i | \omega_j \rangle \neq 0, \quad (i \neq j).$$

Each ω_i is expanded on its own basis $\{\chi_j^{(i)} | j = 1, 2, \dots, m_i\}$,

$$(31) \quad \omega_i = \sum_{j=1}^{m_i} d_{ij} \chi_j^{(i)}.$$

There need not be any connection between the different bases $\{\chi_j^{(i)}\}$ and $\{\chi_j^{(k)}\}$ ($i \neq k$). We find it easier to calculate the ω_i via an equivalent set of Schmidt-orthogonalized orbitals ϕ_i . Define,

$$(32) \quad \phi_1 \equiv \omega_1,$$

$$(33) \quad \phi'_i = \left(1 - \sum_{k=1}^{i-1} |\phi_k\rangle\langle\phi_k|\right) \omega_i;$$

$$(34) \quad \begin{aligned} \phi_i &= \phi'_i \langle\phi'_i | \phi'_i\rangle^{-1/2} \\ &= \sum_{j=1}^{m_i} c_{ij} \chi_j^{(i)} + \sum_{j=1}^{i-1} c_{i,i+j} \phi_j \end{aligned}$$

Except for a constant factor, the determinant of the ϕ_i (Equation 2) is identical with the determinant of the ω_i . By reasoning similar to that in Sections 3 and 4, one would expect ϕ_i still to satisfy Equations (3) and (18). But in order to have consistency and orthogonality, the ϕ_k ($k \leq i$) must all be eigenfunctions of the same Hermitian operator. This can only be achieved if the basis appropriate for the ϕ_i equation is capable of representing ϕ_k ($k \leq i$). Accordingly,* let $\{\chi_1^{(i)}, \chi_2^{(i)}, \dots, \chi_{m_i}^{(i)}, \phi_1, \phi_2, \dots, \phi_{i-1}\} \equiv \{\chi'_1, \chi'_2, \dots, \chi'_{m_i+i-1}\}$ denote the appropriate basis for ϕ_i (cf. Equation 34). Then, with

$$(35) \quad (\mathbf{F}_i)_{ab} \equiv \langle\chi'_a | F_i | \chi'_b\rangle, \quad (a, b \leq m_i + i - 1),$$

$$(36) \quad (\mathbf{S}_i)_{ab} \equiv \langle\chi'_a | \chi'_b\rangle, \quad (a, b \leq m_i + i - 1),$$

and

$$(37) \quad \mathbf{c}_i \equiv \begin{bmatrix} c_{i1} \\ c_{i2} \\ \vdots \\ c_{i, m_i+i-1} \end{bmatrix},$$

instead of Equations (15)–(17), the \mathbf{c}_i (and thus ϕ_i) satisfies Equation (18). Moreover, the ϕ_k ($k < i$) are zero-energy eigenfunctions of Equation (18). Finally, the c_{ij} of Equation (37) with $j \leq m_i$ are identical except for a normalization factor with the d_{ij} of Equation (31), and ω_i is thus determined. It is straightforward to obtain an iterative procedure to calculate the ω_i .

* It is to be understood that if addition of certain ϕ_k to the basis introduces linear dependency, those ϕ_k should be omitted. Thus if $\{\chi_1^{(i)}, \dots, \chi_{m_i}^{(i)}\}$ includes the bases for $\phi_1, \phi_2, \dots, \phi_{i-1}$, then no ϕ_k should be added to the basis.

6. Example

An example for which the present method should be useful is the Be ground state. In this case the exact Hartree-Fock $1s$ orbital has a tail like $\exp\{-r\sqrt{-2\varepsilon_{1s}}\}$ and the exact Hartree-Fock $2s$ orbital has a tail like $\exp\{-r\sqrt{-2\varepsilon_{2s}}\}$, [4], where ε_{1s} and ε_{2s} denote orbital energies. Since $|\varepsilon_{1s}| > |\varepsilon_{2s}|$, the $1s$ orbital should be represented by Slater-type basis functions with no orbital exponent less than, but some equal to $\sqrt{-2\varepsilon_{1s}}$, and similarly for the $2s$ orbital. In particular, the $2s$ basis functions with orbital exponents less than $\sqrt{-2\varepsilon_{1s}}$ should be excluded from the $1s$ orbital to insure correct behavior at large r . *This cannot be achieved in the standard finite basis set expansion method.*

We have performed a calculation for the $Be (1s)^2(2s)^2$ ground state. The results are listed in Table I, together with the results of the standard Hartree-Fock-Roothaan calculation. The basis set is the same as that employed by

TABLE I. Energies and wavefunctions for $Be (1s^2 2s^2)$ computed by various Hartree-Fock methods.^{a,b}

Standard Hartree-Fock finite-basis-set expansion method		
Basis $\{\chi_i\}$	$\varepsilon_{1s} = -4.732\ 683\ 70$	$\varepsilon_{2s} = -0.309\ 271\ 619$
$1s (\zeta = 3.5297)$	0.902 033 074	-0.155 861 437
$1s (6.4072)$	0.083 676 216	-0.019 025 633
$2s (3.2341)$	0.029 052 032	-0.074 504 692
$2s (1.1956)$	0.001 108 642	0.521 217 011
$2s (0.8198)$	-0.000 564 755	0.545 921 226
	$E_{\text{total}} = -14.573\ 0136$	
Nested basis set procedure		
Basis $\{\chi_i\}$	$\varepsilon_{1s} = -4.732\ 688\ 38$	$\varepsilon_{2s} = -0.309\ 271\ 497$
$1s (\zeta = 3.5297)$	0.901 614 477	-0.155 524 479
$1s (6.4072)$	0.083 901 958	-0.018 996 021
$2s (3.2341)$	0.029 599 338	-0.074 496 958
$2s (1.1956)$	—	0.521 214 965
$2s (0.8198)$	—	0.545 923 945
	$E_{\text{total}} = -14.573\ 0130$	
Nested-basis-set Hartree-Fock procedure with long-range forced		
Basis $\{\chi_i\}$	$\varepsilon_{1s} = -4.732\ 786\ 28$	$\varepsilon_{2s} = -0.309\ 285\ 578$
$1s (\zeta = 3.5328)$	-0.911 239 493	-0.165 314 617
$1s (6.5072)$	-0.077 657 434	-0.014 537 772
$2s (3.0766)$	-0.025 914 566	-0.071 245 881
$2s (1.1643)$	—	0.614 918 439
$2s (0.7865)$	—	0.455 854 415
	$E_{\text{total}} = -14.573\ 0066$	

^a See text for description of three methods.

^b Listed under each orbital energy are the linear coefficients of the normalized basis orbitals specified in the leftmost column.

Clementi [5], with the two basis functions having the smallest exponents removed from the $1s$ orbital. In a further calculation the correct long-range behavior of the orbitals has been forced by setting $\zeta_3 = \sqrt{-2\varepsilon_{1s}}$ and $\zeta_5 = \sqrt{-2\varepsilon_{2s}}$ and computing new energies, then changing ζ_3 and ζ_5 again, recomputing the energies, and so on until self consistency was obtained. These orbitals are also reported in Table I.

7. Discussion

The simple beryllium calculation exhibits several interesting features. First it will be noted that the energy loss from excluding the small-orbital-exponent basis functions from the $1s$ orbital is negligible, and further if the correct long range exponential behavior is forced, there is also an equally negligible loss of energy.

TABLE II. Values of $\langle \phi_{1s} | r^n | \phi_{1s} \rangle$ for the $1s$ orbital of Be .

n	Standard Hartree-Fock ^a	Nested Hartree-Fock ^b Long-Range Forced
0	1.0	1.0
2	0.2329	0.2329
4	0.1420	0.1420
6	0.1675	0.1664
8	0.3830	0.3205
10	6.1529	0.9225
12	548.6344	3.7283
14	68751.1067	20.2431

^a First $1s$ orbital of Table I.

^b Last $1s$ orbital of Table I.

In Table II, values of the integrals $\langle \phi_{1s} | r^n | \phi_{1s} \rangle$, $0 \leq n \leq 14$, are compared for the standard Hartree-Fock $1s$ orbital and the nested Hartree-Fock $1s$ orbital with the correct long-range behavior. The large difference in these values at large n illustrates the quite different long-range behavior of these two orbitals.

Finally it will be noticed that the distant node which is present in the standard Hartree-Fock $1s$ orbital disappears in the nested calculations.* The "node" in the $1s$ orbital is a peculiarity of Hartree-Fock calculations: extra nodes, beyond the number of nodes in the corresponding hydrogen orbital and not required for

* A referee has suggested that a simpler method to remove the node in the $1s$ orbital is to put to zero the small coefficients and reorthogonalize the $2s$ orbital to this "corrected" $1s$ orbital. The total energy computed by this method will be above the minimum energy calculated by the nested procedure. The energy computed in this way is -14.5730125 , compared to -14.5730130 by the nested procedure. Although the difference in energy is negligible in this case, for a more general case, where the orbital energies are not so greatly separated, it may be expected to be much more significant. Only the nested basis set method can insure minimization of the energy using the restricted basis sets for certain orbitals.

orthogonality, when present occur at large values of r . The beryllium example leads us to conjecture that such distant extra nodes may be artifacts which result from an approximation procedure which forces the orbitals to behave incorrectly at large r .

For atomic configurations constructed entirely from s orbitals, and for atoms and molecules treated by a Hartree-Fock-Slater approximation or any similar approximation in which the effective local exchange potential goes to zero at large r at least like $1/r$ † the asymptotic behavior [4] of each orbital ϕ_i will be like $\exp(-r\sqrt{-2\varepsilon_i})$, where ε_i is the orbital energy of ϕ_i , and one would expect there to be no distant nodes. But in the not-all- s -orbital Hartree-Fock case, the asymptotic behavior [4] of all the orbitals is uniform (unlike $B\varepsilon$) and our conjecture is more speculative. In any event, the procedure developed in this paper is well suited for calculating Hartree-Fock orbitals accurate for all values of r .

Finally, this work and the previous paper [4] raise an interesting question about the Hartree-Fock model itself. As one goes from $B\varepsilon$ ($1s^22s^2$) to B ($1s^22s^22p$), there is a remarkable change in the long-range behavior of the Hartree-Fock $1s$ orbital: it changes from an asymptotic behavior $\exp(-r\sqrt{-2\varepsilon_{1s}})$ to an asymptotic behavior $\exp(-r\sqrt{-2\varepsilon_{2p}})$. Should one try to modify the model to eliminate this changeover?

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Appendix

For computational convenience we give a formula for $\mathbf{F}_i^{(m-1)}$ in matrix notation. Define

$$(38) \quad (\mathbf{F}^{(m-1)})_{ab} = \langle \chi_a | F^{(m-1)} | \chi_b \rangle,$$

$$(39) \quad (\mathbf{D}_{<i}^{(m-1)})_{ab} = \sum_{j=1}^{i-1} c_{ja}^{(m)} c_{jb}^{(m)*},$$

and

$$(40) \quad (\mathbf{D}_{>i}^{(m-1)})_{ab} = \sum_{j=i+1}^N c_{ja}^{(m-1)} c_{jb}^{(m-1)*},$$

where $c_{ja}^{(m)}$ denotes the coefficient c_{ja} of Equation (3) in the m th iteration. If

† For example the potential used by F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., New Jersey, 1963).

we let \mathbf{S} denote the overlap matrix (cf. Equation 16) we can define the matrices

$$(41) \quad \mathbf{Q}_{<i} = \mathbf{D}_{<i}^{(m-1)} \mathbf{S},$$

and

$$(42) \quad \mathbf{Q}_{>i} = \mathbf{D}_{>i}^{(m-1)} \mathbf{S},$$

where we have suppressed the $(m-1)$ superscript for notational simplicity. All of the matrices so far defined are $M \times M$ matrices ($M = n_N$), possibly having many zero elements. The matrix representation of $\mathbf{F}_i^{(m-1)}$ (Equation 25) in the basis $\{\chi_j | j = 1, 2, \dots, n_i\}$ is

$$(43) \quad \mathbf{F}_i^{(m-1)} = \{n_i \times n_i \text{ principal submatrix of}\} \\ \{[\mathbf{I} - \mathbf{Q}_{<i}^\dagger - \mathbf{Q}_{>i}^\dagger + \mathbf{Q}_{<i}^\dagger \mathbf{Q}_{>i}^\dagger] \mathbf{F}^{(m-1)} [\mathbf{I} - \mathbf{Q}_{<i} - \mathbf{Q}_{>i} + \mathbf{Q}_{>i} \mathbf{Q}_{<i}]\},$$

where the dagger denotes the adjoint (Hermitian conjugate) matrix and \mathbf{I} is the identity matrix. When self consistency is finally achieved, $\mathbf{Q}_{>i} \mathbf{Q}_{<i}$ is a null matrix.

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