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Laboratoire de Chimie et Physique Quantiques

Double excitations with spin-flip methods

Enzo Monino

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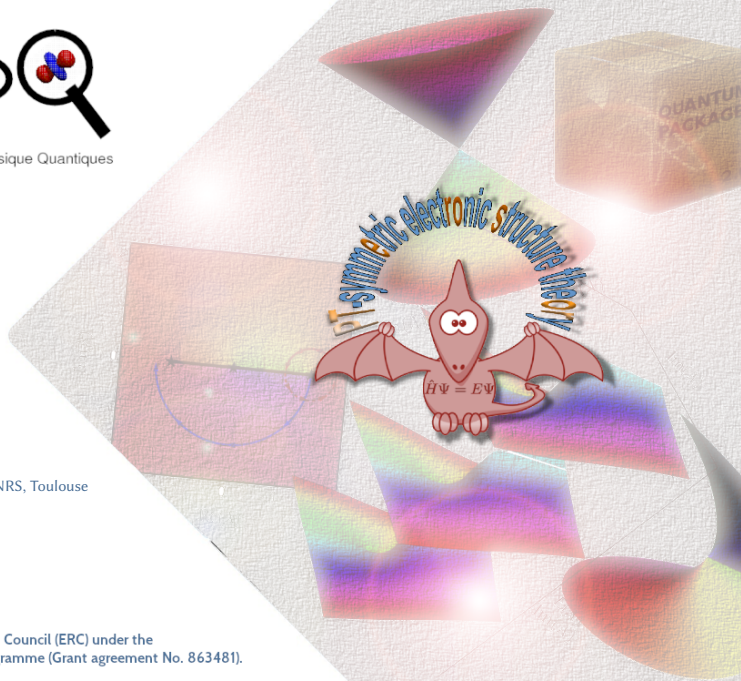
Laboratoire de Chimie et Physique Quantiques, IRSAMC, UPS/CNRS, Toulouse

https://lcpq.github.io/pterosor



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Methods using Casida-like equation 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

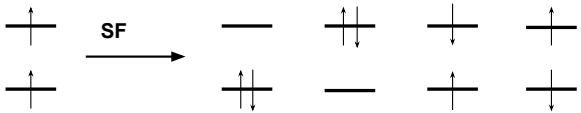
$$R_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a^{KS} - \epsilon_i^{KS}) + 2(ia|bj) + f_{ia,bj}^{xc}$$
$$C_{ia,jb} = 2(ia|jb) + f_{ia,jb}^{xc}$$

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

The solution is to use the spin-flip methods formally introduced by Krylov in 2001 for CI and EOM-CC [12]



[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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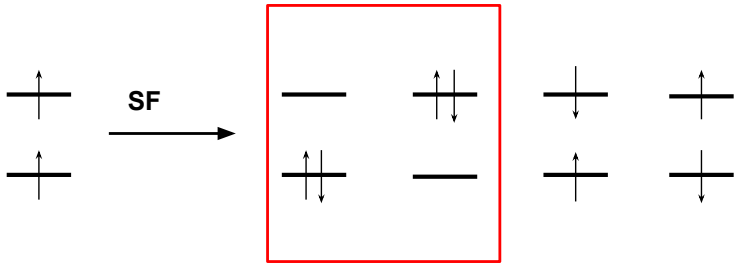
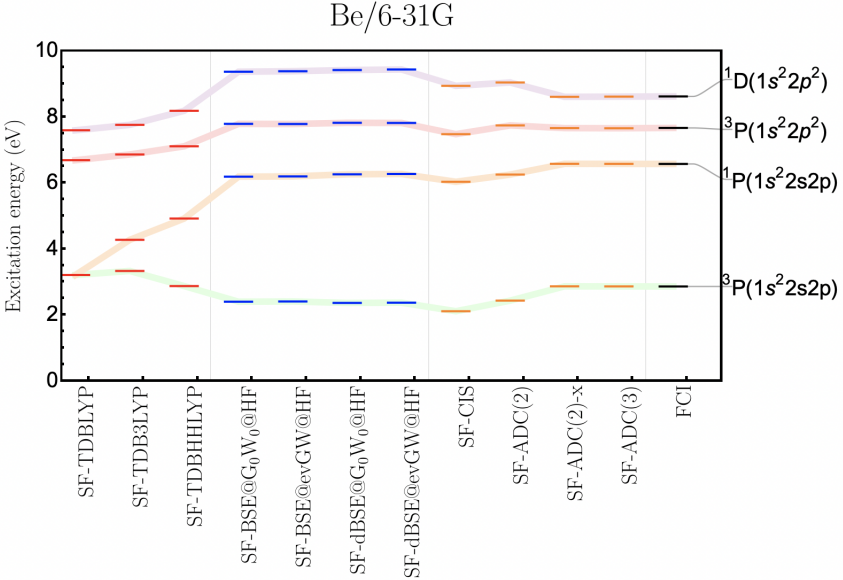
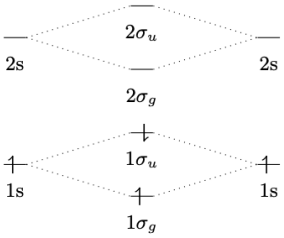
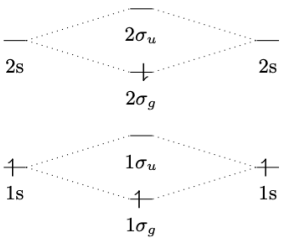
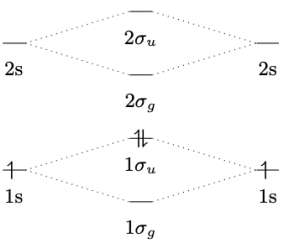


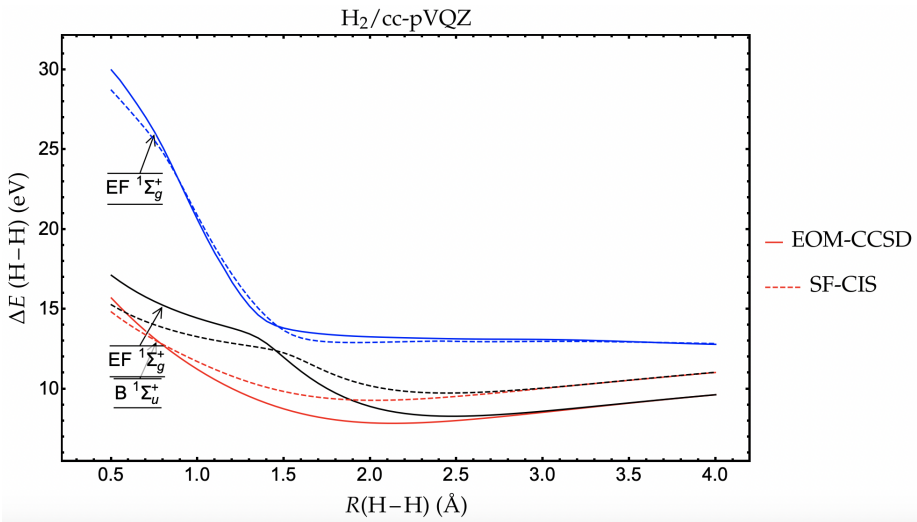

Be/6-31G
Excitation energy (eV)
0
2
4
6
8
10
^{1}D($1s^2 2p^2$)
^{3}P($1s^2 2p^2$)
^{1}P($1s^2 2s2p$)
^{3}P($1s^2 2s2p$)
SF-TDBLYP
SF-TDB3LYP
SF-TDBHHLYP
SF-BSE@G_0W_0@HF
SF-BSE@evGW@HF
SF-dBSE@G_0W_0@HF
SF-dBSE@evGW@HF
SF-CIS
SF-ADC(2)
SF-ADC(2)-x
SF-ADC(3)
FCI

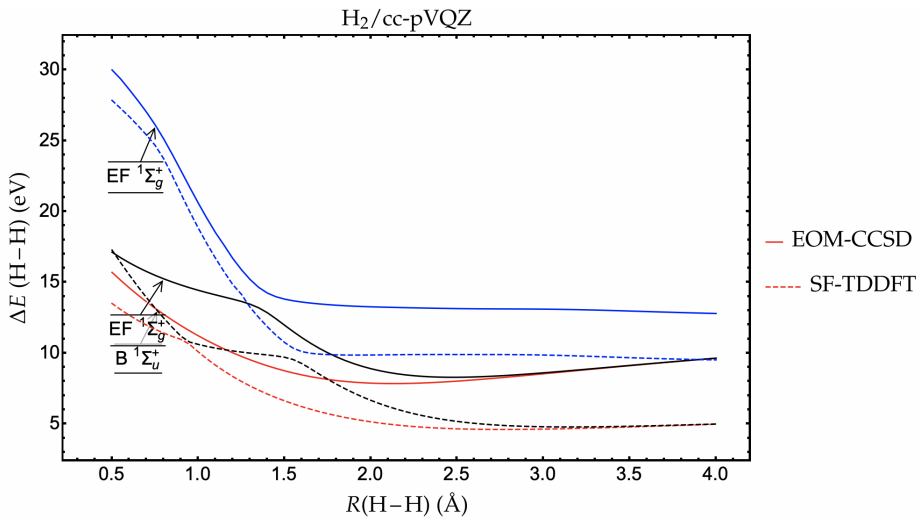
H_2 molecule

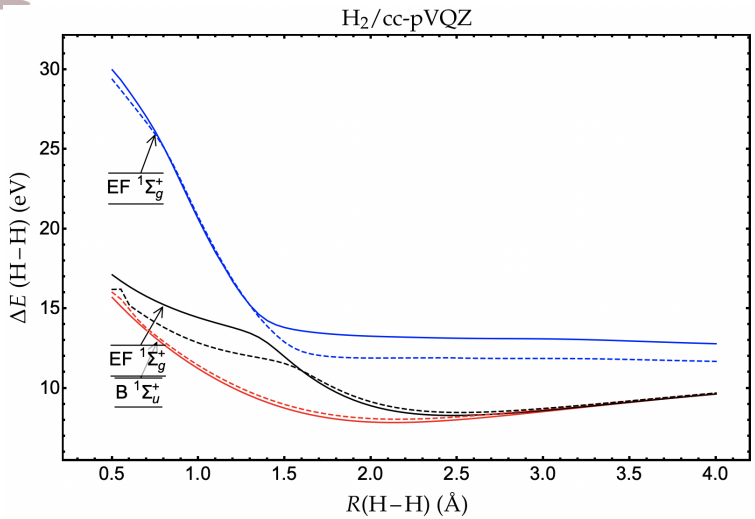

$2\sigma_u$
2s
2s
$2\sigma_g$
$1\sigma_u$
1s
1s
$1\sigma_g$


$2\sigma_u$
2s
2s
$2\sigma_g$
$1\sigma_u$
1s
1s
$1\sigma_g$


$2\sigma_u$
2s
2s
$2\sigma_g$
$1\sigma_u$
1s
1s
$1\sigma_g$


H2/cc-pVQZ
ΔE (H−H) (eV)
R(H−H) (Å)
EF 1Σg+
EF 1Σg+
B 1Σu+
EOM-CCSD
SF-CIS


H2/cc-pVQZ
ΔE (H−H) (eV)
R(H−H) (Å)
EF 1Σg+
EF 1Σg+
B 1Σu+
EOM-CCSD
SF-TDDFT



— EOM-CCSD

----- SF-BSE@G_0W_0@UHF