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Short Communication

Molecular MC SCF Calculations by Direct Minimization

Calculations on H_2CO Using the Single Excitation MC SCF Method in a Full and a Pseudopotential Version

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Calculations on the H_2CO ground state and excited states at the equilibrium planar geometry, using the single excitation MC SCF method, are described for two basis sets. The results obtained by a full calculation including all the electrons are compared with those obtained by a pseudopotential version of the method including only the valence electrons. The results agree quite well both with each other and with the observed values.

Key words: Direct minimization – Pseudopotential MC SCF – Formaldehyde

1. Introduction

The electronic structure of formaldehyde has been the object of extensive investigations, both experimental ([1] and references therein) and theoretical ([2] and references therein). A great number of *ab initio* calculations have been done in order to obtain the properties of the ground state (a MC SCF ground state calculation is given in Ref. [3]); also the electronic spectrum has been theoretically interpreted mainly by means of the usual CI method. Until now, however, no attempt has been made to investigate the nature of the electronic transitions on the basis of a MC wave function. In this context, the aim of this paper is twofold.

1) To test the potentiality of the single excited configuration MC approach, mainly in comparison with the CI method. Moreover we intend to get the feeling of the influence of the basis set on the values of some molecular one-electron properties.
2) To test, in the same context, the applicability of the pseudopotential method, which allows us to describe the low-lying electronic transitions employing a MC wave function relative only to the valence electrons.

In this paper we give the results of a number of calculations on H_2CO at the experimental (ground state) geometry: we have chosen formaldehyde due to the large number of calculations achieved, it being a so convenient well-documented small molecule through which our models can be investigated. The theoretical aspects of the methods are briefly presented in Sect. 2 and the results of the calculations on H_2CO are given in Sect. 3.

2. Computational Methods: All-Electron and Valence-Electron Models

In a previous paper [4] we have described a gradient method for optimizing a singlet MC SCF wave function of the general form

$$ {}^1\psi^{(s)} = a_0^{(s)}\, {}^1\psi_0 + \sum_{I}^{m_0} \sum_{V}^{m_v} {}^1\psi_{I,V}\, a_{VI}^{(s)} \tag{1} $$

where ${}^1\psi_{I,V}$ are single excitation functions obtained by promoting an electron from any of the m_0 orbitals of the set $\{I\}$ occupied in the closed-shell single determinant, ${}^1\psi_0$, to any of the m_v orbitals of the set $\{V\}$ unoccupied in ${}^1\psi_0$; the $a_{VI}^{(s)}$'s are expansion coefficients relative to the state s of the system. The composite set of occupied and unoccupied orbitals is assumed orthonormal. The energy expectation value derived from (1) is given by

$$ {}^1E^{(s)} = \mathrm{tr}\ [h(R)L^{(s)} + \not{f}R + G(Q^{(s)})Q^{(s)\dagger}], \tag{2} $$

where the following matrices have been defined:

$$ R = CC^\dagger, \qquad Q^{(s)} = DA^{(s)}C^\dagger, \qquad h(R) = f + G(R), $$

$$ L^{(s)} = R + \sqrt{2}a_0^{(s)}(Q^{(s)} + Q^{(s)\dagger}) + Q^{(s)}Q^{(s)\dagger} - Q^{(s)\dagger}Q^{(s)}, $$

$$ f_{rs} = \langle r|\not{f}|s\rangle, \qquad [G(R)]_{rs} = \sum_{t,u}^{m} R_{tu}(2\langle ur|ts\rangle - \langle ur|st\rangle). $$

$\not{f}$ is the one-electron part of the Hamiltonian, $A^{(s)}$ is the matrix of the expansion coefficients $a_{VI}^{(s)}$, C and D are the matrices, respectively, of the coefficients of the I and V orbitals in the LCAO approximation, m being the dimension of the atomic basis $r, s, t, u \ldots$.

For a triplet the theory is quite similar.

The energy (2) depends upon the subspace of occupied and unoccupied orbitals and the expansion coefficients via the matrices R and $(a_0^{(s)}, Q^{(s)})$, and our method consists of minimizing directly ${}^1E^{(s)}$, optimizing the density matrix R by a suitable orthogonal transformation of the atomic basis set (assumed orthonormal) and the expansion coefficients, namely $a_0^{(s)}$ and $Q^{(s)}$, by repeated solutions of the corresponding secular equations. When the minimum is reached for the state s, which we now suppose to be the ground state, the desired excited state energies ${}^1E^{(s')}$ ($s' \neq s$, of the same symmetry of s or otherwise) are obtained from the other solutions of the secular determinant. Of course these are the best values, not absolute, but in relation to the matrix R optimized for the state s.

The method outlined above is applied to two models; a full calculation including all the electrons and a pseudopotential calculation including explicitly only the valence electrons, assumed to move in an effective field provided by the atomic cores. Following Kleiner and McWeeny [5], we have chosen the simplest form of the pseudopotential, taking as effective valence-electron Hamiltonian for the valence electron i the expression

$$ \not{f}_{ps}(i) = \not{f}(i) + \sum_{c}^{\text{cores}} \left(\mathscr{J}^{c}(i) + \sum_{t \in c} a_t \mathscr{R}_t^{c}(i) \right), $$

where $\mathscr{J}^c$ is a core Coulomb operator, $\mathscr{R}_t^c$ is a projection operator (with spherical symmetry) for functions of symmetry type t belonging to the core c and a_t are constants to be fitted using atomic term values or taken equal to the atomic ionization potentials[6]. The c summation runs over all the individual cores c in the molecule. Then, the method described above remains the same replacing $f(i)$ with $f_{ps}(i)$ and including explicitly only the valence electrons.

3. The H_2CO Calculations

Calculations were made on the H_2CO (assumed planar) at experimental geometry $CH = 1.102$, $CO = 1.210$ bohr, $H\hat{C}H = 121.1°$, using two different basis sets A and B of Slater-type orbitals. For the full calculations the basis set A consisted of the following orbitals: $1s_C$ (5.6727), $2s_C$ (1.6083), $2p_C$ (1.5679), $1s_O$ (7.6579), $2s_O$ (2.2458), $2p_O$ (2.2266), $1s_H$ (1.0), $1s'_H$ (0.80); for the pseudopotential calculations the change $1s_H\ (1.2) = 1s'_H$ has been made. Basis set B consisted of the same s orbitals as before and of the orbitals $2p_C$ (1.25493), $2p'_C$ (2.72376), $2p_O$ (1.65546), $2p'_O$ (3.68560), both for full and pseudopotential calculations.

The MC results are displayed in Tables 1 and 2: they agree reasonably well with the observed values. As expected, for the inadequacy of the basis the $\pi \rightarrow \pi^*$ transition is too high; in particular, due to the lack of $3s$ orbitals, the ${}^1A_1 \rightarrow {}^1B_2$ transition, usually interpreted as a Rydberg transition $n \rightarrow 3s$, is higher than the $\sigma \rightarrow \pi^*$, at least in the full calculation.

The SCF calculation for the basis set B gives an energy of −113.734 so that the energy gain is of −0.01 Hartree.

The CI results, relative to all single excited configurations, are also reported in Tables 1 and 2: they are less satisfactory than the MC ones. The experimental data are taken from Refs. [1] and [7].

Table 1. Total molecular energy (E, Hartree) and dipole moments (D.M., Debye) for some selected states of the H_2CO molecule

		Full Calculations					
			Basis Set B		Pseudopotential Calculations		
State		Basis Set A	MC-SCF	CI	Basis Set A	Basis Set B	Exp.
${}^1A_1$	E	−113.4560	−113.7440	−113.7340	−8.4159	−8.6887	
	D.M.	1.43	3.00	2.98	0.83	2.75	2.5
${}^3A_2$	E	−112.9330					
	D.M.	1.21					1.29
${}^1A_2$	E		−113.6040				
	D.M.		1.46				1.55

Table 2. Vertical transition energies (eV) and oscillator strengths (in parentheses) for the H_2CO molecule

	Full Calculations					
		Basis Set *B*		Pseudopotential Calculations		
Transitions	Basis Set *A*	MC-SCF	CI	Basis Set *A*	Basis Set *B*	Exp.
$^1A_1\ ^3A_2\ (n, \pi^*)$	4.57					3.54
$^1A_2\ (n, \pi^*)$	5.73	3.81	4.08	3.40	3.85	3.84
$^3B_1$	8.86					
$^3B_2$	9.42					6.7–7.0
$^3A_1\ (\pi, \pi^*)$	9.68					5.6–6.2
$^1B_2\ (n, \sigma^*)$	13.45	9.25	10.73	12.46	8.54	7.08
	(0.49)	(0.059)	(0.186)	(0.116)	(0.066)	(0.038)
$^1B_1\ (\sigma, \pi^*)$	10.39	8.86	8.81	8.83	8.94	9.00
	(0.0007)	(0.018)	(0.005)	(0.0114)	(0.012)	
$^1A_1\ (\pi, \pi^*)$	16.68	17.67	19.25	21.83	17.52	

4. Conclusions

It is seen that the single excitation MC SCF calculations may be carried out successfully yielding satisfactory results both for ground and excited state properties, which compare well with other ones obtained by more elaborate and complete methods. And, more interesting, the less expensive version, including only the valence electrons, gives results that are very close to those of the full version.

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References

1. Moule, D. C., Walsh, A. D.: Chem. Rev. **75**, 67 (1975)
2. Gouyet, J. F., Prat, M. T.: J. Chem. Phys. **64**, 946 (1975)
3. Levy, B.: Chem. Phys. Letters **4**, 17 (1969)
4. Fantucci, P., Polezzo, S., Stabilini, M. P.: Theoret. Chim. Acta (Berl.) **41**, 311 (1976)
5. Kleiner, M., McWeeny, R.: Chem. Phys. Letters **19**, 476 (1973)
6. Zerner, M. C.: Mol. Phys. **23**, 963 (1972)
7. Chutjian, A.: J. Chem. Phys. **61**, 4279 (1974)

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