Double excitations from modified Hartree-Fock equations

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Introduction to the problem

- Double exciatations have become nowadays important as they are related to many technological applications (e.g. increasing the efficiency of solar cells)
- Their description is a great theoretical challenge as they cannot be described in practice by linear response theories based on a single Slater determinant
- Multideterminental approximations can describe multiexcitations, but are comutationally expensive methods
- Hartree-Fock is a ground state approximation. The usual way to expand it for excited states is to occupy virtual orbitals

UHF based approximation for excited states

Usual way to deal with excited states create particle-hole pairs:

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

where $|\Phi^0\rangle$ be the determinant of the HF ground state and $|\Phi^{ed}\rangle$ of double excited state.

Our approach for excited determinants

We do not fix both the virtual and occupied orbitals but obtain them by a minimization of the functional $E(\Phi^{ed}) = \langle\Phi^{ed}|H|\Phi^{ed}\rangle$ with $\langle\Phi^{ed}|\Phi^0\rangle = 0$.

Numerical Implementation

- $\left|\Phi^0\right\rangle = \left|\phi_1, \phi_2, .., \phi_{N\uparrow}; \phi'_1..\phi'_{N\downarrow}\right\rangle \rightarrow$ UHF (ground state)
- $\left|\Phi^{ed}\right\rangle = \left|\chi_1, \chi_2, .., \chi_{N\uparrow}; \chi'_1..\chi'_{N\downarrow}\right\rangle \rightarrow$ excited state

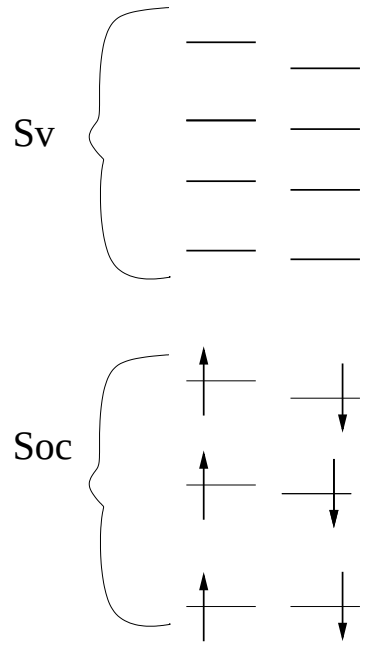
Subpsace distinction

The double excited state has to be orthogonal to the ground state, we impose the appropriate restrictions so that when we have a double exciation from two electrons with different spin

$$\{\chi_1, ..., \chi_{N^\sigma - 1}\} \in S^\sigma_{oc}$$

$$\chi_{N^\sigma} \in S^\sigma_v$$

S^σ_{oc} spanned by $\{\phi^\sigma_1, ..., \phi^\sigma_{N^\sigma}\}$ S^σ_{oc} spanned by $\{\phi^\sigma_{N^\sigma+1}, ..., \phi^\sigma_{N_{basis}}\}$



Diagonalization

$$\boxed{F^{\sigma}\left|\chi_i^{\sigma}\right\rangle = \lambda_i\left|\chi_i^{\sigma}\right\rangle} \tag{2}$$

- Restricting the diagonalization of the Fock matrix F^{σ} in the subspace S_{oc}^{σ} of occupied HF orbitals with spin σ we take the $N^{\sigma} - 1$ lower energy solutions which correspond to the $N^{\sigma} - 1$ excited state orbitals.
- Restricting the diagonalization of F^{σ} to the subspace of virtual HF orbitals S_{v}^{σ}, from the lowest energy solution we find our N_{th}^{σ} excited state orbital.

In the same way we can find an excited state that correspond to an excitation of two electrons with the same spin. The only difference is that we demand two orbitals to belong to S_{v}^{σ}

Excitation energies H_2

Total 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[1]	CI[2]	No Opt.[3]
1.4	-0.073	-0.105	-0.066
	1.060	1.069	1.067
3.0	-0.614	-0.631	-0.503
	0.403	0.426	0.514

[1] M. Tassi, I. Theophilou and S. Thanos, accepted in JCP
[2] A. U. Hazi, C. Derkits and J. N. Bardsley, Phys. Rev. A **27**, 1751 (1983)
[3] without orbital optimization

Excitation energies

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

[a] M. Tassi, I. Theophilou and S. Thanos, accepted in JCP

[b] L. Serrano-Andres, M. Merchan, I. Nebot-Gil, R. Lindh and Bj. O. Roos, J. Chem. Phys. **98**, 3151 (1993).

[c] Experimental data, R. R. Chadwick, M. Z. Zgierski and B. S. Hudson, J. Chem. Phys. **95**, 7204 (1991) and T. Fujii, A. Kamata, M. Shimizu, Y. Adachi and S. Maeda, Chem. Phys. Lett. **115**, 369 (1985)

[d] Excitations energies without any orbital optimization

Summary and Conclusions

- We have developed an approximation for doubly excited states $|\Phi^{ed}\rangle$ that are orthogonal to the ground state UHF $|\Phi^{0}\rangle$
- All excited state orbitals are different from the ground state ones and are derived from minimization in different subspaces
- In this way we obtained excited state orbitals that are self interaction free
- Comparison with literature showed that the method gives good results for the systems tested
- The method is computationally inexpensive

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Thank you for your attention!!