

THE ORTHOGONALITY CONSTRAINED BASIS SET EXPANSION METHOD
FOR TREATING OFF-DIAGONAL LAGRANGE MULTIPLIERS
IN CALCULATIONS OF ELECTRONIC WAVE FUNCTIONS *

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Received 10 June 1969

We propose an alternative to the coupling operator approach for the solution of the self-consistent field equations containing off-diagonal Lagrange multipliers. This method involves a transformation of the basis set after formation of the Hamiltonian matrices and leads to considerable simplification in the equations to be solved, reducing the inhomogeneous equations to pseudo-eigenvalue form. Typical results are reported for the lowest 2A_1 state of H_2O^+ and the lowest 3A_1 and 1A_1 excited states of H_2O .

1. INTRODUCTION

In calculations of the Hartree-Fock wavefunctions for atoms and molecules, the one-electron orbitals which are used to construct the many-electron wavefunction are commonly assumed to be orthogonal. If these orbitals are to be variationally determined, then it is necessary to preserve this orthogonality through the use of Lagrange multipliers. In closed shell systems the wavefunction is invariant to a unitary transformation of the orbitals, and this transformation can be chosen as to eliminate rigorously the off-diagonal Lagrange multipliers. Thus, we may cast the Hartree-Fock equations into pseudo-eigenvalue form [1-3]. However, in open-shell systems the wavefunction is not, in general, invariant to an arbitrary unitary transformation, and so the off-diagonal multipliers must be retained [1, 3].

The present approach, as developed in the following section, does not *explicitly* make use of Lagrange multipliers to maintain orthogonality of the orbitals during the variations. Rather, the orthogonality of a given orbital to the remain-

ing orbitals is ensured by limiting the variations to the space spanned by the functions orthogonal to those orbitals. This technique we call the Orthogonality Constrained Basis Set Expansion (OCBSE) Method.

In the third section we present the results of using OCBSE for the lowest 2A_1 state of H_2O^+ and the lowest excited 3A_1 and 1A_1 states of water. These examples involve up to two open shells of the same symmetry and provide a reasonable test of the efficacy of OCBSE.

Finally, in the last section it is shown that OCBSE can be used to simplify multi-configuration SCF calculations (MC SCF).

2. THE ORTHOGONALITY CONSTRAINED BASIS SET EXPANSION METHOD

The Hartree-Fock wavefunction for a closed shell configuration is

$$\Phi_{\text{HF}} = a[\varphi_1\alpha\varphi_1\beta \dots \varphi_N\alpha\varphi_N\beta],$$

where a is the anti-symmetrizer, φ_i is a one-electron spatial orbital, and α and β are one-particle spin functions. Requiring that the variational expression for orbital φ_i ,

$$I_i = E - \epsilon_{ii}\langle\varphi_i|\varphi_i\rangle - \sum_{j \neq i} [\epsilon_{ij}\langle\varphi_i|\varphi_j\rangle + \epsilon_{ji}\langle\varphi_j|\varphi_i\rangle],$$

be stationary with respect to variations of the orbital, we find that the optimum orbitals satisfy

* Partially supported by a grant (GP-6965) from the National Science Foundation.

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†† Contribution No. 3868.

the set of coupled equations

$$H^{\text{HF}} \phi_i = \epsilon_{ii} \phi_i + \sum_{j \neq i} \epsilon_{ij} \phi_j,$$

where H^{HF} is the one-particle Hartree-Fock Hamiltonian. The diagonal elements of the Lagrange multiplier matrix, ϵ_{ii} , serve to preserve normalization and the off-diagonal elements, ϵ_{ij} , are involved in preserving orbital orthogonality. It is easy to see that the above wavefunction is invariant to a unitary transformation of the orbitals and that this transformation can be chosen such that $\epsilon_{ij} = 0$ ($i \neq j$). Thus, for closed shell systems the Hartree-Fock equations reduce to the familiar pseudo-eigenvalue form [2]

$$H^{\text{HF}} \phi_i = \epsilon_i \phi_i.$$

In an open shell system, on the other hand, while some of the orbitals will be doubly occupied (the closed shell subset), others will only be singly occupied (the open shell subset). It is still possible to eliminate the off-diagonal Lagrange multipliers between the closed shell orbitals [4], but it is not in general possible to eliminate rigorously the off-diagonal multipliers coupling the open shell orbitals* nor those coupling the open and closed shell orbitals. Thus, even in as simple a case as the Hartree-Fock equations for the ground state of the lithium atom, non-zero off-diagonal Lagrange multipliers appear.

Because of the difficulty of solving the Hartree-Fock equations when off-diagonal multipliers are present, early calculations with the Hartree-Fock method often just ignored them [3, 5]. Finally, in 1960 Roothaan [4] showed that for some types of open-shell configurations, *coupling operators* could be defined which incorporate the effect of the off-diagonal Lagrange multipliers. These operators could then be combined with the Hartree-Fock Hamiltonian so as to cast the equations into a pseudo-eigenvalue form. Later, Huzinaga [6, 7], and Birss and Fraga [8] extended this scheme to include a larger class of open-shell configurations. However, calculations on several types of excited states (such as those singlet states involving closed shells and two or more open shells of the same symmetry) have not previously been carried out.

We propose an alternative to the coupling operator technique for calculating the Hartree-Fock wavefunctions for open shell configurations.

* This is the case unless the open shell orbitals of the same symmetry are all associated with the same spin.

Since this method involves constraining the basis set expansion for a given orbital so that it is orthogonal to all of the remaining occupied orbitals, we call this technique the *Orthogonality Constrained Basis Set Expansion* (OCBSE) Method. This new approach simply involves a transformation upon the basis set and the solution of the corresponding equations over a reduced space, without any off-diagonal Lagrange multipliers. This method is applicable only to the case where the SCF equations are solved by expansion techniques.

To illustrate OCBSE we will consider two sets of orbitals of the same symmetry, such as a set of closed shell orbitals and a set of open-shell orbitals. Orthogonality between these orbitals and the remaining orbitals is, of course, ensured by symmetry. An example of such a configuration is the 2A_1 state of the positive ion of water, $[(1a_1)^2(2a_1)^2(3a_1)](1b_1)^2(1b_2)^2$, which will be discussed in the following section. The Hartree-Fock equations are often written as

$$H^A \phi_i^A = \epsilon_{ii}^A \phi_i^A + \sum_q \epsilon_{iq}^A \phi_q^B; \quad (1a)$$

$$H^B \phi_q^B = \epsilon_{qq}^B \phi_q^B + \sum_i \epsilon_{qi}^B \phi_i^A, \quad (1b)$$

$$\langle \phi_i^A | \phi_q^B \rangle = 0;$$

$$i = 1, \dots, n_A; \quad q = 1, \dots, n_B, \quad (1c)$$

where, for example, for the 2A_1 state of H_2O^+

$$H^A = h + 2J_C - K_C + \frac{1}{2}(2J_O - K_O)$$

$$H^B = h + 2J_C - K_C \quad (2a)$$

and J_C , K_C , J_O and K_O are the total Coulomb and exchange operators for the closed and open-shell respectively. In this particular case, $\{\phi_i^A\} = \{\phi(1a_1), \phi(2a_1), \phi(1b_1), \phi(1b_2)\}$ and $\{\phi_q^B\} = \{\phi(3a_1)\}$.

Now, consider a basis set, $\{\chi_\mu; \mu = 1, 2, \dots, M\}$, and project eq. (1b) onto these functions to obtain

$$\langle \chi_\mu | H^B | \phi_q^B \rangle = \epsilon_{qq}^B \langle \chi_\mu | \phi_q^B \rangle + \sum_i \epsilon_{qi}^B \langle \chi_\mu | \phi_i^A \rangle \quad (2b)$$

$$\mu = 1, 2, \dots, M.$$

In OCBSE we choose the basis set $\{\chi_\mu\}$ in eq. (2b) so that the first n_A orbitals are the occupied orbitals of H^A and the remaining $M - n_A$ orbitals are orthogonal to these n_A occupied orbitals. In order to solve eq. (2b) for ϕ_q^B , we expand

$$\varphi_q^B = \sum_{\nu=1}^M \chi_{\nu} C_{\nu q}^B.$$

Since φ_q^B must be orthogonal to the $\{\varphi_i^A; i = 1, \dots, n_A\}$, we have that

$$C_{\nu q}^B = 0 \quad \nu \leq n_A,$$

but for $\mu > n_A$ we have

$$\langle \chi_{\mu} | \varphi_i^A \rangle = 0, \quad (3)$$

and thus, eq. (2b) can be written

$$\sum_{\nu > n_A} H_{\mu\nu}^B C_{\nu q}^B = \sum_{\nu > n_A} S_{\mu\nu} C_{\nu q}^B \epsilon_{qq}^B \quad \mu > n_A. \quad (4)$$

Consequently, we need only solve the usual homogeneous type of SCF equations in the space spanned by those functions which are orthogonal to the occupied orbitals of H^A .

The procedure for solving these equations is to:

- Set up the matrices $\langle \mu | H^A | \nu \rangle$ and $\langle \mu | H^B | \nu \rangle$ in terms of the atomic basis set;
- Construct the transformation matrix, W^A , from the atomic basis to the new basis, where the first n_B columns of W^A are the occupied orbitals of \bar{H}^B from the previous iteration, the next $M - n_A - n_B$ columns are the virtual orbitals of \bar{H}^B and the last n_A columns are the occupied orbitals of \bar{H}^A from the last iteration;
- Transform the Hamiltonian matrix, H^A , over atomic basis functions with W^A , i.e. $\bar{H}^A = \tilde{W}_A H^A W_A$, and diagonalize the lower $M - n_B$ by $M - n_B$ subblock, selecting the desired n_A solutions;
- Construct W_B with the first n_A columns as the occupied orbitals from c, the next $M - n_A - n_B$ columns as the virtual solutions from c, and the last n_B columns as the occupied orbitals of \bar{H}^B from the last iteration;
- Construct $\bar{H}^B = \tilde{W}_B H^B W_B$, solve the lower $M - n_A$ by $M - n_A$ subblock and select the desired n_B solutions;
- Go back to a until the solutions converge.

If there are two open shells, B and C, and a set of closed-shell orbitals, A, we follow the same procedure of constructing the matrices for H^A , H^B , and H^C and then solving these equations by successively transforming to the appropriate basis set. This procedure is sufficiently efficient that each additional open shell leads only to a 25% increase in Hamiltonian formation time over that required for the corresponding (completely) closed-shell calculation. In the case of degener-

ate orbitals, the H^A , H^B , etc. are formed in the usual manner [4].

The OCBSE approach as outlined above has a number of advantages over the coupling operator technique developed by Roothaan. For example, the structure of each of the Hamiltonians is similar to that for closed shell configurations and it is not necessary to form matrix elements over the coupling operator [4]. Consequently, the programming modifications necessary to change a closed shell Hartree-Fock program such as POLYATOM [9] to do open shell calculations are minimal. In addition, all open shell configurations may be handled equivalently. Finally, by Koopmans' theorem the orbital energies, ϵ_{ii} , are approximately the ionization potentials of the system. Note also that for OCBSE it is never necessary to orthogonalize explicitly the occupied orbitals of any iteration*.

The basic idea here of using the orbitals from the i th iteration as the basis for the $(i+1)$ th iteration has also been suggested by Lefebvre [11] and Huzinaga [7]. Lefebvre in 1957 used this approach in his configuration interaction technique for SCF calculations. Huzinaga in the second part of his 1961 paper [7] advanced a method which is conceptually very similar to OCBSE. The major differences are that (a) Huzinaga derived his approach specifically from the energy expression for two open shells, (b) the one- and two-electron integrals are transformed to a new basis at every iteration and (c) only one orbital was solved for in each iteration. Mechanically, (b) above gives rise to a M^5 dependence on the number of basis functions in Huzinaga's scheme rather than M^3 as in OCBSE and (c) requires that a large number of Hamiltonians, say n , be constructed and solved *one at a time*, a process which would be nearly as time-consuming as constructing n groundstate Hamiltonians (even for the simple case of H_2O , 3A_1 , $n = 6$).

3. CALCULATIONS

To illustrate the applicability of the Orthogonality Constrained Basis Set Expansion method to open-shell Hartree-Fock calculations, we have performed such calculations on the lowest 2A_1 state of H_2O^+ and the first excited 3A_1 and 1A_1 Rydberg states of H_2O . These particular ex-

* Such orthogonalization is often required in the coupling operator approach unless the open and closed shell Hamiltonians are combined (e.g., see Selsby and Sukigara [10]).

cited states pose an adequate test of the method since not only do open and closed shells of the same symmetry occur, but also in the excited states the two open-shell orbitals are of the same symmetry (it has not previously been possible to treat such a singlet state with the coupling operator technique). In addition, in the excited states the Rydberg orbital is only loosely bound, which could possibly lead to slower convergence.

The basis set and geometry are the same as used in previous calculations [12].

The results of the open-shell Hartree-Fock calculations on the excited Rydberg states (3A_1 and 1A_1) and the positive ion (2A_1) of the water molecule are given in table 1. Convergence of the open-shell solutions was quite satisfactory, being only slightly slower than that for the closed shell calculation. From these calculations we found that the extra time required to set up each additional Hamiltonian is approximately 25% of that necessary to set up the corresponding ground state Hamiltonian.

It is of interest to note that, for example, the na_1 virtual orbitals of the $4a_1$ Hamiltonian for

the excited singlet state have energies of -0.0862, -0.0640, -0.0408, and -0.0142 (in atomic units) and hence correspond closely to the energies of the higher excited states. In fact, these orbitals are the variationally correct orbitals within the restriction that the core does not change [12]. This is in distinct contrast to the results obtained in the closed shell case [2] and in the open shell case if handled by the coupling operator technique [4-7].

In table 1 the results of the self-consistent field treatment of the open shell states are compared with those obtained in the frozen core approximation (in parentheses) [12]. We note immediately that SCF relaxation of the orbitals has a pronounced effect on both the ionization potential and the excitation energies, but not on the stability. These results indicate that if Rydberg states are to be calculated in the frozen core approximation, it would be better to generate the Rydberg orbitals in the potential of the SCF ion rather than the "Koopmans' theorem" ion [13].

Table 1
Total energies, orbital energies and dipole moment for several states of H_2O and H_2O^+ . All quantities are in Hartree atomic units ^{a)} unless otherwise noted, and all calculations are for the ground state geometry ^{b)}

Configuration symbol	Ground state ^{c)}	Excited states ^{c)}		Ion ^{c)}
	(core) ($3a_1$) ² 1A_1	3A_1	(core) ($3a_1$) ($4a_1$) 1A_1	(core) ($3a_1$) 2A_1
E_{HF}	-76.0143	-75.7160	-75.6992	-75.5348
$\epsilon(1a_1)$	-20.5658	-20.8055	-20.8387	-21.0916
$\epsilon(2a_1)$	- 1.3646	- 1.5455	- 1.5743	- 1.8205
$\epsilon(1b_1)$	- 0.7191	- 0.9132	- 0.9419	- 1.1891
$\epsilon(1b_2)$	- 0.5097	- 0.7248	- 0.7516	- 0.9952
$\epsilon(3a_1)$	- 0.5693	- 0.9358	- 0.9451	- 1.1917
$\epsilon(4a_1)$	- --	- 0.1833	- 0.1653	- --
$\mu(O)$	1.0562	- 0.7623	- 0.7132	1.0942 ^{d)}
ΔE , eV ^{e)}		8.12 (9.82)	8.57 (10.75) ^{f)}	13.05 (15.49) ^{g)}
Stability, eV ^{e)} , ^{h)}		- 4.93 (-5.67)	- 4.47 (- 4.74) ^{f)}	

a) The unit of energy is the Hartree = 27.211 eV, the atomic unit of dipole moment is 2.54158 Debye.

b) W. S. Benedict, N. Gailar and E. K. Plyer, *J. Chem. Phys.* 24 (1956) 1139.

c) Here: (core) = $(1a_1)^2 (2a_1)^2 (1b_1)^2 (1b_2)^2$. These orbitals are slightly different for each state.

d) The origin of the dipole moment operator is at the oxygen.

e) Numbers in parentheses are for the frozen core approximation, see ref. [12].

f) The experimental excitation energy is 9.75 eV and the stability is -4.75 eV, K. Watanabe and M. Zelikoff, *J. Opt. Soc. Am.* 43 (1953) 753.

g) The experimental ionization potential is 14.5 eV. W. C. Price and T. M. Sugden. *Trans. Faraday Soc.* 44 (1948) 108; J. A. R. Samson and G. R. Cook, *Bull. Am. Phys. Soc.* 4 (1959) 454.

h) The stability of a Rydberg state is the energy of the state relative to that of the corresponding ion.

4. OTHER APPLICATIONS

Besides its obvious application to open-shell Hartree-Fock calculations, OCBSE can be used to simplify the solution of the equations for other types of wavefunctions. For example, in multi-configuration SCF (MC SCF) calculations [14-16], there may be many open-shell orbitals of the same symmetry (i.e., orbitals which are not doubly occupied in all configurations). In order to illustrate these simplifications we will consider the case treated by Das and Wahl [15]. Application of the variational principle to the MC SCF wavefunction in its LCAO form leads to equations for the orbital expansion coefficients [15]

$$H_i C_i = S \sum_j C_j \epsilon_{ji}, \quad (5)$$

where, as usual, H_i is the Hamiltonian matrix, C_i is the array of expansion coefficients for orbital ϕ_i , S is the overlap matrix (between basis functions) and ϵ_{ij} is the Lagrange multiplier matrix added again to insure orthonormality of the orbitals. Here H_i contains the average field due to the electrons in the charge distribution of the MC SCF wavefunction. If the off-diagonal Lagrange multipliers are incorporated into the left-hand side of eq. (5), the resulting equations can be written [15]

$$(H^c - R^c) C_i^c = \bar{\epsilon}_i^c S C_i^c, \quad (6a)$$

$$(H_i^o - R_i^o) C_i^o = \bar{\epsilon}_i^o S C_i^o, \quad (6b)$$

where superscript c denotes orbitals which are doubly occupied in *all* configurations and o denotes the various open shell orbitals. The terms R^c and R^o are [15]

$$R^c = \sum_j^{\text{open}} [(S C_j^o) (H_j^c C_j^o)^+ + H^c C_j^o (S C_j^o)]$$

$$R_i^o = \sum_j^{\text{closed}} [(S C_j^c) (H_i^o C_j^c)^+ + H_i^o C_j^c (S C_j^c)^+]$$

$$+ \sum_{j \neq i}^{\text{open}} [(S C_j^o) (H_i^o C_j^o)^+ + (H_i^o C_j^o) (S C_j^o)^+].$$

In contrast, using OCBSE the MC SCF equations to be solved are simply

$$H^c C_i^c = \epsilon_i S C_i^c, \quad (7a)$$

$$H_i^o C_i^o = \epsilon_i S C_i^o, \quad (7b)$$

where each equation of (7) is solved in the space orthogonal to the solutions of the other equations.

Thus, OCBSE would considerably simplify MC SCF calculations. This should make it practical to consider more general classes of configurations. In addition it is likely that convergence would be improved by using eqs. (7) than eqs. (6).

Another application of the OCBSE would be in solving for separated pair equations [17]. Also, for orthogonalized plane wave calculations on solids [18] OCBSE considerably simplifies the construction of the Hamiltonian matrix.

5. CONCLUSION

The solution of self-consistent field equations involving non-trivial orthogonality constraints can be considerably simplified by solving the variational equations in the subspace orthogonal to the appropriate functions. This can be accomplished by a simple transformation on the expansion basis set.

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