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An SCF technique for excited states

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A method for deriving HF-SCF wave functions for excited states is presented here. All the active orbital transformations that are compatible with the orthogonality requirements are performed without unnecessary restrictions on the variational space and within a direct minimization approach. The method has been tested with an application on the first excited singlet state of Be.

Key words: Excited states — Orthogonality conditions

1. Introduction

To have an efficient SCF technique for excited states is of interest at least for two main reasons. First of all it is well known that an SCF wave function with the minimal number of determinants which give the correct space and spin symmetry, usually assures a good quality one-electron density from which one can well approximate not only the mean value of the local monoelectronic operators but also the correlation energy through the integration of a density functional [1]. Note that in the cases in which the HF density is not reliable, a limited MC-SCF wave function usually provides an efficient alternative which still maintains the advantages of an independent-particle description. The second reason is that a CI calculation—at least when limited to single and double excitations—is more reliable and accurate if based on SCF orbitals specifically optimized for the parent configurations [2].

Many variational techniques have been set up for obtaining SCF wave functions for the lowest state of each electronic symmetry [3-10], but of course these approaches cannot be directly applied to the excited states without having a variational collapse.

Two main approaches have been proposed to overcome this problem.

The first one [11-13] introduces explicitly into the variational process the orthogonality constraints to the lower states, i.e. the requirement that the SCF wave function Ψ_i of the ith excited state be orthogonal to the SCF wave functions $(\Psi_j, j=0, \ldots, (i-1)\}$ of the lower states having the same symmetry. Note that, if the SCF wave function Ψ_i were imposed to be orthogonal to the exact lower state wave functions, the approximate energy of the ith state would be an upper bound to the true ith eigenvalue.

The second approach [14-18], instead, is based on the fact that every function which corresponds to the nth root of a linear variation method (CI) furnishes an energy upper bound to the true nth eigenvalue of the Hamiltonian (Hylleras-Undheim-McDonald theorem [19]). In this scheme, then, the SCF wave function for the excited state of interest results orthogonal to and non-interacting with a series of wave functions for the lower states of the same symmetry, which however are not the SCF wave functions effectively used as the best approximations to these states.

For what concerns the upper bound properties of the first approach, we observe that, since the orthogonality constraints are imposed to approximate lower state wave functions, one gets energies $\{E'_i\}$ for which only the "weaker bound", with respect to the exact energies $\{E_i\}$, is satisfied: $E'_i \geq E_i - \sum_{j=1}^{i-1} \varepsilon_j\ (E_i - E_j)$, where $\varepsilon_j = 1 - |\langle \Psi_j | \Phi_j \rangle|^2$ with Φ_j the exact wave function for the jth excited state [13]. To have upper bounds to the exact energies $(E'_i \geq E_i)$, the additional constraints to the Ψ'_is have to be imposed: $\langle \Psi_i | \mathscr{H} | \Psi_j \rangle = 0$, $j=0, \ldots, (i-1)$. In the usual cases the coupling matrix elements $\langle \Psi_i | \mathscr{H} | \Psi_j \rangle$ are negligible, so that it is sufficient to impose only the orthogonality constraints $\langle \Psi_i | \Psi_j \rangle = 0$, $j=0, \ldots, (i-1)$ in the variational process. On the other hand, if these matrix elements cannot be neglected, one has to go beyond the single determinant approach, for example by using MC-SCF wave functions both for the ground and for the excited states [20]. Using such an approach it is again sufficient to impose only the orthogonality constraints among the MC-SCF wave functions.

In this paper we present a new method for deriving SCF wave functions for excited states in which the orthogonality constraints to the lower states of the same symmetry are explicitly introduced. In the existing literature on the subject the orthogonality problem has been usually solved by means of restrictions on the variational space which are stronger than required by the problem itself [11-13]. On the contrary, the method we propose in this article treats the orthogonality constraints in a non-restrictive way, thus allowing to get the true energy minimum compatible with the scheme adopted.

We have chosen an approach of this type for the following reasons. First of all we search for an approximate representation of the various electronic states which still maintains the orthogonality property holding among the exact wave functions, since we think that such a property is important especially when wave functions of different states are simultaneously involved, like in the evaluation of transition probabilities. Furthermore, while in the other approach the Hylleras-Undheim-MacDonald theorem is satisfied only at convergence and this could introduce convergence problems in the iterative process [14, 18], in our approach the orthogonality constraints are satisfied at each step of the SCF process and this fact should guarantee against convergence difficulties related to the introduction of the constraints. It should be stressed, however, that in both the approaches further problems could result for example from inadequacies of the chosen basis set or of the configurations utilized for constructing the wave function in presence of quasi-degeneracies among states.

In this article we present an iterative method for deriving SCF wave functions for excited states, in which all the possible orbital transformations that simultaneously lower the energy and fulfill the orthogonality requirements are performed at each step of the process and without any unnecessary space-restriction. A direct minimization procedure [5] is proposed which does not involve any specific computational difficulty and is free from the convergence problems of the coupling operator techniques [7, 9].

In this paper we do not introduce the constraints $\langle\Psi_i|\mathscr{H}|\Psi_j\rangle = 0, j = 0, \ldots, (i-1)$, which assure the upper bound to the exact energies, nor consider wave functions of the MC-SCF type, but our approach could be generalized in this sense. In Sect. 2 we consider the application of our method to the first two doublet and in Sect. 3. to the first two singlet excited states. In Sect. 4. we discuss the results of our method, as applied to a specific example (first singlet excited state of Be), in comparison with those obtained using different techniques.

2. Doublet states

Let us consider a series of doublet states described by the following RHF wave functions:

$$\Psi^{(\mu)}(1, 2, \ldots, 2n+1) = \sqrt{\frac{1}{(2n+1)!}}\det|\phi_1^{(\mu)}(1)\ldots\bar{\phi}_n^{(\mu)}(2n)\phi_{n+1}^{(\mu)}(2n+1)|, \tag{1}$$

where $j = (\bar{r}_j, s_j)$ denotes the combined spin (s_j) and space coordinates of the electron j, $\phi_1^{(\mu)}, \ldots, \phi_n^{(\mu)}, \phi_{n+1}^{(\mu)}$ are the occupied orbitals of the μth state, constructed in terms of m real basis functions and ordered according to the energy, and $\Psi^{(0)}$ represents the ground state.

The orthogonality constraint on the first excited state wave function $\Psi^{(1)}$ is

$$\langle\Psi^{(0)}|\Psi^{(1)}\rangle = D_{01}^{\mathrm{I}} \cdot D_{01}^{\mathrm{II}} = 0, \tag{2}$$

where

$$D_{01}^{\mathrm{I}} = \det|\langle\phi_1^{(0)}|\phi_1^{(1)}\rangle\cdots\langle\phi_n^{(0)}|\phi_n^{(1)}\rangle\langle\phi_{n+1}^{(0)}|\phi_{n+1}^{(1)}\rangle| = \det|\boldsymbol{S}^{\mathrm{I}}| \tag{3}$$

$$D_{01}^{\mathrm{II}} = \det|\langle\phi_1^{(0)}|\phi_1^{(1)}\rangle\cdots\langle\phi_n^{(0)}|\phi_n^{(1)}\rangle| = \det|\boldsymbol{S}^{\mathrm{II}}|. \tag{4}$$

Since the annihilation of one of the two determinants produces a further node in one of the orbitals involved, from energy considerations we impose such a requirement only on D^{I}_{01}, which involves the occupied orbital highest in energy. Therefore we require that

$$D^{\mathrm{I}}_{01} = \det|\boldsymbol{S}^{\mathrm{I}}| = 0. \tag{5}$$

In what follows we will show that:

(a) constraint (5) is equivalent to the requirement that the occupied orbitals $\phi^{(1)}_1, \ldots, \phi^{(1)}_{n+1}$ be orthogonal to a given vector χ^{I}_{01}, linear combination of the ground state orbitals $\phi^{(0)}_1, \ldots, \phi^{(0)}_{n+1}$.

(b) In the space orthogonal to χ^{I}_{01} the variational process is free from constraints and thus reduced to the solution of the RHF equations for a doublet state.

(c) The full exploitation of the variational degrees of freedom requires the reintroduction of χ^{I}_{01} in the iterative process. For achieving this result we propose a practicable way which implies the use of multiple rotations, as it will be explained later in this Section.

For what concerns point (a) we observe that, since $D^{\mathrm{I}}_{01} = 0$, the rows of $\boldsymbol{S}^{\mathrm{I}}$ must be linearly dependent and therefore at least one of them (only one if $\boldsymbol{S}^{\mathrm{I}}$ has rank n) can be annihilated by means of a unitary transformation among the rows. Such a linear transformation correspondingly defines a normalized vector χ^{I}_{01} orthogonal to all the occupied orbitals $\phi^{(1)}_1, \ldots, \phi^{(1)}_{n+1}$.

Using the Laplace expansion of D^{I}_{01} one can define χ^{I}_{01} as follows

$$D^{\mathrm{I}}_{01} = \sum_{j=1}^{n+1} d^{\mathrm{I}}_{01}(j;\, i)\langle\phi^{(0)}_j|\phi^{(1)}_i\rangle = c_i\langle\chi^{\mathrm{I}}_{01}|\phi^{(1)}_i\rangle, \tag{6}$$

where $d^{\mathrm{I}}_{01}(j;\, i)$ is the complementary cofactor of the (j, i) element of $\mathbf{S}^{\mathrm{I}}$ and c_i is a constant depending on $\phi^{(1)}_i$.

It follows that for a given orthonormal set of occupied orbitals $\phi^{(1)}_1, \ldots, \phi^{(1)}_{n+1}$, which satisfy the condition (5), every linear combination with virtual orbitals orthogonal to χ^{I}_{01} is compatible with (5).

Finally, in order to have a procedure independent of the choice of the trial orbitals, one must perform also linear combinations of χ^{I}_{01} and the occupied orbitals. To this end, we suggest the following procedure, which starts from a set of m orthonormal orbitals $\phi^{(1)}_1, \ldots, \phi^{(1)}_m$ with $\phi^{(1)}_1, \ldots, \phi^{(1)}_{n+1}$ satisfying the condition (5):

(a) Orthogonalization of the virtual orbitals to χ^{I}_{01}. This can be performed for example in the following way:

$$(\phi^{(1)\prime}_k, \phi^{(1)\prime}_{k+1}) = (\phi^{(1)}_k, \phi^{(1)}_{k+1})\begin{pmatrix} c_\theta & s_\theta \\ -s_\theta & c_\theta \end{pmatrix}, \tag{7}$$

where $c_\theta = \cos(\theta)$, $s_\theta = \sin(\theta)$ and

$$\theta = \tan^{-1}\left(\frac{\langle\chi^{\mathrm{I}}_{01}|\phi^{(1)}_k\rangle}{\langle\chi^{\mathrm{I}}_{01}|\phi^{(1)}_{k+1}\rangle}\right). \tag{8}$$

These linear combinations, which are to be done in sequence, guarantee that $\langle\phi_k^{(1)\prime}|\chi_{01}^{\mathrm{I}}\rangle=0$, $k=n+2,\ldots,m-1$ and give $\phi_m^{(1)\prime}=\chi_{01}^{\mathrm{I}}$.

(b) Energy optimization in the space of the occupied and virtual orbitals orthogonal to χ_{01}^{I}, according to one of the standard procedures for the solution of the RHF equations.

(c) Energy optimization in the space $\{\phi_1^{(1)},\ldots,\phi_{n+1}^{(1)},\chi_{01}^{\mathrm{I}}\}$. For this step we suggest to perform a series of double rotations [5], that are the simplest multiple rotations, which allow to minimize the energy and simultaneously to fulfill the orthogonality requirement. Note that in this case a two-parameter linear combination is equivalent to the use of a general (3×3) unitary transformation.

In our scheme each double rotation is made beteen χ_{01}^{I} and an occupied orbital ϕ_l $(l=1,\ldots,(n+1))$ with an angle α and between the resulting $\chi_{01}^{\mathrm{I}}(\alpha)$ and a different occupied orbital $\phi_{l'}$ with an angle β:

$$(\chi_{01}^{\mathrm{I}},\phi_l,\phi_{l'})_\alpha^\beta\equiv[\alpha;(\chi_{01}^{\mathrm{I}},\phi_l^{(1)})]\otimes[\beta;(\chi_{01}^{\mathrm{I}}(\alpha),\phi_{l'}^{(1)})]. \tag{9}$$

The angles α and β are obtained by solving the following system of equations:

$$d[\Delta E(\alpha,\beta)]=0 \tag{10}$$

$$D_{01}^{\mathrm{I}}=\langle c_\alpha\phi_l^{(1)}+s_\alpha\chi_{01}^{\mathrm{I}}|\mathcal{O}_{ll'}|c_\beta\phi_{l'}^{(1)}+s_\beta(c_\alpha\chi_{01}^{\mathrm{I}}-s_\alpha\phi_l^{(1)})\rangle=0 \tag{11}$$

$$\mathcal{O}_{ll'}=\sum_{p,q=1}^{n+1}|\phi_p^{(0)}\rangle d(p,q;l,l')\langle\phi_q^{(0)}|, \tag{12}$$

where in (12) $d(p,q;l,l')$ is the second-order generalized minor [21] deriving from the Laplace expansion of D_{01}^{I} and in (10) $\Delta E(\alpha,\beta)$ represents the variation of the energy E given by

$$E=\sum_p\langle p|\tfrac{1}{2}\omega_p\mathscr{h}+\mathscr{F}_p|p\rangle=\sum_p\omega_p\mathscr{h}_{pp}+\sum_{pq}(\mu_{pq}\mathscr{T}_{pq}-\nu_{pq}\mathscr{K}_{pq}), \tag{13}$$

$$\mathscr{F}_p=\tfrac{1}{2}\omega_p\mathscr{h}+\sum_q(\mu_{pq}\mathscr{T}_q-\nu_{pq}\mathscr{K}_q). \tag{14}$$

In (13)-(14) $\{\omega\}$, $\{\mu\}$, $\{\nu\}$ are state parameters and $\mathscr{h}_{pp}$, $\mathscr{T}_{pq}$, $\mathscr{K}_{pq}$ are the matrix elements of the well known monoelectronic ($\mathscr{h}$), Coulomb ($\mathscr{T}_q$), exchange ($\mathscr{K}_q$) operators. The relationship between α and β, which follows from (11), is

$$t_\beta=s_\alpha\frac{\langle\chi_{01}^{\mathrm{I}}|\mathcal{O}_{ll'}|\phi_{l'}^{(1)}\rangle}{\langle\chi_{01}^{\mathrm{I}}|\mathcal{O}_{ll'}|\phi_l^{(1)}\rangle}=s_\alpha\frac{D_{01}^{\mathrm{I}}(\chi_{01}^{\mathrm{I}}\rightarrow\phi_l^{(1)})}{D_{01}^{\mathrm{I}}(\chi_{01}^{\mathrm{I}}\rightarrow\phi_{l'}^{(1)})}=s_\alpha\cdot\varepsilon, \tag{15}$$

where $t_\beta=\tan(\beta)$ and $D_{01}^{\mathrm{I}}(\chi\rightarrow\phi)$ represents the determinant of the superposition matrix S^{I} in which the orbital ϕ has been substituted by χ.

The second order approximate solution of the Eqs. (10)-(11), labeling χ_{01}^{I}, $\phi_l^{(1)}$, $\phi_{l'}^{(1)}$ respectively with i, j,k and utilizing the formalism of Ref. [5], is the following

$$(2\alpha)\simeq-\frac{E_1(i,j)+\varepsilon\cdot E_1(i,k)}{E_2(i,j)+2\varepsilon\cdot G(i,j;i,k)+\varepsilon^2\cdot E_2(i,k)}, \tag{16}$$

where

$$E_1(i, j) = 4\langle i|(\mathscr{F}_j - \mathscr{F}_i)|j\rangle \tag{17}$$

$$\begin{aligned} E_2(i, j) = 2[&\langle i|(\mathscr{F}_j - \mathscr{F}_i) + (A_{ij} - \tfrac{1}{2}B_{ij})\mathscr{K}_j - \tfrac{1}{2}B_{ij}\mathscr{T}_j|i\rangle \\ &+ \langle j|(\mathscr{F}_i - \mathscr{F}_j) + (A_{ij} - \tfrac{1}{2}B_{ij})\mathscr{K}_i - \tfrac{1}{2}B_{ij}\mathscr{T}_i|j\rangle] \end{aligned} \tag{18}$$

$$G(i, j; k, l) = 4A_{ij;kl}(ij|kl) - 2B_{ij;kl}[(ik|jl) + (il|jk)] \tag{19}$$

$$A_{ij} = \mu_{ii} - 2\mu_{ij} + \mu_{jj} \tag{20}$$

$$B_{ij} = \nu_{ii} - 2\nu_{ij} + \nu_{jj} \tag{21}$$

$$A_{ij;kl} = \mu_{ik} - \mu_{il} - \mu_{jk} + \mu_{jl} \tag{22}$$

$$B_{ij;kl} = \nu_{ik} - \nu_{il} - \nu_{jk} + \nu_{jl}. \tag{23}$$

In (17)-(18) the Hartree-Fock operators $\mathscr{F}$'s are defined by (14), in (20)-(23) the μ, ν's are the state parameters which define the energy - see (13) - and $(ij|kl)$ is a bielectronic integral in the charge notation.

If a more accurate solution is required one can use α and β from (15)-(16) as the initial guess of an iterative process.

Let us now consider the second excited state wave function $\Psi^{(2)}$, for which the orthogonality requirements are

$$\langle\Psi^{(0)}|\Psi^{(2)}\rangle = D^{\mathrm{I}}_{02} \cdot D^{\mathrm{II}}_{02} = 0 \tag{24}$$

$$\langle\Psi^{(1)}|\Psi^{(2)}\rangle = D^{\mathrm{I}}_{12} \cdot D^{\mathrm{II}}_{12} = 0, \tag{25}$$

where $D^{\mathrm{I,II}}_{i,2}$, $i = 0, 1$ are defined as in (3)-(4).

From energy considerations we require that $D^{\mathrm{I}}_{02} = 0$ and $D^{\mathrm{I}}_{12} = 0$.

For a given set of trial orbitals $\{\phi^{(2)}_1, \ldots, \phi^{(2)}_n, \phi^{(2)}_{n+1}\}$, which satisfy the conditions (24)-(25), utilizing the Laplace expansions of D^{I}_{02} and D^{I}_{12}, we can define two vectors χ^{I}_{02}, χ^{I}_{12} linear combinations respectively of $\phi^{(0)}_1, \ldots, \phi^{(0)}_{n+1}$ and of $\phi^{(1)}_1, \ldots, \phi^{(1)}_{n+1}$, which are orthogonal to $\phi^{(2)}_1, \ldots, \phi^{(2)}_{n+1}$ but in general not mutually orthogonal.

The first step of our procedure consists now in a sequence of two by two rotations - see (7)-(8) - in the space $\{\phi^{(2)}_{n+2}, \ldots, \phi^{(2)}_m\}$ for getting virtual orbitals $\phi^{(2)'}_{n+2}, \ldots, \phi^{(2)'}_{m-1}$ orthogonal to χ^{I}_{02} and then in rotating these orbitals to obtain new virtual orbitals $\phi^{(2)''}_{n+2}, \ldots, \phi^{(2)''}_{m-2}$ orthogonal to χ^{I}_{12}. We observe that $\phi^{(2)'}_m = \chi^{\mathrm{I}}_{02}$, while $\phi^{(2)''}_{m-1}$ is the component of χ^{I}_{12} orthogonal to χ^{I}_{02}. Every linear combination of the occupied orbitals with $\phi^{(2)''}_{n+2}, \ldots, \phi^{(2)''}_{m-2}$ is then compatible with the constraints (24)-(25) and can be used for the energy optimization as in the previous step (b).

For a complete energy minimization however we must also perform those linear combinations in the space $\{\phi^{(2)}_1, \ldots, \phi^{(2)}_{n+1}, \phi^{(2)''}_{m-1}, \phi^{(2)'}_m\}$ which are compatible with the constraints (24)-(25). To this end one can repeat the operations described in step (c) - see before - respectively in the space $\{\phi^{(2)}_1, \ldots, \phi^{(2)}_{n+1}, \phi^{(2)''}_{m-1}\}$ and in the space $\{\phi^{(2)'}_1, \ldots, \phi^{(2)'}_{n+1}, \phi^{(2)''}_m\}$, where now $\phi^{(2)''}_m$ is the normalized component of

$\phi_m^{(2)'}$ orthogonal to the reference vector $\chi_{12}^{I'}$ defined by the new occupied orbitals $\phi_1^{(2)'}, \dots, \phi_{n+1}^{(2)'}$ and by the condition $D_{12}^{I}=0$.

Extension of this method to higher doublet excited states is straightforward. A completely equivalent procedure can also be applied to all those excited states that can be described by a one determinant wave function.

3. Singlet states

Let us consider a closed shell, ground state wave function

$$\Psi^{(0)}(1,2,\dots,2n)=\sqrt{\frac{1}{(2n)!}}\det|\phi_1^{(0)}(1)\bar{\phi}_1^{(0)}(2)\cdots\phi_n^{(0)}(2n-1)\bar{\phi}_n^{(0)}(2n)| \tag{26}$$

and a series of excited singlet state wave functions $\Psi^{(\mu)}$ having the same spatial symmetry of $\Psi^{(0)}$:

$$\begin{aligned}\Psi^{(\mu)}(1,2,\dots,2n)=\sqrt{\frac{1}{(2n)!2}}\{&\det|\phi_1^{(\mu)}(1)\cdots\bar{\phi}_{n-1}^{(\mu)}(2n-2)\phi_n^{(\mu)}(2n-1)\\&\times\bar{\phi}_{n+1}^{(\mu)}(2n)|\\&+\det|\phi_1^{(\mu)}(1)\cdots\bar{\phi}_{n-1}^{(\mu)}(2n-2)\phi_{n+1}^{(\mu)}(2n-1)\bar{\phi}_n^{(\mu)}(2n)|\}.\end{aligned} \tag{27}$$

The orthogonality requirement in the optimization of $\Psi^{(1)}$ is

$$\langle\Psi^{(0)}|\Psi^{(1)}\rangle=\sqrt{2}D_{01}^{I}\cdot D_{01}^{II}=0, \tag{28}$$

where

$$D_{01}^{I}=\det|\langle\phi_1^{(0)}|\phi_1^{(1)}\rangle\cdots\langle\phi_{n-1}^{(0)}|\phi_{n-1}^{(1)}\rangle\langle\phi_n^{(0)}|\phi_{n+1}^{(1)}\rangle|=\det|\boldsymbol{S}^{I}| \tag{29}$$

$$D_{01}^{II}=\det|\langle\phi_1^{(0)}|\phi_1^{(1)}\rangle\cdots\langle\phi_{n-1}^{(0)}|\phi_{n-1}^{(1)}\rangle\langle\phi_n^{(0)}|\phi_n^{(1)}\rangle|=\det|\mathbf{S}^{II}|. \tag{30}$$

As for the doublet state, from energy considerations we require that $D_{01}^{I}=0$, and we suggest a procedure quite similar to that previously proposed:

(a) optimization of the lower orbital of the singlet pair, i.e. energy minimization in the space $\{\phi_n^{(1)}, \phi_{n+2}^{(1)}, \dots, \phi_m^{(1)}\}$. It can be freely performed since it leaves $D_{01}^{I}=0$.

(b) Orthogonalization of $\phi_{n+2}^{(1)}, \dots, \phi_m^{(1)}$, as in (7)–(8), to the reference vector χ_{01}^{I} which is defined by the condition $D_{01}^{I}=0$ and energy optimization in the space $\{\phi_1^{(1)}, \dots, \phi_{n-1}^{(1)}, \phi_{n+1}^{(1)}, \phi_{n+2}^{(1)}, \dots, \phi_{m-1}^{(1)}\}$.

(c) Reintroduction of the excluded virtual orbital $\phi_m^{(1)}$ in the variational space, i.e. energy minimization in the space $\{\phi_1^{(1)}, \dots, \phi_{n-1}^{(1)}, \phi_{n+1}^{(1)}, \phi_n^{(1)}, \phi_m^{(1)}\}$. To this end one can repeat the sequence of double rotations described in the previous step (c) for the first doublet state, in the spaces $\{\phi_1^{(1)}, \dots, \phi_{n-1}^{(1)}, \phi_{n+1}^{(1)}, \phi_m^{(1)}\}$, $\{\phi_1^{(1)}, \dots, \phi_{n-1}^{(1)}, \phi_n^{(1)}, \phi_{n+1}^{(1)}\}$, $\{\phi_1^{(1)}, \dots, \phi_{n-1}^{(1)}, \phi_n^{(1)}, \phi_m^{(1)}\}$ and in the space $\{\phi_n^{(1)}, \phi_{n+1}^{(1)}, \phi_m^{(1)}\}$.

Let us consider now the orthogonality requirements in the optimization of $\Psi^{(2)}$:

$$\langle\Psi^{(0)}|\Psi^{(2)}\rangle=\sqrt{2}D_{02}^{\mathrm{I}}\cdot D_{02}^{\mathrm{II}}=0 \tag{31}$$

$$\langle\Psi^{(1)}|\Psi^{(2)}\rangle=D_{12}^{\mathrm{I}}\cdot\bar{D}_{12}^{\mathrm{I}}+D_{12}^{\mathrm{II}}\cdot\bar{D}_{12}^{\mathrm{II}}=0, \tag{32}$$

where $D_{i,2}^{\mathrm{I,II}}$, $i=0,1$, are defined as in (29)–(30) and

$$\bar{D}_{12}^{\mathrm{I}}=\det|\langle\phi_1^{(1)}|\phi_1^{(2)}\rangle\cdot\cdots\langle\phi_{n-1}^{(1)}|\phi_{n-1}^{(2)}\rangle\langle\phi_{n+1}^{(1)}|\phi_n^{(2)}\rangle|=\det|\bar{S}^{\mathrm{I}}| \tag{33}$$

$$\bar{D}_{12}^{\mathrm{II}}=\det|\langle\phi_1^{(1)}|\phi_1^{(2)}\rangle\cdots\langle\phi_{n-1}^{(1)}|\phi_{n-1}^{(2)}\rangle\langle\phi_{n+1}^{(1)}|\phi_{n+1}^{(2)}\rangle|=\det|\bar{S}^{\mathrm{II}}|. \tag{34}$$

From energy consideration we satisfy the condition (31) by requiring that D_{02}^{I} be equal to zero; this condition defines a vector χ_{02}^{I} orthogonal to $\phi_1^{(2)},\ldots,\phi_{n-1}^{(2)},\phi_{n+1}^{(2)}$. Let us assume for simplicity to optimize the energy in a space orthogonal to χ_{02}^{I}, so that we can ignore (31) and analyze in detail the condition (32). The inclusion of χ_{02}^{I} in the variational space can be performed afterwards in a way analogous to that described in the previous step (c) for the first excited singlet state.

The orthogonality requirement (32) can be cast in the form

$$\langle\phi_n^{(2)}|\mathscr{Q}|\phi_{n+1}^{(2)}\rangle=0, \tag{35}$$

where

$$\mathscr{Q}=|\chi\rangle\langle\bar{\chi}|+|\bar{\chi}\rangle\langle\chi| \tag{36}$$

or, equivalently,

$$\langle\phi_n^{(2)}|\{|\chi\rangle\langle\bar{\chi}|\phi_{n+1}^{(2)}\rangle+|\bar{\chi}\rangle\langle\chi|\phi_{n+1}^{(2)}\rangle\}=\langle\phi_n^{(2)}|\chi_n\rangle=0 \tag{37}$$

$$\langle\phi_{n+1}^{(2)}|\{|\chi\rangle\langle\bar{\chi}|\phi_n^{(2)}\rangle+|\bar{\chi}\rangle\langle\chi|\phi_n^{(2)}\rangle\}=\langle\phi_{n+1}^{(2)}|\chi_{n+1}\rangle=0. \tag{38}$$

In (36)–(38) χ and $\bar{\chi}$ are defined through the Laplace expansions with respect to the last column respectively of D_{12}^{I} (or D_{12}^{II}) and $\bar{D}_{12}^{\mathrm{I}}$ (or $\bar{D}_{12}^{\mathrm{II}}$) and are orthogonal to the doubly occupied orbitals, while χ_n and χ_{n+1} are linear combinations of χ and $\bar{\chi}$.

For a given set of trial orbitals $\{\phi_1^{(2)},\ldots,\phi_{n-1}^{(2)},\phi_n^{(2)},\phi_{n+1}^{(2)}\}$ which satisfy the condition (32), one can easily prove that linear combinations of the doubly occupied orbitals with virtual orbitals orthogonal to χ and $\bar{\chi}$ are compatible with constraint (32) and can be used for the energy minimization. Analogously from (37)–(38) it follows that the energy can be freely optimized by means of linear combinations between $\phi_n^{(2)}$ and virtual orbitals orthogonal to χ_n, and linear combinations between $\phi_{n+1}^{(2)}$ and virtual orbitals orthogonal to χ_{n+1}.

The remaining combinations of interest are those in the space $\{\phi_1^{(2)},\ldots,\phi_{n-1}^{(2)},\phi_n^{(2)},\phi_{n+1}^{(2)},\phi_{m-1}^{(2)},\phi_m^{(2)}\}$ where $\phi_{m-1}^{(2)},\phi_m^{(2)}$ are those virtual orbitals, projections of χ and $\bar{\chi}$ onto the virtual space, that have been excluded in the optimization of the doubly occupied orbitals.

The suggested procedure consists of the following steps:

(a) optimization of the singlet pair with the two excluded virtual orbitals, i.e. double rotations in the space $\{\phi_n^{(2)},\phi_{n+1}^{(2)},\phi_{m-1}^{(2)},\phi_m^{(2)}\}$.

First of all we rotate $\phi_{m-1}^{(2)}$ and $\phi_m^{(2)}$ to get new $\phi_{m-1}^{(2)'}$ and $\phi_m^{(2)'}$ having the largest possible superposition respectively with χ_n and χ_{n+1}. Then we perform a double rotation between $\phi_n^{(2)}$ and $\phi_{m-1}^{(2)'}$ with an angle α and between $\phi_{n+1}^{(2)}$ and $\phi_m^{(2)'}$ with an angle β:

$$(\phi_n^{(2)}, \phi_{m-1}^{(2)'}; \phi_{n+1}^{(2)}, \phi_m^{(2)'})_\alpha^\beta \equiv [\alpha; (\phi_n^{(2)}, \phi_{m-1}^{(2)'})] \otimes [\beta, (\phi_{n+1}^{(2)}, \phi_m^{(2)'})], \tag{39}$$

where α and β are obtained by solving the following system of equations:

$$d[\Delta E(\alpha, \beta)] = 0 \tag{40}$$

$$\langle c_\alpha \phi_n^{(2)} - s_\alpha \phi_{m-1}^{(2)'} | \mathcal{Q} | c_\beta \phi_{n+1}^{(2)} - s_\beta \phi_m^{(2)'} \rangle = 0. \tag{41}$$

In (40) $\Delta E(\alpha, \beta)$ represents the energy variation.

The relationship between α and β is given by (41)

$$t_\beta = -\frac{\langle \phi_{m-1}^{(2)'} | \mathcal{Q} | \phi_{n+1}^{(2)} \rangle t_\alpha}{\langle \phi_n^{(2)} | \mathcal{Q} | \phi_m^{(2)'} \rangle - t_\alpha \langle \phi_{m-1}^{(2)'} | \mathcal{Q} | \phi_m^{(2)'} \rangle} = -\frac{a t_\alpha}{c + d t_\alpha}, \tag{42}$$

The second order approximate solution of the equations (40)-(41) is the following:

$$(2\alpha) \simeq -\frac{E_1(\phi_n^{(2)}, \phi_{m-1}^{(2)'}) - \frac{a}{c} E_1(\phi_{n+1}^{(2)}, \phi_m^{(2)'})}{E_2(\phi_n^{(2)}, \phi_{m-1}^{(2)'}) + \left(\frac{a}{c}\right)^2 E_2(\phi_{n+1}^{(2)}, \phi_m^{(2)'}) + \frac{ad}{c^2} E_1(\phi_{n+1}^{(2)}, \phi_m^{(2)'})},$$

$$-\frac{2a}{c} G(\phi_n^{(2)}, \phi_{m-1}^{(2)'}; \phi_{n+1}^{(2)}, \phi_m^{(2)'}) \tag{43}$$

where $E_1(i, j)$ and $E_2(i, j)$ are defined as in (17)-(18) and $G(i, j; k, l)$ as in (19). If a more accurate solution is required one can use α and β from (42)-(43) as the initial guess of an iterative process.

(b) Optimization of all occupied orbitals with the two excluded virtual orbitals, i.e. double rotations of the type:

$$(\phi_l^{(2)}, \phi_k^{(2)}; \phi_n^{(2)}, \phi_{n+1}^{(2)})_\alpha^\beta \equiv [\alpha; (\phi_l^{(2)}, \phi_k^{(2)})] \otimes [\beta; (\phi_n^{(2)}, \phi_{n+1}^{(2)})], \tag{44}$$

with $l = 1, \ldots, n-1$ and $k = m-1, m$.

The angles α and β are obtained from the solution of the system of equations

$$d[\Delta E(\alpha, \beta)] = 0 \tag{45}$$

$$\langle c_\beta \phi_n^{(2)} - s_\beta \phi_{n+1}^{(2)} | c_\alpha^2 \mathscr{P}_{ll}^{(l)} + s_\alpha^2 \mathscr{P}_{kk}^{(l)} - 2 s_\alpha c_\alpha \mathscr{P}_{lk}^{(l)} | c_\beta \phi_{n+1}^{(2)} + s_\beta \phi_n^{(2)} \rangle = 0. \tag{46}$$

In (45) $\Delta E(\alpha, \beta)$ represents the energy variation, while in (46) the operators $\mathcal{P}_{ij}^{(l)}$ are defined as follow:

$$\mathcal{P}_{ij}^{(l)} = \tfrac{1}{2}\{\mathcal{O}_l[|\phi_i^{(2)}\rangle\langle\phi_j^{(2)}| + |\phi_j^{(2)}\rangle\langle\phi_i^{(2)}|]\bar{\mathcal{O}}_l + \bar{\mathcal{O}}_l[|\phi_i^{(2)}\rangle\langle\phi_j^{(2)}| + |\phi_j^{(2)}\rangle\langle\phi_i^{(2)}|]\mathcal{O}_l\} \tag{47}$$

$$\mathcal{O}_l = \sum_{p,q=1}^{n} |\phi_p^{(1)}\rangle d(p, q; l, k)\langle\phi_q^{(1)}| \tag{48}$$

$$\bar{\mathcal{O}}_l = \sum_{\substack{p,q=1\\(\neq n)}}^{n+1} |\phi_p^{(1)}\rangle \bar{d}(p, q; l, k)\langle\phi_q^{(1)}|, \tag{49}$$

where $d(p, q; l, k)$, $\bar{d}(p, q; l, k)$ are the second order generalized minors [21] respectively of D_{12}^{I} (or D_{12}^{II}) and $\bar{D}_{12}^{\mathrm{I}}$ (or $\bar{D}_{12}^{\mathrm{II}}$) and k denotes the last column of $S^{\mathrm{I,II}}$ and $\bar{S}^{\mathrm{I,II}}$. Note the χ, $\bar{\chi}$ defined in (36) have simple expressions in terms of these operators: $\mathcal{O}_l|\phi_l^{(2)}\rangle = \chi$, $\bar{\mathcal{O}}_l|\phi_l^{(2)}\rangle = \bar{\chi}$.

The condition (46) can be cast in the form

$$\begin{aligned} t_{2\beta} &= -2\frac{\langle\phi_n^{(2)}|2\mathcal{P}_{lk}^{(l)} - t_\alpha\mathcal{P}_{kk}^{(l)}|\phi_{n+1}^{(2)}\rangle t_\alpha}{\langle\phi_{n+1}^{(2)}|[\mathcal{P}_{ll}^{(l)} - 2t_\alpha\mathcal{P}_{lk}^{(l)} + t_\alpha^2\mathcal{P}_{kk}^{(l)}]|\phi_{n+1}^{(2)}\rangle - \langle\phi_n^{(2)}|[\mathcal{P}_{ll}^{(l)} - 2t_\alpha\mathcal{P}_{lk}^{(l)} + t_\alpha^2\mathcal{P}_{kk}^{(l)}]|\phi_n^{(2)}\rangle} \\ &= -2\frac{(a + bt_\alpha)t_\alpha}{c + dt_\alpha + gt_\alpha^2}. \end{aligned} \tag{50}$$

The second-order approximate solution of (45)–(46) is

$$(2\alpha) \simeq -\frac{E_1(\phi_l^{(2)}, \phi_k^{(2)}) - \frac{a}{c}E_1(\phi_n^{(2)}, \phi_{n+1}^{(2)})}{E_2(\phi_l^{(2)}, \phi_k^{(2)}) + \left(\frac{a}{c}\right)^2 E_2(\phi_n^{(2)}, \phi_{n+1}^{(2)}) + \left(\frac{ad}{c^2} - \frac{b}{c}\right)E_1(\phi_n^{(2)}, \phi_{n+1}^{(2)}) - \frac{2a}{c}G(\phi_l^{(2)}, \phi_k^{(2)}; \phi_n^{(2)}, \phi_{n+1}^{(2)})}, \tag{51}$$

where we have used the same definitions as in (17)–(19).

(c) Optimization of the occupied orbitals among themselves, i.e. double rotations of the type:

$$(\phi_n^{(2)}, \phi_l^{(2)}, \phi_{n+1}^{(2)})_\alpha^\beta \equiv [\alpha; (\phi_n^{(2)}, \phi_l^{(2)})] \otimes [\beta; (\phi_n^{(2)}(\alpha), \phi_{n+1}^{(2)})] \tag{52}$$

with $l = 1, \ldots, n-1$.

The angles α and β are obtained from the solution of the system of equations

$$d[\Delta E(\alpha, \beta)] = 0 \tag{53}$$

$$\begin{aligned} t_{2\beta} &= -2\frac{\langle\phi_l^{(2)}|\mathcal{P}_{nn}^{(l)}|\phi_{n+1}^{(2)}\rangle t_\alpha\sqrt{1 + t_\alpha^2}}{[\langle\phi_{n+1}^{(2)}|\mathcal{P}_{ll}^{(l)}|\phi_{n+1}^{(2)}\rangle - \langle\phi_n^{(2)}|\mathcal{P}_{ll}^{(l)}|\phi_n^{(2)}\rangle] + 2t_\alpha\langle\phi_{n+1}^{(2)}|\mathcal{P}_{ln}^{(l)}|\phi_{n+1}^{(2)}\rangle + [\langle\phi_{n+1}^{(2)}|\mathcal{P}_{nn}^{(l)}|\phi_{n+1}^{(2)}\rangle - \langle\phi_l^{(2)}|\mathcal{P}_{nn}^{(l)}|\phi_l^{(2)}\rangle]t_\alpha^2} \\ &= -\frac{2a\sqrt{1 + t_\alpha^2} \cdot t_\alpha}{c + dt_\alpha + gt_\alpha^2}. \end{aligned} \tag{54}$$

In (53) $\Delta E(\alpha, \beta)$ represents as usual the energy variation and the operators $\mathscr{P}_{ll}^{(l)}$, $\mathscr{P}_{ln}^{(l)}$, $\mathscr{P}_{nn}^{(l)}$ are defined by (47)-(49).

The second-order approximate solution of these equations is

$$(2\alpha) \simeq -\frac{E_1(\phi_n^{(2)}, \phi_l^{(2)}) - \frac{a}{c} E_1(\phi_n^{(2)}, \phi_{n+1}^{(2)})}{E_2(\phi_n^{(2)}, \phi_l^{(2)}) + \left(\frac{a}{c}\right)^2 E_2(\phi_n^{(2)}, \phi_{n+1}^{(2)}) + \frac{ad}{c^2} E_1(\phi_n^{(2)}, \phi_{n+1}^{(2)}) - 2\left(\frac{a}{c}\right) G(\phi_n^{(2)}, \phi_l^{(2)}; \phi_n^{(2)}, \phi_{n+1}^{(2)})} . \quad (55)$$

A similar set of double rotations can be performed exchanging $\phi_n^{(2)}$ with $\phi_{n+1}^{(2)}$ in (52). The procedure is the same as in step (c).

We observe that this sequence of double rotations inside the space $\{\phi_1^{(2)}, \ldots, \phi_{n-1}^{(2)}, \phi_n^{(2)}, \phi_{n+1}^{(2)}, \phi_{m-1}^{(2)}, \phi_m^{(2)}\}$ is not univocally defined. In our scheme we use the linear combinations between $\phi_n^{(2)}$ and $\phi_{n+1}^{(2)}$ essentially as a tool for satisfying the orthogonality requirement.

Extension of this procedure to higher excited states is straightforward.

4. Applications

In this section we compare the results obtained by using our method in the case of the first singlet excited state of Be (2s→3s), with those obtained by using techniques more restrictive in the exploitation of the variational space [11-13]. We observe that in this case the general approach proposed by Davidson and Stenkamp [14] for RHF wave functions gives an energy which in principle is not an upper bound to the exact one whereas the corresponding wave function can be regarded as intermediate between those for the ground and the first excited state.

For what concerns our method, we have applied the procedure described in Sect. 3. without finding any convergence problem. Starting from the orbitals of the ground state or from other orbital sets which satisfied from the beginning the orthogonality constraint (28) the number of iterations required for convergence up to 10^{-6} a.u. never exceeded 12.

For comparison, we have also introduced the orthogonality constraint (28) in more restrictive ways. The first one (A) consisted in freezing the lower singly occupied orbital ($\phi_n^{(1)}$) and corresponded to the annihilation of a row of $\boldsymbol{S}^{\mathrm{I}}$, see (29). In the second one (B) the orthogonality constraint was satisfied by a proper restriction in the variational space of $\phi_{n+1}^{(1)}$ [12]. Note that using method B the results depend on the choice of the starting orbitals, that we chose as those of the ground state.

The results of such calculations, given in Table 1, show that because of the greater variational freedom allowed by our method we get an excited state energy lower than the other ones by about 0.2-0.6 eV (≈3-10% of the HF excitation energy).

Table 1. Comparison of the results obtained using the methods described in Sect. 4. in the case of the first singlet excited state of Be. In the second column E represents the energy of the state given in atomic units. In the third and fourth columns we give the absolute values of the superposition elements of $\phi_{n+1}^{(1)}$ with the ground state occupied orbitals. In the last column ΔE represents the HF transition energy, given in eV, with respect to the ground state energy ($E_0 = -14.572842$ a.u.)

Method	E(a.u.)	$\langle 3s^{(1)} \| 1s^{(0)} \rangle$	$\langle 3s^{(1)} \| 2s^{(0)} \rangle$	E (eV)
Our method	−14.355127	0.00051923	0.00000024	5.92
Method A	−14.347434	0.00059620	0.0	6.13
Method B	−14.333696	0.00000002	0.0	6.51

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