Theoret. Chim. Acta (Berl.) 53, 197–201 (1979)

THEORETICA CHIMICA ACTA

Note on the *ab initio* PUHF Treatment of Open-Shell Systems

John C. Schug

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Va. 24061, USA

Ab initio projected-unrestricted Hartree–Fock calculations have been carried out on a number of excited and ionic states of the water molecule. Results have been compared with large-scale CI calculations, with IVO calculations, and with those of Mrozek and Golebiewski obtained by the 2 × 2 rotation method applied to orbitals. It is concluded that the PUHF method may provide the most useful alternative to large-scale CI for calculating properties of open-shell systems. But it will not be generally useful for calculating spectral transition energies.

Key words: Projected-unrestricted *ab initio* HF treatment of open-shell systems – Open-shell systems, *ab initio* PUHF treatment of ~

1. Introduction

In the last few years we have published several papers dealing with projected-unrestricted Hartree–Fock (PUHF) theory. Approximate pi-electron theory was used to calculate spin distributions and electronic transition energies in pi-electron systems [1]; the INDO formalism was employed to calculate electronic spectra of several small molecules of C_{2v} symmetry [2]. *Ab initio* calculations were made of the nuclear hyperfine splittings in the methyl radical and on the ordering of the lowest electronic states of the ozone molecule [3]. The encouraging nature of these earlier results led to further interest in the utility of PUHF theory for making *ab initio* calculations of wavefunctions for electronically excited molecules. Several calculations were therefore carried out for the water molecule, and these will be presented in this note.

The present study is not complete, but a sufficient number of results are presented so that the PUHF method can be viewed in perspective along with several other

0040-5744/79/0053/0197/$01.00

calculational methods. Primarily, the method is viewed as an alternative to large-scale configuration-interaction (CI) calculations. As expected, the PUHF theory gives considerably worse results than do large scale CI calculations. However, the present and earlier [3] results indicate that the PUHF method does a creditable job on open-shell systems. Unfortunately, because the ground and excited states of a closed-shell molecule are not subjected to comparable corrections, it does a poor job of predicting spectral transition energies.

2. Calculations

The geometry chosen for the water molecule was the same as that used by Goddard and Hunt. The basis set consisted solely of atom-centered Gaussian-type orbitals. The Dunning [4] contracted $[4s3p/2s]$ Gaussian basis was augmented with polarization functions [5] (two-term expansion of a $3d$ Slater function for oxygen, one set of $2p$ functions for hydrogen) and diffuse oxygen orbitals [6] (two s-orbitals with exponents of 0.08, 0.02 and two sets of p-orbitals with exponents of 0.05, 0.0125). This gave a total basis set of 37 contracted Gaussians. The symmetry orbitals constructed from these number 36, there being, respectively, 17, 2, 7, and 10 which belong to the irreducible representations a_1, a_2, b_1, and b_2.

All calculations were carried out using the IBM version of the POLYATOM package [7]. This was supplemented with a spin-projection program that was written at this laboratory [8].

The PUHF method has been described in detail in a number of papers [1–3], so it will not be outlined here. However, two points should be noted with respect to computational techniques.

All excited-state calculations were started from the Hartree–Fock ground-state, $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$. Only excitations from the $1b_1$, $3a_1$, and $1b_2$ orbitals were carried out, but of course all orbitals were iterated to self-consistency in the UHF treatments of the excited states. When the excitation involves ground-state occupied and virtual orbitals of different symmetries, the excited state is automatically orthogonal to the ground-state. This is not the case when the orbitals have the same symmetry, so an orthogonality constraint must be included. In the present calculations, $a_1 \rightarrow a_1$ and $b_1 \rightarrow b_1$ transitions were treated by means of the OCBSE procedure suggested by Hunt *et al.* [9].

The SCF calculations are carried out in an orthogonalized basis which can be developed in a number of ways. In this instance, the ground-state SCF orbitals represent a convenient orthogonal set. For a particular irreducible representation, it is straightforward to impose orthogonality by eliminating the highest ground-state occupied orbital from the UHF expansion of the excited-state orbitals.

Only one UHF calculation was performed for each type of excitation considered. But since a complete set of virtual orbitals is obtained, a whole series of excited states is obtainable by populating these in turn. The orthogonality constraint described in the preceding paragraph could be generalized and applied successively to each higher state, but it will be seen that the present results do not warrant such treatment.

3. Results

Some typical results are listed in Table 1. The present results, labelled PUHF, are compared with those of several calculations. All results have been arbitrarily referenced to the ground-state energy obtained from the present calculation (−76.04519 hartrees). All calculations shown are slightly different in their basis sets, but the nature of the results is obvious.

As was evident from their paper, the CI calculations of Winter, Goddard, and Bobrowicz [10] (labelled WGB) are the best of the lot in every respect. They provide the lowest ground-state and excited state energies and the best energy differences. The transition energies that have been well-established experimentally are listed in the last column of Table 1; the CI transition are in excellent agreement with these. Others included are the improved virtual orbital (IVO) results of Goddard and Hunt (GH) and those obtained by Mrozek and Golebiewski [11] (MG) using the 2 × 2 rotation technique. As far as excited-state energies are concerned, it is evident that the projected UHF calculation is appreciably more effective than the IVO and the 2 × 2 rotation methods. This is true in spite of the fact that Goddard and Hunt employed several more diffuse orbitals than did the present work.

The single-triplet separations are consistently underestimated by the PUHF results, while the IVO calculations tend to overestimate them.

Table 1. Energies of excited states (eV) relative to the ground-state of the present calculation

Transition	State	WGB[a] (CI)	PUHF	GH[b] (IVO)	MG[c]	Observed[d] excitation energy (eV)
	Ground	−2.48	0	0.88	0.91	0
$1b_1 \rightarrow 4a_1$	$^3B_1$	4.78	6.01	7.52	7.85	7.14
	$^1B_1$	5.13	6.35	8.14	8.19	7.49
$1b_1 \rightarrow 2b_2$	$^3A_2$	6.86	8.08	9.52		9.1
	$^1A_2$	6.98	8.09	9.84		9.1
$3a_1 \rightarrow 4a_1$	$^3A_1$	6.96	8.56	9.86	9.61	9.35
	$^1A_1$	7.54	8.97	10.76	10.12	9.73
$1b_1 \rightarrow 2b_1$	$^3A_1$	7.26	8.46	10.54		9.81
	$^1A_1$	7.68	8.69	11.06		10.17
$1b_1 \rightarrow 5a_1$	$^3B_1$	7.51	8.85	10.80		9.93
	$^1B_1$	7.58	8.76	10.88		10.00
$3a_1 \rightarrow 5a_1$	$^3A_1$	9.29	11.15	12.68		
	$^1A_1$	9.60	11.15	13.39		

[a] Ref. [10].

[b] Ref. [6].

[c] Ref. [11].

[d] See Ref. [10] for detailed references and discussion.

It appears that if one is interested in calculating excited state properties, then the PUHF theory should be considered as the most useful alternative to large scale CI. On the other hand, if one wants to assign spectral transitions, the PUHF method is not as useful as the IVO. In fact, the IVO method is more useful just because it does not provide as much correlation in the excited states.

In order to effectively use the PUHF method to predict spectra, it is necessary to introduce the appropriate amount of correlation in the ground-state. This has been found to be possible in several cases in the past [12], but no means has yet been found for the water molecule. There are no Hartree–Fock instabilities to exploit in the ground-state wavefunction, but it is possible that the Half-Projected Hartree–Fock [13] procedure would be useful for this.

The two lowest vertical ionization energies were calculated using the PUHF method. UHF calculations were performed for the cation obtained by removing either an a_1 or a b_1 electron, spin projections were carried out, and the resulting energies then compared to the ground-state energy. The resulting energies were 10.90 eV for formation of the ${}^2B_1$ ion and 13.24 eV for the ${}^2A_1$ ion. The experimental vertical ionization energies are 12.62 and 14.68 eV, respectively [14]. To place these numbers on the same energy scale as all others in this paper, it is assumed that the CI calculation of Winters *et al.* gave the correct molecular ground-state energy. Thus, subtracting 2.48 eV from the experimental energies yields 10.14 and 12.20 eV as the ion energies on the present scale. These are in reasonable agreement with the calculated values. Since the ions are open-shell systems, they are reasonably treated by the PUHF method.

It is of interest to investigate the dependence of energy on nuclear geometry. Winter *et al.* have not yet published their potential energy curves for the excited states of neutral H_2O, so it was decided to make a comparison with the multi-configuration SCF plus CI calculations of Fortune and co-workers on the ${}^2B_1$ cation, H_2O^+. Table 2 lists the differences between our calculated energies and theirs over a range of bond lengths and bond angles. The difference in energy is considerable, but

Table 2. Comparison of PUHF and MCSCF/CI energies of the ${}^2B_1$ cation H_2O^+

R_{OH} (a_0)	HOH (degrees)	$E_{PUHF}-E_{MCSCF/CI}$ [a] (hartrees)
1.90	103	0.07700
1.90	109	0.07658
1.90	115	0.07616
1.84	109	0.07477
1.96	109	0.07843

[a] The MCSCF/CI results were taken from Ref. [15].

remains fairly constant over the entire range so that force constants and vibrational energy levels would be quite similar.

References

1. Phillips, D. H., Schug, J. C.: J. Chem. Phys. **61**, 1031 (1974);
Schug, J. C., Brewer, D. A.: J. Phys. Chem. **81**, 161 (1977)
2. Schug, J. C., Lengsfield, B. H., Brewer, D. A.: Intern. J. Quantum Chem. **11**, 591 (1977)
3. Lengsfield, B. H., Schug, J. C.: Mol. Phys. **35**, 1113 (1978)
4. Dunning, T. H.: J. Chem. Phys. **53**, 2823 (1970)
5. Dunning, T. H.: J. Chem. Phys. **55**, 3958 (1971)
6. Goddard, W. A., Hunt, W. J.: Chem. Phys. Letters **24**, 464 (1974)
7. Metzgar, T. D., Bloor, J. E.: POLYATOM (Version II), QCPE No. 238 (1974), Quantum Chemistry Program Exchange, Bloomington, Indiana, 47401
8. Brewer, D. A.: Ph.D. dissertation, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, (1977)
9. Hunt, W. J., Dunning, T. H., Goddard, W. A.: Chem. Phys. Letters **3**, 606 (1969)
10. Winter, N. W., Goddard, W. A., Bobrowicz, F. W.: J. Chem. Phys. **62**, 4325 (1975)
11. Mrozek, J., Golebiewski, A.: Intern. J. Quantum Chem. **12**, 207 (1977)
12. Schug, J. C., Lengsfield, B. H., Brewer, D. A.: J. Phys. Chem. **82**, 1436 (1978); Bendazzoli, G. L., Bernardi, F., Geremia, A., Palmieri, P.: Theoret. Chim. Acta (Berl.) **27**, 63 (1972)
13. Cox, P. A., Wood, M. H.: Theoret. Chim. Acta (Berl.) **41**, 269 (1976)
14. Turner, D. W., Baker, C., Baker, A. D., Brundle, C. R.: Molecular photoelectron spectroscopy. New York: Wiley, 1970
15. Fortune, P. J., Rosenburg, B. R., Wahl, A. C.: J. Chem. Phys. **65**, 2201 (1976)

Received October 19, 1978/May 8, 1979