

Open-Shell SCF Calculations with a Model Potential Method

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A model potential proposed by Huzinaga and his coworkers has been incorporated into the generalized coupling operator for open-shell SCF. With this modified operator, valence-only calculations have been performed on the ground and Rydberg excited states of the water molecule and compared with the *ab initio* SCF results previously reported.

Key words: Open-shell SCF with model potential

1. Introduction

In recent years, there have been many *ab initio* SCF calculations of polyatomic molecules [1]. In the closed-shell case, the Hartree-Fock-Roothaan SCF method is usually straightforward [2]. However, in the open-shell case, the situation becomes more complicated due to the existence of off-diagonal Lagrange multipliers which couple the open shells with the closed shells and other open shells [3, 4]. The principal problem is the elimination of the off-diagonal Lagrange multipliers in the Euler equations for the linearization of the equations to be solved. The coupling operator method developed by Roothaan [3] and extended by Huzinaga [4] has overcome this problem and the method has been applied to open-shell systems in both *ab initio* and semiempirical frameworks.

The generalized form of the coupling operator method which satisfies the correct variational condition has recently been discussed by Huzinaga [5] and also by Hirao and Nakatsuji [6]. In a previous paper [7], the author has modified their operator into a unique form taking into account the fact that the Hermitian conditions for the Lagrange multipliers among closed shells are automatically fulfilled and some *ab initio* applications for open-shell systems were reported [8].

As the number of electrons in the system increases, the *ab initio* method becomes expensive even for molecules of moderate size. Because of the computational problem associated with the *ab initio* method, attempts have been made to use the method of pseudo or model potential for valence-only calculations of polyatomic molecules [9–15]. The formalism of pseudopotential theory for one electron outside of a core is well known. The theory has recently been extended to the case in which the valence

electrons lie in a closed shell outside the inner cores in the molecule [13, 16], and applications to closed-shell polyatomic molecules have been reported [9-15]. Huzinaga and his coworkers gave a promising approach for the construction of the model potential in atoms and molecules by the use of Gaussian-type functions [14, 15]. The present work incorporates their model potential method into the unique coupling operator for open-shell SCF as previously given [7]. The open-shell states of polyatomic molecules can then be treated by valence-only calculations.

This work outlines the necessary formalism and its application to the ground state and Rydberg excited states of the water molecule.

2. Theoretical

The molecular model potential method proposed by Huzinaga and his coworkers [14, 15] will be outlined to show the development of our formalism for open-shell states of polyatomic molecules.

Consider a molecular system which contains N atoms with individual core regions numbered as $C1, C2, \dots, CI, \dots, CN$. The I th core, CI , contains N_{CI} electrons and the valence region of the whole molecular system contains N_v electrons.

The total wavefunction is now assumed to have the form;

$$\Psi = MA_P[\Phi_{C1}\Phi_{C2}\dots\Phi_{CI}\dots\Phi_{CN}\Phi_v]$$

where M is the normalization constant and A_p represents partial antisymmetrizer [17]. Here, all the core wavefunctions assume an antisymmetrized and normalized Slater determinant of doubly occupied atomic core orbitals, $\{\phi_i^{CI}\}$:

$$\Phi_{CI} = (1/N_{CI}!)^{1/2} \det[\phi_1^{CI}(1)\alpha(1)\phi_1^{CI}(2)\beta(2)\dots\phi_{N_{CI}/2}^{CI}(N_{CI}-1)\alpha(N_{CI}-1)\phi_{N_{CI}/2}^{CI}(N_{CI})\beta(N_{CI})]; \quad I = 1, 2, \dots, N$$

For the system in which the valence manifold contains both closed and open shells, the wavefunction, $\Phi_v = \Phi_v(\{\phi_k^v\})$ is generally a linear combination of Slater determinants appropriately constructed to be an eigenfunction of symmetry and spin for the particular state under study. Here the $\{\phi_k^v\}$ are the molecular valence orbitals which are to be expanded in terms of the atomic valence orbitals brought in from the preparatory works on atoms.

Assuming the following orthogonality conditions [14, 17];

$$\begin{aligned} \langle \phi_i^{CI} | \phi_j^{CJ} \rangle &= \delta_{ij} \delta_{IJ} \\ \langle \phi_i^{CI} | \phi_j^v \rangle &= 0 \\ \langle \phi_i^v | \phi_j^v \rangle &= \delta_{ij} \end{aligned} \quad (1)$$

the total energy of the system can be written as [14, 15]:

$$E = \langle \Phi_v | \tilde{H}_v | \Phi_v \rangle + \sum_I^N E_{CI} + \sum_{I>J}^N E_{CI,CJ} \quad (2)$$

The third term has been approximated by the simple expression:

$$E_{CI,CJ} \cong \frac{(Z_I - N_{CI})(Z_J - N_{CJ})}{R_{IJ}}$$

Since the component wavefunctions for the cores are assumed to be the Slater determinants of doubly occupied atomic core orbitals, the second term in the total energy expression is given by:

$$E_{CI} = 2 \sum_k^{N_{CI}/2} H_{kk}^{CI} + \sum_{k,1}^{N_{CI}/2} (2J_{k1}^{CI} - K_{k1}^{CI})$$

Now the Hamiltonian, \tilde{H}_v , in the first term of Eq. (2) can be written as:

$$\tilde{H}_v = \sum_i^{N_v} \left(-\frac{1}{2} \Delta_i - \sum_I^N \frac{Z_I}{r_{Ii}} \right) + \sum_I^N \sum_k^{N_{CI}/2} (2J_k^{CI} - K_k^{CI}) + \sum_{i>j}^{N_v} \frac{1}{r_{ij}}$$

Huzinaga and his coworkers [14, 15] have shown that the above \tilde{H}_v can be safely replaced by the model Hamiltonian, \tilde{H}_{vm} .

$$\tilde{H}_{vm} = \sum_i^{N_v} h_m(i) + \sum_{i>j}^{N_v} \frac{1}{r_{ij}} \quad (3)$$

where

$$h_m(i) = -\frac{1}{2} \Delta_i - \sum_I^N V_m^{CI}(r_{Ii}) + \sum_I^N \sum_k^{N_{CI}} B_k^{CI} |\phi_k^{CI}\rangle \langle \phi_k^{CI}|$$

with

$$V_m^{CI}(r_{Ii}) = \frac{Z_I - N_{CI}}{r_{Ii}} [1 + A_1^I \exp\{-a_1^I r_{Ii}^2\} + A_2^I \exp\{-a_2^I r_{Ii}^2\}]$$

With the above model Hamiltonian and Φ_v , the Hartree-Fock-Roothaan molecular valence orbitals, $\{\phi_k^v\}$, for open-shell systems can be determined by the introduction of the generalized coupling operator method in the following manner.

The valence energy

$$E_v \equiv \langle \Phi_v | \tilde{H}_{vm} | \Phi_v \rangle$$

can be written in general as:

$$E_v = 2 \sum_{i \in C} H_{ii}^v + \sum_{i,j \in C} (2J_{ij}^v - K_{ij}^v) + \sum_{k \in O} \nu_k [H_{kk}^v + \sum_{i \in C} (2J_{ik}^v - K_{ik}^v)] \\ + \sum_{k,l \in O} (2\alpha_{kl} J_{kl}^v - \beta_{kl} K_{kl}^v) \quad (4)$$

where the occupied valence orbitals are now split into two classes; C and O for closed shell and open shell respectively [7]. α_{kl} and β_{kl} are the coupling constants dependent on the state under study. ν_k is the fractional occupancy of the k th MO.

H_{ii}^v, J_{ij}^v and K_{ij}^v represent core, Coulomb and exchange integrals of the valence MO's respectively, and they are given as:

$$H_{ii}^v = \langle \phi_i^v | h_m | \phi_i^v \rangle$$

$$J_{ij}^v = \langle \phi_i^v | J_j^v | \phi_i^v \rangle$$

$$K_{ij}^v = \langle \phi_i^v | K_j^v | \phi_i^v \rangle$$

with

$$J_j^v(\mu)\phi(\mu) = \int [\bar{\phi}_j^v(\nu)\phi_j^v(\nu)/r_{\mu\nu}] d\nu\phi(\mu)$$

$$K_j^v(\mu)\phi(\mu) = \int [\bar{\phi}_j^v(\nu)\phi(\nu)/r_{\mu\nu}] d\nu\phi_j^v(\mu)$$

Here h_m in the core integral is the one-electron part of the model Hamiltonian given in (3).

The Euler equations derived from the valence energy variation are:

$$F_c^v | \phi_i^v \rangle = \sum_{j \in \mathbf{N}} \epsilon_{ji} | \phi_j^v \rangle; \quad i \in \mathbf{C}$$

and

$$F_k^v | \phi_k^v \rangle = \sum_{j \in \mathbf{N}} \epsilon_{jk} | \phi_j^v \rangle; \quad k \in \mathbf{O}$$

where

$$F_c^v = h_m + \sum_{i \in \mathbf{C}} (2J_i^v - K_i^v) + \sum_{k \in \mathbf{O}} \frac{\nu_k}{2} [2J_k^v - K_k^v]$$

and

$$F_k^v = \frac{\nu_k}{2} \left[h_m + \sum_{i \in \mathbf{C}} (2J_i^v - K_i^v) \right] + \sum_{l \in \mathbf{O}} (2\alpha_{kl} J_l^v - \beta_{kl} K_l^v)$$

Here \mathbf{N} is a manifold generated by a set of SCF occupied valence orbitals. The $\{\epsilon_{ij}\}$ are the Lagrange multipliers which ensure the orthogonality of the valence orbitals.

Projectors are now defined corresponding to the above Fock operators:

$$\Pi_c^v = P_c + P_u, \quad \Pi_k^v = P_k + P_u$$

with

$$P_c = \sum_{i \in \mathbf{C}} | \phi_i^v \rangle \langle \phi_i^v |, \quad P_k = | \phi_k^v \rangle \langle \phi_k^v |$$

$$P_u = \sum_{u \in \mathbf{V}} | \phi_u^v \rangle \langle \phi_u^v |$$

where the $\{\phi_u^v\}$ are the set of SCF virtual orbitals generating the manifold, \mathbf{V} within the valence region.

We can now build a unique coupling operator using the projectors defined above [7]:

$$R_v = R_{ov} + T_v$$

with

$$R_{ov} = \Pi_c^v F_c^v \Pi_c^v + \sum_{k \in O} \Pi_k^v F_k^v \Pi_k^v$$

and

$$T_v = \sum_{k \in O} \{(\lambda_{ck} - \lambda_{kc})P_c(F_k^v - F_c^v)P_k + (\lambda_{kc} - \lambda_{ck})P_k(F_c^v - F_k^v)P_c\} \\ + \sum_{k \neq l} (\lambda_{lk} - \lambda_{kl})P_l(F_k^v - F_l^v)P_k$$

where the $\{\lambda_{ij}\}$ are the arbitrary non-zero numbers with the condition: $\lambda_{ij} \neq \lambda_{ji}$. They are chosen such that:

$$\lambda_{kc} - \lambda_{ck} = 1, \quad \lambda_{kl} - \lambda_{lk} = 1(l > k)$$

This choice has been found to give satisfactory convergence in the previous *ab initio* works [7, 8].

The term T_v in the above coupling operator ensures the Hermiticity of the Lagrange multipliers during the SCF iterative process, and the coupling operator satisfies the correct variational condition for the valence orbital SCF.

With this operator, the Hartree-Fock equations for valence-only calculations are reduced into a single pseudo-secular equation:

$$R_v |\phi_i^v\rangle = \epsilon_{ii} |\phi_i^v\rangle; \quad i \in N$$

With the above scheme, the open-shell states as well as the closed-shell state can be handled without the limitation on the number of open shells in the valence region. As an example, calculations on the ground and Rydberg excited states of the water molecule have been performed.

3. Calculations

The model potentials used for the cores in a molecule have to be brought in from the preparatory work on atoms. McWilliams and Huzinaga [15] adapted the so-called Pople 4-31G Gaussian-type basis [18] for use with model potential calculations.

In the present work, we have used their contraction scheme for the oxygen core and valence orbitals, together with the model potential parameters they have proposed (see Tables I and IV in Ref. [15]). Pople's basis set with the scale factors, $\zeta' = 1.27$ and $\zeta'' = 1.25$ (in Pople's notation), has been used for the hydrogens [18]. The above basis set has been augmented with one set of diffuse *s* and *p* Gaussians on the oxygen atom with an exponent of 0.028 in order to get a better description of the Rydberg excited states [19].

The geometrical parameters used in this work are the same as those used in the previous *ab initio* study [7].

4. Results and Discussion

The water molecule has been studied in many calculations both in *ab initio* and semi-empirical frameworks due to its chemical importance [19]. In a previous paper, a unique generalized coupling operator for open-shell SCF has been discussed and applied to *ab initio* calculations of the ground and lower excited states of the water molecule [7]. The basis set used in the calculations was a double zeta basis set of contracted Gaussians from Dunning [20] and Huzinaga [21], augmented with two diffuse *s* functions and a set of diffuse *p* functions. The vertical transition energies obtained and the known experimental data [22] are reproduced in columns III and IV of the table.

With the coupling operator scheme for the valence-only SCF discussed in the previous section, the valence energies, E_v 's, have been optimized for the ground and the lower excited states. For the 1A_1 ground state, $E_v = -23.9802$ a.u. Energies for the vertical transitions from the ground state to the Rydberg excited states are calculated from the valence energy differences between the ground and the excited states, and they are shown in column I of the table.

Using a basis set comparable to that used in the valence-only calculations, the *ab initio* SCF calculations were repeated. The Pople 4-31G basis [18] set augmented with a set of diffuse *s* and *p* functions on the oxygen atom with an exponent of 0.028 were used for the calculations. Only the hydrogen basis set was scaled [18], i.e., $\zeta' = 1.27$ and $\zeta'' = 1.25$. These *ab initio* results, as seen in column II of the table, may then be directly compared with the results of the present valence-only calculations.

McWilliams and Huzinaga studied the geometry and the orbital energies of the ground state of the water molecule with their model potential method [15]. The orbital energies they obtained from the valence-only calculation agree well with the *ab initio* results. It is seen from the table that the model potential they proposed is also able to reproduce the *ab initio* SCF results for the excited states of the water molecule as well. According to the above formulation, the attractive local model potential should be the same for the ground and excited states of the system, and by using the common model potential both for the ground and excited states, *ab initio* SCF results for the excited states may be reproduced equally well.

Table 1. SCF results

	I Present Valence- only Calculations	II Pople 4-31G	III Previous <i>ab initio</i>	IV Experimental
Total energy of 1A_1 ground state (a.u.)		-75.913	-76.003	
Excitation energy (eV)				
$^1A_1 \rightarrow ^3B_1$	5.92	5.95	6.27	7.2
$^1A_1 \rightarrow ^1B_1$	6.32	6.33	6.70	7.4
$^1A_1 \rightarrow ^3A_2$	8.05	8.09	8.13	-
$^1A_1 \rightarrow ^1A_2$	8.17	8.20	8.26	9.1

Comparison of experimental and computed transition energies shows that the theoretical transition energies have lower values both for *ab initio* and valence-only calculations. This trend has been attributed to be the effect of electron correlation [19], which has not been taken into account in the present scheme. Recently, Freed discussed the possibility for the inclusion of the correlation effect in valence-only calculations [23], which is beyond the scope of the present work.

Because of the computational problems associated with the *ab initio* calculations of polyatomic molecules, it is desirable to use a model potential such as this in order to calculate the approximate excited states of large molecules. The present scheme handles any number of open shells together with the closed shell and is expected to be very useful for the calculations of open-shell states of large organic molecules and transition metal complexes. Applications of the present method to large polyatomic systems will be reported elsewhere.

References

1. Schaefer III, H. F.: The electronic structure of atoms and molecules; A survey of rigorous quantum mechanical results. Reading: Addison-Wesley 1972
2. Roothaan, C. C. J.: Rev. Mod. Phys. **23**, 69 (1951)
3. Roothaan, C. C. J.: Rev. Mod. Phys. **32**, 179 (1960)
4. Huzinaga, S.: Phys. Rev. **120**, 866 (1960)
5. Huzinaga, S.: J. Chem. Phys. **51**, 3971 (1969)
6. Hirao, K., Nakatsuji, H.: J. Chem. Phys. **59**, 1457 (1973)
7. Ishikawa, Y.: Chem. Phys. Letters **37**, 597 (1976)
8. Ishikawa, Y., Binning, Jr., R. C.: Chem. Phys. Letters, in press
9. Switalski, J. D., Schwartz, M. E.: J. Chem. Phys. **62**, 1521 (1975)
10. Simons, G.: Chem. Phys. Letters **18**, 315 (1973)
11. Coffey, P., Ewig, C. S., Van Wazer, J. R.: J. Am. Chem. Soc. **97**, 1656 (1975)
12. Melius, C. F., Goddard III, W. A.: Phys. Rev. **10**, 1528 (1974)
13. Kleiner, M., McWeeny, R.: Chem. Phys. Letters **19**, 476 (1973)
14. Bonifacic, V., Huzinaga, S.: J. Chem. Phys. **62**, 1509 (1975)
15. McWilliams, D., Huzinaga, S.: J. Chem. Phys. **63**, 4678 (1975)
16. Huzinaga, S., Cantu, A. A.: J. Chem. Phys. **55**, 5543 (1971)
17. McWeeny, R.: Proc. Roy. Soc. (London) **A253**, 242 (1959)
18. Ditchfield, R., Hehre, W. J., Pople, J. A.: J. Chem. Phys. **54**, 724 (1971)
19. Winter, N. W., Goddard III, W. A., Bobrowicz, F. W.: J. Chem. Phys. **62**, 4325 (1975)
20. Dunning, Jr., T. H.: J. Chem. Phys. **53**, 2823 (1970)
21. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)
22. Knoop, F. W. E., Brongersma, H. H., Oosterhoff, C. J.: Chem. Phys. Letters **13**, 20 (1972)
23. Freed, K. F.: Chem. Phys. Letters **29**, 143 (1974)

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