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Double excitations from modified Hartree Fock subsequent minimization scheme

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Doubly excited states have nowadays become important in technological applications, e.g., in increasing the efficiency of solar cells and therefore, their description using *ab initio* methods is a great theoretical challenge as double excitations cannot be described by linear response theories based on a single Slater determinant. In the present work we extend our recently developed Hartree-Fock (HF) approximation for calculating singly excited states [M. Tassi, I. Theophilou, and S. Thanos, Int. J. Quantum Chem. **113**, 690 (2013)] in order to allow for the calculation of doubly excited states. We describe the double excitation as two holes in the subspace spanned from the occupied HF orbitals and two particles in the subspace of virtual HF orbitals. A subsequent minimization of the energy results to the determination of the spin orbitals of both the holes and the particles in the occupied and virtual subspaces, respectively. We test our method, for various atoms, H_2 and polyene molecules which are known to have excitations presenting a significant double excitation character. Importantly, our approach is computationally inexpensive. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4797466]

I. INTRODUCTION

The description of multielectron excited states is a great theoretical challenge, since they are important in many research fields such as the purpose of increasing the efficiency of solar cells with the multiexciton generation in quantum dots[1–3] and the photophysics/photochemistry of polyenes. Particularly, in the early 1970s it was experimentally demonstrated[4] that there exists a state 2^1A_g in long polyenes which is of significant double excitation character and is located lower than their absorbing state. Since then, the description of their doubly excited states has become a subject of many theoretical[5–7] and experimental works.[8,9] This is due to the fact that these excitations in polyenes can be used for technological applications, such as organic electronics[10] and photonics[11] and play an important role in biological processes such as vision and photosynthesis.[12] Although, multielectron excited states can be modeled using multideterminantal methods such as configuration interaction (CI),[5] Second-Order Perturbation Theory (PT2D),[13] complete active space self-consistent field method (CASSCF),[13,14] its second order perturbation theory (CASPT2),[14,15] and symmetry adapted cluster CI (SAC-CI),[16,17] these kinds of calculations are prohibitively computationally expensive for large molecules. Therefore, there is still need for development of faster computational methods that can successfully describe double excitations.

While singly excited states have been successfully described using single determinantal approximations such as time-dependent Density-Functional theory (TDDFT)[18–22] and time-dependent Hartree-Fock (TDHF),[23–26] it has been shown that linear response TDDFT/TDHF suffer from a number of shortcomings which restrict their applicability in the multielectron excitations.[26–30] In the Dyson equation, which connects the true response function with the Kohn-Sham response function, the response of the Kohn-Sham system does not contain multielectron excitations and an adiabatic exchange correlation kernel does not create additional poles.[31] Recently, there are numerous attempts for development of methodologies that can successfully describe double excitations.[32–39]

At this point, it is worth to note that one could apply the subspace theory for excited states developed initially by Theophilou[40,41] for density functional calculation and applied by Stoddart and Davis[42] to Hartree Fock (HF) in order to derive an expression for the exchange and correlation energy density functional. Further developments on the subspace HF have been developed by Gidopoulos and Theophilou.[43] This method however, does not give excited state determinants orthogonal to the ground state.

Recently, a single determinantal approach has been developed by Glushkov and Assfeld,[44] using the constrained optimized effective potential (COEP) method.[45–47] In this series of papers, the hole in the space of occupied orbitals is fixed. This is an advantage for excitation from core states since hole optimization would demand a series of calculations where all excitations above a core state had to be determined.[48] Further, this choice is intuitively comprehensible and most experimental results label these excitations by the core orbital removed, in the case of ionization.

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In a recent paper,[49] we proposed a variational single determinantal approach for singly excited states, based on Unrestricted Hartree-Fock (UHF) equations,[50] where we choose a Slater determinant (SD), by creating a particle in the subspace spanned by the virtual ground state orbitals and a hole in the subspace of occupied ground state orbitals. These orbitals were determined by applying the variational theory, e.g., we minimized the energy of this Slater determinant by varying these orbitals within the ground state occupied and virtual subspaces. Thus, all excited state orbitals are chosen variationally in contrast to COEP where the holes are fixed.[44] In the same way we calculated higher singly excited states. A higher excited state is calculated by minimization in the virtual and occupied subspaces spanned by the orbitals of the previous lower energy state. In this way, we derive excited states that are not only orthogonal to the ground state, but also mutually orthogonal.

In the present work, we extend the above approach to doubly excited states. The resulting doubly excited states are orthogonal to the ground and the singly excited ones, which is a property of the exact solution of the many body Schrödinger equation as well. The variations of the minimization procedure have to be performed on subspaces that depend on the character of the doubly excited state, we would like to describe. In case we describe two excited orbitals with different spin, we search for one of the spin up orbitals of the excited state in the subspace of the spin up virtual orbitals of the ground state and the rest of spin up orbitals in the subspace of occupied ground state spin up orbitals. In analogy we treat the spin down orbitals. If we have a doubly excited state resulting from the excitation of two orbitals with the same spin (e.g., spin up), we find both of the orbitals with the largest energy from minimization in the subspace of the virtual spin up orbitals and the rest of spin up orbitals by minimization in the subspace of occupied spin up orbitals. The spin down orbitals are determined by minimization of the whole space of spin down orbitals. Thus, the space of occupied spin down orbitals is redetermined so as to give the lowest energy.

We tested the current methodology by calculating excited states of double excitation character of Be, Na, Mg, and K atoms and compared them to experimental results, where we found that they are in remarkable agreement. We further checked our method by calculating the lowest doubly excited states of the hydrogen molecule for different internuclear distances and the doubly excited state of two polyene molecules (C_4H_6 and C_6H_8) known for having excited states of strongly double excitation character. The comparison of the present results with the ones obtained by multideterminantal approximations (CASSCF, CI), COEP as well as with the experimental ones, showed that our method, which is computationally inexpensive, can give accurate enough results for double excitations.

This paper is organized as follows. In Sec. II we explain the main idea of the methodology and we derive the amended equations needed for the doubly excited states. In Sec. III we present our results for the excited state energies. Finally, in Sec. IV we give some concluding remarks.

II. METHODOLOGY AND NUMERICAL IMPLEMENTATION

As a first approach for the calculation of excitation energies $\Delta\varepsilon$, one can consider excitations from the occupied to virtual orbitals. Then, for two particle excitations $\Delta\varepsilon = \varepsilon_{v,k} + \varepsilon_{v,l} - \varepsilon_{oc,i} - \varepsilon_{oc,j}$, where the occupied orbitals $|\varphi^{\sigma_1}_{oc,i}\rangle$, $|\varphi^{\sigma_2}_{oc,j}\rangle$ have been substituted by the virtual ones $|\varphi^{\sigma_1}_{v,k}\rangle$, $|\varphi^{\sigma_2}_{v,l}\rangle$. However, this is only a poor approximation. The above excitations correspond to a N-particle Slater Determinant $|\Phi_{ed}\rangle$ where the orbitals $|\varphi^{\sigma_1}_{oc,i}\rangle$, $|\varphi^{\sigma_2}_{oc,j}\rangle$ of the UHF ground state $|\Phi_0\rangle$ have been replaced by $|\varphi^{\sigma_1}_{v,k}\rangle$, $|\varphi^{\sigma_2}_{v,l}\rangle$. Then the energy difference of these states is $\Delta E = \langle\Phi_{ed}|\hat{H}|\Phi_{ed}\rangle - \langle\Phi_0|\hat{H}|\Phi_0\rangle$, and after taking the single particle UHF equations into account one finds

$$\begin{aligned}\Delta E = \varepsilon_{v,k} + \varepsilon_{v,l} - \varepsilon_{oc,i} - \varepsilon_{oc,j} - \frac{1}{2}\big[\langle\varphi^{\sigma_1}_{v,k}|\hat{V}_h + \hat{V}_x|\varphi^{\sigma_1}_{v,k}\rangle \\ + \langle\varphi^{\sigma_2}_{v,l}|\hat{V}_h + \hat{V}_x|\varphi^{\sigma_2}_{v,l}\rangle\big] + \frac{1}{2}\big[\langle\varphi^{\sigma_1}_{oc,i}|\hat{V}_h + \hat{V}_x|\varphi^{\sigma_1}_{oc,i}\rangle \\ + \langle\varphi^{\sigma_2}_{oc,j}|\hat{V}_h + \hat{V}_x|\varphi^{\sigma_2}_{oc,j}\rangle\big], \qquad (1)\end{aligned}$$

where $\hat{V}_h$ is the Hartree potential and $\hat{V}_x$ is the exchange operator. (Note that the σ upper indices are used for the ↑ and ↓ spin states.) This is an easy way to have a rough estimate of excitation energies. However, in the HF single particle equations the occupied orbitals are repelled correctly by an electrostatic charge of $N - 1$ electrons, while the unoccupied orbitals are repulsed not by the correct charge of $N - 1$ electrons but by the wrong one of N electrons. This makes the HF virtual orbitals artificially diffuse and their energy eigenvalues too large. As these orbitals enter the expression of the excitation energy ΔE in Eq. (1) it is not surprising that this energy tends to be too large in comparison to the true excitation energy. Nevertheless, ΔE is not necessarily an upper bound to the excitation energy since the Rayleigh Ritz variational principle allows the lowest HF excited state energy to be lower than the exact excited state energy. In the present HF approach, the doubly excited states are obtained by a variational procedure under the condition that they are orthogonal to the ground state, as in the case of exact excited states. This means that the $|\chi^{\sigma_1}_{v,N+1}\rangle$, $|\chi^{\sigma_2}_{v,N+2}\rangle$ from the space S^v of the virtual orbitals corresponding to the creation operators $\hat{\alpha}^{\sigma_1\dagger}_{v,N+1}$ and $\hat{\alpha}^{\sigma_2\dagger}_{v,N+2}$ and the $|\chi^{\sigma_1}_{oc,N}\rangle$, $|\chi^{\sigma_2}_{oc,N-1}\rangle$ from the space S^{oc} of the occupied orbitals corresponding to the annihilation operators orbitals $\hat{\alpha}^{\sigma_1}_{oc,N}$ and $\hat{\alpha}^{\sigma_2}_{oc,N-1}$ must be chosen variationally, so that the doubly excited Slater Determinant

$$|\Phi_{ed}\rangle = \hat{\alpha}^{\sigma_1\dagger}_{v,N+1}\hat{\alpha}^{\sigma_2\dagger}_{v,N+2}\hat{\alpha}^{\sigma_1}_{oc,N}\hat{\alpha}^{\sigma_2}_{oc,N-1}|\Phi_0\rangle \qquad (2)$$

minimizes the energy functional $\langle\Phi_{ed}|\hat{H}|\Phi_{ed}\rangle$. Since the $|\chi^{\sigma_1}_{oc,N}\rangle$, $|\chi^{\sigma_2}_{oc,N-1}\rangle$ do not coincide with the UHF orbitals $|\phi_i\rangle$ the new basis of the $N - 2$ occupied orbitals does not coincide with that spanned by the $|\phi_i\rangle$ for $i = 1 \ldots N - 2$. However, once the $|\chi^{\sigma_1}_{oc,N}\rangle$, $|\chi^{\sigma_2}_{oc,N-1}\rangle$ are determined, the subspace of occupied states normal to these orbitals is uniquely determined and a new orthogonal basis can be chosen. The same comments hold for the space of virtual states. In this way described above, one can obtain an excitation energy ΔE in which the energy given in Eq. (1) is an upper bound.

Importantly, the orbitals that give the excitation energy are now self-interaction free as they are obtained from one electron equations that they contribute themselves to the Hartree and the Exchange terms.

Before going into the details of the calculation, let us see some properties of the HF operator. Note first that when $|\Phi\rangle$ is a determinant then

$$\begin{aligned} E^{UHF}(\Phi) = \langle\Phi|\hat{H}|\Phi\rangle &= \langle\Phi|\hat{T}+\hat{V}|\Phi\rangle \\ &+ \frac{1}{2}\iint d^3\mathbf{r}d^3\mathbf{r}'\rho(\mathbf{r};\Phi)\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r}';\Phi) \\ &- \frac{1}{2}\iint d^3\mathbf{r}d^3\mathbf{r}'\rho^{\uparrow}(\mathbf{r},\mathbf{r}';\Phi)\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho^{\uparrow}(\mathbf{r}',\mathbf{r};\Phi) \\ &- \frac{1}{2}\iint d^3\mathbf{r}d^3\mathbf{r}'\rho^{\downarrow}(\mathbf{r},\mathbf{r}';\Phi)\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho^{\downarrow}(\mathbf{r}',\mathbf{r};\Phi), \end{aligned} \tag{3}$$

where $\rho^{\sigma}(\mathbf{r},\mathbf{r}';\Phi) = \langle\Phi|\hat{\rho}^{\sigma}(\mathbf{r},\mathbf{r}')|\Phi\rangle$ and $\rho(\mathbf{r};\Phi) = \rho^{\uparrow}(\mathbf{r},\mathbf{r};\Phi) + \rho^{\downarrow}(\mathbf{r},\mathbf{r};\Phi)$. Then the UHF ground state energy E_0^{UHF} is obtained by minimizing the above total energy whereas the doubly excited state is obtained by minimization under orthogonality constraint $\langle\Phi_{ed}|\Phi_0\rangle = 0$. By keeping the variations corresponding to the creation operators in the virtual space, $|\Phi_{ed}\rangle$ is orthogonal to the ground state $|\Phi_0\rangle$. In the numerical implementation we do not have to use a projection operator for the occupied and virtual spaces, because in practice we can limit the variations in the corresponding spaces.

The doubly excited state can result either of excitation of one electron with spin up and one electron with spin down or of excitation of two electrons of the same spin.

A. Imposed restrictions to the excited state determinant for the excitation of two electrons with different spin

Next we shall deal with the numerical implementation of excitations for two different spins, denoting the excitation orbitals in the virtual space by $\chi_{N+1}^{\uparrow}$, $\chi_{N+1}^{\downarrow}$ and the new basis in the space of occupied orbitals by $\chi_i^{\uparrow}$, $i = 1 \ldots N^{\uparrow}$ and $\chi_i^{\downarrow}$, $i = 1 \ldots N^{\downarrow}$. The constraints are

(a) $\langle\chi_i^{\uparrow}|\varphi_j^{\uparrow}\rangle = 0$, for $i \leq N^{\uparrow} - 1$ and $j > N^{\uparrow}$
(b) $\langle\chi_i^{\downarrow}|\varphi_j^{\downarrow}\rangle = 0$, for $i \leq N^{\downarrow} - 1$ and $j > N^{\downarrow}$
(c) $\langle\chi_i^{\uparrow}|\varphi_j^{\uparrow}\rangle = 0$, for $i = N^{\uparrow}$ and $j \leq N^{\uparrow}$
(d) $\langle\chi_i^{\downarrow}|\varphi_j^{\downarrow}\rangle = 0$, for $i = N^{\downarrow}$ and $j \leq N^{\downarrow}$.

These conditions lead to the minimization of the following quantities:

$$\langle\Phi_{ed}|\hat{H}|\Phi_{ed}\rangle + \sum_{i<N^{\uparrow}}\sum_{j>N^{\uparrow}}\mu_{i,j}^{\uparrow}\langle\chi_i^{\uparrow}|\varphi_j^{\uparrow}\rangle + \sum_{j\leq N^{\uparrow}}\mu_j^{\prime\uparrow}\langle\chi_{N^{\uparrow}}^{\uparrow}|\varphi_j^{\uparrow}\rangle + \sum_{i=1}^{N^{\uparrow}}\lambda_i^{\uparrow}\langle\chi_i^{\uparrow}|\chi_i^{\uparrow}\rangle, \tag{4}$$

$$\langle\Phi_{ed}|\hat{H}|\Phi_{ed}\rangle + \sum_{i<N^{\downarrow}}\sum_{j>N^{\downarrow}}\mu_{i,j}^{\downarrow}\langle\chi_i^{\downarrow}|\varphi_j^{\downarrow}\rangle + \sum_{j\leq N^{\downarrow}}\mu_j^{\prime\downarrow}\langle\chi_{N^{\downarrow}}^{\downarrow}|\varphi_j^{\downarrow}\rangle + \sum_{i=1}^{N^{\downarrow}}\lambda_i^{\downarrow}\langle\chi_i^{\downarrow}|\chi_i^{\downarrow}\rangle, \tag{5}$$

where $\mu_{i,j}^{\uparrow}$, $\mu_j^{\prime\uparrow}$, $\lambda_i^{\uparrow}$, $\mu_{i,j}^{\downarrow}$, $\mu_j^{\prime\downarrow}$, $\lambda_i^{\downarrow}$ are Lagrange multipliers. After the minimization we get two matrix equations for the orbitals with spin up and two matrix equations for the orbitals with spin down:

(a) For $i < N^{\uparrow}$ then $|\chi_i^{\uparrow}\rangle$ belongs to the subspace of occupied orbitals with spin up $S_{oc}^{\uparrow}$ and the matrix equation is

$$\hat{F}^{\uparrow}|\chi_i^{\uparrow}\rangle + \sum_{j>N^{\uparrow}}\mu_{i,j}^{\uparrow}|\varphi_j^{\uparrow}\rangle = \lambda_i^{\uparrow}|\chi_i^{\uparrow}\rangle. \tag{6}$$

For $i = N^{\uparrow}$ then $|\chi_i^{\uparrow}\rangle$ belongs to the subspace of virtual orbitals with spin $S_v^{\uparrow}$ and the matrix equation is

$$\hat{F}^{\uparrow}|\chi_i^{\uparrow}\rangle + \sum_{j<N^{\uparrow}}\mu_j^{\prime\uparrow}|\varphi_j^{\uparrow}\rangle = \lambda_i^{\uparrow}|\chi_i^{\uparrow}\rangle. \tag{7}$$

(b) For the orbitals with spin down the same equations hold. Thus:
for $i < N^{\downarrow}$

$$\hat{F}^{\downarrow}|\chi_i^{\downarrow}\rangle + \sum_{j>N^{\downarrow}}\mu_{i,j}^{\downarrow}|\varphi_j^{\downarrow}\rangle = \lambda_i^{\downarrow}|\chi_i^{\downarrow}\rangle \tag{8}$$

and for $i = N^{\downarrow}$

$$\hat{F}^{\downarrow}|\chi_i^{\downarrow}\rangle + \sum_{j<N^{\downarrow}}\mu_j^{\prime\downarrow}|\varphi_j^{\downarrow}\rangle = \lambda_i^{\downarrow}|\chi_i^{\downarrow}\rangle. \tag{9}$$

Equation (8) refers to the $|\chi_i^{\downarrow}\rangle$ belonging to the subspace of occupied orbital with spin down $S_{oc}^{\downarrow}$ and Eq. (9) refers to the $|\chi_i^{\downarrow}\rangle$ belonging to the subspace of virtual orbital with spin down $S_v^{\downarrow}$.

In the above Eqs. (6)–(9), $\hat{F}^{\uparrow}$ and $\hat{F}^{\downarrow}$ are the Fock operators for the electrons with spin up and spin down, respectively, for which the following relations corresponding to Φ_{ed} hold:

$$\begin{aligned} \hat{F}^{\uparrow}\chi_i^{\uparrow}(\mathbf{r}) = \hat{h}\chi_i^{\uparrow}(\mathbf{r}) &+ \int d\mathbf{r}'\frac{\rho(\mathbf{r}';\Phi_{ed})}{|\mathbf{r}-\mathbf{r}'|}\chi_i^{\uparrow}(\mathbf{r}) \\ &- \int d\mathbf{r}'\frac{\rho_{\uparrow}(\mathbf{r},\mathbf{r}';\Phi_{ed})}{|\mathbf{r}-\mathbf{r}'|}\chi_i^{\uparrow}(\mathbf{r}'), \end{aligned} \tag{10}$$

$$\begin{aligned} \hat{F}^{\downarrow}\chi_i^{\downarrow}(\mathbf{r}) = \hat{h}\chi_i^{\downarrow}(\mathbf{r}) &+ \int d\mathbf{r}'\frac{\rho(\mathbf{r}';\Phi_{ed})}{|\mathbf{r}-\mathbf{r}'|}\chi_i^{\downarrow}(\mathbf{r}) \\ &- \int d\mathbf{r}'\frac{\rho_{\downarrow}(\mathbf{r},\mathbf{r}';\Phi_{ed})}{|\mathbf{r}-\mathbf{r}'|}\chi_i^{\downarrow}(\mathbf{r}'), \end{aligned} \tag{11}$$

where $\hat{h}(\mathbf{r}) = \frac{1}{2}\nabla^2 + \hat{V}(\mathbf{r})$ is the kinetic plus external potential operator, which is equal to the one of the UHF ground state and $\rho(\mathbf{r}';\Phi_{ed})$ is the spin density matrix of $|\Phi_{ed}\rangle$:

$$\rho_s(\mathbf{r},\mathbf{r}';\Phi_{ed}) = \sum_{i=1}^{N^{\sigma}}\chi_i^{\sigma}(\mathbf{r})\chi_i^{\sigma}(\mathbf{r}'), \tag{12}$$

where N^{σ} stands for the number of orbitals with spin ↑ and spin ↓. Finally, $\rho(\mathbf{r};\Phi_{ed}) = \rho_{\uparrow}(\mathbf{r},\mathbf{r};\Phi_{ed}) + \rho_{\downarrow}(\mathbf{r},\mathbf{r};\Phi_{ed})$ is the electron density of the state $|\Phi_{ed}\rangle$.

B. Minimization equations

Now let us show how we can solve the matrix equations (6)–(9). At first we will show the procedure for $i < N^{\sigma}$ and afterwards for $i = N^\sigma$. Thus, we can get from recombination of the above equations the Lagrange multipliers $\mu^\uparrow_{i,k}$ and $\mu^\downarrow_{i,k}$ (see Appendix A) and introducing them to Eqs. (6) and (8), respectively. Then, we have

$$\hat{F}^\uparrow|\chi_i^\uparrow\rangle - \sum_{j>N^\uparrow} |\varphi_j^\uparrow\rangle\langle\varphi_j^\uparrow|\hat{F}^\uparrow|\chi_i^\uparrow\rangle = \lambda_i^\uparrow|\chi_i^\uparrow\rangle, \tag{13}$$

$$\hat{F}^\downarrow|\chi_i^\downarrow\rangle - \sum_{j>N^\downarrow} |\varphi_j^\downarrow\rangle\langle\varphi_j^\downarrow|\hat{F}^\downarrow|\chi_i^\downarrow\rangle = \lambda_i^\downarrow|\chi_i^\downarrow\rangle, \tag{14}$$

where the $\sum_{j>N^\uparrow}|\varphi_j^\uparrow\rangle\langle\varphi_j^\uparrow|$ and $\sum_{j>N^\downarrow}|\varphi_j^\downarrow\rangle\langle\varphi_j^\downarrow|$ represent the identity operators of the subspace of virtual orbitals with spin up and spin down, respectively. Therefore, if we restrict the minimization (see Appendix B) to the $S^\uparrow_{oc}$ and $S^\downarrow_{oc}$, respectively, from the above equations we take

$$\hat{F}^\uparrow|\chi_i^\uparrow\rangle = \lambda_i^\uparrow|\chi_i^\uparrow\rangle, \tag{15}$$

$$\hat{F}^\downarrow|\chi_i^\downarrow\rangle = \lambda_i^\downarrow|\chi_i^\downarrow\rangle. \tag{16}$$

From Eqs. (15) and (16) we understand that in the subspaces $S^\uparrow_{oc}$ and $S^\downarrow_{oc}$, $|\chi^\uparrow\rangle$, is an eigenstate of the operator $\hat{F}^\uparrow$ and $|\chi^\downarrow\rangle$, is an eigenstate of the operator $\hat{F}^\downarrow$, respectively. Thus, from the $N^\uparrow - 1$ lowest energy solutions of Eq. (15) and the $N^\downarrow - 1$ lowest energy solutions of Eq. (16) we can find the $N^\uparrow - 1$ $\chi_i^\uparrow$ and the $N^\downarrow - 1$ $\chi_i^\downarrow$, respectively.

Additionally, the same procedure holds if $i = N^\sigma$ and one can easily see that also $|\chi^\uparrow_{N^\uparrow}\rangle$ and $|\chi^\downarrow_{N^\downarrow}\rangle$ are the eigenstates with the lowest eigenvalue of the operators $\hat{F}^\uparrow$ and $\hat{F}^\downarrow$, respectively, in the subspaces, $S^\uparrow_v$ and $S^\downarrow_v$ of virtual orbitals.

C. Distinction of subspaces in which Fock matrix diagonalization is performed

Consequently, the solution of Eqs. (6)–(9) can be obtained, if we diagonalize separately in the subspaces of virtual and occupied orbitals. Therefore, in order to distinguish the subspaces for finding the excited states we express the Fock matrix in the basis of ground state canonical orbitals and not the "original" Gaussian basis, x_k. The matrix elements of the Fock matrix expressed in Gaussian basis set are

$$\langle x_k|\hat{F}^\uparrow|x_l\rangle = \langle x_k|(\hat{h} + \int d\mathbf{r}'\frac{\rho(\mathbf{r}';\Phi_{ed})}{|\mathbf{r}-\mathbf{r}'|} - \int d\mathbf{r}'\frac{\rho^\uparrow(\mathbf{r},\mathbf{r}';\Phi_{ed})}{|\mathbf{r}-\mathbf{r}'|})|x_l\rangle, \tag{17}$$

$$\langle x_k|\hat{F}^\downarrow|x_l\rangle = \langle x_k|(\hat{h} + \int d\mathbf{r}'\frac{\rho(\mathbf{r}';\Phi_{ed})}{|\mathbf{r}-\mathbf{r}'|} - \int d\mathbf{r}'\frac{\rho^\downarrow(\mathbf{r},\mathbf{r}';\Phi_{ed})}{|\mathbf{r}-\mathbf{r}'|})|x_l\rangle. \tag{18}$$

In this way the matrix elements of the new Fock matrix $F'^\uparrow$ with respect to the ground state orbitals are

$$F'^\uparrow_{ji} = \langle\varphi_j^\uparrow|\hat{F}^\uparrow|\varphi_i^\uparrow\rangle = \left\langle \sum_{k=1}^{L} c_{jk}x_k|\hat{F}^\uparrow|\sum_{l=1}^{L} c_{il}x_l \right\rangle = \sum_{k,l=1}^{L} c_{jk}c_{il}\langle x_k|\hat{F}^\uparrow|x_l\rangle \tag{19}$$

and the same equation holds for the $F'^\downarrow$:

$$F'^\downarrow_{ji} = \langle\varphi_j^\downarrow|\hat{F}^\downarrow|\varphi_i^\downarrow\rangle = \left\langle \sum_{k=1}^{L} d_{jk}x_k|\hat{F}^\downarrow|\sum_{l=1}^{L} d_{il}x_l \right\rangle = \sum_{k,l=1}^{L} d_{jk}d_{il}\langle x_k|\hat{F}^\downarrow|x_l\rangle, \tag{20}$$

where c_{ij} and d_{ij} are the coefficients of the basis set x_k and L is the dimension of basis set. From Eqs. (B1) and (B2) one can see that we have to diagonalize the $(\hat{I}^\sigma - \sum_{j>N^\sigma}|\varphi_j^\sigma\rangle\langle\varphi_j^\sigma|)\hat{F}^\sigma$ and $(\hat{I}^\sigma - \sum_{j<N^\sigma}|\varphi_j^\sigma\rangle\langle\varphi_j^\sigma|)\hat{F}^\sigma$ in the subspaces S^σ_{oc} and S^σ_v, respectively. The matrix elements of the above operators are the same with the matrix elements of the new Fock matrices F'^σ (see Eqs. (19) and (20)) in the corresponding subspaces. Therefore, instead of having to diagonalize two different matrices (Eqs. (B1) and (B2)), we diagonalize the F'^σ, separately in the subspaces of virtual and occupied orbitals, ignoring the matrix elements that are between the two subspaces S^σ_{oc} and S^σ_v. Thus, it is like we perform a diagonalization of the block diagonal matrices:

$$F'^\uparrow_{i,j} = \langle\varphi_i^w|\hat{F}^\uparrow|\varphi_j^{w'}\rangle = \begin{cases} F'^\uparrow_{i,j}, & \text{if } \varphi_i^\uparrow, \varphi_j^\uparrow \epsilon S_v^\uparrow \text{ or } \varphi_i^\uparrow, \varphi_j^\uparrow \epsilon S_{oc}^\uparrow \\ 0, & \text{if } \varphi_i^\uparrow \epsilon S_v^\uparrow \text{ and } \varphi_j^\uparrow \epsilon S_{oc}^\uparrow \end{cases}, \tag{21}$$

$$F'^\downarrow_{ij} = \langle\varphi_i^w|\hat{F}^\downarrow|\varphi_j^{w'}\rangle = \begin{cases} F'^\downarrow_{i,j}, & \text{if } \varphi_i^\downarrow, \varphi_j^\downarrow \epsilon S_v^\downarrow \text{ or } \varphi_i^\downarrow, \varphi_j^\downarrow \epsilon S_{oc}^\downarrow \\ 0, & \text{if } \varphi_i^\downarrow \epsilon S_v^\downarrow \text{ and } \varphi_j^\downarrow \epsilon S_{oc}^\downarrow \end{cases}, \tag{22}$$

where S^σ_v, S^σ_{oc} are the subspaces of virtual and occupied orbitals with spin up or spin down. Then, we evaluate the new orbitals $|\chi_i^\uparrow\rangle$ and $|\chi_i^\downarrow\rangle$ of the doubly excited state:

$$|\chi_i^\uparrow\rangle = \sum_j c'_{ij}|\varphi_j^\uparrow\rangle = \sum_{jk} c'_{ij}c_{jk}|x_k\rangle = \sum_k c''_k|x_k\rangle, \tag{23}$$

$$|\chi_i^\downarrow\rangle = \sum_j d'_{ij}|\varphi_j^\downarrow\rangle = \sum_{jk} d'_{ij}d_{jk}|x_k\rangle = \sum_k d''_k|x_k\rangle, \tag{24}$$

where c'_{ij} and d'_{ij} are the coefficients that resulted from the diagonalization of $F'^\uparrow$ and $F'^\downarrow$, respectively. The above doubly excited state is not only orthogonal to the ground state but also orthogonal to the singly excited states. One can show this in the same way as Ref. 49 where we proved that the singly excited state is orthogonal to the ground state.

TABLE I. Excitation energies in hartree for the doubly excited states.

Atom	GS configuration[a]	ES configuration[b]	This work	NIST[c]	No Opt.[d]
Be	$1s^22s^2$	$1s^12s^12p^2$	4.386	4.343	4.810
Na	$1s^22s^22p^63s^1$	$1s^22s^22p^53p^2$	1.371	1.417	1.604
Mg	$1s^22s^22p^63s^2$	$1s^22s^22p^63p^2$	2.093	2.046	2.434
K	$1s^22s^22p^63s^23p^64s^1$	$1s^22s^22p^63s^23p^53d^15s^1$	0.965	0.975	1.053

[a] Configuration of the ground state.

[b] Configuration of the doubly excited state.

[c] See Ref. 58.

[d] Excitation energies without any orbital optimization.

D. Excitation of two electrons with same spin

In case that two electrons with spin up are excited, the orthogonality constraints are

(a) $\langle\chi_i^\uparrow|\varphi_j^\uparrow\rangle = 0$, for $i \le N^\uparrow - 2$ and $j > N^\uparrow$

(b) $\langle\chi_i^\uparrow|\varphi_j^\uparrow\rangle = 0$, for $i = N^\uparrow, N^\uparrow + 1$ and $j \le N^\uparrow$.

Therefore, the procedure to be followed is the same as that in the previous case, the difference being that one has to deal only with the equations for the orbitals with spin up while the orbitals with spin down are treated in the same way as in the ground state. Note that in the end, the spin down orbitals derived will not be the same as the ground state ones, meaning that the subspace $S^\downarrow$ will change, since the spin down UHF operator is different because of the change of the Hartree potential due to the change of the spin up orbitals. In particular, the quantities under minimization are

$$\langle\Phi_{ed}|\hat{H}|\Phi_{ed}\rangle + \sum_{i<N^\uparrow-1}\sum_{j>N^\uparrow}\mu_{i,j}^\uparrow\langle\chi_i^\uparrow|\varphi_j^\uparrow\rangle$$
$$+\sum_{i=N^\uparrow}^{N^\uparrow+1}\sum_{j\le N^\uparrow}\mu_{i,j}'^\uparrow\langle\chi_i^\uparrow|\varphi_j^\uparrow\rangle + \sum_{i=1}^{N^\uparrow}\lambda_i^\uparrow\langle\chi_i^\uparrow|\chi_i^\uparrow\rangle, \qquad (25)$$

$$\langle\Phi_{ed}|\hat{H}|\Phi_{ed}\rangle + \sum_{i=1}^{N^\downarrow}\lambda_i^\downarrow\langle\chi_i^\downarrow|\chi_i^\downarrow\rangle. \qquad (26)$$

Thus, in order to solve the problem of the doubly excited state that is produced by the excitation of two orbitals with spin up, we have to diagonalize the Fock matrix $F^\uparrow$ iteratively in the subspace $S_{oc}^\uparrow$ and $S_v^\uparrow$ to find the orbitals with spin up. For the spin down orbitals we diagonalize the Fock matrix $F^\downarrow$ in the whole space of occupied and virtual orbital, $S^\downarrow$, of the electrons with spin down. In this case also the doubly excited state is orthogonal to the singly excited state (see Appendix C).

III. RESULTS AND DISCUSSION

We applied the method presented in Sec. II to the Be, Na, Mg, and K atoms and the H_2, C_4H_6 (1,3-butadiene) and C_6H_8 (trans-1,3,5-hexatriene) molecules. For the atoms mentioned above two electrons with spin up were excited, while for the molecules we excited one electron with spin up and one with spin down. For the numerical implementation of the above method we developed a code for doubly excited states, using GAMESS US[51] for the UHF ground state.

We adopted the cc-pVQZ[52] basis set for Be and Mg, the aug-cc-pVTZ[52] for Na and Sadlej-pVTZ[53–57] for K. In Table I, we present our results for the excitation energies from the UHF ground state for the atoms mentioned above and in the next column the corresponding reference data from the NIST database.[58] In the last column, the excitation energies from the UHF ground state obtained without orbital optimization are given for comparison, i.e., we directly evaluate Eq. (1). That is to say, if we just create two holes in the subspace of occupied orbitals and two particles in the subspace of virtual orbitals with spin up for the case of excited orbitals with same spin, or one hole in the subspace of occupied orbitals with spin up and another one in the subspace of occupied orbitals with spin down and one particle in the corresponding virtual subspaces for the case of excited orbitals with different spin. One can easily realize that the results of the present method are very near to the reference data and they are better than those obtained without optimization.

For H_2 we used the cc-pVTZ[52] basis. In Table II we see the total energies of the doubly excited state ${}^1\Sigma_g^+$ of H_2 and the corresponding excitation energies from the UHF ground state for some points of the potential curve. In the first column we include the results for the total and excitation energies of our method and compare them with those obtained by CI[59] and COEP[44] in the next columns. One can see that our results are reasonable, while they differ from those obtained without optimization given in the last column. We can see that the excited energies that were found variationally are higher than the CI excited energies and as expected were lower than those obtained without any variation. Thus, for all

TABLE II. Energies in hartree of the doubly excited state, ${}^1\Sigma_g^+$, of H_2 and corresponding excitation energies from the ground state.

R (bohr)	This work	CI[a]	COEP[b]	No Opt.[c]
1.4	− 0.073	− 0.105	− 0.106	− 0.066
	1.060[d]	1.069[d]	1.073[d]	1.067[d]
2.0	− 0.374	− 0.397	− 0.403	− 0.282
	0.717[d]	0.741[d]	0.740[d]	0.809[d]
2.5	− 0.523	− 0.540	− 0.549	− 0.425
	0.519[d]	0.594[d]	0.544[d]	0.617[d]
3.0	− 0.614	− 0.631	− 0.641	− 0.503
	0.403[d]	0.426[d]	0.400[d]	0.514[d]

[a] See Ref. 59.

[b] See Ref. 44.

[c] Energies and excitation energies without any orbital optimization.

[d] Corresponding excitation energies.

TABLE III. Geometry of 1,3-butadiene and trans-1,3,5-hexatriene.

Geometry (Angstrom, deg)
(A) 1,3-Butadiene ($H_2C_aC_bHC_bHC_aH_2$)
$r(C_aC_b) = 1.343$, $r(C_bC_b) = 1.467$,
$r(CH) = 1.094$,
angle (HC_aC_b) = 119.5, angle ($C_aC_bC_b$) = 122.8
(B) Trans-1,3,5-hexatriene ($H_2C_aC_bHC_cHC_cHC_bHC_aH_2$)
$r(C_aC_b) = 1.337$, $r(C_bC_c) = 1.457$,
$r(C_cC_c) = 1.343$, $r(HC) = 1.103$,
angle (HC_aC_b) = 120.5, angle (C_aC_bH) = 117.0,
angle ($HC_{c\ c}$) = 115.0, angle($C_aC_bC_c$) = 122.4

internuclear distances the energies of the doubly excited state were closer to the CI result than the corresponding energies without optimization. Moreover, as one can realize from the results the corresponding excitation energies were smaller than the ones obtained by CI. This is due to the fact that the CI ground state energies are much lower than the UHF ones, while the CI excited energies are not that much lower than the excited states of our method. For instance, in the distance of 1.4 bohrs the energy difference between the HF and CI ground state is 0.041 hartree and between our doubly excited state and CI excited state is 0.032, resulting our method to give smaller excitation energy than CI. For two internuclear distances $R = 1.4$ and $R = 2.5$ bohrs we see that the excitation energies without optimization are closer to those obtained by CI than the ones using the variational principle. At these distances the difference between the excited energies without optimization and the CI excited energies is very close to the difference between the UHF and CI ground states, e.g., for $R = 1.4$ bohrs the excited energy without optimization difference is 0.039 hartree instead of 0.032 for the optimized value, while the ground state HF and CI energy difference is 0.041 hartree, resulting to a non-optimized excitation energy that is closer to the one obtained by CI. Nevertheless, in these two internuclear distances as one can see the excitation energy without optimization is already quite good and the optimization does not change that much its value, so it is still good. Thus, the optimization seems to give in many cases a much better excitation energy than the non-optimized one and even when it seems that it does not significantly deteriorate the result.

Finally, for C_4H_6 and C_6H_8 molecules we used the 6-311G[60] basis and their experimental structure[61] which is given in Table III. In the first column of Table IV, we can see the excitation energies of the 2^1A_g doubly excited state from the ground state of the above molecules. We compare our methodology with CASSCF[13] and experimental values[8,9] given in the next columns. In the last column the results before the orbital optimization are given. One can conclude that our results are in good agreement with those given in the above references and that the optimization is necessary, in order to have reasonable results for the double excitation energies. Especially in the case of C_4H_6, we can see that the non-optimized excitation energy is twice as large from the one in the literature.

TABLE IV. Excitation energies in hartree from the ground state for the doubly excited state, 2^1A_g, of the 1,3-butadiene and trans-1,3,5-hexatriene.

System	This work	CASSCF[a]	Expt.[b]	No Opt.[c]
C_4H_6	0.256	0.244	0.208	0.432
C_6H_8	0.204	0.208	0.191	0.393

[a] See Ref. 13.

[b] Experimental data, see Ref. 9 for C_4H_6 and Ref. 8 for C_6H_8.

[c] Excitations energies without any orbital optimization.

TABLE V. Number of self-consistent field iterations needed for energy convergence.

System	Be	Na	Mg	K	H_2	C_4H_6	C_6H_8
Iterations	11	62	52	6	7[a], 7[b], 13[c], 30[d]	13	20

[a] $R = 1.4$ bohrs

[b] $R = 2.0$ bohrs

[c] $R = 2.5$ bohrs

[d] $R = 3.0$ bohrs

The fact that the excitation energies without optimization tend to be larger than the true excitation energies is not surprising as we have already discussed in Sec. II. The virtual orbital obtained from the HF ground state calculation give poor approximations of excited electron orbitals with too high energy eigenvalues. This is due to the self-interaction of the virtual HF orbitals. In our method all the orbitals are self-interaction free, giving a much more reasonable approximation to the excited state energy than the non-optimized ones.

Finally, our approach is computationally inexpensive since without any mixing scheme, and for a convergence threshold 10^{-8} on total energy, the number of required self-consistent field iterations is quite small (see Table V).

IV. CONCLUSIONS

In this paper, we presented an efficient variational single determinantal approach based on UHF equations, for the calculation of doubly excited states. Our approach is based on separate subsequent minimizations in the subspaces of virtual and occupied orbitals of the ground state UHF $|\Phi_0\rangle$ of the functional $\langle\Phi_{ed}|\hat{H}|\Phi_{ed}\rangle$, where $|\Phi_{ed}\rangle = \hat{\alpha}^{\sigma_1\dagger}_{v,N+1}\hat{\alpha}^{\sigma_2\dagger}_{v,N+2}\hat{\alpha}^{\sigma_1}_{oc,N}\hat{\alpha}^{\sigma_2}_{oc,N-1}|\Phi_0\rangle$, $\hat{\alpha}^{\sigma_1\dagger}_{v,N+1}$, $\hat{\alpha}^{\sigma_2\dagger}_{v,N+2}$ are creation operators corresponding to two orbitals of the virtual subspace of certain spin σ of the ground state, and $\hat{\alpha}^{\sigma_1}_{oc,N}$, $\hat{\alpha}^{\sigma_1}_{oc,N-1}$ annihilation operators corresponding to the space of occupied ones. Since the excited state has to be orthogonal to the ground state and the subspaces of virtual and occupied orbitals are mutually orthogonal, we imposed the appropriate constraints in the minimization of the UHF functional. As doubly excited states can result either from the excitation of one electron with spin up and one with spin down or from the excitation of two electrons with the same spin, we treated the two cases separately. In the first case, we performed subsequent minimization in the subspaces of virtual and occupied orbitals of the electron with spin up and spin down and in the second one the minimization of the two separate subspaces is done only for the electrons with the same spin as they are the excited ones, while for the others the minimization is in the whole space.

We compared our results with those given in the NIST database[58] for the Be, Na, Mg, and K atoms and for H_2 molecule with those obtained by CI[59] and COEP.[44] For polyenes (1,3-butadiene and trans-1,3,5-hexatriene) comparison was made with experimental results[8,9] and with those obtained by CASSCF.[13] In all cases we found that our results were in satisfactory agreement with those given in the above literature. In addition, we compared our results with the excitation energies obtained without orbital optimization and concluded that the latter, in general, deviate from the values in literature. This is because the excitation energy that one derives when no optimization is performed in the virtual space, contains contributions from the virtual orbitals which are not self-interaction free. Contrary, with our optimization scheme, all orbitals that enter the excitation energy expression are self-interaction free. Therefore, we conclude that the optimization is necessary in order to obtain a good estimation of the double excitation energies. Finally, we stress the fact that our approach is very efficient computationally. This is a result of its single determinantal character and the small number of self-consistent field iterations that are needed in order to have successful convergence.

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APPENDIX A: CALCULATION OF THE LAGRANGE MULTIPLIERS μ_{ij}

At first, we will find the Lagrange multiplier μ_{ij} for $i < N^\sigma$, while the same procedure holds for $i = N^\sigma$. Thus, for $i < N^\sigma$, multiplying Eqs. (6) and (8) with $\langle\varphi_k^\uparrow|$ and $\langle\varphi_k^\downarrow|$ respectively we find

$$\begin{cases} \langle\varphi_k^\uparrow|\hat{F}^\uparrow|\chi_i^\uparrow\rangle = \lambda_i^\uparrow \tilde{c}_{k,i}^\uparrow, & k \le N^\uparrow \\ \langle\varphi_k^\uparrow|\hat{F}^\uparrow|\chi_i^\uparrow\rangle + \mu_{i,k}^\uparrow = 0, & k > N^\uparrow \end{cases}, \tag{A1}$$

$$\begin{cases} \langle\varphi_k^\downarrow|\hat{F}^\downarrow|\chi_i^\downarrow\rangle = \lambda_i^\downarrow \tilde{c}_{k,i}^\downarrow, & k \le N^\downarrow \\ \langle\varphi_k^\downarrow|\hat{F}^\downarrow|\chi_i^\downarrow\rangle + \mu_{i,k}^\downarrow = 0, & k > N^\downarrow \end{cases}, \tag{A2}$$

where $\tilde{c}_{k,i}^\sigma = \langle\varphi_k^\sigma|\chi_i^\sigma\rangle$. From the equations above one can see that

$$\begin{cases} \mu_{i,k}^\uparrow = -\langle\varphi_k^\uparrow|\hat{F}^\uparrow|\chi_i^\uparrow\rangle, & k > N^\uparrow \\ \mu_{i,k}^\downarrow = -\langle\varphi_k^\downarrow|\hat{F}^\downarrow|\chi_i^\downarrow\rangle, & k > N^\downarrow \end{cases}. \tag{A3}$$

APPENDIX B: MINIMIZING EQUATIONS IN DISTINCT SUBSPACES

If $\hat{I}^\uparrow$ and $\hat{I}^\downarrow$ are the identity operators of the whole space of the virtual and occupied orbitals, then Eqs. (13) and (14) become

$$\left(\hat{I}^\uparrow - \sum_{j>N^\uparrow} |\varphi_j^\uparrow\rangle\langle\varphi_j^\uparrow|\right)\hat{F}^\uparrow|\chi_i^\uparrow\rangle = \lambda_i^\uparrow|\chi_i^\uparrow\rangle, \tag{B1}$$

$$\left(\hat{I}^\downarrow - \sum_{j>N^\downarrow} |\varphi_j^\downarrow\rangle\langle\varphi_j^\downarrow|\right)\hat{F}^\downarrow|\chi_i^\downarrow\rangle = \lambda_i^\downarrow|\chi_i^\downarrow\rangle. \tag{B2}$$

But

$$\hat{I}^\uparrow - \sum_{j>N^\uparrow} |\varphi_j^\uparrow\rangle\langle\varphi_j^\uparrow| = \sum_{j\le N^\uparrow} |\varphi_j^\uparrow\rangle\langle\varphi_j^\uparrow| \tag{B3}$$

$$\hat{I}^\downarrow - \sum_{j>N^\downarrow} |\varphi_j^\downarrow\rangle\langle\varphi_j^\downarrow| = \sum_{j\le N^\downarrow} |\varphi_j^\downarrow\rangle\langle\varphi_j^\downarrow|, \tag{B4}$$

therefore, introducing the above equations into Eqs. (B1) and (B2), we find

$$\sum_{j\le N^\uparrow} |\varphi_j^\uparrow\rangle\langle\varphi_j^\uparrow|\hat{F}^\uparrow|\chi_i^\uparrow\rangle = \lambda_i^\uparrow|\chi_i^\uparrow\rangle, \tag{B5}$$

$$\sum_{j\le N^\downarrow} |\varphi_j^\downarrow\rangle\langle\varphi_j^\downarrow|\hat{F}^\downarrow|\chi_i^\downarrow\rangle = \lambda_i^\downarrow|\chi_i^\downarrow\rangle. \tag{B6}$$

In the occupied subspace, we have $\sum_{j\le N^\uparrow} |\varphi_j^\uparrow\rangle\langle\varphi_j^\uparrow| = \hat{I}$ and $\sum_{j\le N^\downarrow} |\varphi_j^\downarrow\rangle\langle\varphi_j^\downarrow| = \hat{I}$.

APPENDIX C: ORTHOGONALITY OF DOUBLY EXCITED STATES, RESULTING FROM THE EXCITATION OF TWO ORBITALS WITH THE SAME SPIN, WITH THE CORRESPONDING SINGLY EXCITED STATES

Let $|\Phi_0\rangle = |\varphi_1, \varphi_2, \ldots, \varphi_{N^\uparrow}; \varphi_1', \varphi_2', \ldots, \varphi_{N^\downarrow}'\rangle$ be the HF Slater determinant of the ground state, $|\Phi_{ed}\rangle = |\xi_1, \xi_2, \ldots, \xi_{N^\uparrow}; \xi_1', \xi_2', \ldots, \xi_{N^\uparrow}'\rangle$ and $|\Phi_{ed}\rangle = |\chi_1, \chi_2, \ldots, \chi_{N^\uparrow-1}, \chi_{N^\uparrow}; \chi_1', \chi_2', \ldots, \chi_{N^\uparrow-1}', \chi_{N^\uparrow}'\rangle$ be the Slater determinants of the singly and doubly excited states of our method, respectively. In the following we omit the spin down part of the Slater determinants as it is not changing. Then, the $\xi_{N^\uparrow}$ orbital of the singly excited state can be expressed as

$$|\xi_{N^\uparrow}\rangle = k_{N^\uparrow-1}|\chi_{N^\uparrow-1}\rangle + k_{N^\uparrow}|\chi_{N^\uparrow}\rangle + k''|\chi''\rangle. \tag{C1}$$

The above equation holds because $|\xi_{N^\uparrow}\rangle$ belongs to the subspace of virtual orbitals, S_v and $|\chi_{N^\uparrow-1}\rangle$, $|\chi_{N^\uparrow}\rangle$ are elements of the new orthogonal basis set of the S_v, while $|\chi''\rangle$ belongs to the complementary part of the new basis set of S_v. Therefore, $|\Phi_{ed}\rangle$ becomes

$$\begin{aligned} |\Phi_{ed}\rangle = {} & k_{N^\uparrow-1}|\xi_1, \xi_2, \ldots, \chi_{N^\uparrow-1}\rangle + k_{N^\uparrow}|\xi_1, \xi_2, \ldots, \chi_{N^\uparrow}\rangle \\ & + k''|\xi_1, \xi_2, \ldots, \chi''\rangle. \end{aligned} \tag{C2}$$

The $|\chi_{N^\uparrow}\rangle$ orbital of $|\Phi_{ed}\rangle$ is orthogonal to all the orbitals of the first determinant $|\xi_1, \xi_2, \ldots, \chi_{N^\uparrow-1}\rangle$ in Eq. (C2), the $|\chi_{N^\uparrow-1}\rangle$ is orthogonal to all the orbitals of the second determinant $|\xi_1, \xi_2, \ldots, \chi_{N^\uparrow}\rangle$ in Eq. (C2), while both of them are orthogonal to all the orbitals of the third determinant $|\xi_1, \xi_2, \ldots, \chi''\rangle$ in Eq. (C2). Therefore,

$$\langle \Phi_{ed} | \Phi_{ed} \rangle = \langle \xi_1, \xi_2, \ldots, \xi_{N^{\uparrow}} | \chi_1, \chi_2, \ldots, \chi_{N^{\uparrow}-1}, \chi_{N^{\uparrow}} \rangle = 0. \tag{C3}$$

Thus, we showed that the doubly excited state resulting from the excitation of two orbitals with same spin is orthogonal to the corresponding singly excited state.

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