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Test applications of a new SCF method for excited states

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In order to test a recently proposed technique for deriving orthogonality-constrained HF wave functions for excited states, several applications to molecular systems, have been made and the results compared with those provided by other SCF techniques.

Key words: Excited states — Orthogonality conditions

1. Introduction

In this article we discuss some test applications of a new method, recently proposed by the authors [1], for deriving Hartree–Fock (HF) wave functions for excited states. In this method the energy of the excited state is minimized subject to the requirement that the corresponding HF wave function be orthogonal to all the HF wave functions of the lower states; the advantages of the method stem from its full exploitation of all the degrees of freedom in the variational space which are compatible with the orthogonality constraints.

Other SCF techniques for excited states which do not explicitly maintain orthogonality to the approximate lower state wave functions have been proposed in the literature [2, 3], but we believe that a representation of the electronic states which maintains the orthogonality property among the exact wave functions is advantageous, especially in the evaluation of quantities like the transition probabilities, which simultaneously involve the wave functions of the two different states.

It should also be noted that to have an SCF method which gives variationally correct energies for the excited states is very important, not only because the independent-particle approximation allows a clearer physical interpretation of the wave function, but also because an HF-SCF approach usually makes possible a reasonably accurate optimization of the molecular geometry with far less effort than do the MC-SCF or CI methods [4]. Furthermore it is well known that CI calculations - at least when limited to single and double excitations - are more reliable and accurate when based on SCF orbitals that are specifically optimized for the parent configurations [5].

As to the convergence properties of our technique we observe that in the examples discussed in this article we have used a first order direct minimization procedure, based on different Fock-like operators for the different types of orbital rotations [6], which makes it possible to satisfy both the orthogonality requirements and the correct variational conditions at each step of the process, as discussed in [1]. Such a procedure represents a simplified version of a general direct minimization approach and can be easily implemented, while at the same time it does not introduce any more convergence difficulties than those of a standard open shell SCF process. Furthermore in this procedure the convergence of the iterative process can be accelerated by means of one of the various techniques proposed in the literature (see, e.g. [7]).

In the following sections we test our method by calculating the HF wave functions for the excited states of a few interesting molecular systems and point out some features of the energy minimization and the convergence properties of our technique. Comparisons with the results of other SCF approaches are also given.

2. One-determinant wave functions

2.1. Doublet states

As the first test application of our method we have studied a few electronic vertical transitions in the spectrum of the ethyl radical chosen at the HF ground state geometry (C_s molecular point group) [8]. This molecule represents a well characterized system which is appropriate for testing the capabilities of our method in comparison with other approaches; both the evaluation of the transition energy and the quality of the wave function will be considered. In particular, this molecule possesses low-lying excited states of the same symmetry as the ground state and which are nearly degenerate, so that the use of second-order SCF procedures to derive the corresponding HF wave functions has been thought necessary [7]. We will compare our results with those obtained by using two different approaches: (1) the method proposed in [2, 3] (hereafter referred to as Davidson's method), chosen as an example of the techniques in which orthogonality to the lower state wave functions is not explicitly introduced, and (2) a simplified approach (referred to as the "space-restricted" method) in which the orthogonality constraints are imposed in a more restrictive way (see, e.g. [9]), i.e. by excluding the singly occupied orbitals of the lower states from the variational space of the excited state of interest. The transition energies are also compared with those calculated in [8] using a second-order HF procedure (referred to as Lengsfield's method).

In Table 1 we give the results obtained using the four different approaches described above. The calculations have been performed using the Dunning's double-zeta plus polarization valence basis [10] augmented with double-zeta $3s, 3p$ and single-zeta $3d$ functions centered on the radical site, as explained in the footnote of Table 1.

We observe that in this case our transition energies are practically coincident with those obtained via Davidson's and Lengsfield's methods. This equivalence is also confirmed by the analysis of the form of the occupied orbitals resulting from Davidson's method and ours, which mutually overlap by at least 0.9998. However, the "space-restricted" method appears to become less appropriate as one goes to higher excitation energies. We also stress the fact that the application of Davidson's method via a coupling operator technique, as proposed in [3] and applied to the case of the ethyl radical in [7], gives rise to serious convergence difficulties in the derivation of the second excited state of A_1 symmetry, while the third excited state of that symmetry cannot be obtained at all. In contrast, by using this same method with different Fock-like operators for the different types of orbital rotations [6], we have obtained a smooth convergence for both the states in spite of their quasi-degeneracy. (It will be noted that in the coupling operator technique the effective angles used for some types of orbital rotations are not optimal with respect to the energy minimization process [13]).

To conclude the discussion of this example we observe that our method can also be applied to higher excited states with essentially the same computational effort as in a standard open shell SCF procedure, since it only requires a proper definition of the variational space for each excited state. Further, when we started from the doubly occupied plus the first virtual orbitals of the next lower state, the number of iteration steps needed to get an accuracy of $\sim 10^{-8}$ a.u. in the energy value never exceeded 14.

Table 1. Vertical excitation energies for the ethyl radical at the SCF geometry [8], calculated by using our method (ΔE_m), Davidson's method (ΔE_D), Lengsfield's method (ΔE_L), and a "space-restricted" method (ΔE_{SR}). The exponent for the uncontracted d polarization function on the carbon atom is 0.75, while the exponents of the Rydberg functions are $\alpha_s = 0.0437$ and 0.01725, $\alpha_p = 0.0399$ and 0.01575, and $\alpha_d = 0.015$. Such a basis set is similar to the SCF1 basis set of [8] except for the use of Hermite Gaussian functions [11, 12] instead of Cartesian Gaussian functions; the ground state energy is $E_{HF} = -78.605\,250$ a.u.

State	ΔE_m (eV)	ΔE_D (eV)	ΔE_{SR} (eV)	ΔE_L (eV)
$2\,^2A_1(3s)$	4.91	4.91	5.08	4.88
$3\,^2A_1(3p)$	5.68	5.69	5.92	5.67
$4\,^2A_1(3p)$	5.82	5.84	6.03	5.83
$5\,^2A_1(3d)$	6.50	6.50	6.85	6.49
$1\,^2A_2(3p)$	5.70	—	—	5.68
$2\,^2A_2(3d)$	6.59	6.59	6.59	6.59

As a more stringent test of the ability of our method to give the proper excited state wave function, we have calculated the three lowest RHF wave functions of $^2\Sigma^+$ symmetry of the OH radical, which correspond to the following orbital occupancies: $A(^2\Sigma^+)$: $1\sigma^2 2\sigma^2 3\sigma^1 \pi^4$, $B(^2\Sigma^+)$: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 \pi^2$, $C(^2\Sigma^+)$: $1\sigma^2 2\sigma^2 4\sigma^1 \pi^4$. In particular, we are interested in the third state (C), since the first excited state of $^2\Sigma^+$ symmetry (B) is automatically orthogonal to both the A and C states because of differences in the orbital occupation numbers. Hence, in our approach, the only orthogonality constraint which must be imposed in the SCF process involves the states A and C. Furthermore the ionic dissociation of the C state and the anti-bonding character of the singly occupied orbital make the construction of the HF energy curve for this state a difficult task.

The calculations, results of which are given in Table 2, have been performed in a range of internuclear distances between 3 and 6 a.u., which contains the position of the minimum of the C state, and inside which the three states (A, B and C) are sufficiently well separated ($\Delta E \sim 1$-3 eV).

Starting with trial orbitals taken from the A state, we have not encountered any convergence difficulty in the SCF process for the C state, although a larger number (about 25) of iteration steps were necessary to obtain a convergence of 10^{-8} a.u. in the energy value. The HF energy curve so obtained is a smooth function of the internuclear distance R which can be well fitted by a polynomial, and qualitatively reproduces the behaviour of the CI energy curve as obtained

Table 2. Behaviour of the energy differences (ΔE) and of the dipole moment (μ) of the $C(^2\Sigma^+)$ state of the OH radical as functions of the internuclear distance R. The ΔE_ms are the energy differences obtained using our method and calculated with respect to the energy value at $R = 4$ a.u., $E = -74.991\,510$ a.u., while the ΔE_{CI}s are the corresponding values obtained in [14] by using a CI approach. The calculations have been performed by using the [5s, 4p] and the [3s] contracted basis sets of Dunning [10a] for the oxygen and the hydrogen atoms respectively. Both the basis sets have been then augmented as suggested in [14], but Spherical Gaussian functions have been used instead of Cartesian Gaussian functions

R (a.u.)	ΔE_m (eV)	ΔE_{CI} (eV)	μ (Debye)
3.00	1.056 588	0.79	4.054 604
3.25	0.489 381	0.32	5.447 873
3.50	0.157 013	0.06	6.636 898
3.75	0.012 354	−0.03	7.675 150
4.00	0.	0.	8.607 464
4.25	0.074 398	—	9.465 926
4.50	0.202 376	0.16	10.272 160
4.75	0.361 076	—	11.041 096
5.00	0.535 178	0.51	11.782 756
5.25	0.714 805	—	12.504 543
5.50	0.893 588	0.84	13.211 569
5.75	1.067 636	—	13.907 414
6.00	1.234 717	1.20	14.594 827

in [14] using the same basis set; the difference between the HF and the CI results becomes appreciable only at $R = 3$ a.u., and this is due to increased correlation effects. The same considerations also apply to the HF dipole moment, whose values as function of R are given in Table 2; this fact confirms the correct nature of our SCF orbitals.

For comparison we tried to derive the RHF wave function of the state C by using Davidson's method, but we ran into serious convergence difficulties in the iterative process: the convergence was quite slow and was characterized by progressively damped oscillations. When starting from trial orbitals taken from the A state, after about 20 iterations the process seems to converge to an energy value higher than that obtained by using our method (e.g. at $R = 4$ a.u., $E_D = -74.984\,154$ a.u.). Furthermore the singly occupied orbital so obtained exhibits an irregular behaviour of the expansion coefficients as functions of the orbital exponents. These convergence problems still remain if one utilizes different Fock-like operators for the different types of orbital rotations and cannot be attributed to a quasi-degeneracy among the states, since between $R = 4$ a.u. and $R = 6$ a.u. the other HF states are appreciably far away in energy ($\Delta E \geq 3$ eV), but they are presumably due to the anti-bonding and highly polarized nature of the singly occupied orbital.

2.2. *Triplet states*

From a technical point of view, we observe that the procedures required for the application of our method to the triplet states, and in general to every high-spin state that can be described by a single-determinant wave function, are analogous to those necessary for the doublet states. Therefore we have considered only one other molecular example to compare our technique with those referred to as Davidson's and the "space-restricted" methods. The example we chose is from the spectrum of the ketene molecule (CH_2CO) - a system well studied in the literature, and which will also be considered in the next section - and concerns

Table 3. Vertical excitation energies for various electronic transitions of the ketene molecule at the experimental geometry [15], calculated using our method (ΔE_m), the Davidson's method with orthogonal (ΔE_{or}) or non-orthogonal (ΔE_{nor}) orbitals and a "space-restricted" method (ΔE_{SR}). Note that the value of ΔE_{nor} has been taken from [17] and refers to the SCF ground state geometry. The calculations have been performed with a DZ plus polarization basis set augmented by Rydberg functions as described in [15], but utilizing Hermite Gaussian functions instead of Cartesian Gaussian functions

State	ΔE_m (eV)	ΔE_{or} (eV)	ΔE_{SR} (eV)
$1\,^3A_1(2b_1 \to 3b_1)$	4.99	—	—
$2\,^3A_1(2b_1 \to 4b_1)$	6.56	6.58	6.57
	ΔE_m (eV)	ΔE_{nor} (eV)	ΔE_{SR} (eV)
$2\,^1A_1(2b_1 \to 3b_1)$	6.65	6.58	6.89
$3\,^1A_1(2b_2 \to 3b_2)$	10.90		

the second triplet excited state of A_1 symmetry obtained through the promotion of one electron from the highest occupied orbital ($2b_1$) of the ground state ($^1A_1$: $\ldots 7a_1^2 \ldots 2b_2^2 \ldots 2b_1^2$); the constraint of orthogonality to the first A_1 triplet state ($\ldots 7a_1^2 \ldots 2b_2^2 \ldots 2b_1^1 3b_1^1$) was imposed.

In Table 3 we report the results of the calculations performed with the three methods; note that in the "space-restricted" one the highest singly occupied orbital of the lower triplet state is excluded from the variational space. In this case we did not find any convergence difficulty in the application of the three methods. Furthermore, as can be seen from the results of Table 3, our technique gives practically the same results as the other two.

3. Singlet excited states

The derivation of the wave function for the first excited singlet state of the same symmetry as the closed shell ground state does not present any particular technical difficulty within our approach. Contrary to this, the Davidson's method cannot be applied using orthogonal orbitals because of the possibility of variational collapse onto the ground state wave function, and its generalization to non-orthogonal open shell orbitals is required [3]; such a generalization corresponds to the use of a two-configuration SCF wave function [3, 4].

As a significant test for the application of our method to such a case we have chosen the first excited singlet state of A_1 symmetry of the ketene molecule - corresponding to the ($2b_1 \rightarrow 3b_1$: $\pi \rightarrow \pi^*$) promotion from the ground state configuration - a problem much studied both experimentally and theoretically [7, 15-17]: the corresponding transition has not been clearly located in the spectrum, and furthermore, it is still controversial whether it is possible to describe this state correctly at an RHF level using orthogonal orbitals.

We have employed our method to calculate the vertical excitation energy for such a transition using the same geometry and basis set as for the $^3A_1$ states. The result, given in Table 3 is compared with that obtained in [17] using the non-orthogonal generalization of the Davidson's method, and with that obtained through a "space-restricted" procedure by freezing the highest doubly occupied orbital of the ground state. In applying our method we have not found any convergence difficulty in the iterative process; furthermore, as in the previous cases, our result does not depend on the trial orbitals used as starting point.

The value we get for the transition energy is very close to that obtained via Davidson's method, although the latter - based on a two-configuration SCF wave function - includes some energy contributions due to the correlation of the two unpaired electrons. The reason for this agreement probably rests on the Rydberg nature of the highest singly occupied orbital ($3b_1$), which makes such correlation contributions negligible; this nature is confirmed by the fact that the expectation value of $\langle x^2 \rangle$ (where x is the axis perpendicular to the plane of the molecule) is ~48 a.u. for the $3b_1$ orbital, compared with a value of ~2 a.u. for the $2b_1$ orbitals of the ground and the singlet excited state. Such results are in agreement with the conclusions of Allen and Schaefer [17].

For testing the capabilities of our method in deriving the SCF wave function for higher excited states we have considered the state of ${}^1A_1$ symmetry obtained through the promotion $(2b_2 \rightarrow 3b_2)$ from the ground state configuration of the ketene molecule. In this case one has to impose two orthogonality constraints in the derivation of the excited state wave function ψ_2, one with respect to the ground state wave function ψ_0 and the other with respect to the first singlet excited state wave function ψ_1 derived above:

$$\langle \psi_2 | \psi_0 \rangle = D \cdot \det |\langle 1b_2^{(2)} | |b_2^{(0)}\rangle \langle 3b_2^{(2)} | 2b_2^{(0)}\rangle| = D \cdot d_2 = 0, \tag{1}$$

$$\begin{aligned} \langle \psi_2 | \psi_1 \rangle = D' \cdot \det |\langle 1b_2^{(2)} | 2b_2^{(1)}\rangle \langle 3b_2^{(2)} | 2b_2^{(1)}\rangle| \\ \cdot \det |\langle 1b_1^{(2)} | 1b_1^{(1)}\rangle \langle 2b_1^{(2)} | 3b_1^{(1)}\rangle| = D' \cdot d_2' \cdot d_1' = 0, \end{aligned} \tag{2}$$

where D and D' are defined by the relations

$$\begin{aligned} D = \sqrt{2}[\det{}^2 |\langle 1a_1^{(2)} | 1a_1^{(0)}\rangle \cdots \langle 7a_1^{(2)} | 7a_1^{(0)}\rangle| \cdot \det{}^2 |\langle 1b_1^{(2)} | 1b_1^{(0)}\rangle \langle 2b_1^{(2)} | 2b_1^{(0)}\rangle| \\ \cdot \det |\langle 1b_2^{(2)} | 1b_2^{(0)}\rangle \langle 2b_2^{(2)} | 2b_2^{(0)}\rangle|], \end{aligned} \tag{3}$$

$$\begin{aligned} D' = 2[\det{}^2 |\langle 1a_1^{(2)} | 1a_1^{(1)}\rangle \cdots \langle 7a_1^{(2)} | 7a_1^{(1)}\rangle| \cdot \det |\langle 1b_1^{(2)} | 1b_1^{(1)}\rangle \langle 2b_1^{(2)} | 2b_1^{(1)}\rangle| \\ \cdot \det |\langle 1b_2^{(2)} | 1b_2^{(1)}\rangle \langle 2b_2^{(2)} | 2b_2^{(1)}\rangle|], \end{aligned} \tag{4}$$

The constraints (1) and (2) can be satisfied by requiring either (a) $d_2 = d_2' = 0$ or (b) $d_2 = d_1' = 0$. Following our approach, condition (a) defines two reference vectors of the same symmetry (b_2) that are to be excluded initially from the variational space in order to satisfy the orthogonality conditions, and then reincluded through the use of double rotations in order to exploit all the variational degrees of freedom. This can be performed by following the scheme suggested in [1] for the second excited singlet state. Using the condition (b) instead, the two reference vectors belong to different symmetries (b_1 and b_2) and for each of these one can use the same procedure as for the first singlet excited state. We have thus calculated the transition energy for the $3\ {}^1A_1(2b_2 \rightarrow 3b_2)$ state by imposing the conditions (a) and (b) separately, and in Table 3 we report the result obtained through the less restrictive one, (b); however, we stress that the transition energy obtained via condition (a) is only slightly higher (by about 0.03 eV). Note that the application of Davidson's method to such a case is not straightforward and probably requires the generalization to a four-configuration wave function.

In addition, to test the dependence of our results on the ordering of the states, i.e. on the number of constraints imposed in the SCF process for each excited state wave function, we have first derived the wave function for the ${}^1A_1(2b_2 \rightarrow 3b_2)$ state by requiring orthogonality to the ground state wave function only, and then derived the wave function for the ${}^1A_1(2b_1 \rightarrow 3b_1)$ state by requiring orthogonality both to the ground and to the ${}^1A_1(2b_2 \rightarrow 3b_2)$ wave functions. The transition energies obtained in this way are very similar to the ones obtained previously and are, respectively, $\Delta E(2b_2 \rightarrow 3b_2) = 10.85$ eV and $\Delta E(2b_1 \rightarrow 3b_1) = 6.66$ eV. This fact indicates that, at least in problems in which the excited state wave functions are well separate in energy, the ordering of the states does not change even if one imposes an incorrect sequence of orthogonality constraints.

Another interesting problem, significant for testing the properties of our method, is given by the derivation of the HF wave function for the lowest singlet open shell state ($n \to \pi^*$) of formaldehyde, which in the ground state C_{2V} geometry, corresponds to the configuration $^1A_2$: $\ldots 5a_1^2 1b_1^2 1b_2^2 2b_1^1 2b_2^1$. This problem becomes particularly delicate - both as regards the ordering of the states and the convergence of the iterative process - when the molecule is completely distorted, since the open shell state is of the same symmetry and nearly degenerate with the closed shell one. In this sense it has been mentioned as a case in which inversion of the roots is possible within a CAS-SCF calculation [7].

To study this problem we have performed separate SCF calculations for the singlet open and closed shell states at three different geometries: (a) the experimental ground state geometry, (b) the experimental singlet excited state geometry [18] (obtained from (a) through an out-of-plane bending of the CH_2 group), and (c) a completely distorted geometry, obtained from (b) through a rotation of the oxygen atom by 30 degrees around an axis perpendicular to the C–O bond and containing the carbon atom. The experimental ground state geometry and the basis set have been taken from [19], and Hermite Gaussian functions have been used. The HF energies obtained using our method are given in Table 4; note that the value of the vertical excitation energy of the open shell state agrees very well with the corresponding value given in [7].

We note that, in order to have the correct order of the states at the distorted geometry (c) we have first derived the two HF wave functions without any constraint, finding the open shell state lower than the closed shell one by about 0.13 eV, and then repeated the calculation for the closed shell wave function by maintaining orthogonality to the open shell lower one. The inclusion of the orthogonality raises the energy of the upper state by about 0.19 eV, but greatly improves the convergence properties of the process (the number of iteration steps is reduced by a factor ~3) because it includes the variational constraint properly. We also stress the fact that, in such a delicate case, our method easily converges to a variationally stable single-determinant representation of the excited state of interest.

Table 4. HF energies (E_{HF}) of the lowest closed shell (cs) and open shell (os) singlet states of formaldehyde, calculated at the three different geometries (a), (b) and (c) explained in the text; the energies are given in atomic units. ΔE represents the energy difference, $\Delta E = E_{HF}(os) - E_{HF}(cs)$, calculated in electron volts

Geometry	E_{HF} (cs)	E_{HF} (os)	ΔE (eV)
(a)	−113.891 124	−113.775 503	3.15
(b)	−113.795 804	−113.785 424	0.28
(c)	−113.745 122	−113.756 922	−0.32

4. Conclusions

We have applied our method to a few of the molecular excited states concerning which there are controversies in the literature. In particular, we have tested the quality of the results and the convergence properties of the method in cases in which there are problems due to quasi-degeneracies among different states, critical nature of the orbitals, or problems related to the applicability of an RHF approach with orthogonal orbitals to the singlet excited states.

The results lead us to make the following remarks.

(a) Using a first order direct minimization procedure, which is very simple to implement, we have not found any convergence difficulties in the application of of our method also to higher excited states: good results have been obtained for both the energy and the quality of the wave function.

(b) Where comparison with other SCF methods was possible, our technique gave essentially analogous results, though usually with better convergence properties.

(c) Our method can also be applied directly to the singlet excited states of the same symmetry as the closed shell ground state, thus also allowing one to derive variationally correct HF wave functions for such states without resort to more complicated multi-configuration wave functions, and without problems of root-flipping.

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