Obtain double excitations with spin-flip methods

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What's the problem ?

Methods using Casida-like equations are blind to double excitations :

$$\begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix} \begin{pmatrix} X_m \\ Y_m \end{pmatrix} = \Omega_m \begin{pmatrix} X_m \\ Y_m \end{pmatrix}$$

With

$$R_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a^{KS} - \epsilon_i^{KS}) + 2(ia|bj) + f_{ia,bj}^{xc}$$
$$C_{ia,jb} = 2(ia|jb) + f_{ia.jb}^{xc}$$

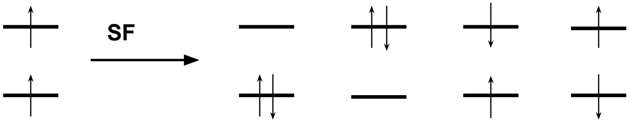
for TD-DFT, and with

$$R_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a^{GW} - \epsilon_i^{GW}) + 2(ia|bj) - W_{ij,ba}^{stat}$$
$$C_{ia,jb} = 2(ia|jb) - W_{ib,ja}^{stat}$$

for BSE

What's the solution ?

The solution is to use the spin-flip methods formally introduced by Krylov in 2001 for CI and EOM-CC [1] [2]



1. A. I. Krylov, Chem. Phys. Lett., 2001, 338, 375–384.
2. A. I. Krylov, Chem. Phys. Lett., 2001, 350, 522–530.

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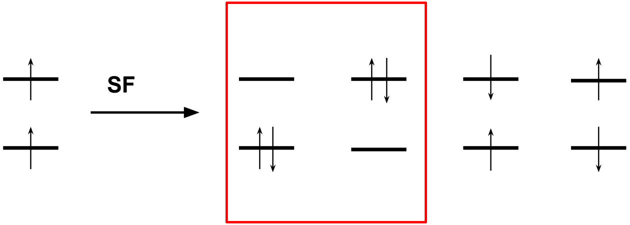

State	TD-BLYP	TD-BHHLYP	CIS	BSE@G0W0	FCI
^{3}P $(1s^2 2s^1 2p^1)$	3.210	2.874	2.111	2.399	2.862
^{1}P $(1s^2 2s^1 2p^1)$	3.210	4.922	6.036	6.191	6.577
^{3}P $(1s^2 2p^2)$	6.691	7.112	7.480	7.792	7.669
^{1}D $(1s^2 2p^2)$	7.598	8.188	8.945	9.373	8.624

Table – Spin-flip excitations (in eV) of Be obtained for various methods with the 6-31G basis.

Effect of the exact exchange [a]

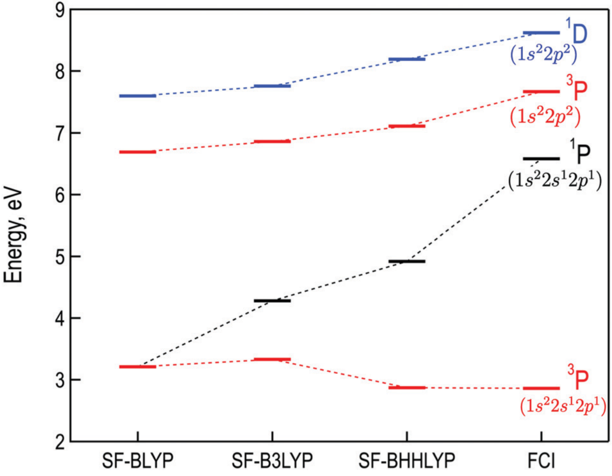

Figure – Electronic states of Be

a. Phys. Chem. Chem. Phys., 2020,22, 4326-4342