BARCELONA 2019
HANDS-ON DFT AND BEYOND: HIGH-THROUGHPUT SCREENING AND BIG-DATA ANALYTICS, TOWARDS EXASCALE COMPUTATIONAL MATERIALS SCIENCE
University of Barcelona, Barcelona, Spain, August 26th to September 6th, 2019

The use of spin-flip excitation in DFT: theory and applications

David Casanova

Thursday August 29, 2019
Barcelona

ikerbasque
Basque Foundation for Science

david.casanova@ehu.eus

Motivation: molecular low-lying electronic states

Framework: molecular photophysics and photochemistry with **DFT**

Electronic states

- ground state
- excited states

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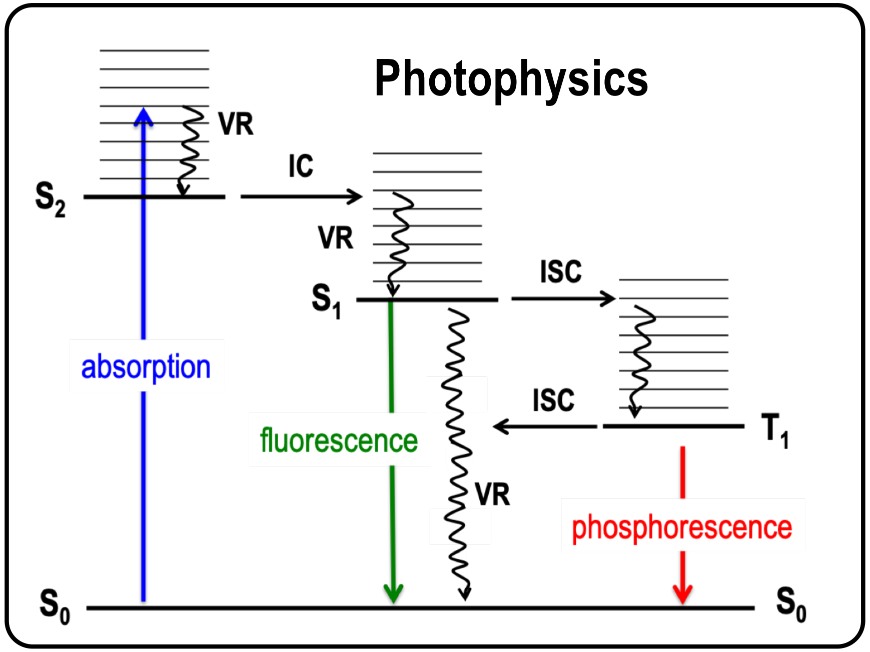
- ground state
- excited states

Processes
- photophysics



Excited generation
- photo absorption
- charge recombination

Radiative
- fluorescence
- phosphorescence

Non-radiative
- physical process: IC, ISC

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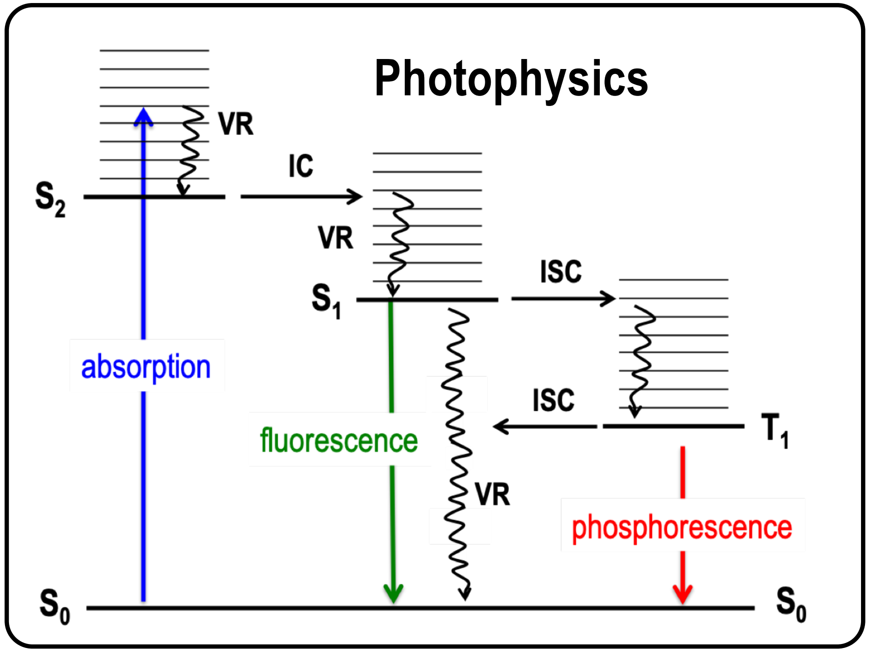

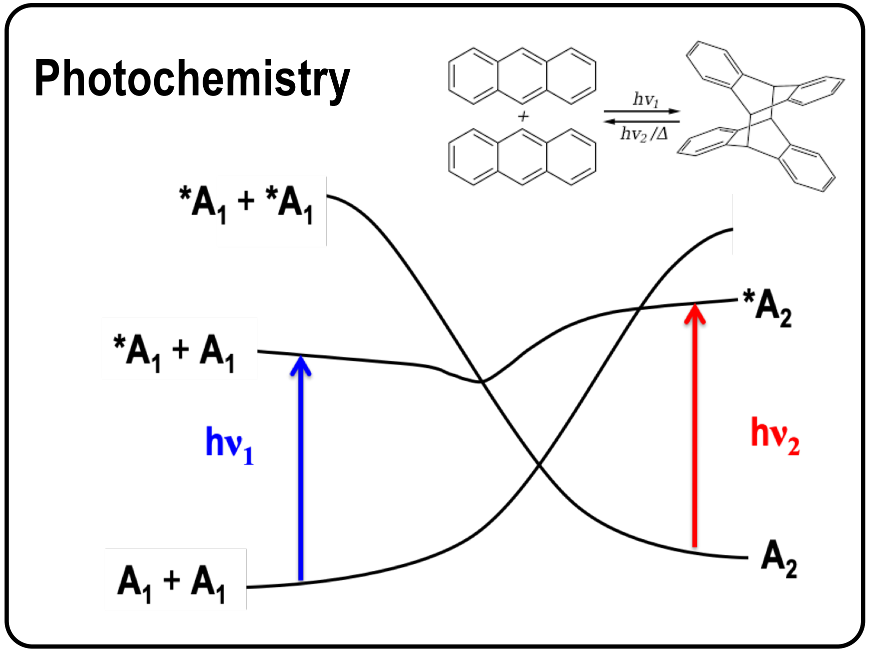

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Outline

- Sketch of TDDFT
  properties and limitations
- Introduction of the spin-flip operator
- Spin-flip in TDDFT (SF-TDDFT)
- Noncollinear SF-TDDFT
- Source of spin contamination
- Spin adapted solutions

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Monday September 2nd Day 6: Quasiparticle approaches: DFT and beyond		
09:00 - 10:00	Patrick Rinke	Charged excitation (GW)
10:00 - 11:00	Claudia Draxl	Neutral Excitation (BSE)
11:00 - 11:30	Coffee Break	
11:30 - 12:30	Miguel Alexandre Marques	Neutral Excitations (TDDFT)
12:30 - 14:30	Lunch Break	
14:30 - 15:30	Xinguo Ren	RPA and Beyond
15:30 - 19:30	Dorothea Golze	Tutorial 5: Excited states and spectroscopy

Time-dependent density functional

Time-independent DFT

HK-1 mapping

$$\rho(r) \leftrightarrow v[\rho](r) \leftrightarrow \Psi[\rho](r)$$

exact ground state

Time-dependent DFT

Runge-Gross theorem

PRL 52 (1984) 997

$$\rho(r,t) \leftrightarrow v[\rho](r,t) + C(t) \leftrightarrow \Psi[\rho;\Psi_0](r,t)$$

exact time-dependent state

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HK-2 variational principle

$$\exists \text{ of a VP} \Longrightarrow \rho(r)$$

$$\delta\langle\Psi[\rho](r)|\hat{H} - E|\Psi[\rho](r)\rangle = 0$$

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exact time-dependent state

Stationary principle

$$\exists \text{ of a ST} \Longrightarrow \rho(r,t)$$

$$\frac{\delta A[\rho;\Psi_0]}{\delta\rho(r,t)} = 0$$

Action integral

$$A[\rho;\Psi_0] = \int_{t_0}^{t_1} dt \langle\Psi[\rho;\Psi_0](r,t)|i\partial_t - \hat{H}(t)|\Psi[\rho;\Psi_0](r,t)\rangle$$

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Time-independent Kohn-Sham equations ⟵ Non-interacting system ⟶ Time-dependent Kohn-Sham equations

Time-dependent Kohn-Sham equations

Non-interacting system

$$v_S(r,t) \rightarrow \rho(r,t) = \rho_S(r,t)$$

$$v_S(r,t) = v_{ext}(r,t) + \int d^3r' \frac{\rho(r',t)}{|r-r'|} + v_{xc}(r,t)$$

1p potential

Time-dependent Kohn-Sham equations

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$$v_S(r,t) \rightarrow \rho(r,t) = \rho_S(r,t) = \sum_i |\phi_i(r,t)|^2$$

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1p orbitals

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time-dependent 1p SE

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$$\phi_i(r,t) = \sum_l^{N_B} c_{li}(t)\chi_l(r)$$

→

TDKS equation

$$i\partial_t \mathbf{C} = \mathbf{FC}$$

$$\mathbf{FP} - \mathbf{PF} = i\partial_t \mathbf{P}$$

Density matrix (Dirac) form

$$\rho(r,t) = \sum_{p,q}^{N_B} P_{pq}\chi_p(r)\chi_q^*(r)$$

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- Real time TDDFT
- Linear response TDDFT

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1st order

$$\mathbf{P} = \mathbf{P}^{(0)} + \mathbf{P}^{(1)}$$

$$\mathbf{F} = \mathbf{F}^{(0)} + \mathbf{F}^{(1)}$$

oscillatory TD field

$$\mathbf{H}^{(1)} = \frac{1}{2}(\mathbf{g}e^{-i\omega t} + \mathbf{g}^\dagger e^{i\omega t})$$

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idempotency

zero-frequency limit

(infinitesimal perturbation)

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

non-Hermitian eigenvalue eq.

(Casida's form)

Time-dependent Kohn-Sham equations

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x_{ai} : virtual-occupied $\quad i \in O, a \in V$

y_{ai} : occupied-virtual

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \frac{\partial F_{ia}}{\partial P_{jb}}$$

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Adiabatic approximation

$$v_{xc}(r,t) = \frac{\delta A_{xc}[\rho, \Psi_0]}{\delta \rho(r,t)}$$

$$f_{xc}(r,r';\omega) = \int_{-\infty}^{\infty} d(t-t') e^{i\omega(t-t')} \frac{\delta^2 A_{xc}[\rho,\Psi_0]}{\delta\rho(r,t)\delta\rho(r',t')}$$

→

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}$$

$$f_{xc}(r,r') = \frac{\delta^2 E_{xc}[\rho]}{\delta\rho(r)\delta\rho(r')}$$

Instantaneous change xc potential

- use of time-independent xc kernel
- no retardation/memory effects
- single electron excitations

TDDFT in Quantum Chemistry

Casida's formulation of TDDF

Advantages

- Good accuracies (absorption and emission properties)
- Low computational cost → large compounds
- Easy to implement and use
- Coupled to environmental models

Method of choice in computational spectroscopy

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Method of choice in computational spectroscopy

Disadvantages

- Poor description transitions with sizeable hole/electron spatial separation

  charge transfer and Rydberg states
- Unable to deal with degeneracies or near-degeneracies

  dissociations, diradicals, transition states, conical intersections
- Missing doubly or highly-excited states (adiabatic approximation)

  dark states, multi-excitons,...

Strong limitations for photochemistry and photobiology

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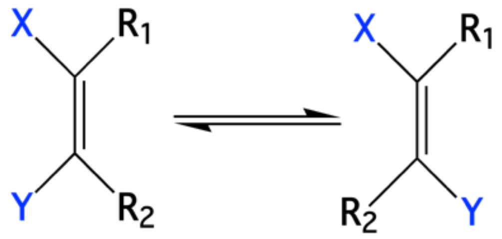
LR-TDDFT failures

Electronic degeneracy

Double bond torsion

- light ⇒ mechanical motion
- photobiological systems (vision)
- technological uses (optical memories)



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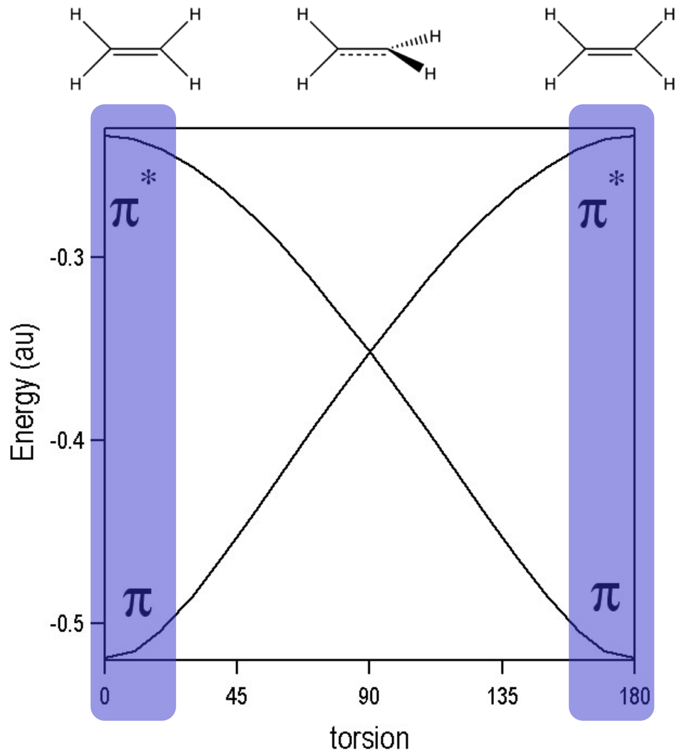

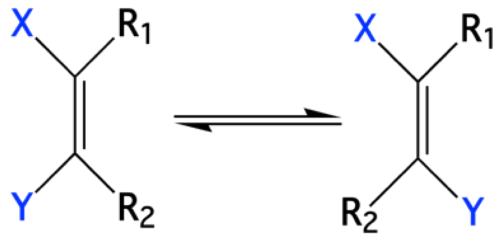

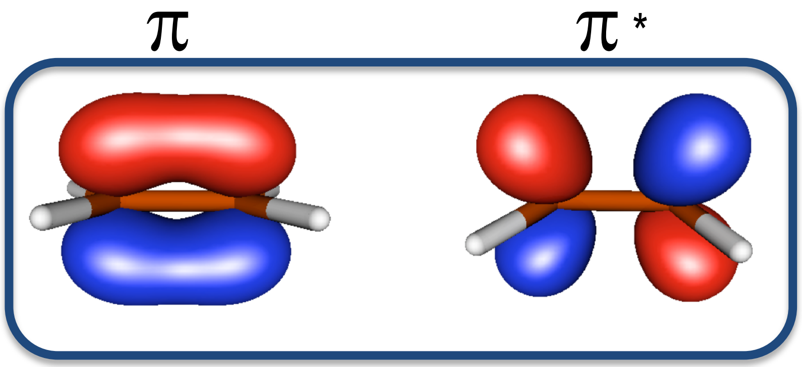

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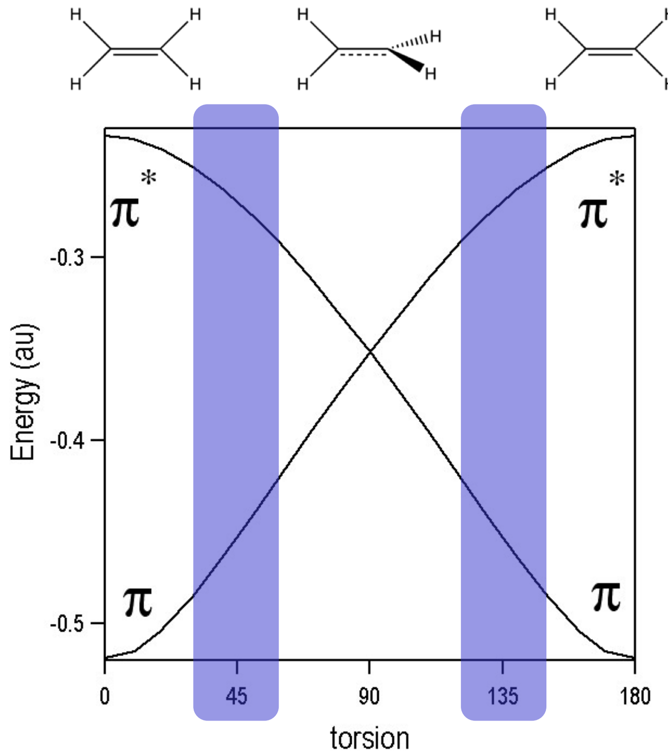

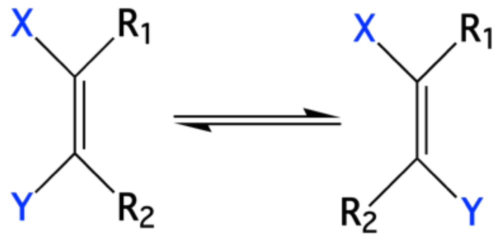

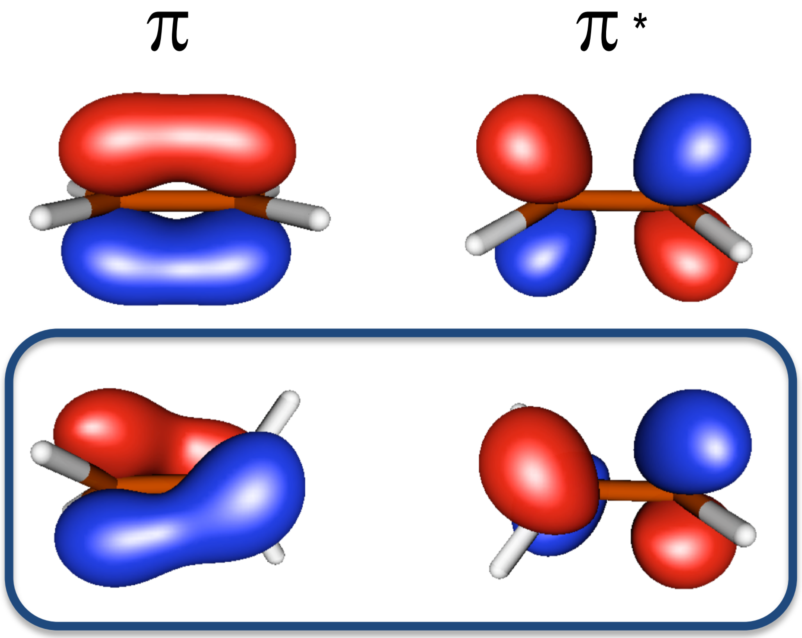

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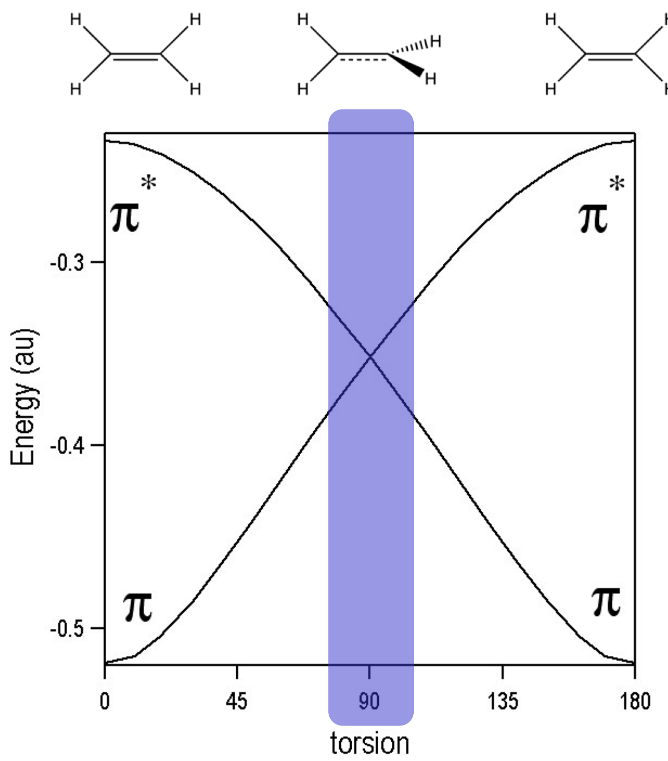
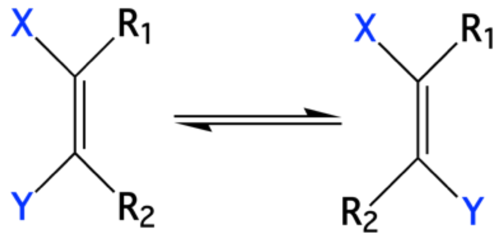
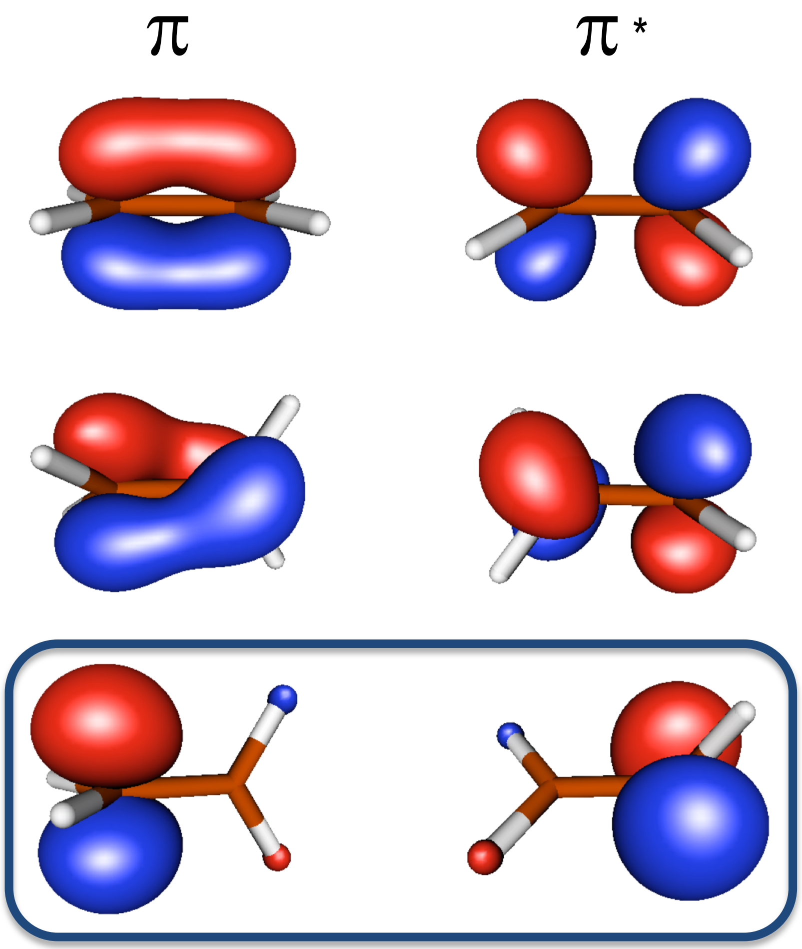


KS ground state is ill-defined





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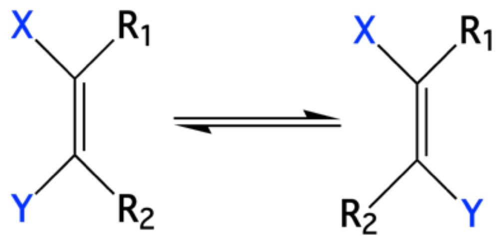
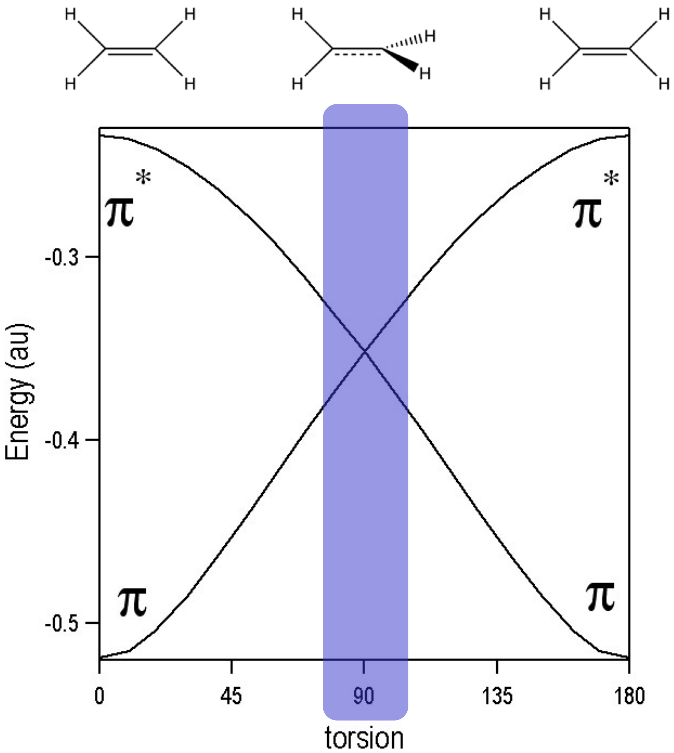




B3LYP/DZP

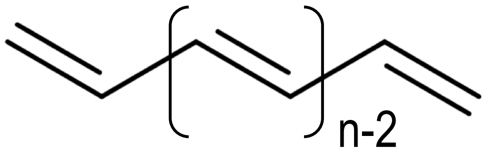
```
---------------------------------------------------
        TDDFT/TDA Excitation Energies
---------------------------------------------------

Excited state   1: excitation energy (eV) =   -1.0654
Total energy for state  1:                  -78.47809856 au
   Multiplicity: Triplet
   Trans. Mom.:  0.0000 X   0.0000 Y   0.0000 Z
   Strength   :     0.0000000000
   D(  8) --> V(  1) amplitude =  0.9964

Excited state   2: excitation energy (eV) =    1.6800
Total energy for state  2:                  -78.37720765 au
   Multiplicity: Singlet
   Trans. Mom.:  0.7975 X   0.0000 Y   0.0000 Z
   Strength   :     0.0261748746
   D(  8) --> V(  1) amplitude =  0.9748
```

KS ground state is ill-defined → linear response fails

LR-TDDFT failures

Double excitations

Example: all-*trans* polyenes



n-2

LR-TDDFT failures

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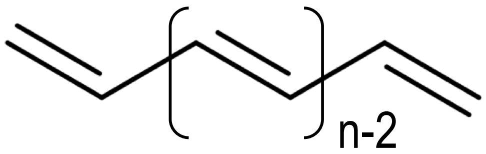
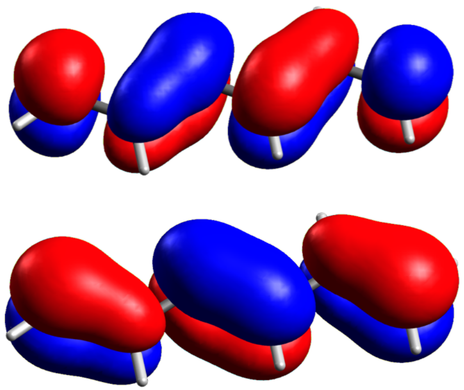
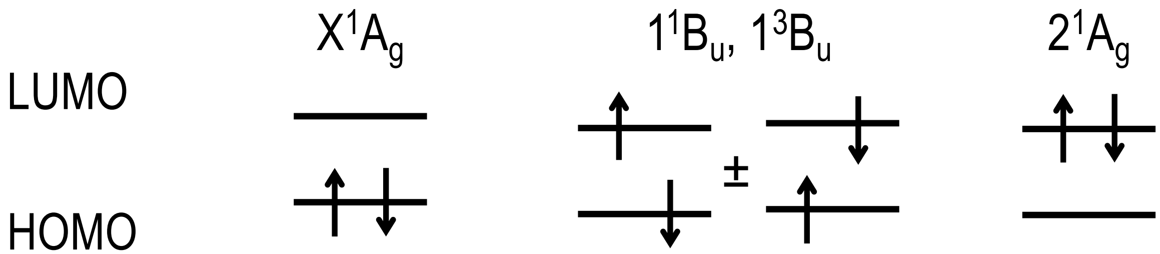


Hexatriene (n=3)





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Int. J. Quantum Chem. 66 (1998) 157
J. Phys. Chem. A 105 (2001) 451

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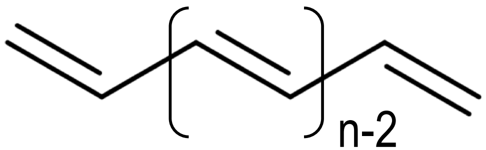
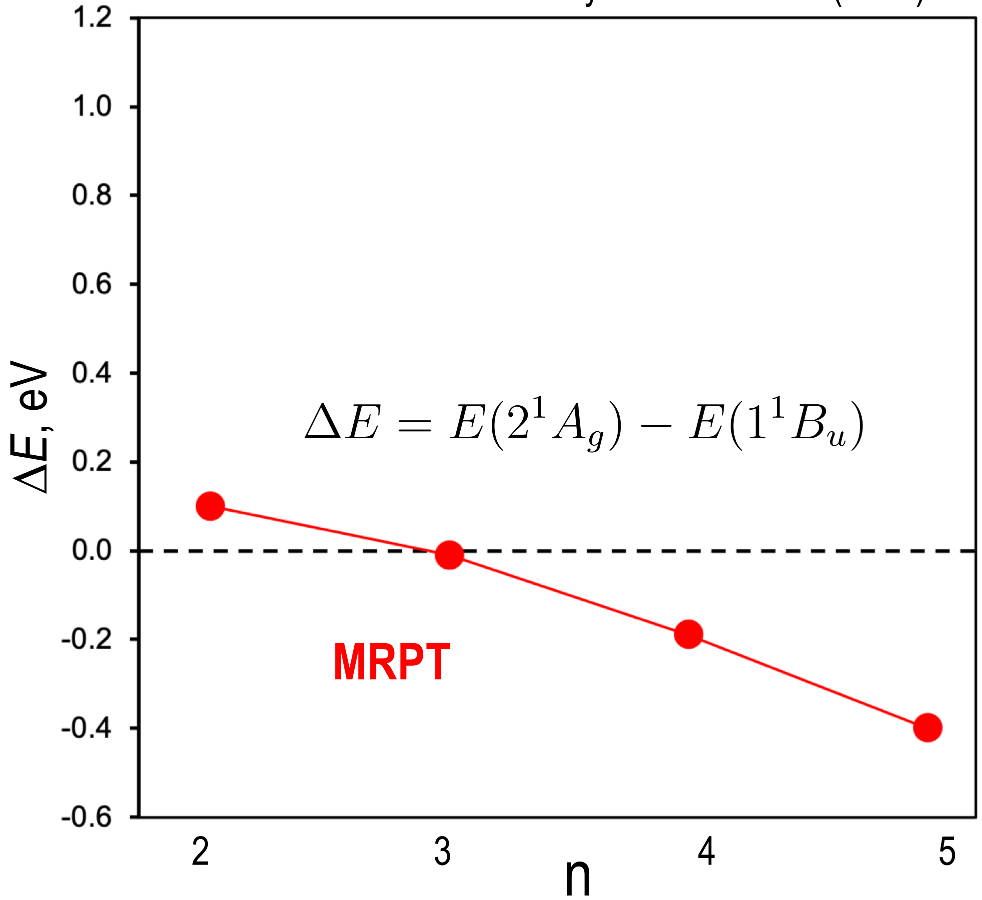
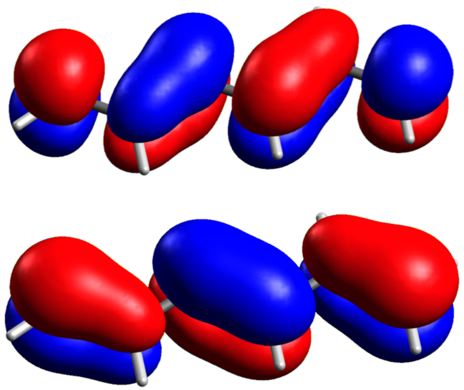
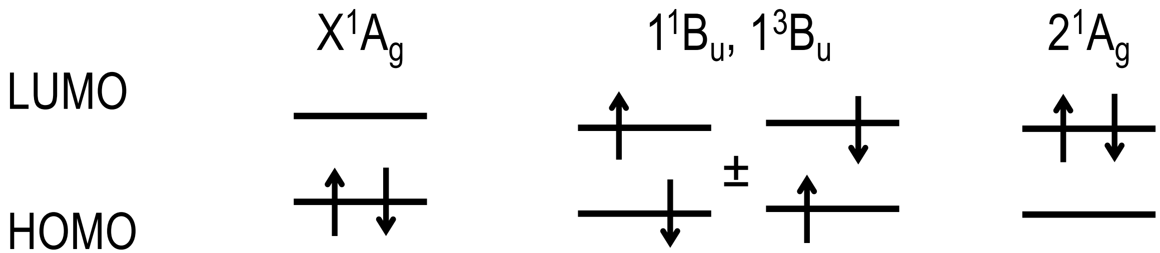




Hexatriene (n=3)



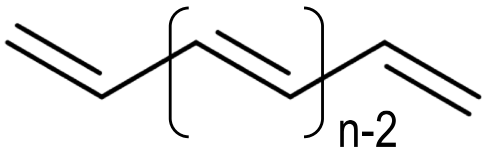


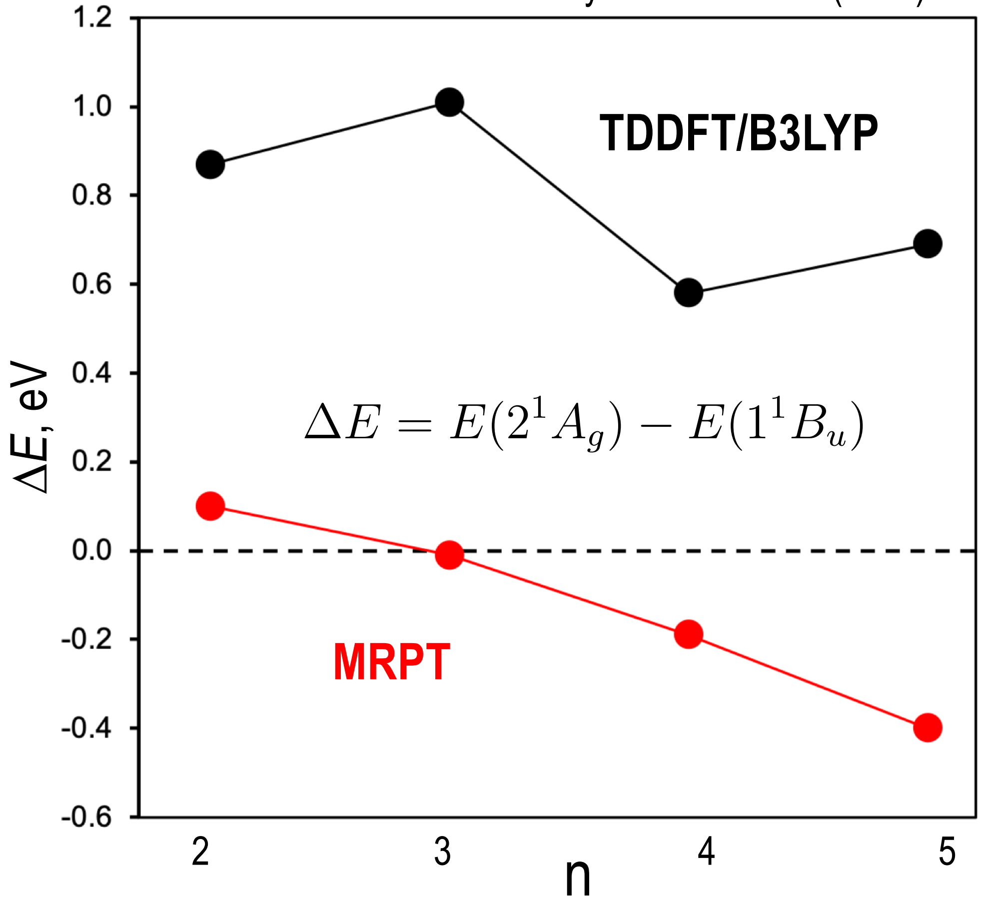
LR-TDDFT failures

Int. J. Quantum Chem. 66 (1998) 157
J. Phys. Chem. A 105 (2001) 451

Double excitations

Example: all-*trans* polyenes





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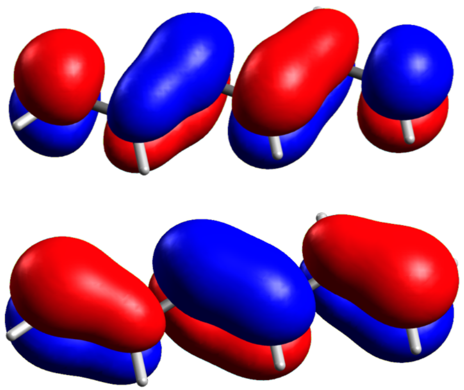

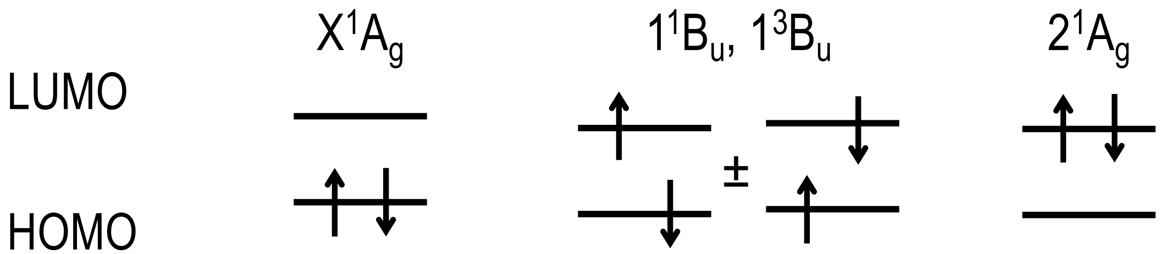

Spin-flip excitation operator

Spin-flip in CC and CI

Chem. Phys. Lett. 338 (2001) 375
Chem. Phys. Lett. 350 (2001) 522

$$[\hat{\bar{H}}, \hat{R}]|\Psi_0\rangle = \omega \hat{R}|\Psi_0\rangle \qquad |\Psi_f\rangle = \hat{R}|\Psi_0\rangle \qquad \hat{\bar{H}} = e^{-T}\hat{H}e^{T}$$

Spin-flip excitation operator

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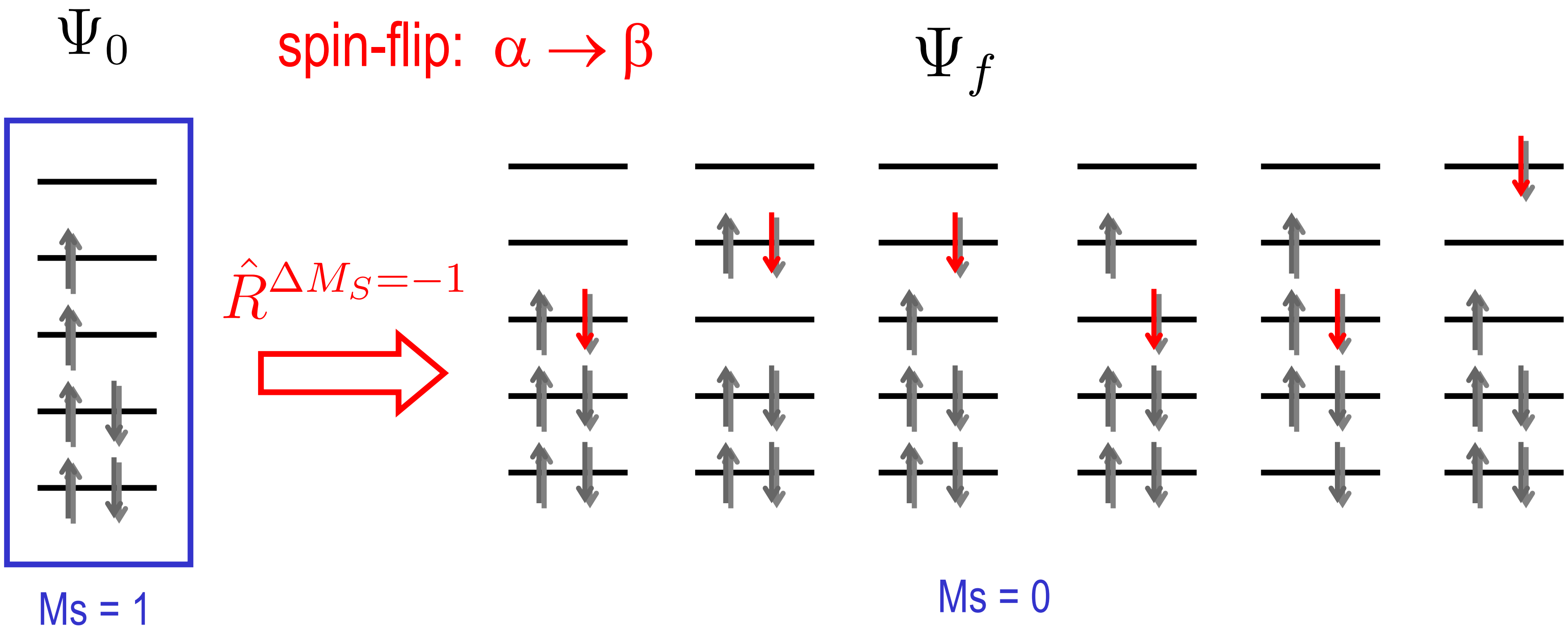

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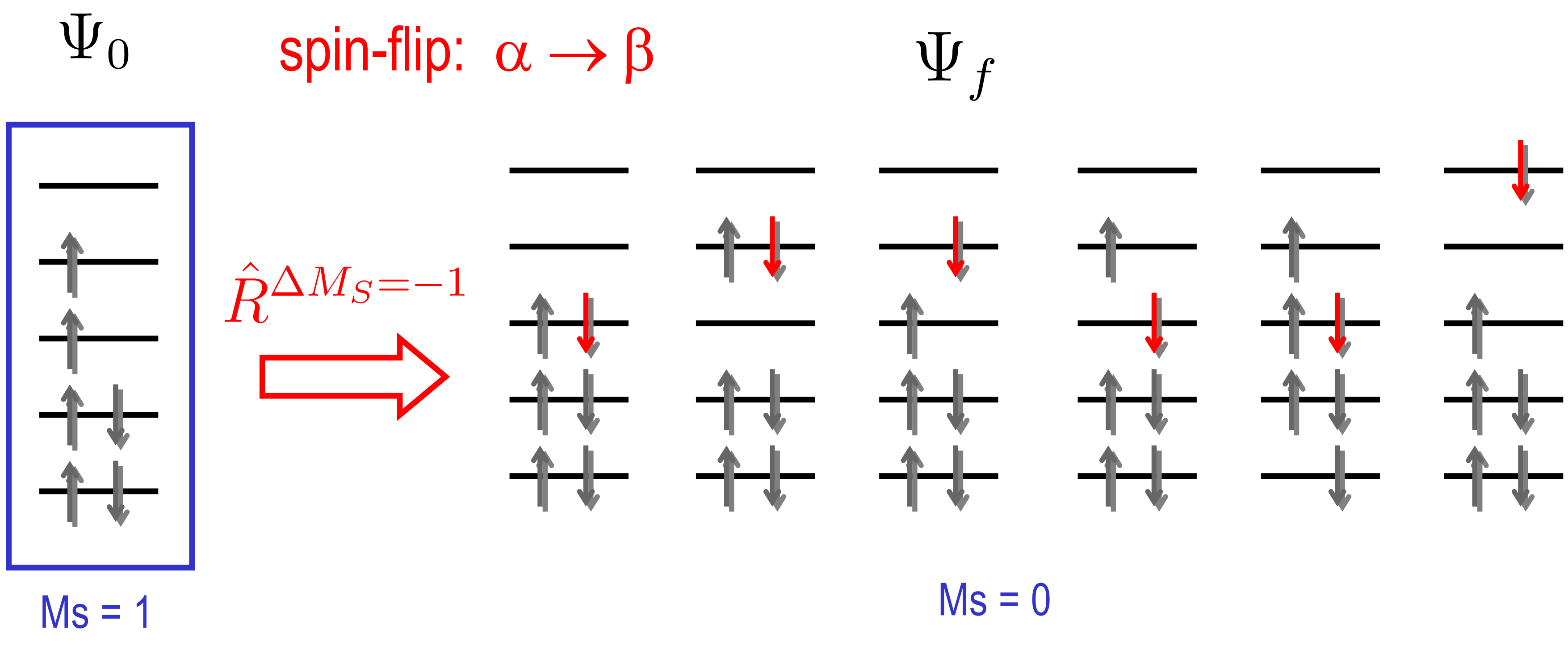


Characterization of diradicals

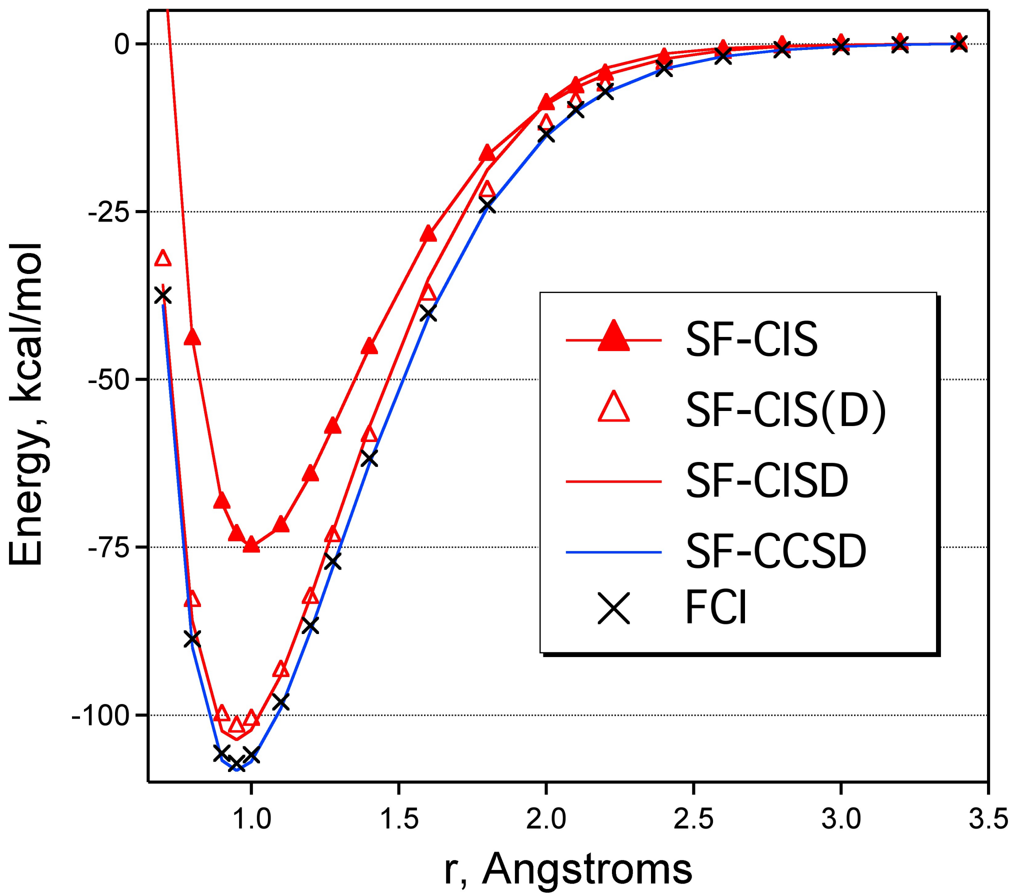
Ground and low-lying excited states

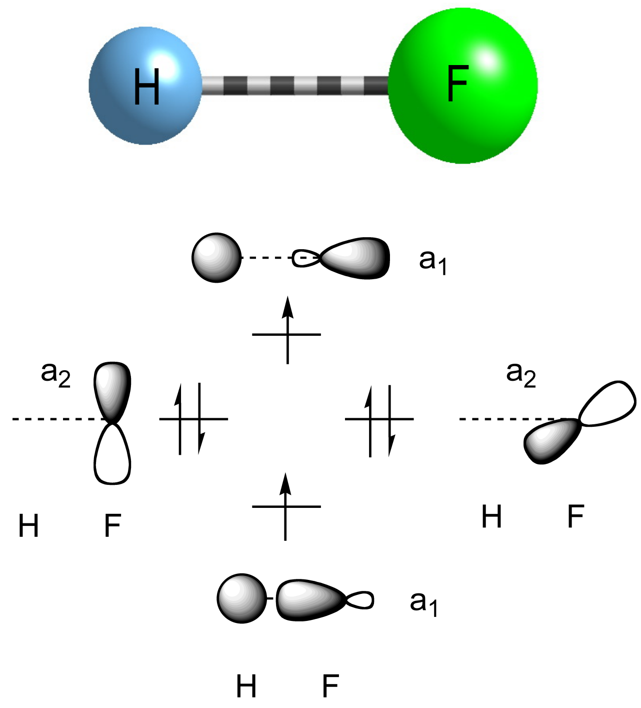
Double excitations

Examples: SF in wave function methods

Ground state

Diradicals, triradicals, bond-breaking



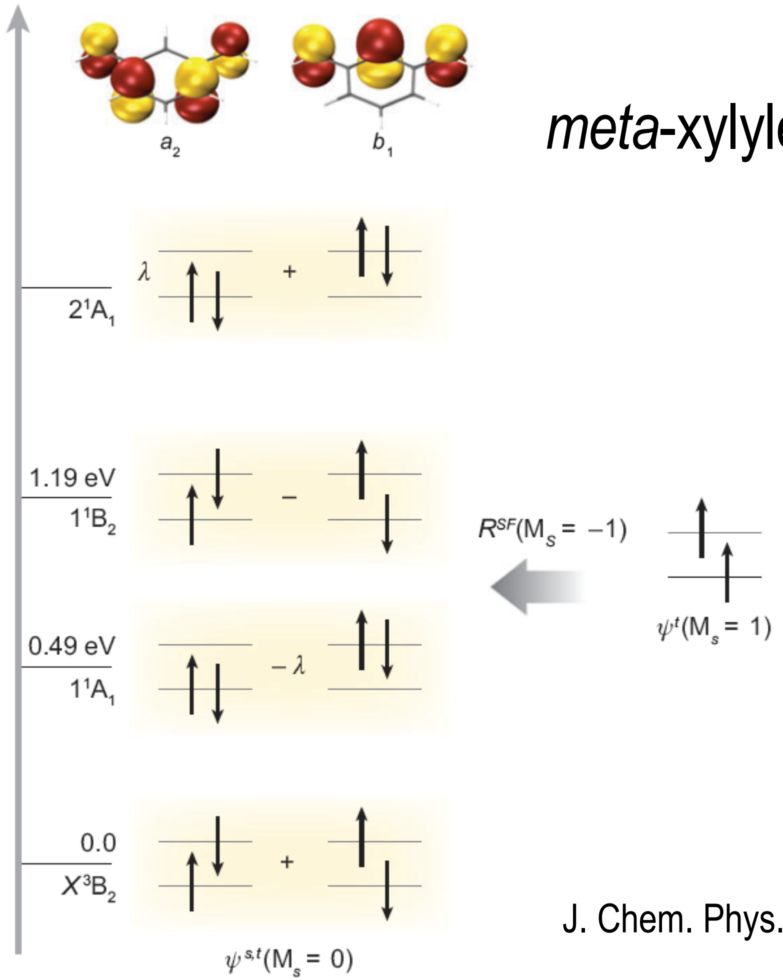


$^3\Sigma^+$ reference

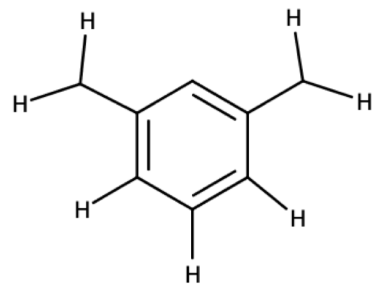
Examples: SF in wave function methods

Excited states

Diradicals, triradicals, bond-breaking



meta-xylylene



Excited states in open-shell molecules

EOM-SF-CCSD

J. Chem. Phys. 117 (2002) 4694

Spin-flip in DFT: SF-TDDFT

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

$x_{\bar{a}i}$: virtual-occupied $\quad i \in O(\alpha), \bar{a} \in V(\beta)$

$y_{a\bar{i}}$: occupied-virtual $\quad \bar{i} \in O(\beta), a \in V(\alpha)$

$$A_{i\bar{a},j\bar{b}} = \delta_{ij}\delta_{\bar{a}\bar{b}}(\epsilon_{\bar{a}} - \epsilon_i) + \frac{\partial F_{i\bar{a}}}{\partial P_{j\bar{b}}}$$

$$B_{i\bar{a},b\bar{j}} = \frac{\partial F_{i\bar{a}}}{\partial P_{b\bar{j}}}$$

$$\begin{aligned} A_{i\bar{a},j\bar{b}} &= \delta_{ij}\delta_{\bar{a}\bar{b}}(\epsilon_{\bar{a}} - \epsilon_i) + (i\bar{a}|f_H|j\bar{b}) + (i\bar{a}|f_{xc}|j\bar{b}) \\ B_{i\bar{a},\bar{j}b} &= (i\bar{a}|f_H|b\bar{j}) + (i\bar{a}|f_{xc}|b\bar{j}) \end{aligned}$$

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$$(i\bar{a}|f_H|j\bar{b}) = \int \phi_i(r_1)\phi_a(r_1)\frac{1}{|r_1 - r_2|}\phi_j(r_2)\phi_b(r_2)dr_1dr_2 \ \langle\alpha_1|\beta_1\rangle\langle\alpha_2|\beta_2\rangle = 0$$

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Spin-flip in DFT: SF-TDDFT

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Pure xc-functional

$$\begin{aligned} A_{i\bar{a},j\bar{b}} &= \delta_{ij}\delta_{\bar{a}\bar{b}}(\epsilon_{\bar{a}} - \epsilon_i) \\ B_{i\bar{a},\bar{j}b} &= 0 \end{aligned}$$

No coupling between SF states

Spin-flip in DFT: SF-TDDFT

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

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No coupling between SF states

Hybrid xc-functional

$$\begin{aligned} A_{i\bar{a},j\bar{b}} &= \delta_{ij}\delta_{\bar{a}\bar{b}}(\epsilon_{\bar{a}} - \epsilon_i) - c_{HF}(ij|f_H|\bar{a}\bar{b}) \\ B_{i\bar{a},\bar{j}b} &= -c_{HF}(ib|f_H|\bar{a}\bar{j}) \end{aligned}$$

Spin-flip in DFT: SF-TDDFT

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

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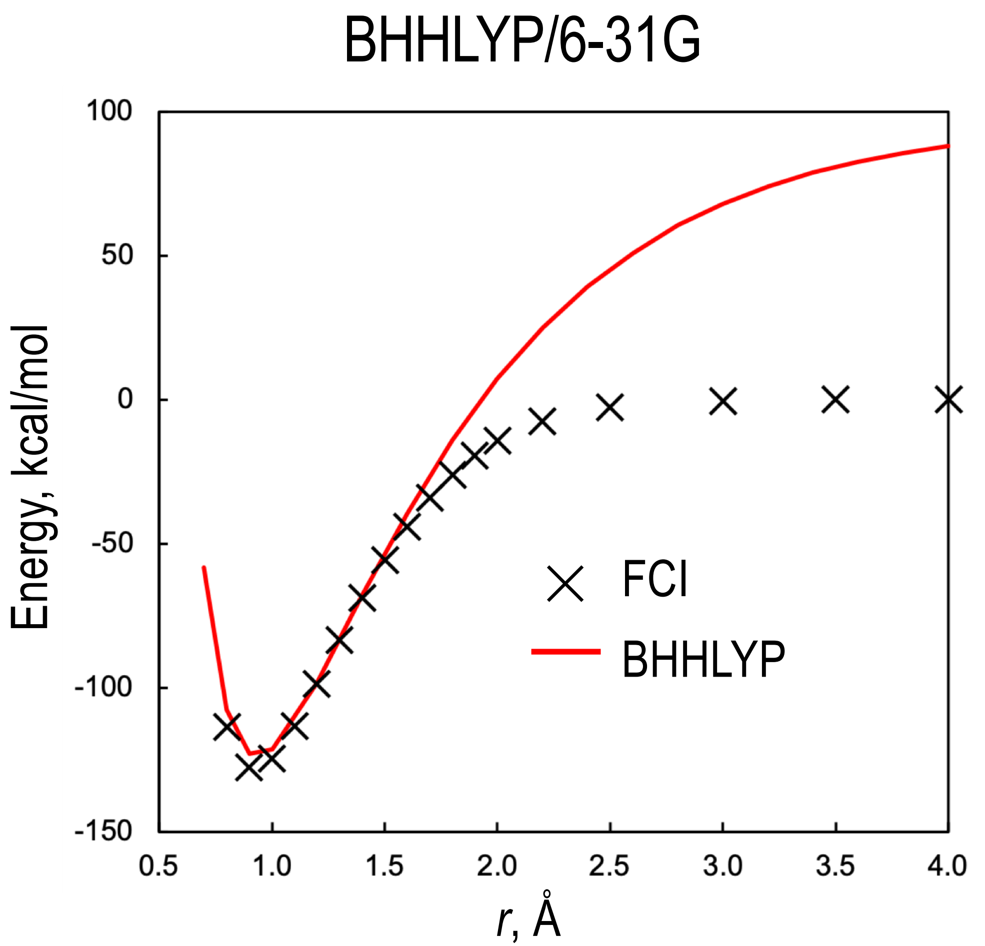
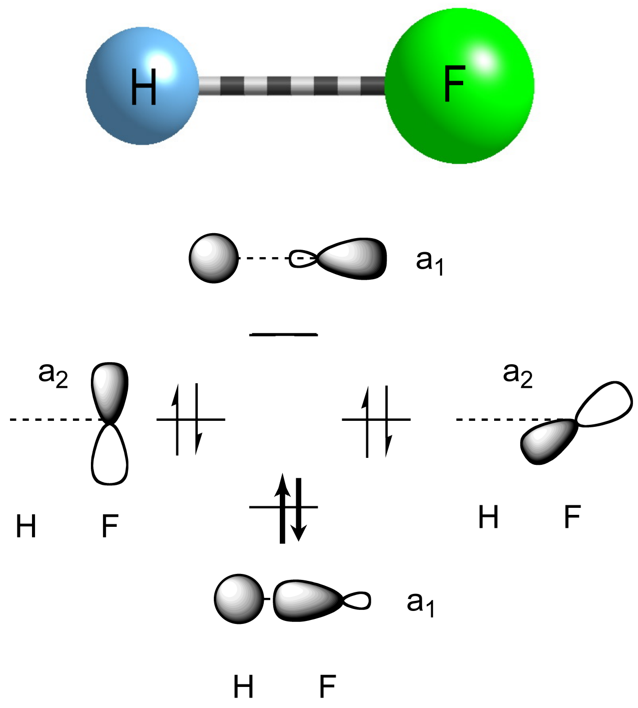
Best performance of SF-TDDFT achieved with functionals with large amounts of HF exchange

BHHLYP, 50-50 or PBE50 (50%)

Example: HF dissociation

Ground state dissociation

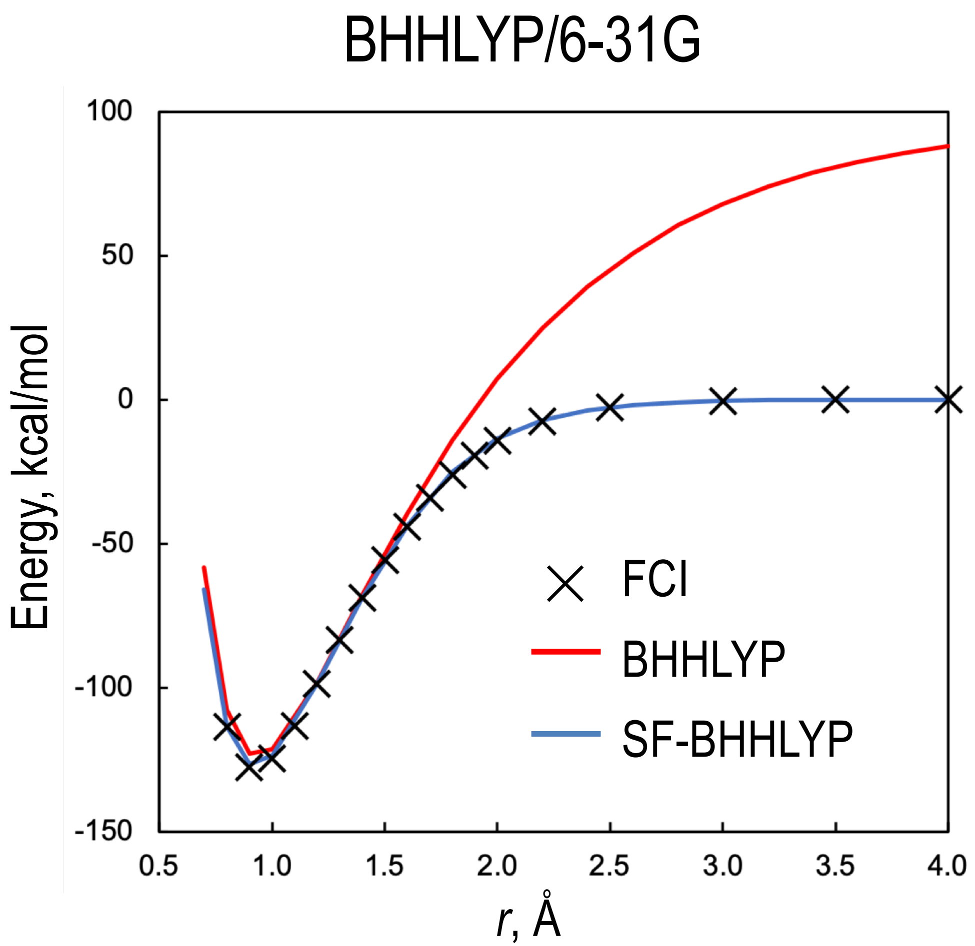


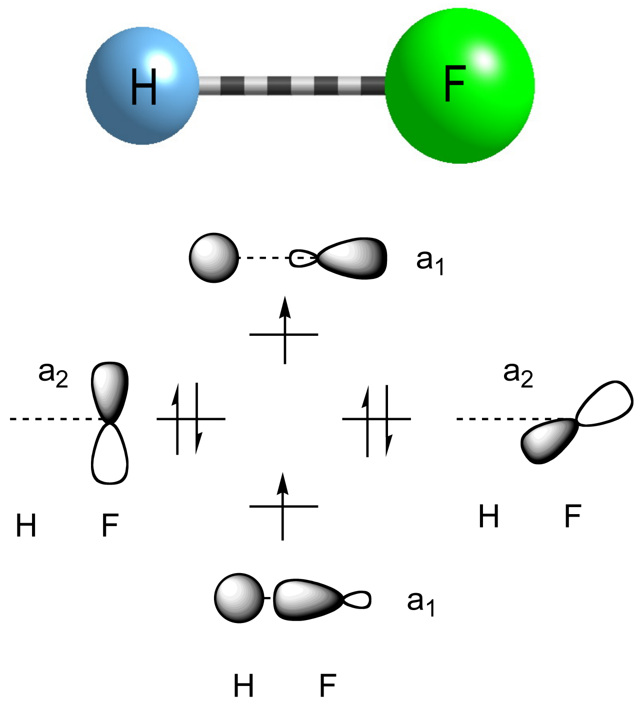


$^1\Sigma^+$ ground state

Example: HF dissociation

Ground state dissociation



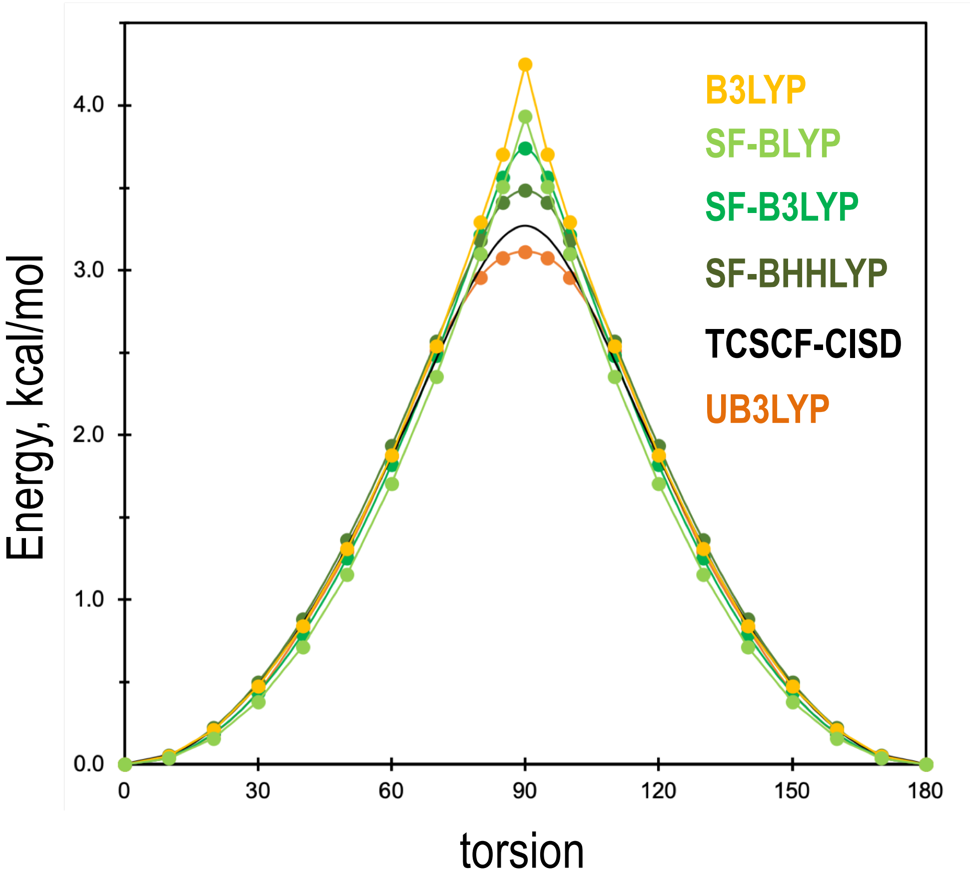


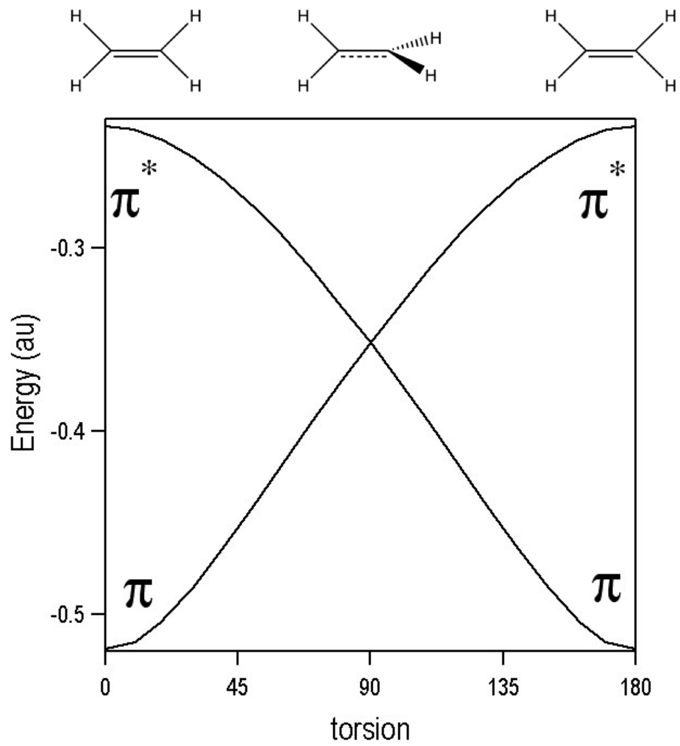
$^3\Sigma^+$ reference

Example: ethene torsion

Ground state PES

Basis set: DZP





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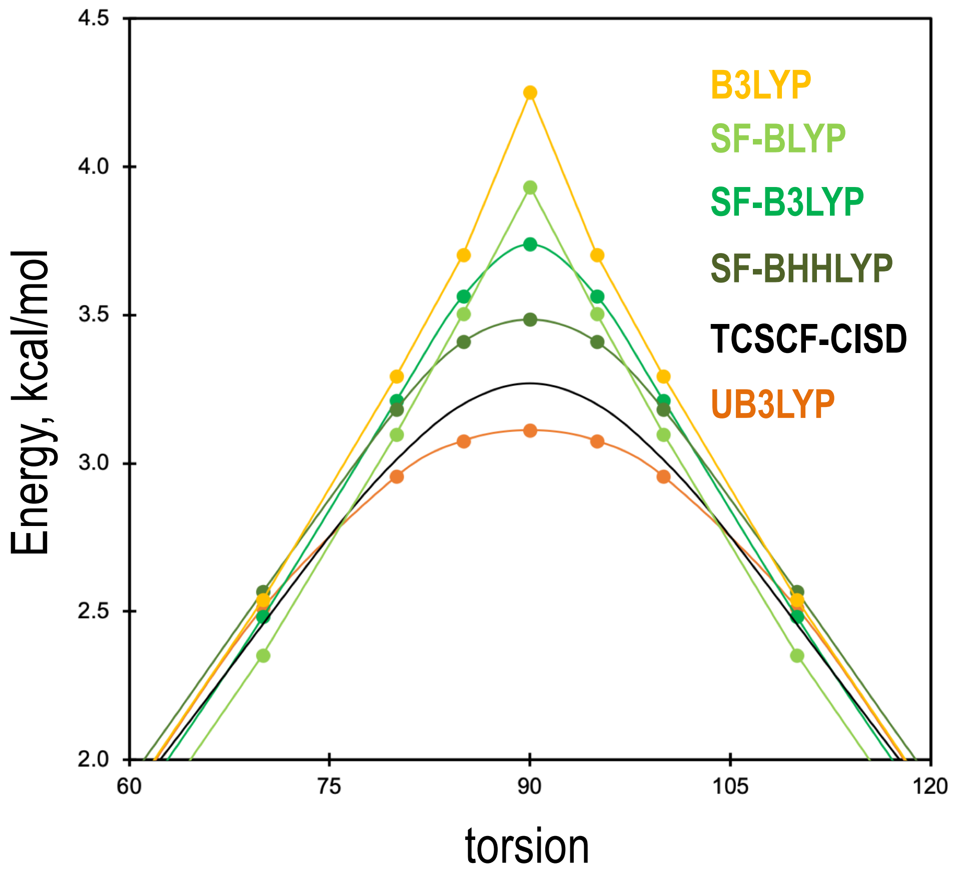

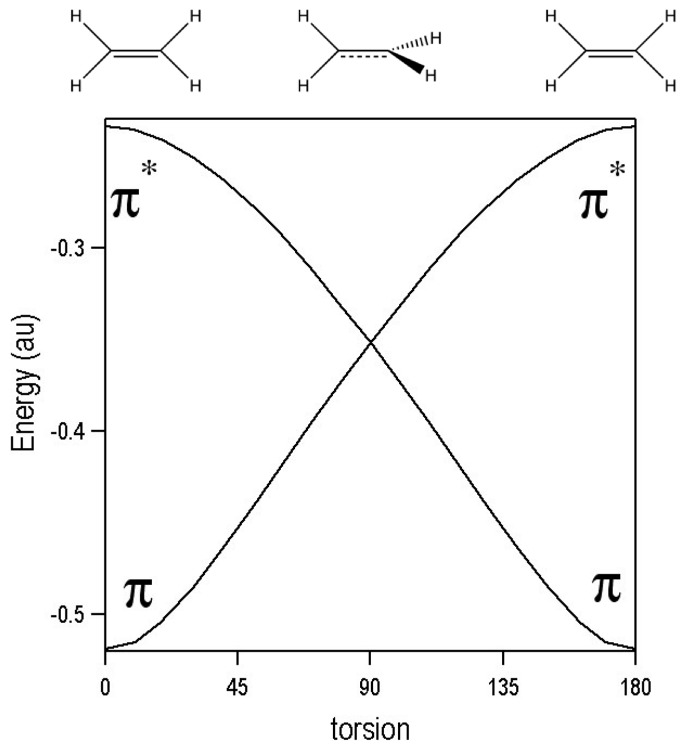

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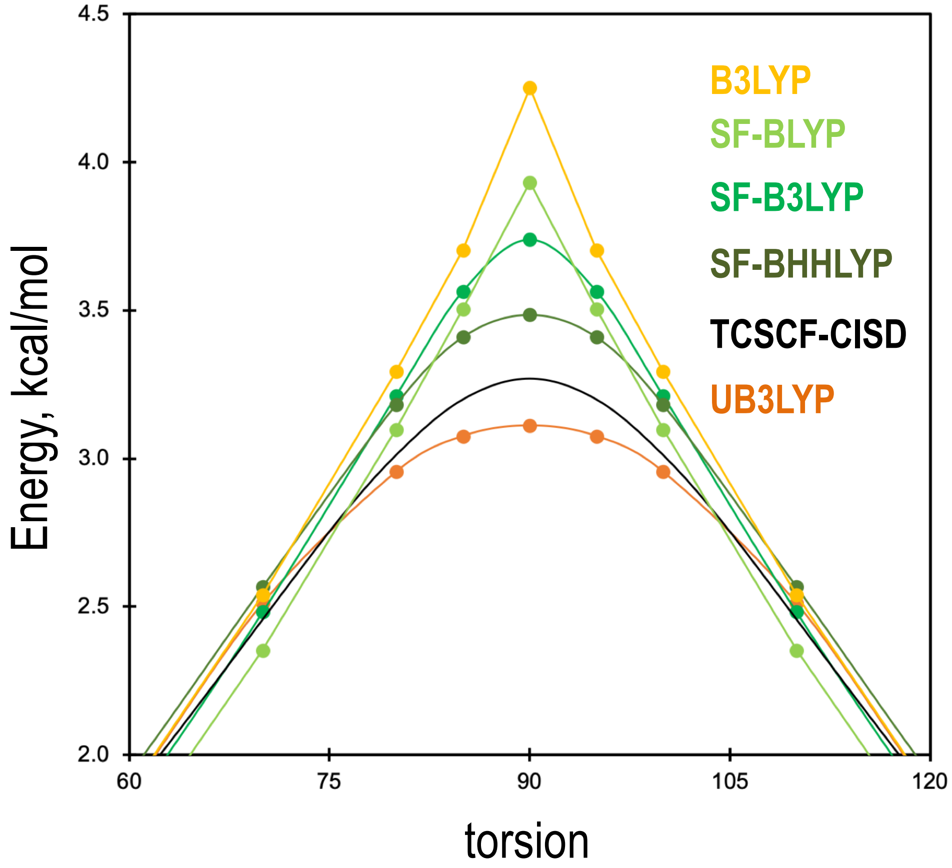
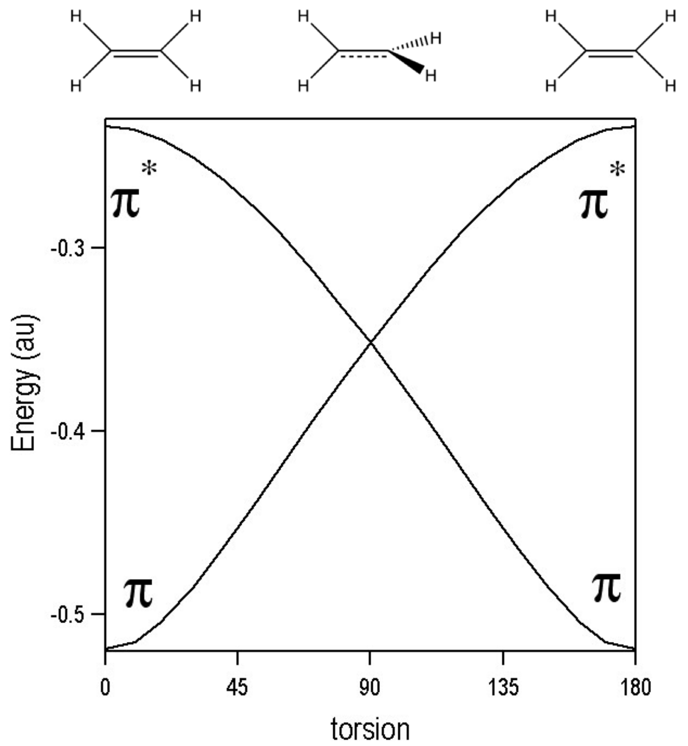


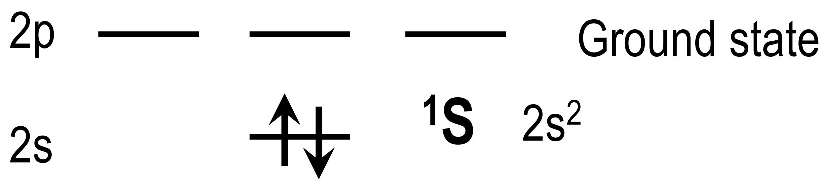
SF-TDDFT

- PES in chemical reactions
- Transition state characterization



Example: Excitation energies

Be atom



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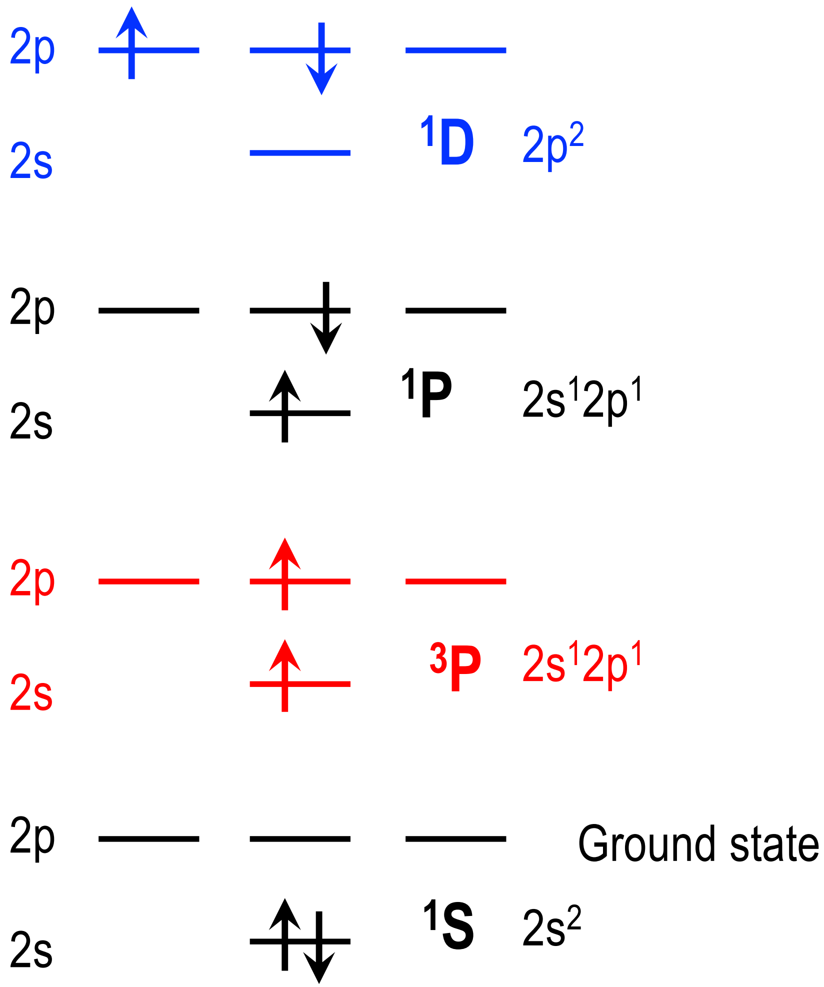

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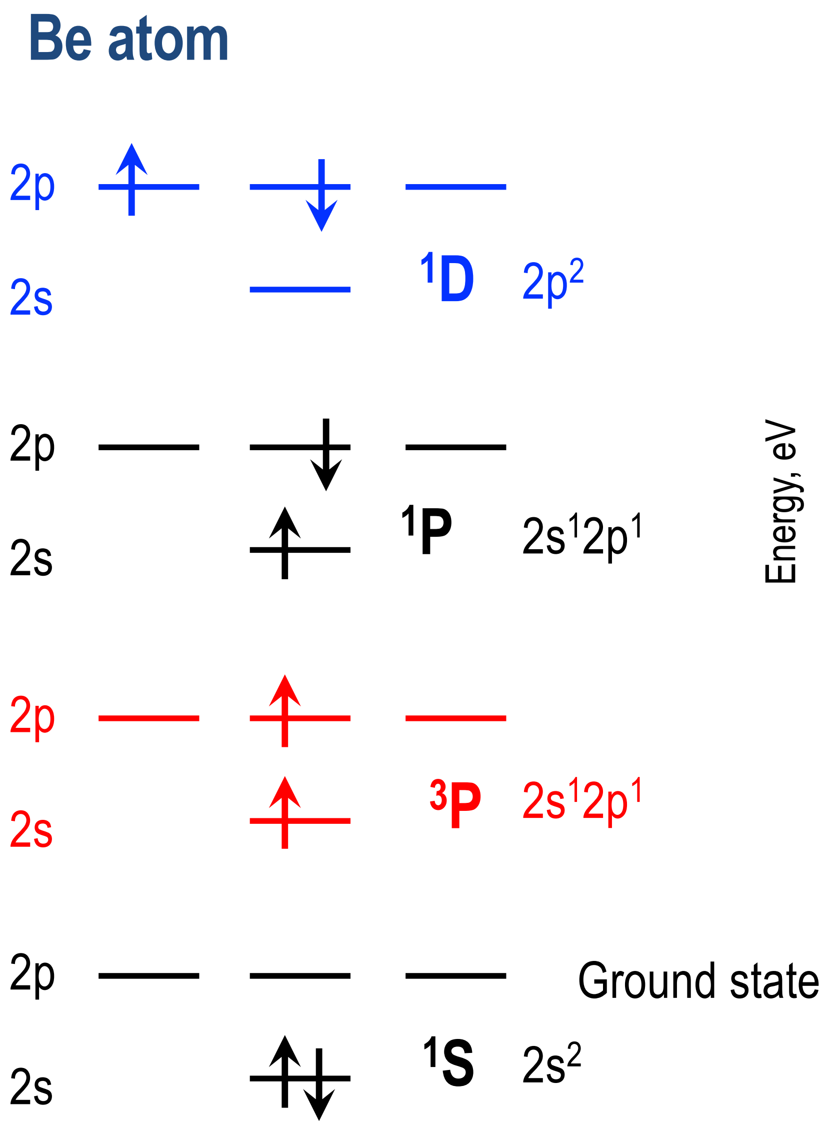

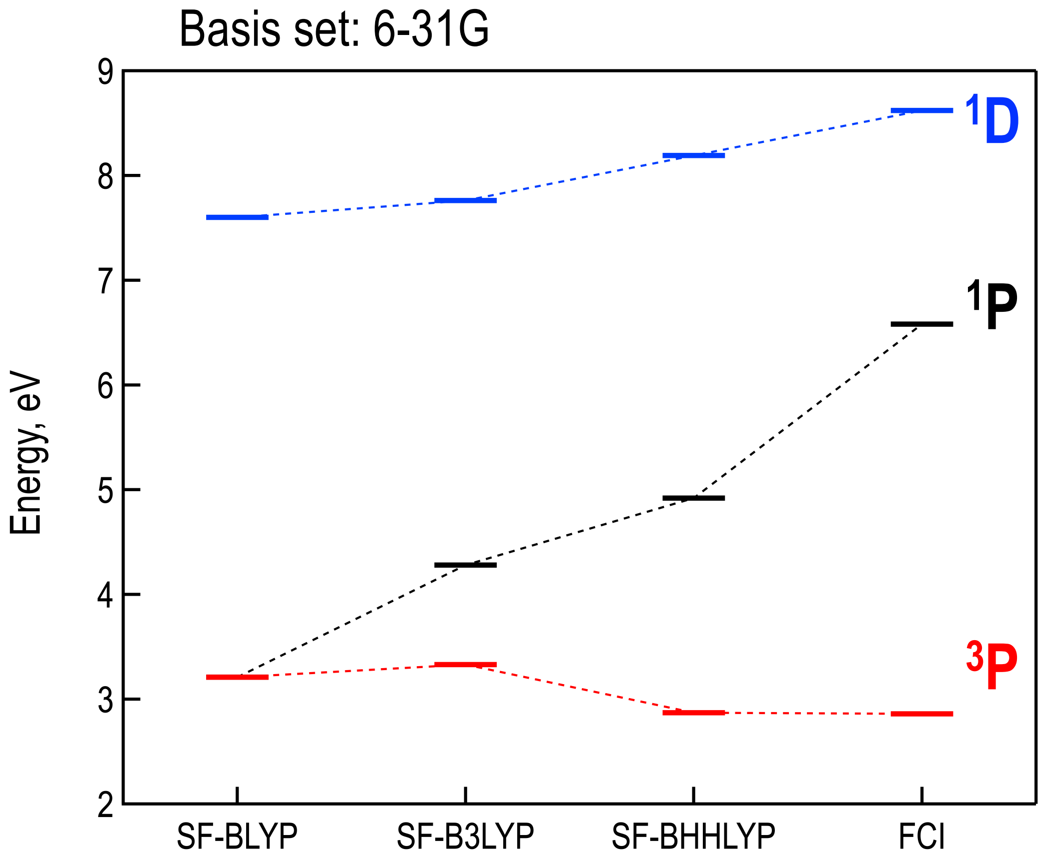

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Noncollinear SF-TDDFT

		XC potential
non-relativistic TDDFT	collinear	$v_{xc}^{C} = \frac{\delta E_{XC}[\rho]}{\delta \rho}$
relativistic TDDFT	noncollinear	$v_{xc}^{NC} = \frac{\delta E_{XC}[\rho]}{\delta \rho} + \frac{\delta E_{XC}[\rho]}{\delta s} \frac{\mathbf{m} \cdot \sigma}{s}$

s: spin density

m: magnetic vector

$\boldsymbol{\sigma}$: Pauli matrices

J. Chem. Phys. 121 (2004) 6658

Noncollinear SF-TDDFT

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J. Chem. Phys. 121 (2004) 6658

IF SOC = 0, α/β spin-orbitals ⇒ $v_{xc}^{NC} = v_{xc}^{C}$

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J. Chem. Phys. 121 (2004) 6658

IF SOC = 0, α/β spin-orbitals ⇒ $v_{xc}^{NC} = v_{xc}^{C}$ **BUT** TD perturbation ⇒ 1st order change in $\rho_{\alpha\beta}$ and v_{xc}^{NC} (spin-flip transition)

J. Chem. Phys. 121 (2004) 12191

Noncollinear SF-TDDFT

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J. Chem. Phys. 121 (2004) 12191

NC-SF-TDDFT

$$\begin{bmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B}^* & \mathbf{A}^*\end{bmatrix}\begin{bmatrix}\mathbf{X}\\ \mathbf{Y}\end{bmatrix}=\omega\begin{bmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & -\mathbf{1}\end{bmatrix}\begin{bmatrix}\mathbf{X}\\ \mathbf{Y}\end{bmatrix}$$

$x_{\bar{a}i}$: virtual-occupied $\quad i\in O(\alpha),\bar{a}\in V(\beta)$

$y_{a\bar{i}}$: occupied-virtual $\quad \bar{i}\in O(\beta),a\in V(\alpha)$

$$A_{i\bar{a},j\bar{b}}=\delta_{ij}\delta_{\bar{a}\bar{b}}(\epsilon_{\bar{a}}-\epsilon_i)+\frac{\partial F_{i\bar{a}}}{\partial P_{j\bar{b}}}$$

$$B_{i\bar{a},b\bar{j}}=\frac{\partial F_{i\bar{a}}}{\partial P_{b\bar{j}}}$$

$$\frac{\partial F_{i\bar{a}}}{\partial P_{j\bar{b}}}=(ia|\varpi|jb)=\int\phi_i(\mathbf{r})\phi_a(\mathbf{r})\frac{1}{\rho_\alpha-\rho_\beta}\left(\frac{\delta E_{XC}}{\delta\rho_\alpha}-\frac{\delta E_{XC}}{\delta\rho_\beta}\right)\phi_j(\mathbf{r})\phi_b(\mathbf{r})d\mathbf{r}$$

Noncollinear SF-TDDFT

		XC potential
non-relativistic TDDFT	collinear	$v_{xc}^{C} = \frac{\delta E_{XC}[\rho]}{\delta \rho}$
relativistic TDDFT	noncollinear	$v_{xc}^{NC} = \frac{\delta E_{XC}[\rho]}{\delta \rho} + \frac{\delta E_{XC}[\rho]}{\delta s}\frac{\mathbf{m}\cdot\sigma}{s}$

s: spin density
m: magnetic vector
$\boldsymbol{\sigma}$: Pauli matrices
J. Chem. Phys. 121 (2004) 6658

IF SOC = 0, α/β spin-orbitals ⇒ $v_{xc}^{NC} = v_{xc}^{C}$ **BUT** TD perturbation ⇒ 1st order change in $\rho_{\alpha\beta}$ and v_{xc}^{NC} (spin-flip transition)

J. Chem. Phys. 121 (2004) 12191

NC-SF-TDDFT

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

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$$\frac{\partial F_{i\bar{a}}}{\partial P_{j\bar{b}}} = (ia|\varpi|jb) = \int \phi_i(\mathbf{r})\phi_a(\mathbf{r})\frac{1}{\rho_\alpha - \rho_\beta}\left(\frac{\delta E_{XC}}{\delta \rho_\alpha} - \frac{\delta E_{XC}}{\delta \rho_\beta}\right)\phi_j(\mathbf{r})\phi_b(\mathbf{r})d\mathbf{r}$$

Pure xc-functional

$$A_{i\bar{a},j\bar{b}} = \delta_{ij}\delta_{\bar{a}\bar{b}}(\epsilon_{\bar{a}} - \epsilon_i) + (ia|\varpi|jb)$$

$$B_{i\bar{a},\bar{j}b} = (ia|\varpi|bj)$$

Hybrid xc-functional

$$A_{i\bar{a},j\bar{b}} = \delta_{ij}\delta_{\bar{a}\bar{b}}(\epsilon_{\bar{a}} - \epsilon_i) - c_{HF}(ij|f_H|\bar{a}\bar{b}) + (1 - c_{HF})(ia|\varpi|jb)$$

$$B_{i\bar{a},\bar{j}b} = -c_{HF}(ib|f_H|\bar{a}\bar{j}) + (1 - c_{HF})(ia|\varpi|bj)$$

Examples: NC-SF-TDDFT

Atomic excitation energies: **open-shell** ground state

Carbon, Oxygen, Silicon, Sulfur

Ground state: ^3P

Excited state: ^1D

Nitrogen, Phosphorus

Ground state: ^4S

Excited state: ^2D, ^2P

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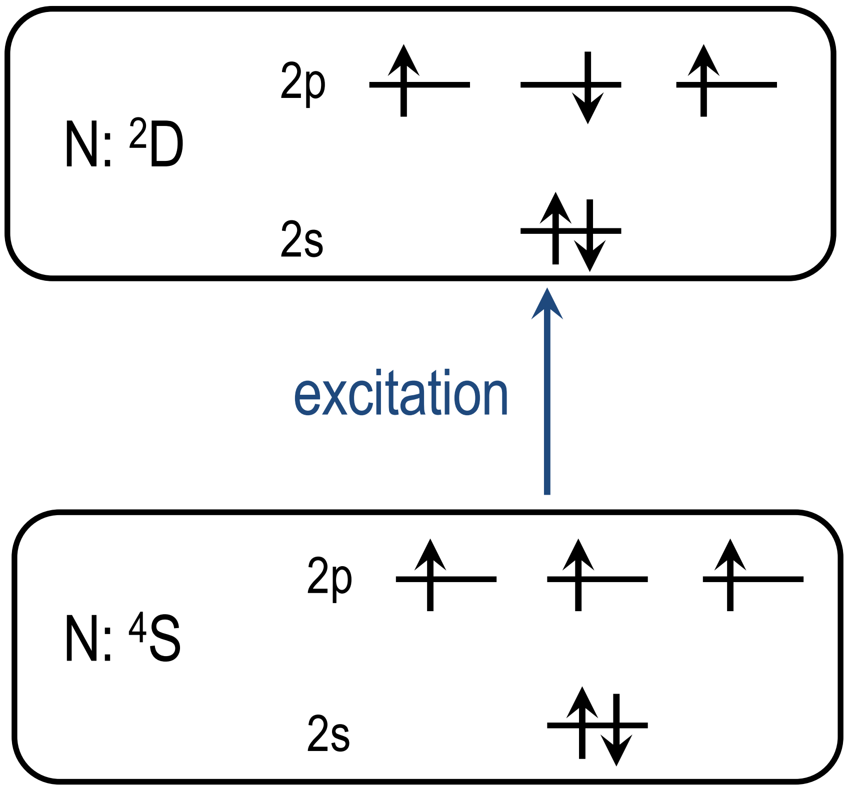

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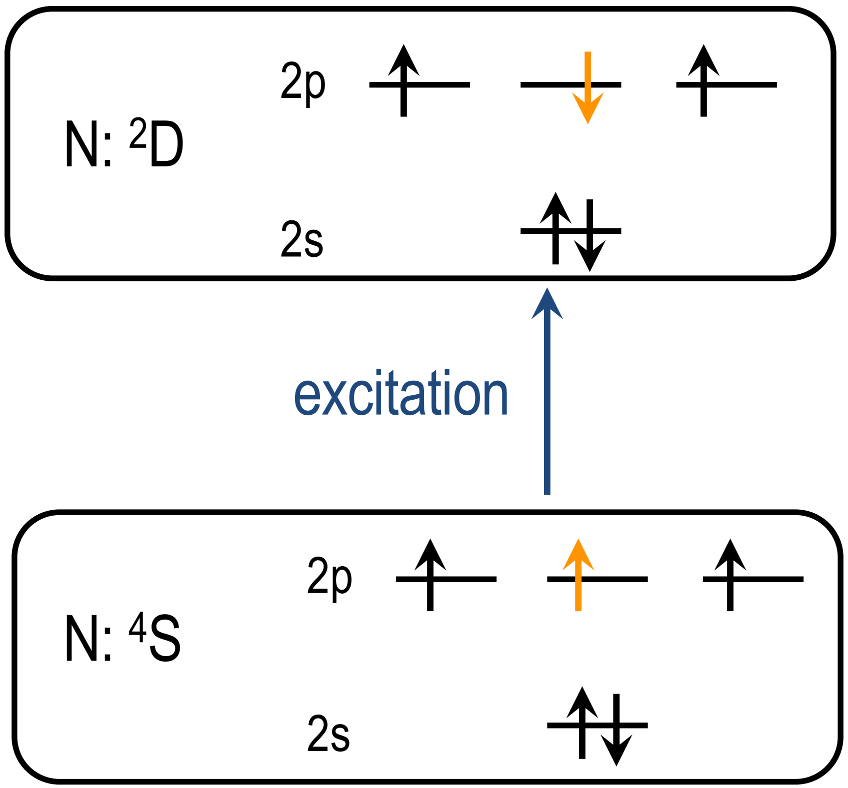

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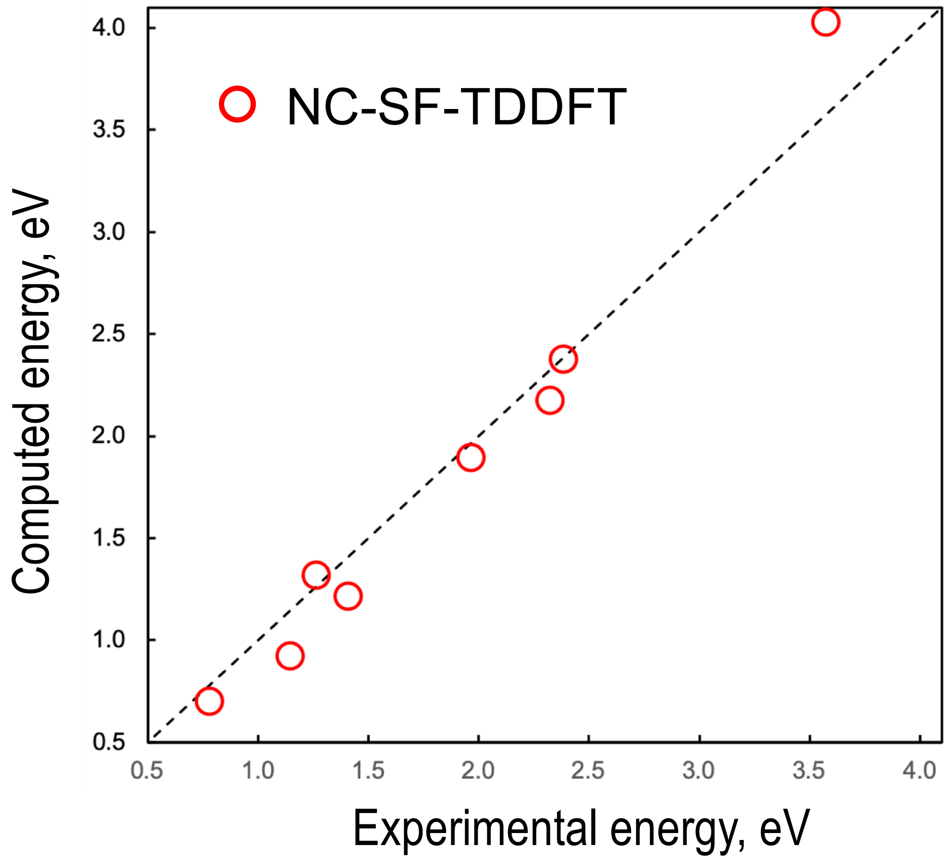
LDA/TZ2P

J. Chem. Phys. 121 (2004) 12191



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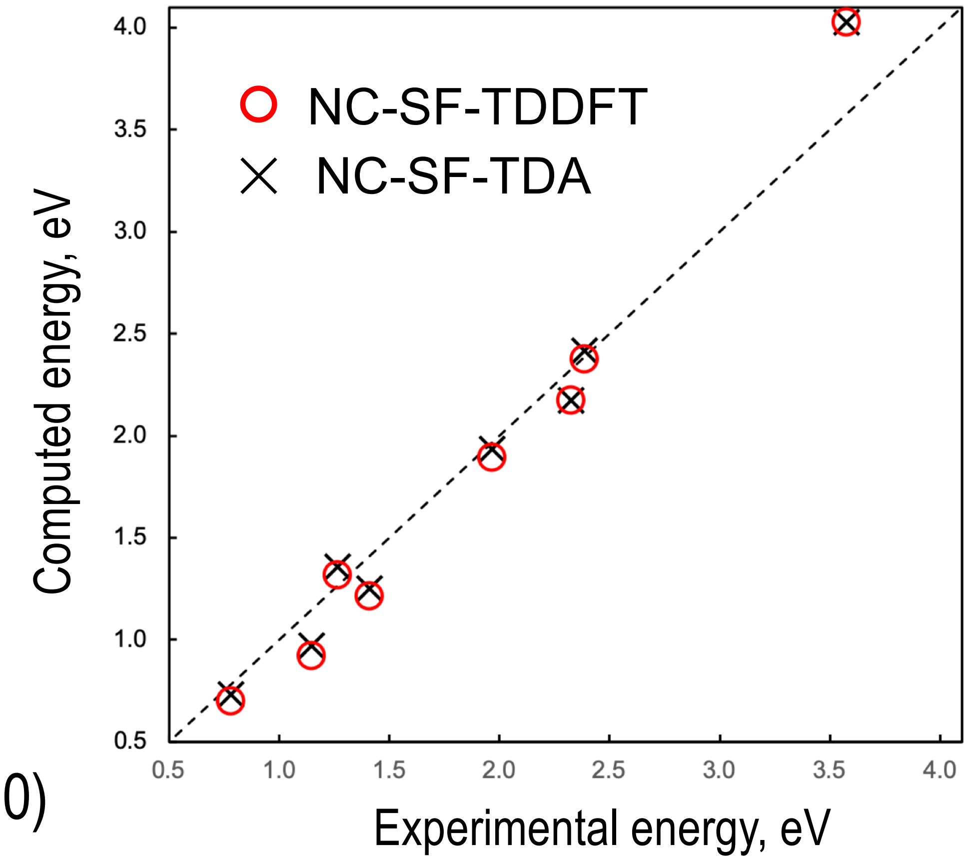


NC-SF-TDDFT vs. NC-SF-TDA (B = 0)

TDA in SF-TDDFT ✓

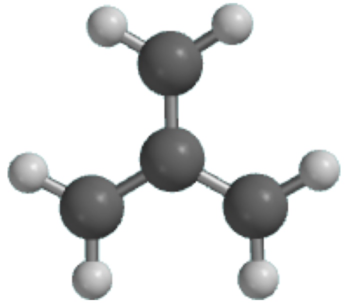
$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix}$$

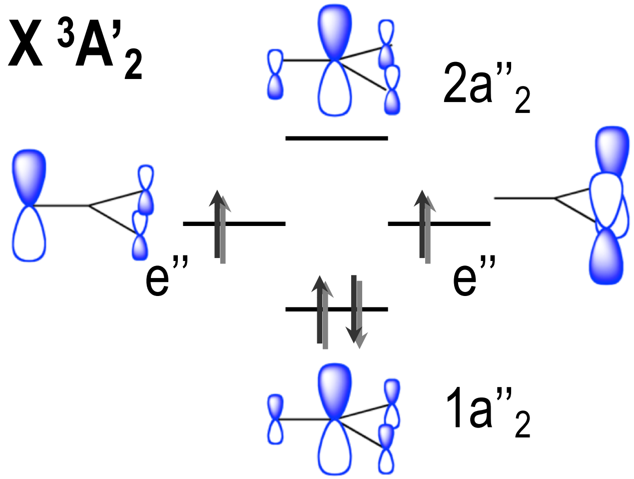
Examples: NC-SF-TDDFT

TMM diradical

Geometry: D_{3h}

Ground state: $^3A'_2$





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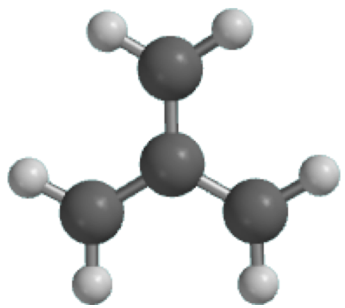
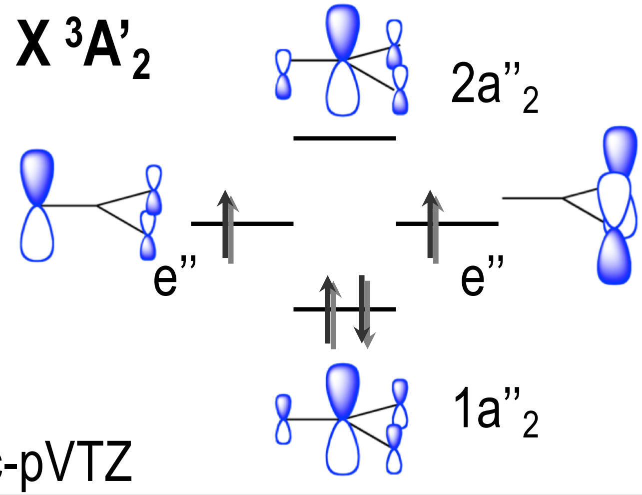
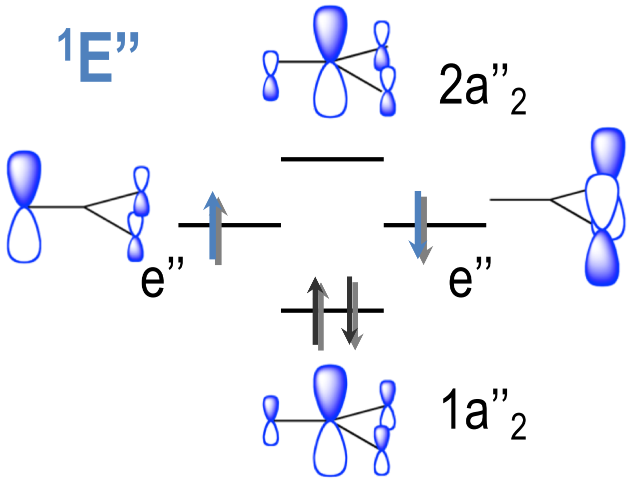
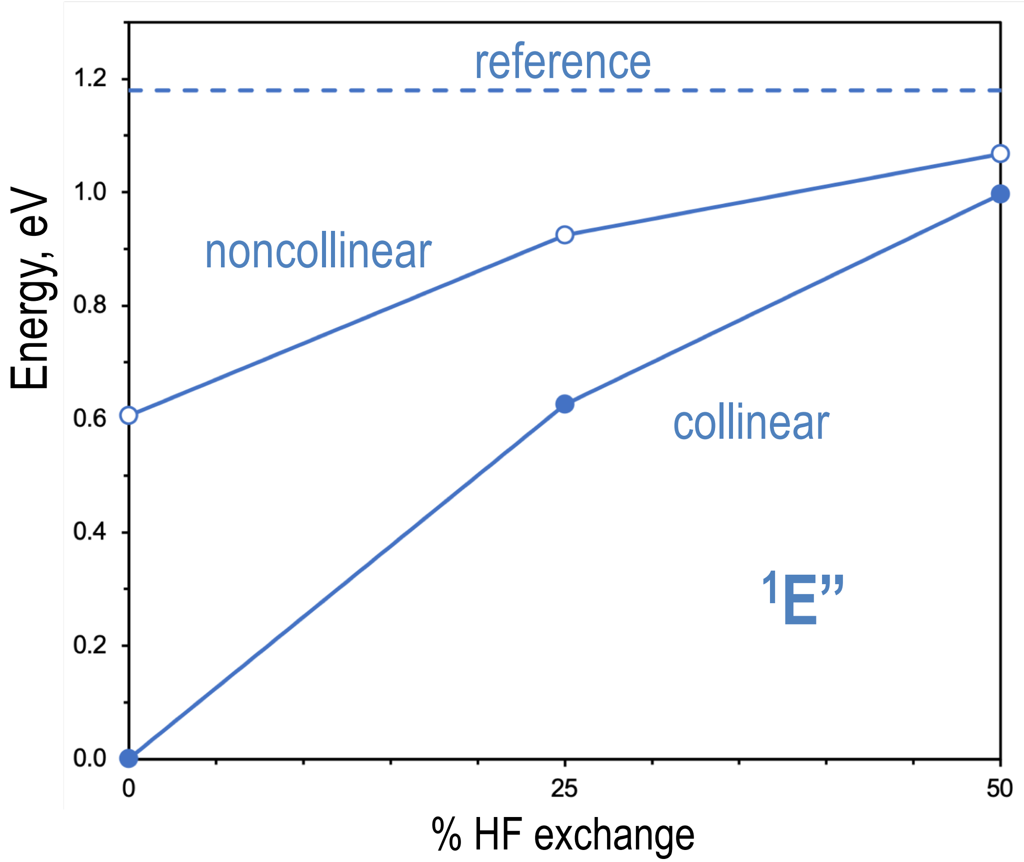




SF-PBE/cc-pVTZ





J. Chem. Phys. 117 (2002) 4694

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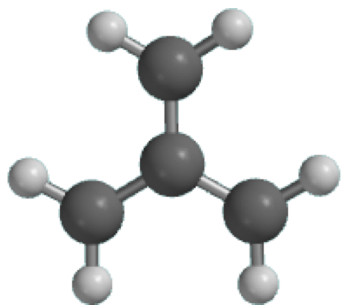

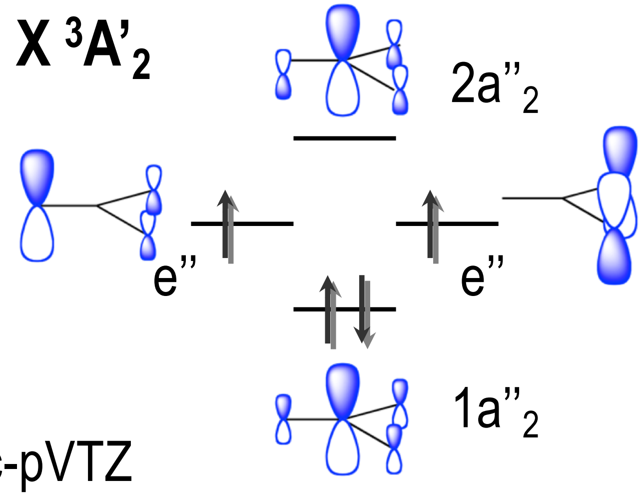

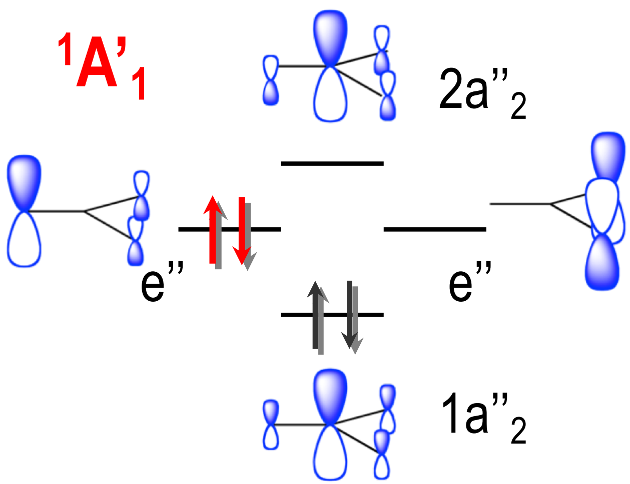

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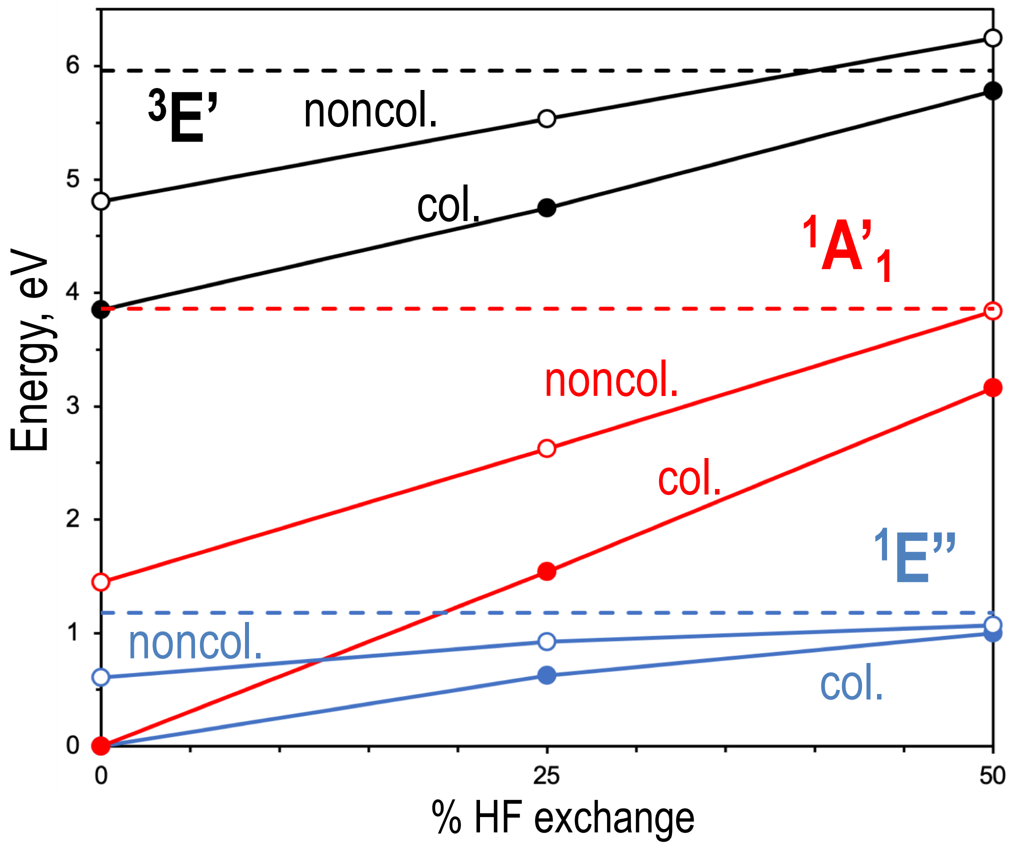

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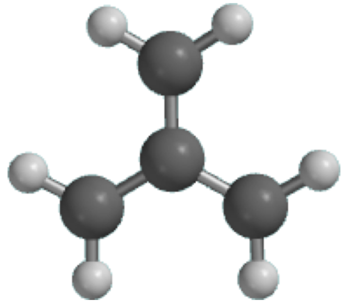
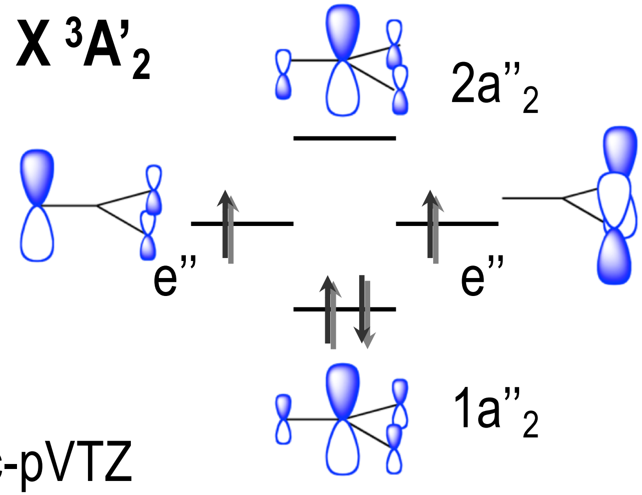
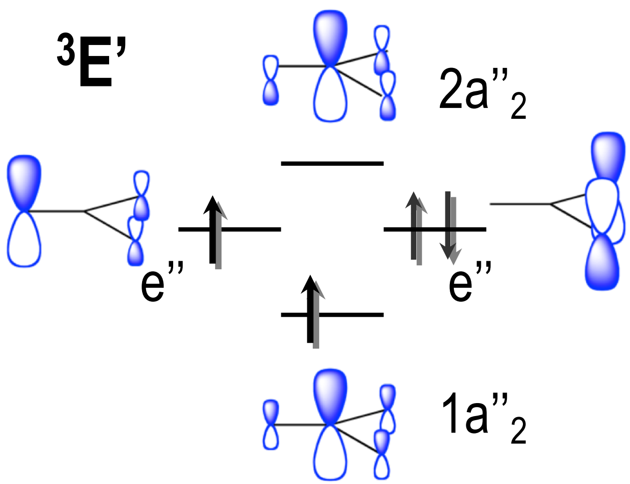
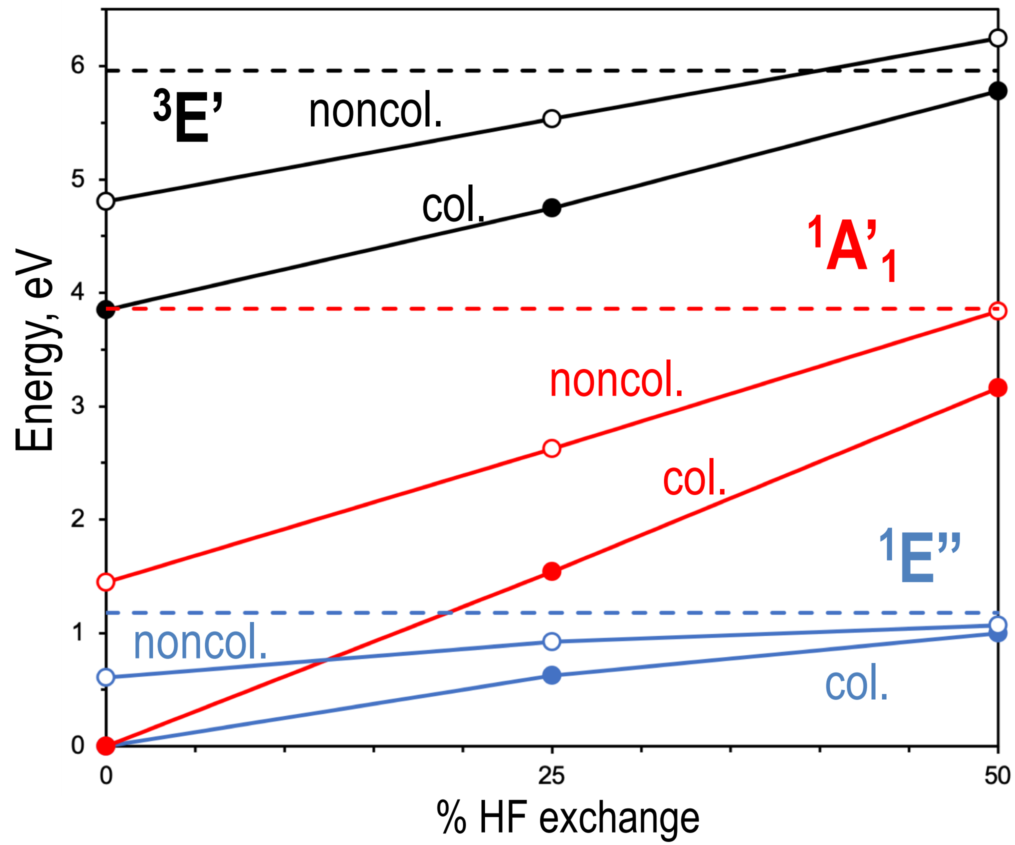






HF exchange in NC-SF-TDDFT ✓

SF-PBE/cc-pVTZ

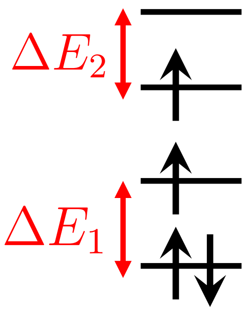


J. Chem. Phys. 117 (2002) 4694

Spin contamination in SF-TDDFT

Sources of spin contamination

- Spin-unrestricted KS reference



KS triplet ill-defined

⇓

$\langle \hat{S}^2 \rangle > 2.0$

ΔE_1 and/or ΔE_2 small

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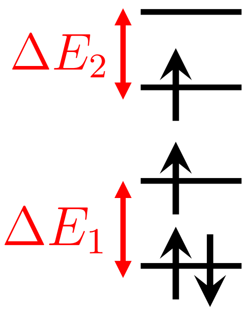

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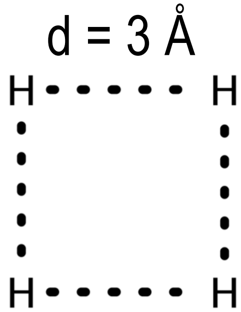

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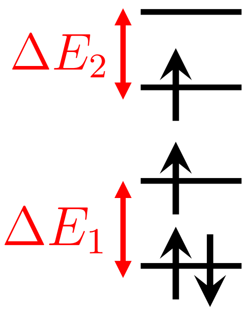

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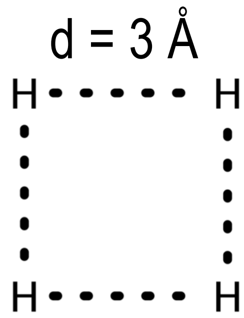

4 electrons in
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FCI

state	E, meV
S_0	0
T_1	24
T_2	50
S_1	64
T_3	76
Q_1	87

SF-PBE50

$\langle S^2 \rangle$	E, meV
1.02	0
2.22	2912
1.00	2953
0.99	4695
0.85	5924
...	...

$\langle S^2 \rangle_{ref} = 2.26$

Spin contamination in SF-TDDFT

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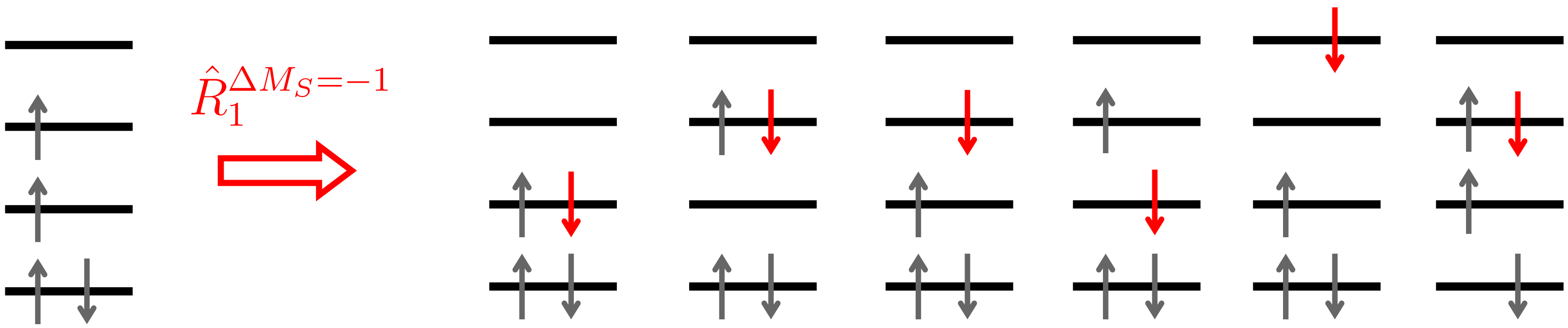
- Spin-incompleteness of SF (1-elec) operator



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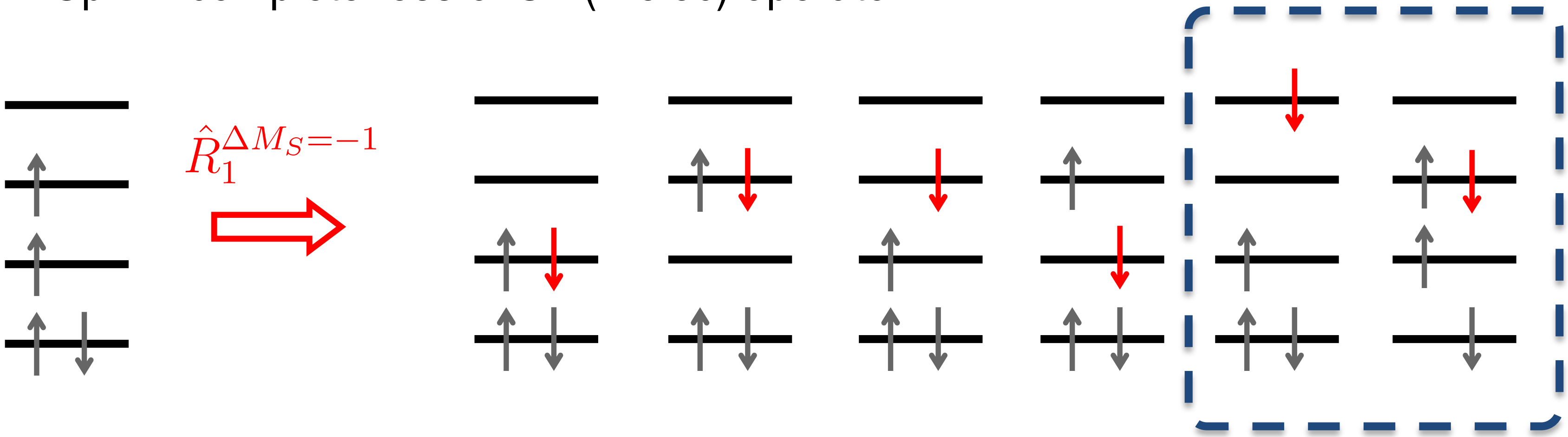

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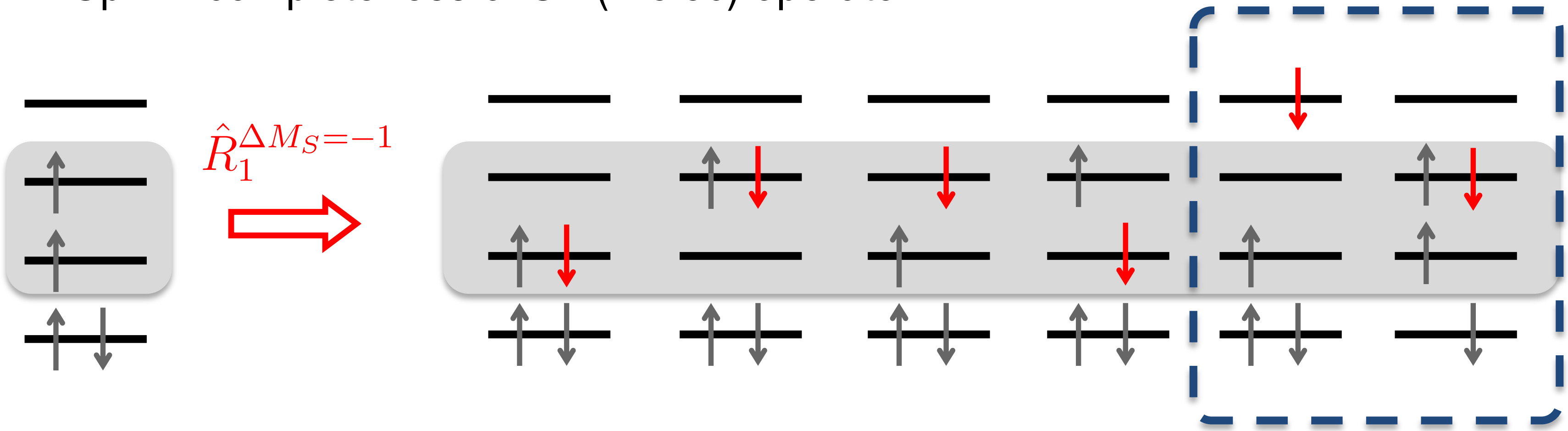

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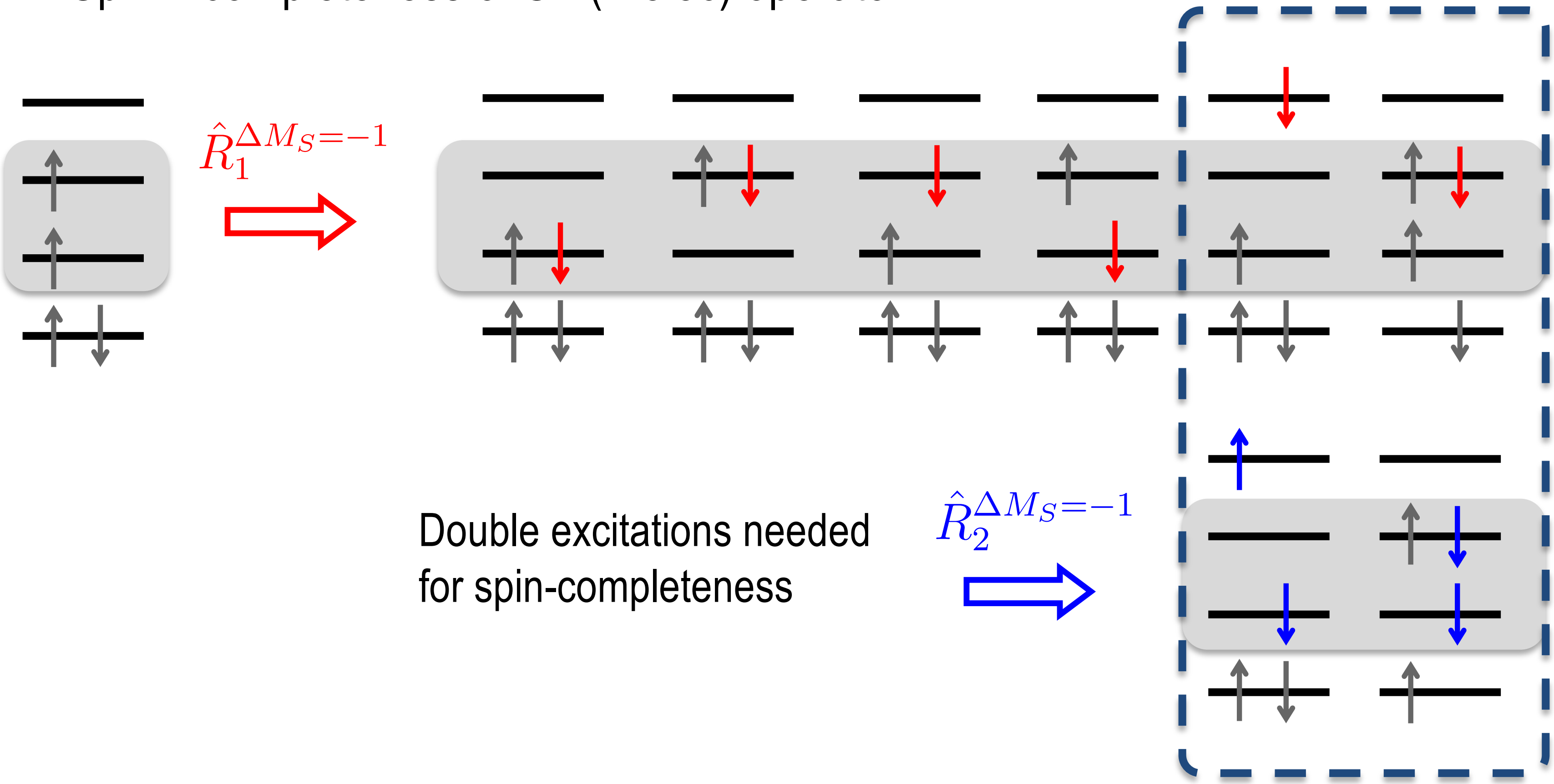

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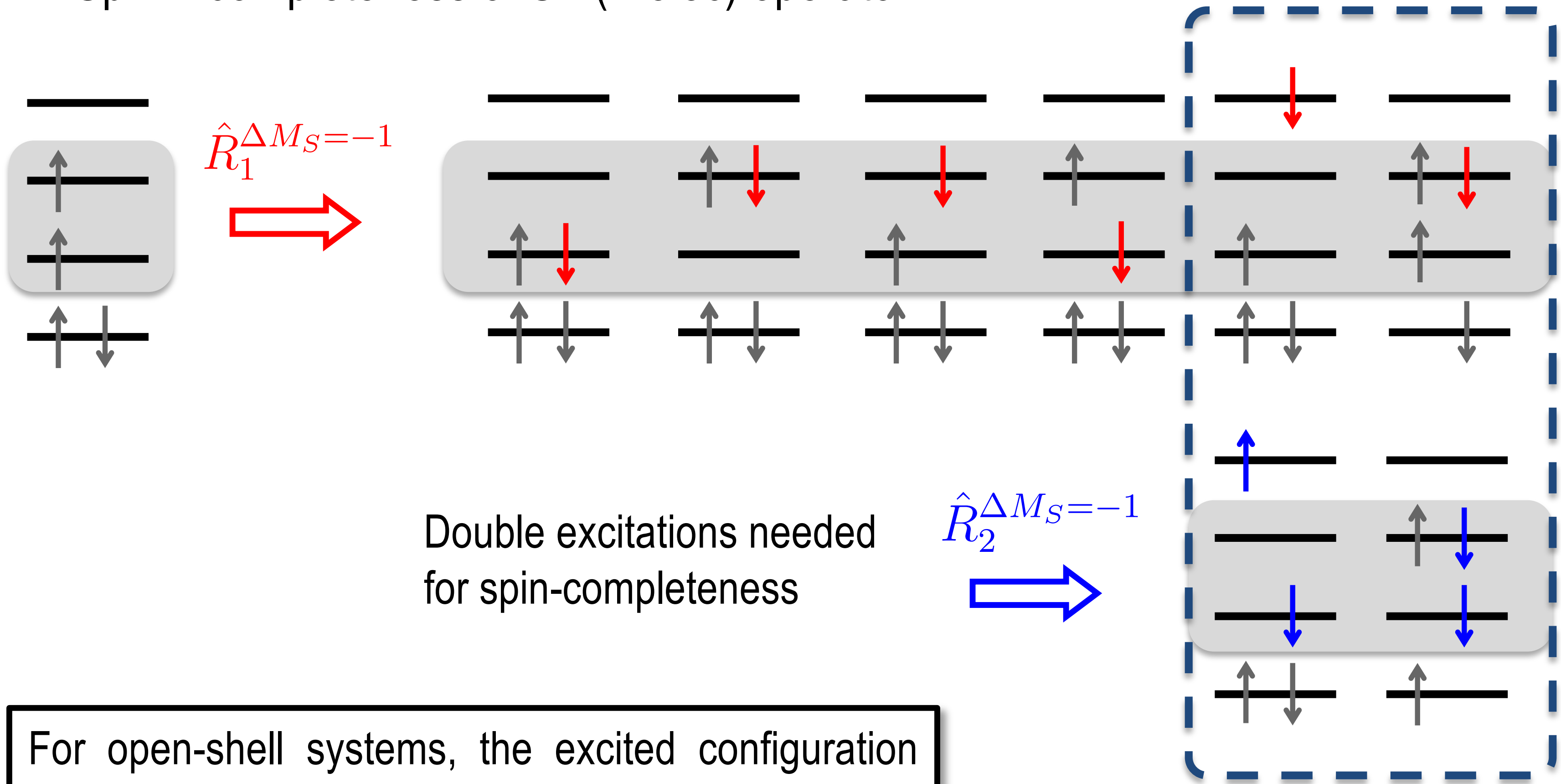

For open-shell systems, the excited configuration space cannot be made spin-adapted within the truncated rank.

Spin contamination in SF-TDDFT

Spin adaptation in SF-TDDFT

higher-rank
excitations

$\hat{R}_2, \hat{R}_3, ...$

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$\hat{R}_2, \hat{R}_3, \ldots$

✓ WFT

✗ TDDFT ⇐ Adiabatic approximation

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Spin adaptation in SF-TDDFT

higher-rank excitations $\hat{R}_2, \hat{R}_3, \ldots$

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- "Dressed" TDDFT ⇐ corrections to AA (frequency dependent XC kernel)

J. Chem. Phys. 122 (2005) 054111

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  J. Chem. Phys. 122 (2005) 054111

- "Transfer rule"

  J. Chem. Phys. 133 (2010) 064106
  J. Chem. Phys. 149 (2018) 104101

  SA-TDHF → SA-TDDFT

$$F_{pq} \rightarrow F_{pq}^{KS}$$

$$(pq|sr) - (pr|sq) \rightarrow (pq|sr) + (pq|f_{xc}|sr)$$

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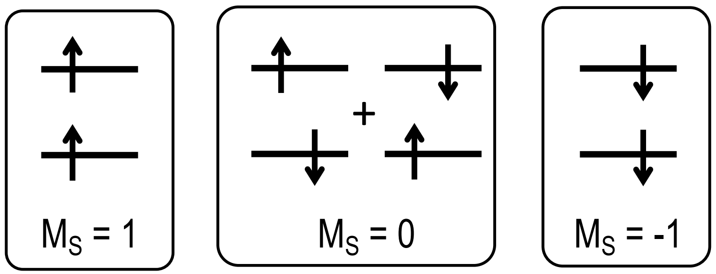
tensor/mixed reference



generalized excitations

$$\hat{R}_1^{\Delta M_S = -1,0,+1}$$

Wrapping up

- SF-TDDFT near degeneracies and double excitations within DFT
- Ground and excited state method
- Collinear kernel requires exact exchange (%50)
- Noncollinear kernel naturally couples SF excitations
- Computational cost scales as TDDFT
- Spin contamination: reference and target states
- Limited to low-lying states