Basic aspects of the spin-Restricted Ensemble-referenced Kohn-Sham (REKS) method

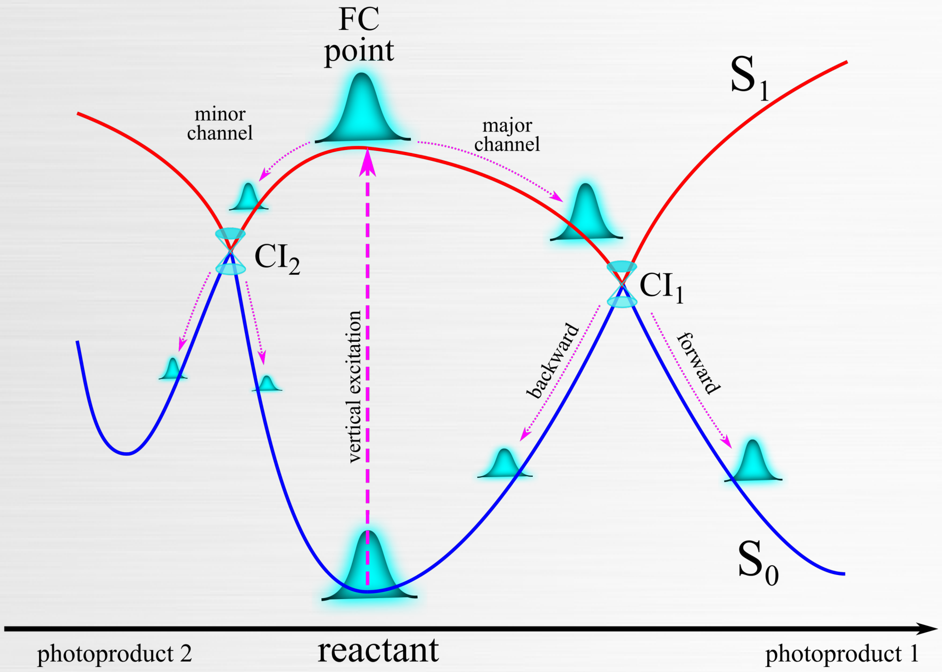
Part 2

Excited States

Content

- Excited states and non-adiabatic dynamics
    - conical intersections
    - quantum chemical methods for non-adiabatic dynamics
    - KS-DFT and non-adiabatic dynamics
- DFT for excited states
    - time-dependent DFT
    - ensemble DFT for excited states
- Practical implementation of eDFT for excited states
    - state-averaged REKS method
        - benchmarks
        - examples of excited state calculations
        - REKS and conical intersections
        - extensions of REKS for excited states

Non-Adiabatic Molecular Dynamics (NAMD)



Ultrafast (<1ps) phenomena in the excited states:

- excitation energy transfer
- photo-chemical reactions

Multi-state dynamics

Goes beyond the BO approximation

Non-adiabatic couplings btw states

Population transfer btw states

Input from *ab initio* calculations

- energies
- forces
- non-adiabatic couplings
- Hessians

Conical Intersections (CIs) – true crossings btw electronic state of the same symmetry

CIs – efficient funnels for population transfer

Quantum vs Semi-classical NAMD

QMD:

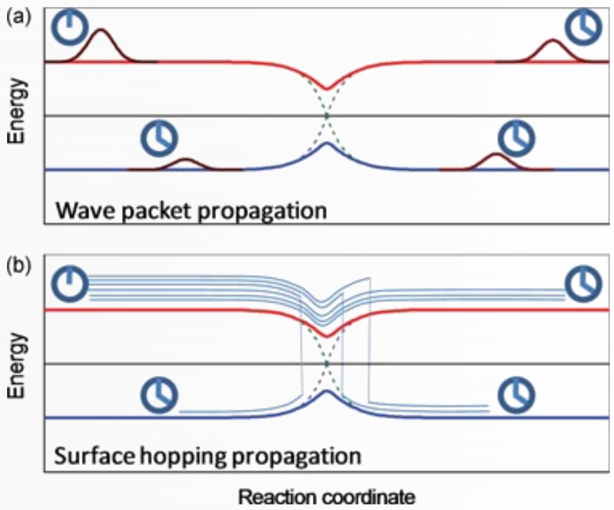
$$-i\partial_t \Phi(\mathbf{Q},t) = \left\{\sum_k -\frac{\vec{\nabla}_k^2}{2M_k} + \mathbf{V}(\mathbf{Q})\right\}\Phi(\mathbf{Q},t)$$

$$\mathbf{V}(\mathbf{Q}) = \frac{1}{2}\,tr\,\mathbf{V}(\mathbf{Q}) + \begin{pmatrix} v_1(\mathbf{Q}) & v_2(\mathbf{Q}) \\ v_2(\mathbf{Q}) & -v_1(\mathbf{Q}) \end{pmatrix}$$

Input:

electronic energies, forces, Hessians,
non-adiabatic couplings

$$\mathbf{F}_{kl} = \left\langle \Psi_k(\mathbf{r};\mathbf{Q}) \middle| \vec{\nabla}_{\mathbf{Q}} \Psi_l(\mathbf{r};\mathbf{Q}) \right\rangle_{\mathbf{r}}$$



TSH dynamics: Solves classical nuclear EOM

Initial sampling → Classical transport → Surface hopping → Final evaluation

sampling of the Wigner function at T

$$\dot{\mathbf{P}} = -\vec{\nabla}_{\mathbf{Q}} V(\mathbf{Q})$$

$$\mathbf{P} = \dot{\mathbf{Q}}$$

$$E_k, \vec{\nabla}_{\mathbf{Q}} E_k, \mathbf{F}_{kl}$$

probability depends on $\mathbf{F}_{kl}$

statistical averaging of observables

Egorov theorem: $W(\Phi(t)) \approx W(\Phi(0)) \circ f_t$ f_i – flow (classical transport)

Input for NAMD simulations

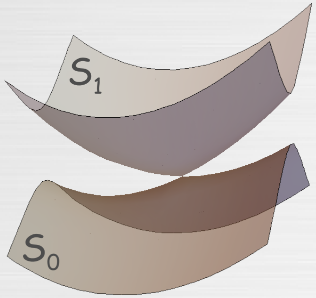
Electronic energies (PESs), forces, non-adiabatic couplings (NACs)

$$E_k(\mathbf{Q}),\quad \vec{\nabla}_{\mathbf{Q}} E_k,\quad \mathbf{F}_{kl}$$

Correct topography of PESs: include all types of electron correlation, dynamic & static

static correlation → multi-reference effects

Correct topology of conical intersections; double cone, not linear crossing



non-adiabatic coupling (NAC):

$$\left\langle S_0 \middle| \vec{\nabla} S_1 \right\rangle = \frac{\left\langle S_0 \middle| \vec{\nabla}\hat{H} \middle| S_1 \right\rangle}{E_1 - E_0}$$

becomes singular at a CI

transition probability (Landau-Zener):

$$P(S_1 \to S_0) = \exp\left[-\frac{\pi}{4\hbar} \cdot \frac{E_1 - E_0}{\vec{\mathrm{V}} \cdot \left\langle S_0 \middle| \vec{\nabla} S_1 \right\rangle} \right]$$

reaches maximum at a CI

Electronic states must be *coupled* with each other

uncoupled states – wrong topology (linear crossing)

Conical intersections

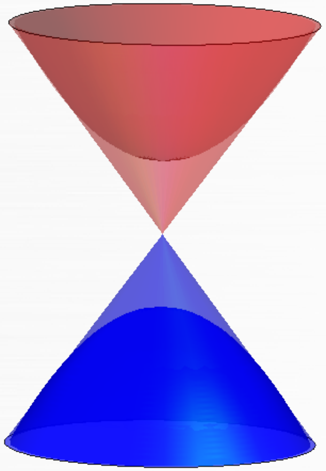
True crossings btw 2 (or more) states of the same symmetry

Occur in the space of N-2 internal dof's (CI seam)

diabatic

adiabatic

$$\begin{vmatrix} E_0 & h_{01} \\ h_{01} & E_1 \end{vmatrix} \Rightarrow \begin{vmatrix} E_0 & 0 \\ 0 & E_1 \end{vmatrix}$$



Conical Intersection

$$E_0 = E_1$$

$$h_{01} = 0$$

PESs depend *linearly* on displacement

topology of a double cone

Avoided Crossing

$$E_0 = E_1$$

$$h_{01} \neq 0$$

quadratic dependence

CI's branching plane

$$\vec{x}_1 = \tfrac{1}{2}\vec{\nabla}(E_0 - E_1) \qquad \vec{x}_1 = \tfrac{1}{2}\vec{\nabla}(E_0 - E_1)$$

$$\vec{x}_2 = \vec{\nabla} h_{01} \qquad \vec{x}_2 = \left\langle \Psi_0 \middle| \vec{\nabla}\hat{H} \middle| \Psi_1 \right\rangle$$

define all displacements lifting the degeneracy

Electronic states must be *coupled* with each other

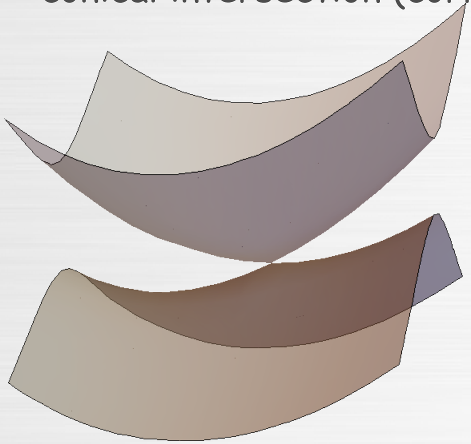
uncoupled states – wrong topology (linear crossing)

Importance of Conical Intersections

Proper methodology

e.g., MS-CASPT2

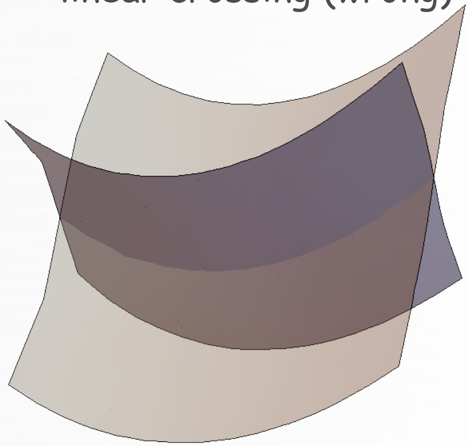
conical intersection (correct)



Improper methodology

e.g., TD-DFT

linear crossing (wrong)



non-adiabatic coupling:

$$\left\langle S_0 \middle| \vec{\nabla} S_1 \right\rangle = \frac{\left\langle S_0 \middle| \vec{\nabla} \hat{H} \middle| S_1 \right\rangle}{E_1 - E_0}$$

singular in the
space of N-2 dof's

singular in the
space of N-1 dof's

correct dynamics

wrong dynamics

JCP, 155, 124111 (2021)

Computational methods for direct dynamics

Should include dynamic and static correlation

Should correctly describe CIs and NACs

type	method(s)	pro	contra
all state methods	full CI (FCI)	good for everything	not affordable
multi-state methods	SA-CASSCF MS-PT2 MRCI(SD)	yield correct CI topology; appropriate for NAMD	no dynamic correlation underestimate dynamic correlation not size-consistent
single-state methods	CASSCF CASPT2	inappropriate for NAMD	wrong CI topology; not a double cone
response methods	TD-DFT ADC(n) CCn	not generally appropriate for NAMD	no coupling btw the reference (ground) state and response (excited) states; wrong topology of S_1/S_0 CIs

DFT and excited states

DFT – ground state theory (H-K theorems)

Excited states – from response to time-dependent perturbation (TD-DFT)

Disadvantages of standard TD-DFT:

- Limited class of excitations can be treated
    - no multiple excitations
- No coupling btw the ground state and response states
    - no avoided crossings
    - no conical intersections
- Insufficient orbital relaxation
    - poor charge transfer (CT) excitations
- Single-reference ground state
    - poor excitations of strongly correlated systems

KS DFT vs. Ensemble DFT

	KS DFT	**Ensemble DFT**
Applicability:	ground state only	ground and excited states
Existence of V_{xc}:	assumed	rigorously proved
Non-interacting reference:	single-determinant; fixed occupations	multi-reference; fractional occupations
Bond breaking:	brakes symmetry and/or wrong	doesn't brake symmetry
Excited states:	perturbational only (response formalism)	perturbational (response) and variational (ΔSCF)
S_0/S_1 PES crossings (avoided and real):	no	yes
multiple excitations:	no	yes

Variational principle for excited states

variational principle: $\widetilde{E}(\boldsymbol{\lambda})=\dfrac{\langle\Phi(\boldsymbol{\lambda})|\hat{H}|\Phi(\boldsymbol{\lambda})\rangle}{\langle\Phi(\boldsymbol{\lambda})|\Phi(\boldsymbol{\lambda})\rangle};\quad \boldsymbol{\lambda}=\{\lambda_1,\lambda_2,\ldots\};\quad \dfrac{\partial\widetilde{E}(\boldsymbol{\lambda})}{\partial\lambda_n}=0,\ \forall\lambda_n$

let: $|\,\theta_0(\boldsymbol{\lambda})\rangle=\Phi(\boldsymbol{\lambda})\big/\langle\Phi(\boldsymbol{\lambda})|\,\Phi(\boldsymbol{\lambda})\rangle^{1/2}=\sum_k|\,k\,\rangle\langle\,k\,|\,\theta_0(\boldsymbol{\lambda})\rangle$ where $|\,k\,\rangle$ eigenfunctions of $\hat{H}$

then $\widetilde{E}(\boldsymbol{\lambda})=\sum_{k,l}\langle\,\theta_0(\boldsymbol{\lambda})\,|\,l\,\rangle\langle\,l\,|\hat{H}|\,k\,\rangle\langle\,k\,|\,\theta_0(\boldsymbol{\lambda})\rangle=\sum_k\left|\langle\,\theta_0(\boldsymbol{\lambda})\,|\,k\,\rangle\right|^2E_k=E_0+\sum_k\left|\langle\,\theta_0(\boldsymbol{\lambda})\,|\,k\,\rangle\right|^2(E_k-E_0)\geq E_0$

---

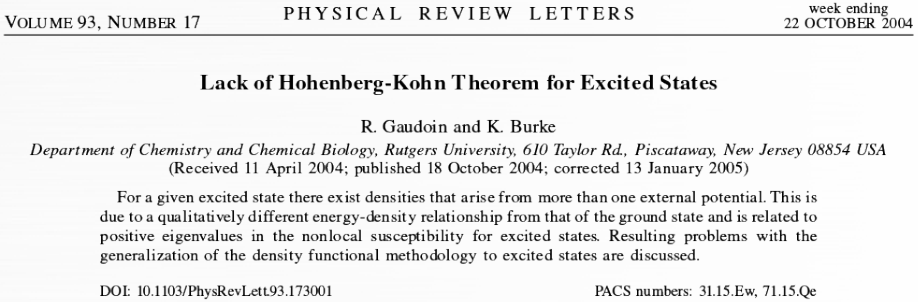
ground state $|\,\theta_0(\boldsymbol{\lambda})\rangle$, excited state $|\,\theta_1(\boldsymbol{\lambda})\rangle$

under constraint $\langle\,\theta_0(\boldsymbol{\lambda})\,|\,\theta_1(\boldsymbol{\lambda})\rangle=0$

$$\widetilde{E}_1(\boldsymbol{\lambda})=\sum_k\left|\langle\,\theta_1(\boldsymbol{\lambda})\,|\,k\,\rangle\right|^2E_k=0+E_1+\sum_{k>1}\left|\langle\,\theta_1(\boldsymbol{\lambda})\,|\,k\,\rangle\right|^2(E_k-E_1)\geq E_1$$

Must know the lower state(s) first!

$$\langle\,\theta_j(\boldsymbol{\lambda})\,|\,\theta_i(\boldsymbol{\lambda})\rangle=0,\ \forall j<i$$



VOLUME 93, NUMBER 17 PHYSICAL REVIEW LETTERS week ending 22 OCTOBER 2004

Lack of Hohenberg-Kohn Theorem for Excited States

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(Received 11 April 2004; published 18 October 2004; corrected 13 January 2005)

For a given excited state there exist densities that arise from more than one external potential. This is due to a qualitatively different energy-density relationship from that of the ground state and is related to positive eigenvalues in the nonlocal susceptibility for excited states. Resulting problems with the generalization of the density functional methodology to excited states are discussed.

DOI: 10.1103/PhysRevLett.93.173001 PACS numbers: 31.15.Ew, 71.15.Qe

Linear-response TD-DFT for excited states

Not interested in time dependence, but in frequency dependence!

Heisenberg equations of motion: $-i\frac{d\hat{O}}{dt}=\left[\hat{H},\hat{O}\right]$

time domain → frequency domain $\frac{d}{dt} \to -i\omega$

$$\omega\hat{O}=\left[\hat{H},\hat{O}\right] \qquad \hat{O}=\sum_{i,a}X_{ia}\,\hat{a}^{\dagger}\,\hat{i}+\sum_{j,b}Y_{jb}\,\hat{j}^{\dagger}\,\hat{b}$$

excitation/de-excitation amplitudes

only one-electron transitions are included

$$\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B}^{*} & \mathbf{A}^{*}\end{pmatrix}\begin{pmatrix}\vec{X}\\ \vec{Y}\end{pmatrix}=\begin{pmatrix}\boldsymbol{\omega} & \mathbf{0}\\ \mathbf{0} & -\boldsymbol{\omega}\end{pmatrix}\begin{pmatrix}\vec{X}\\ \vec{Y}\end{pmatrix}$$

linear-response TD-HF/TD-DFT equations

$$A_{ia,jb}=\delta_{ij}\,\delta_{ab}\left(\varepsilon_a-\varepsilon_i\right)+\left(i\,a\middle|f_{Hxc}\middle|b\,j\right)-\left(i\,j\middle|f_{Hxc}\middle|b\,a\right)$$

electron-hole interaction

$$B_{ia,jb}=\left(i\,a\middle|f_{Hxc}\middle|\,j\,b\right)-\left(i\,b\middle|f_{Hxc}\middle|\,j\,a\right)$$

coupling btw excitations and de-excitations

Tamm-Dancoff approximation ($\mathbf{B}=0$) $\mathbf{A}\,\vec{X}=\boldsymbol{\omega}\,\vec{X}$ Hermitian eigenvalue equation

TD-DFT and conical intersections

TD-DFT – response of the ground state to obtain excited states

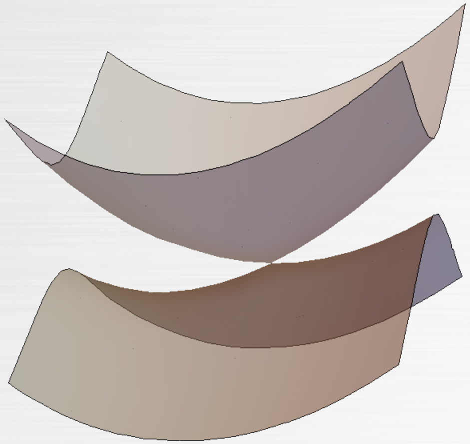
no interaction btw the ground and excited states (Brillouin’s theorem)

no S_1/S_0 avoided crossings

no S_1/S_0 conical intersections (real crossings)

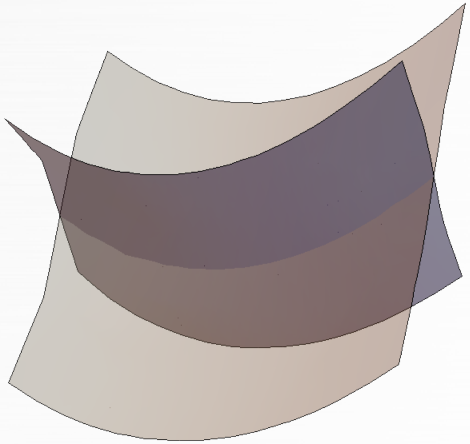
Brillouin’s theorem $\left\langle \Phi_0 \middle| \hat{H} \middle| \Phi_i^a \right\rangle = 0$ reference state (S_0) is uncoupled from response states (S_n)

correct conical intersection



correct dynamics

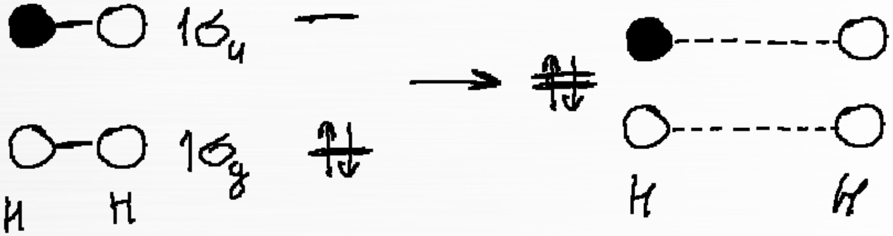
TD-DFT (linear crossing)



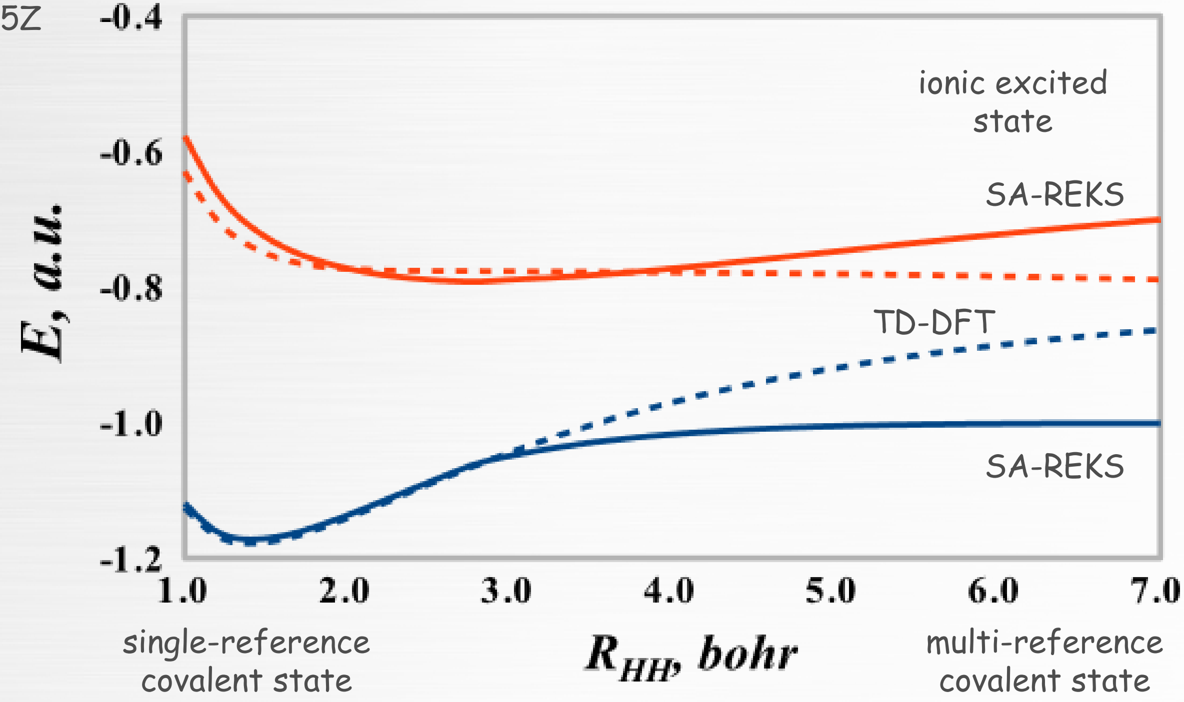
wrong dynamics

TD-DFT and bond dissociation: H_2

Bond dissociation in H_2

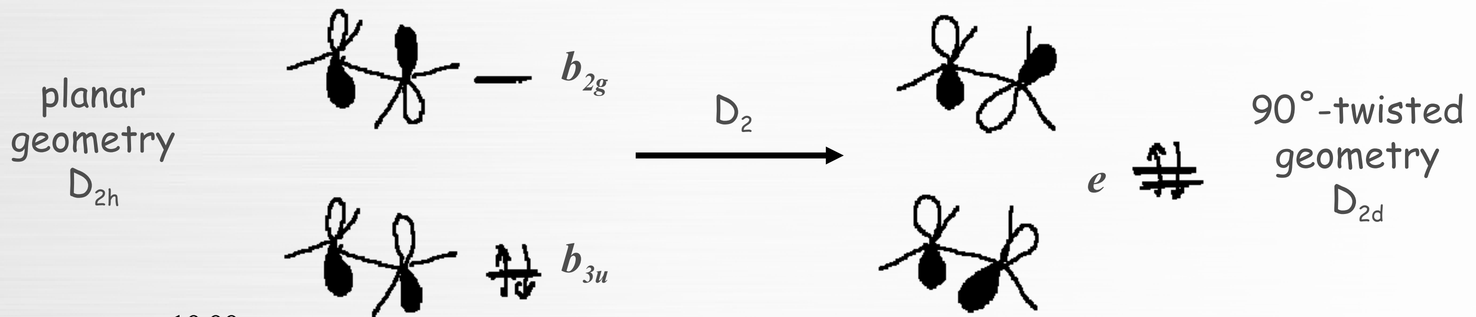


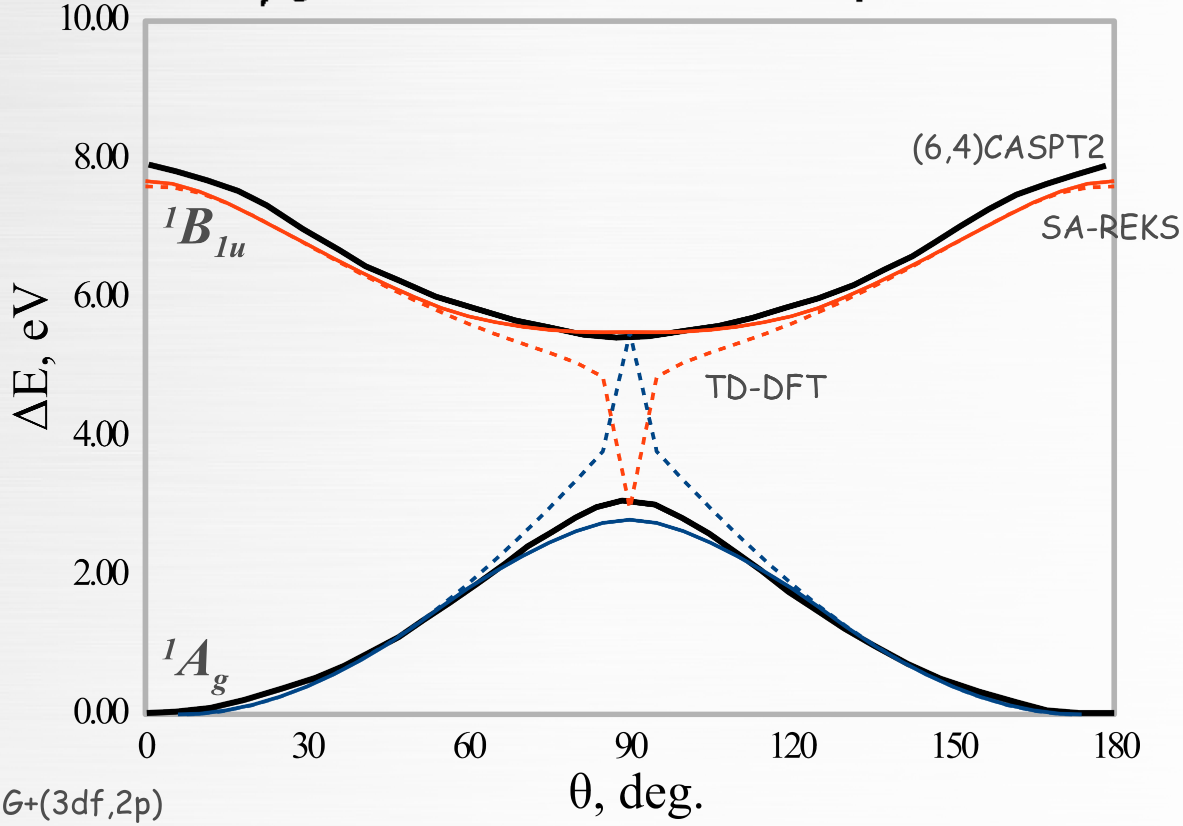
LC-ωPBE/cc-pV5Z



TD-DFT failure: single-determinant KS DFT cannot describe bond dissociation

TD-DFT and bond dissociation: C_2H_4





BH&HLYP/6-311G+(3df,2p)

Ensemble DFT for excited states

TD-DFT: response theory (usually, linear response)

eDFT: variational theory

Gross, Oliveira, Kohn (1988): variational principle for ensembles

$$\sum_k \omega_k \left\langle \Phi_k \middle| \hat{H} \middle| \Phi_k \right\rangle \geq \sum_k \omega_k E_k$$

basis for variational DFT for excited states

REKS formulation (SA-REKS): E_0 approximated by REKS PPS

E_1 approximated by REKS OSS

ensemble energy $$E_{ens}(\omega) = (1-\omega)E_0 + \omega E_1$$ variationally optimized

excitation energy: $$\Delta E = E_1 - E_0 = \frac{E_{ens}(\omega) - E_0}{\omega} = \frac{d\,E_{ens}(\omega)}{d\,\omega}$$

Types of states described by REKS

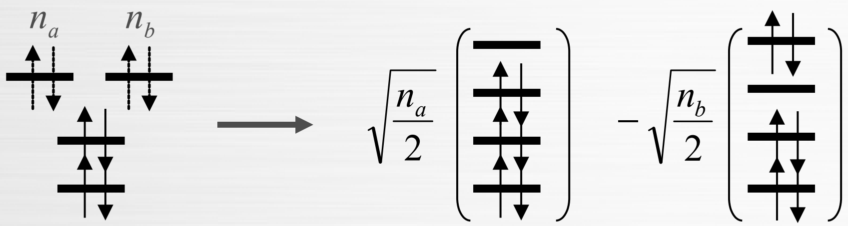
REKS ↔ GVB in DFT context

MF, T.J. Martínez, K. S. Kim, PCCP 18, 21040 (2016)
MF, F. Liu, K. S. Kim, T. J. Martínez, JCP 145, 244104 (2016)
MF, T. J. Martínez, K. S. Kim, JCP 147, 064104 (2017)

(2,2) active space:

Perfectly spin-Paired Singlet (PPS) state

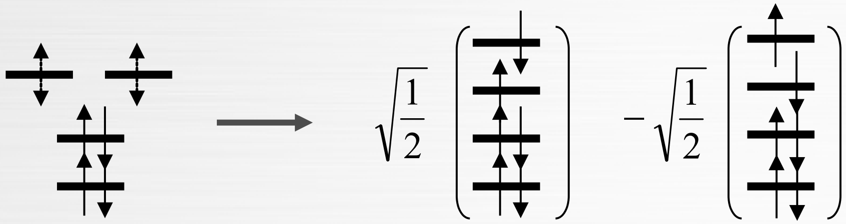
$\lambda = 0$ $\lambda \approx 0$



$$\Phi_0^{GVB}(1,2) = \sqrt{\frac{n_a}{2}}\left|\phi_a \bar{\phi}_a\right\rangle - \sqrt{\frac{n_b}{2}}\left|\phi_b \bar{\phi}_b\right\rangle$$

FONs variationally optimized

Open-Shell Singlet (OSS) state



$$\Phi_1^{GVB}(1,2) = \sqrt{\frac{1}{2}}\left|\phi_a \bar{\phi}_b\right\rangle - \sqrt{\frac{1}{2}}\left|\bar{\phi}_a \phi_b\right\rangle$$

FONs fixed by (spin-)symmetry

(N,M) active space:

and many more…

State-Averaged REKS method

SA-REKS energy

$$E_{SA-REKS}(\omega) = (1-\omega)E_{PPS} + \omega E_{OSS}$$

state-averaged REKS energy

“ground” state (PPS) energy

“excited” state (OSS) energy

is variationally optimized (w.r.t. the KS orbitals and FONs)

The PPS and OSS energies are calculated using the common set of optimized orbitals.

Excitation energy

$$\Delta E = \frac{E_{SA-REKS}(\omega) - E_{PPS}}{\omega}$$

$\omega = ½$ (usually)

A. Kazaryan, J. Heuver, and M. Filatov, J. Phys. Chem. A 112, 12980 (2008)

State-Interaction SA-REKS (SI-SA-REKS)

Homosymmetric molecule: ***a*** and ***b*** - different symmetry species (H_2, C_2H_4, etc.)

PPS $C_1|\uparrow\downarrow\;-\rangle - C_2|-\;\uparrow\downarrow\rangle \;\cancel{\longleftrightarrow}\; \frac{1}{\sqrt{2}}|\uparrow\;\downarrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\;\uparrow\rangle$ OSS

No coupling btw the states; PPS & OSS yield S_0 and S_1 energies

Heterosymmetric molecule: ***a*** and ***b*** - same symmetry species

PPS $C_1|\uparrow\downarrow\;-\rangle - C_2|-\;\uparrow\downarrow\rangle \;\longleftrightarrow\; \frac{1}{\sqrt{2}}|\uparrow\;\downarrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\;\uparrow\rangle$ OSS

PPS & OSS are coupled; not S_0 and S_1 energies

State-Interaction SA-REKS (SI-SA-REKS)

SSR method derived from analogy with GVB/RCI (restricted conf. interaction)

REKS states – *diabatic states* for GVB-like secular problem

$$\begin{pmatrix} E_0^{PPS} & h_{01} & \cdots \\ h_{01} & E_1^{OSS} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \\ \vdots \end{pmatrix} = \begin{pmatrix} E_0^{SSR} & 0 & \cdots \\ 0 & E_1^{SSR} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \\ \vdots \end{pmatrix}$$

KS orbitals and FONs – from minimization of state-averaged (SA) functional (equiensemble)

$$E_{SA-REKS} = \omega_0 \, E_0^{PPS} + \omega_1 \, E_1^{OSS} + \ldots; \qquad \omega_0 = \omega_1 = \ldots$$

SSR(2,2)

$$E_{SA-REKS} = \tfrac{1}{2} E_0^{PPS} + \tfrac{1}{2} E_1^{OSS}$$

WIREs: Comp. Mol. Sci. 5, 146 (2015);
Top. Curr. Chem. 368, 97 (2016)
and references therein

State-Interaction SA-REKS (SI-SA-REKS)

Assume non-interacting system ($\lambda = 0$)

Apply quasi-degenerate PT ($\lambda \approx 0$) :

E_0 $\quad C_1|\uparrow\!\downarrow\ -\rangle - C_2|-\ \uparrow\!\downarrow\rangle$

E_1 $\quad \frac{1}{\sqrt{2}}|\uparrow\ \downarrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\ \uparrow\rangle$

$$\begin{pmatrix} E_0^\lambda & h_{01}^\lambda \\ h_{01}^\lambda & E_1^\lambda \end{pmatrix} \longleftarrow$$

$$h_{01}^\lambda = \left(\sqrt{n_a^\lambda} - \sqrt{n_b^\lambda}\right)\varepsilon_{ab}^\lambda$$

$$\varepsilon_{ab}^\lambda = \left\langle a \middle| n_a^\lambda \hat{F}_a^\lambda \middle| b \right\rangle = \left\langle a \middle| n_b^\lambda \hat{F}_b^\lambda \middle| b \right\rangle$$

open-open Lagrange multiplier in SA-REKS

apply λ-integration

same assumptions
as in REKS

$$\begin{pmatrix} E_0^{PPS} & h_{01} \\ h_{01} & E_1^{OSS} \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \end{pmatrix} = \begin{pmatrix} E_0^{SSR} & 0 \\ 0 & E_1^{SSR} \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \end{pmatrix}$$

$$h_{01} = \left(\sqrt{n_a} - \sqrt{n_b}\right)\varepsilon_{ab}$$

$$\varepsilon_{ab} = \left\langle a \middle| n_a \hat{F}_a \middle| b \right\rangle = \left\langle a \middle| n_b \hat{F}_b \middle| b \right\rangle$$

- E_0, E_1 give S_0 and S_1 energies
- if $\varepsilon_{ab} = 0$, SI-SA-REKS is equivalent to SA-REKS
- $\omega = ½$ should be used in SA-REKS

Interstate coupling in SI-SA-REKS

Near $\lambda \to 0$

$$\Phi_0^\lambda = \sqrt{\frac{n_a^\lambda}{2}}\left|\ldots a\,\bar{a}\right\rangle - \sqrt{\frac{n_b^\lambda}{2}}\left|\ldots b\,\bar{b}\right\rangle \qquad \Phi_1^\lambda = \sqrt{\frac{1}{2}}\left|\ldots a\,\bar{b}\right\rangle + \sqrt{\frac{1}{2}}\left|\ldots b\,\bar{a}\right\rangle$$

$$\hat{H}^\lambda = -\tfrac{1}{2}\sum_i \nabla_i^2 + \sum_i V_{ext}^\lambda(\vec{r}_i) + \lambda \sum_{i<j} r_{ij}^{-1}$$

$$\begin{aligned}
h_{01}^\lambda = \left\langle \Phi_0^\lambda \middle| \hat{H}^\lambda \middle| \Phi_1^\lambda \right\rangle &= \frac{\sqrt{n_a^\lambda}}{2}\left\langle a\,\bar{a} \middle| \hat{H}^\lambda \middle| a\,\bar{b} \right\rangle + \frac{\sqrt{n_a^\lambda}}{2}\left\langle a\,\bar{a} \middle| \hat{H}^\lambda \middle| b\,\bar{a} \right\rangle - \frac{\sqrt{n_b^\lambda}}{2}\left\langle b\,\bar{b} \middle| \hat{H}^\lambda \middle| a\,\bar{b} \right\rangle - \frac{\sqrt{n_b^\lambda}}{2}\left\langle b\,\bar{b} \middle| \hat{H}^\lambda \middle| b\,\bar{a} \right\rangle \\
&= \frac{\sqrt{n_a^\lambda}}{2}\left\langle \bar{a} \middle| \hat{F}^\lambda \middle| \bar{b} \right\rangle + \frac{\sqrt{n_a^\lambda}}{2}\left\langle a \middle| \hat{F}^\lambda \middle| b \right\rangle - \frac{\sqrt{n_b^\lambda}}{2}\left\langle b \middle| \hat{F}^\lambda \middle| a \right\rangle - \frac{\sqrt{n_b^\lambda}}{2}\left\langle \bar{b} \middle| \hat{F}^\lambda \middle| \bar{a} \right\rangle \\
&= \left(\sqrt{n_a^\lambda} - \sqrt{n_b^\lambda}\right)\varepsilon_{ab}^\lambda
\end{aligned}$$

Fock operator:

$$\hat{F}^\lambda \phi_k^\sigma = \frac{\delta E^\lambda}{\delta\left(\phi_k^\sigma\right)^*} \qquad \left(\phi_k^\sigma\right)^* \hat{F}^\lambda = \frac{\delta E^\lambda}{\delta \phi_k^\sigma}$$

$$\left\langle \phi_p^\sigma \middle| \hat{F}^\lambda \middle| \phi_q^\sigma \right\rangle = \left\langle \frac{\delta E^\lambda}{\delta \phi_p^\sigma} \middle| \phi_q^\sigma \right\rangle \approx \left\langle \frac{\delta E^0}{\delta \phi_p^\sigma} \middle| \phi_q^\sigma \right\rangle + d\lambda \left\langle \frac{\delta \dot{E}^\lambda}{\delta \phi_p^\sigma} \middle| \phi_q^\sigma \right\rangle, \quad \dot{E}^\lambda = \frac{dE^\lambda}{d\lambda}$$

λ-integration:

$$\left\langle \phi_p^\sigma \middle| \hat{F}^1 - \hat{F}^0 \middle| \phi_q^\sigma \right\rangle = \int_0^1 d\lambda \left\langle \frac{\delta \dot{E}^\lambda}{\delta \phi_p^\sigma} \middle| \phi_q^\sigma \right\rangle$$

SSR(2,2): How does it work…

1st: Optimize orbitals using SA-REKS(2,2)

$$E_{SA-REKS} = \tfrac{1}{2} E_0^{PPS} + \tfrac{1}{2} E_1^{OSS}$$

2nd: Build the SSR(2,2) secular equation using the common set of KS orbitals

$$\begin{pmatrix} E_0^{PPS} & h_{01} \\ h_{01} & E_1^{OSS} \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \end{pmatrix} = \begin{pmatrix} E_0^{SSR} & 0 \\ 0 & E_1^{SSR} \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \end{pmatrix}$$

3rd: Solve the SSR(2,2) secular equation and obtain the adiabatic SSR energies

SSR(2,2): Analytical energy derivatives

The KS orbitals optimized for averaged state $E_{SA-REKS} = \frac{1}{2} E_0^{PPS} + \frac{1}{2} E_1^{OSS}$

The variational condition $\left\langle \phi_p \middle| n_q \hat{F}_q \middle| \phi_q \right\rangle = \left\langle \phi_q \middle| n_p \hat{F}_p \middle| \phi_p \right\rangle$ is NOT fulfilled for PPS and OSS

The analytical derivatives, X = PPS, OSS, need orbital derivatives $\phi_i^\lambda = \sum_j^{all} \phi_j U_{ji}^\lambda$

$$\frac{\partial E_{SA}^X}{\partial \lambda} = \sum_{L=L_{min}}^{L_{max}} C_L^X \frac{\partial' E_L}{\partial \lambda} - \frac{1}{2} \sum_{i,j}^{all} \left({}^i\epsilon_{ij}^X + {}^j\epsilon_{ij}^X \right) S_{ji}^\lambda + \sum_{i,j}^{all} \left({}^i\epsilon_{ij}^X - {}^j\epsilon_{ij}^X \right) U_{ji}^\lambda$$

Coupled-perturbed (CP) REKS equation (CP-REKS) $\sum_{ij} A_{pq,ij} U_{ji}^\lambda = B_{pq}^\lambda$

- Solve SA-REKS SCF equations
- Solve CP-REKS equations
- Calculate derivatives of SA-REKS PPS and OSS states
- Calculate derivatives of SSR states SSR$_0$ and SSR$_1$

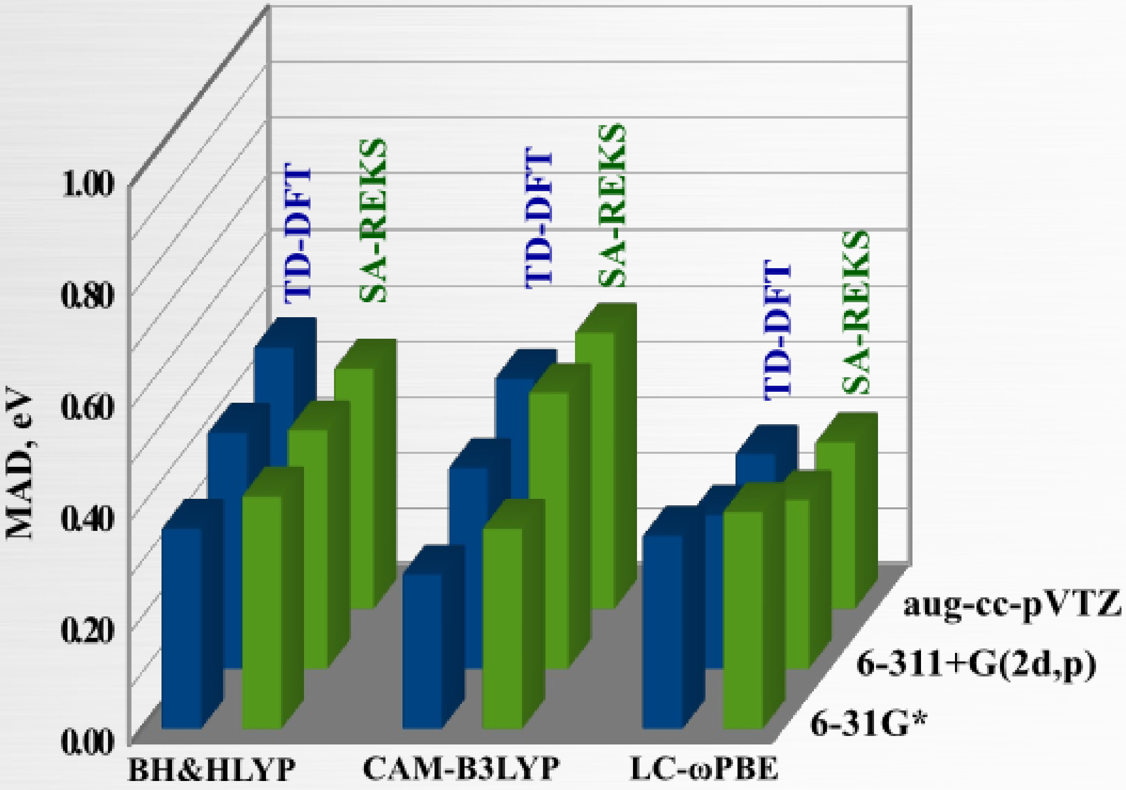
Analytical derivatives used for geometry optimizations and molecular dynamics

Applications of REKS to excited states

- Benchmarking: SA-REKS vs. experimental excitation energies
- Bond breaking: Excitations in molecules undergoing bond breaking
- PES crossings: conical intersections and photochemistry
- Conjugated systems: lowest excited states of π-conjugated molecules
- Charge transfer transitions: lowest excited states of donor-acceptor systems and charge transfer
- Double excitations and crossings between excited states

Benchmarking SA-REKS for excitation energies (eV)

Mean absolute deviations (eV) for 15 π-π^* and n-π^* transitions in simple organic molecules. Experimental data from Schreiber et al, JCP 128, 134110 (2008)

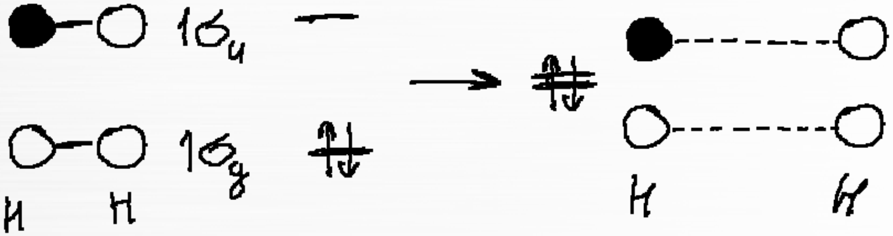


ethylene	π-π^*	7.80
butadiene	π-π^*	6.18
hexatriene	π-π^*	5.10
octatetraene	π-π^*	4.66
cyclopropene	π-π^*	7.06
cyclopentadiene	π-π^*	5.55
norbornadiene	π-π^*	5.34
furan	π-π^*	6.32
pyrrole	π-π^*	6.57
imidazole	π-π^*	6.19
imidazole	n-π^*	6.81
pyridine	π-π^*	4.85
pyridine	n-π^*	4.59
uracil	π-π^*	5.35
uracil	n-π^*	4.80

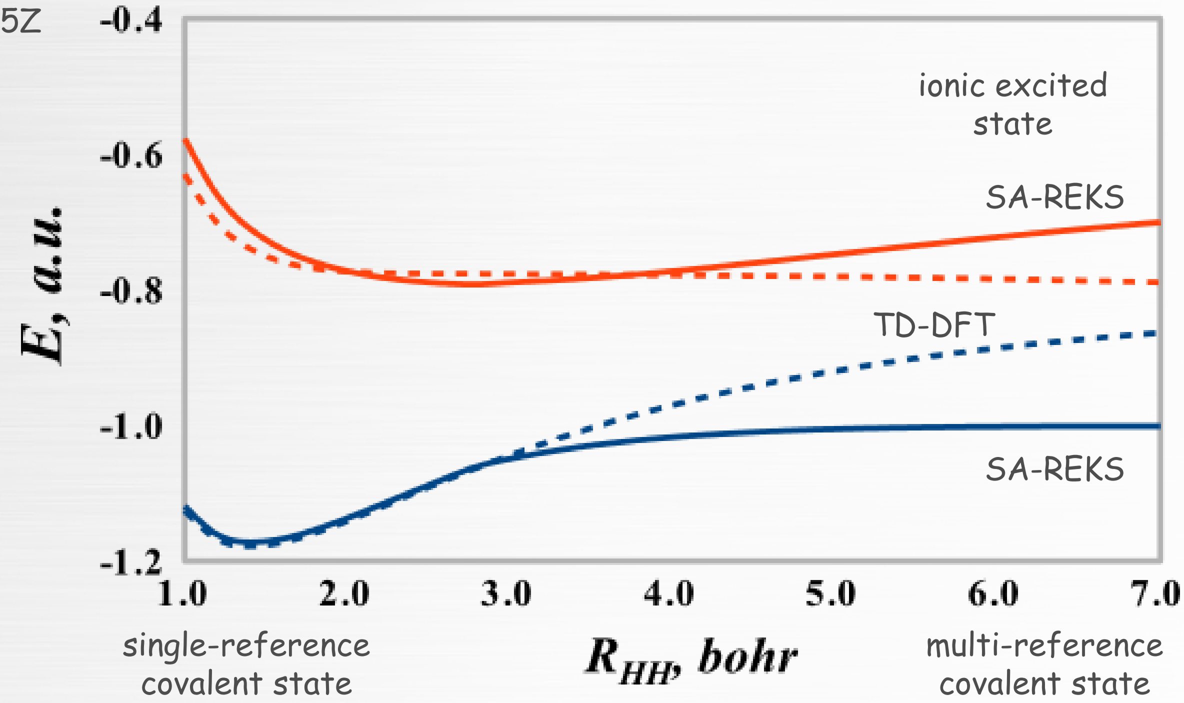
SA-REKS and TD-DFT are equally good for simple molecules

Bond dissociation in a homosymmetric molecule

Bond dissociation in H_2

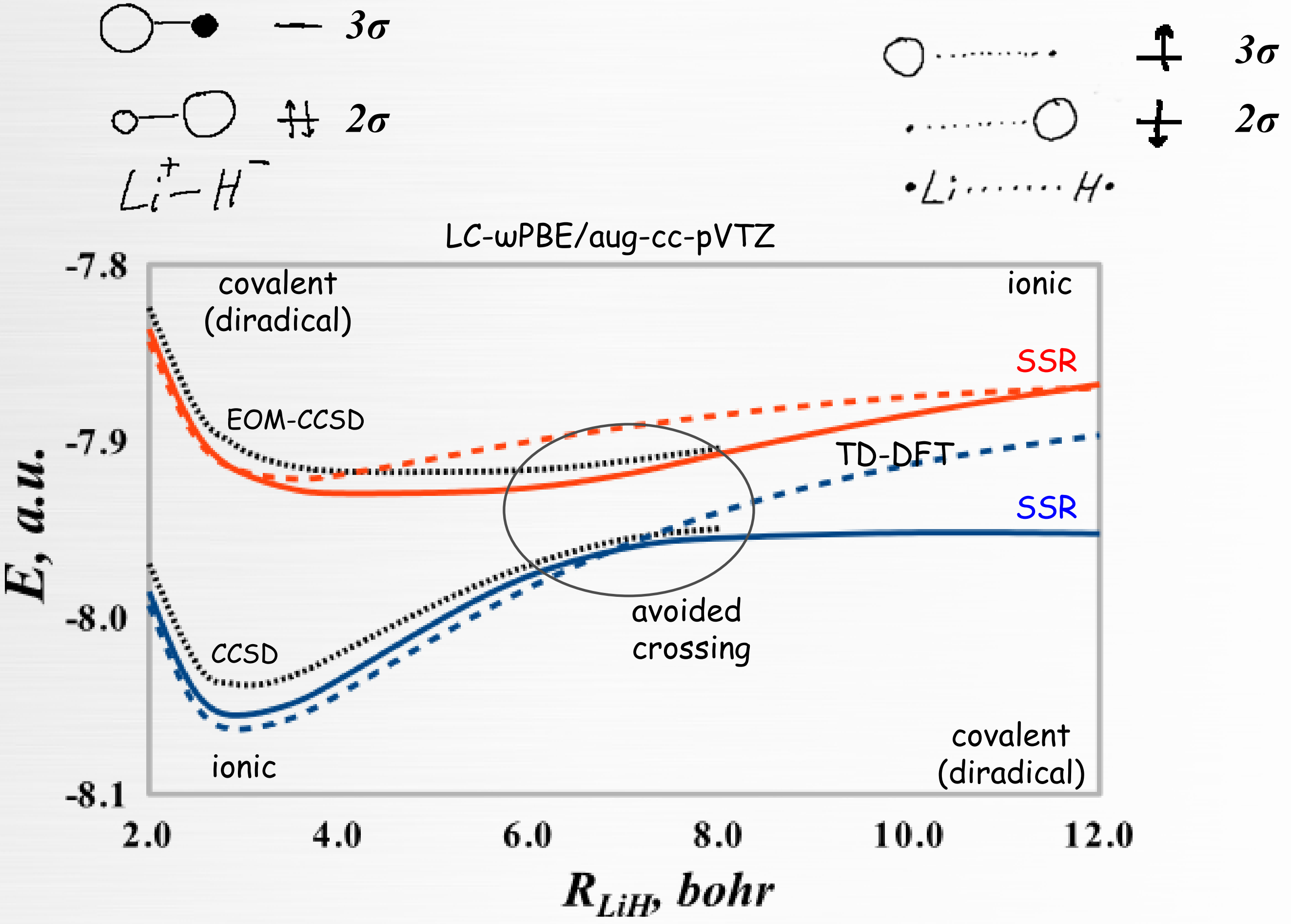


LC-ωPBE/cc-pV5Z

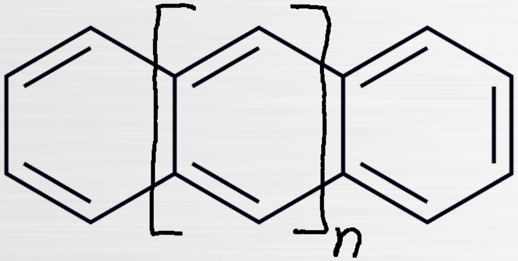


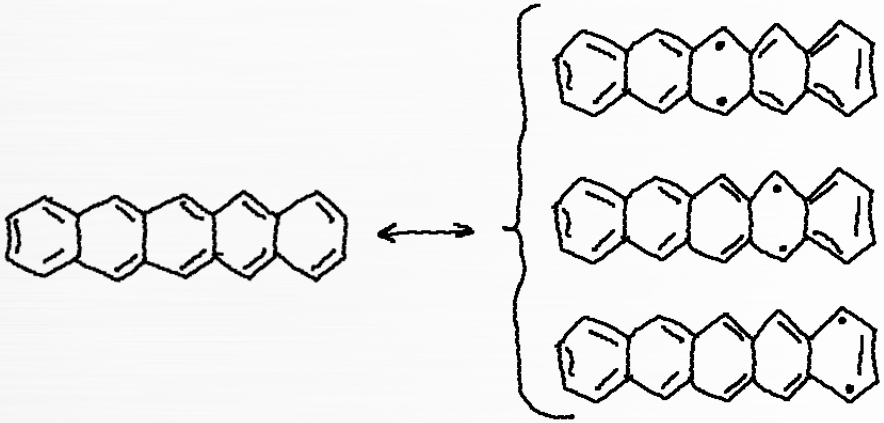
<u>TD-DFT failure</u>: single-determinant KS DFT cannot describe bond dissociation

Bond dissociation in a heterosymmetric molecule



Extended π-conjugated systems: polyacenes





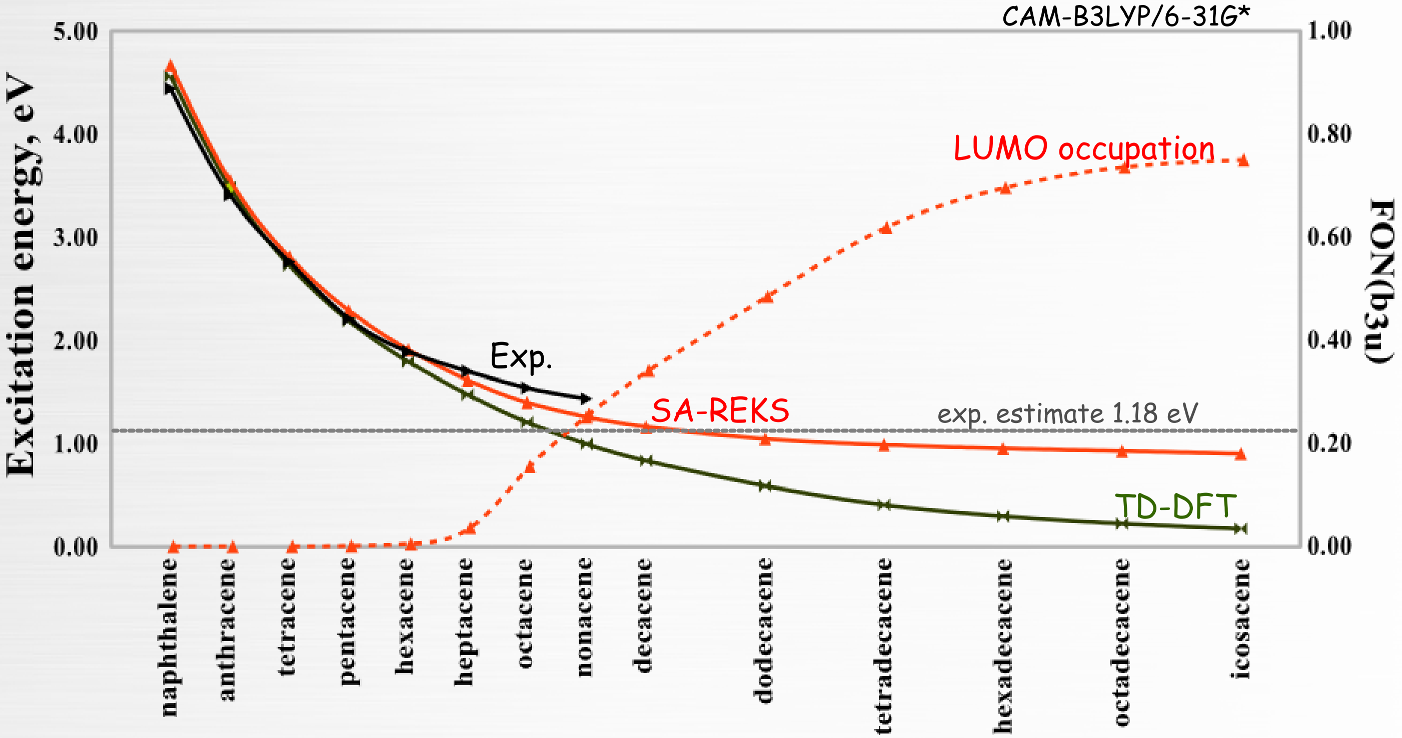
Strongly correlated singlet ground state (experiment up to n=9),

Low singlet-triplet gap is expected in longer acenes

Interesting for non-linear optics, photovoltaics

Lowest excitation energy of polyacenes

^1L_a state: HOMO-LUMO transition ($b_{2g} \rightarrow b_{3u}$)



SA-REKS: accurate excitation energies for all n

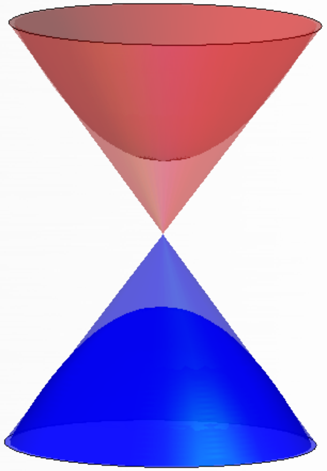
TD-DFT: fails after n ~ 7

Conical intersections

Most important mechanistic features of photochemical reactions
True crossings btw 2 (or more) states of the same symmetry

$$\begin{vmatrix} E_1 & h_{12} \\ h_{12} & E_2 \end{vmatrix}$$

E_1, E_2 - arbitrary diabatic states



Conical Intersection

$$E_1 = E_2$$
$$h_{12} = 0$$

Avoided Crossing

$$E_1 = E_2$$
$$h_{12} \neq 0$$

CI's branching plane

$$\vec{x}_1 = \tfrac{1}{2}\vec{\nabla}\left(E_1 - E_2\right)$$
$$\vec{x}_2 = \vec{\nabla}\, h_{12}$$

Branching plane vectors:

- define all directions of escape from CI
- similar to transition vector in TST

Ruedenberg et al., JCP 95, 1862 (1991)

SSR: conical intersections, non-adiabatic couplings

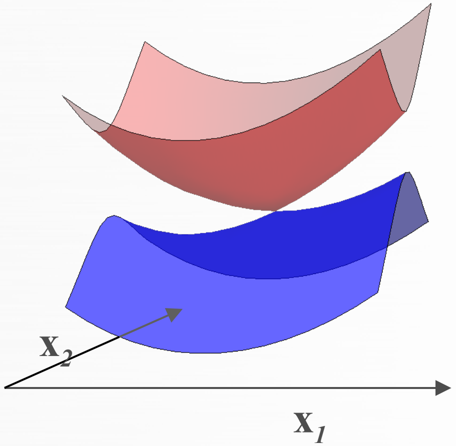
SSR(2,2) secular equation:

$$\begin{pmatrix} E_0^{PPS} & h_{01} \\ h_{01} & E_1^{OSS} \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \end{pmatrix} = \begin{pmatrix} E_0^{SSR} & 0 \\ 0 & E_1^{SSR} \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \end{pmatrix}$$

@ a CI:

$$E_0^{PPS} = E_1^{OSS}$$

$$h_{01} = 0$$



CI's BP vectors:

$$\mathbf{x}_1 = \tfrac{1}{2}\vec{\nabla}\left(E_0^{PPS} - E_1^{OSS}\right)$$

$$\mathbf{x}_2 = \vec{\nabla}\, h_{01}$$

MECI geometries and BP vectors tested against MRCISD

RMSD 0.061 Å

Non-adiabatic coupling (NAC) vector:

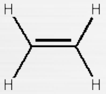
$$\mathbf{F}_{01} = \frac{\left(C_{00}\,C_{01} - C_{10}\,C_{11}\right)\mathbf{x}_1 + \left(C_{00}\,C_{11} + C_{10}\,C_{01}\right)\mathbf{x}_2}{E_1^{SSR} - E_0^{SSR}}$$

Analytic gradients for S_0 and S_1 available

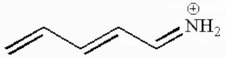
NAC is done analytically

JCP 147, 034113 (2017)

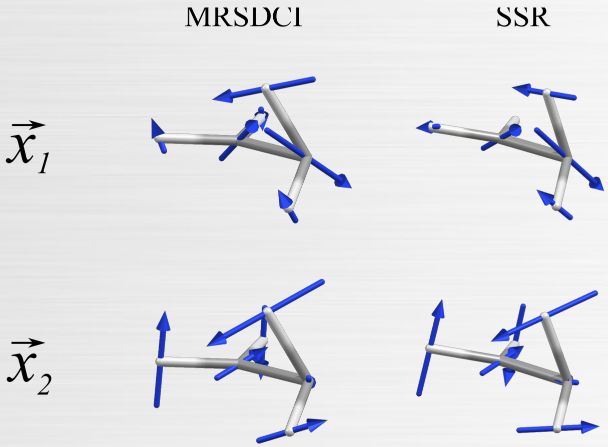
CI's and BP vectors of simple molecules

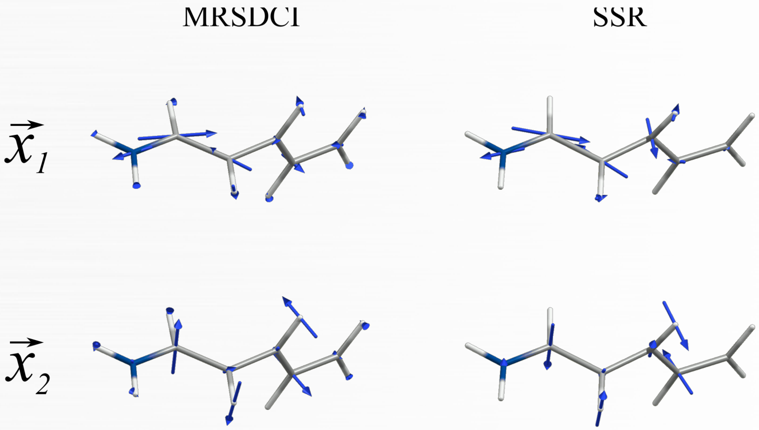


ethylene

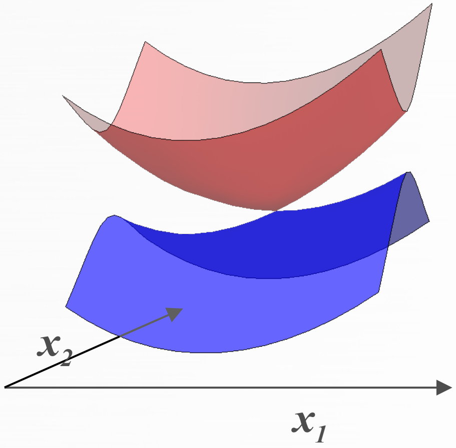


penta-2,4-dieniminium



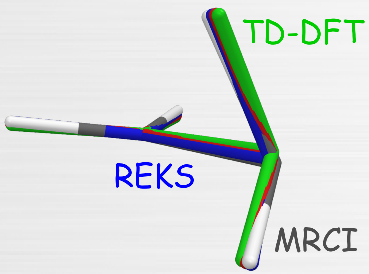


PES's scan around
MECI of PSB3



SSR-BH&HLYP/6-31G*

Shape of S_0 and S_1 PES's around a CI



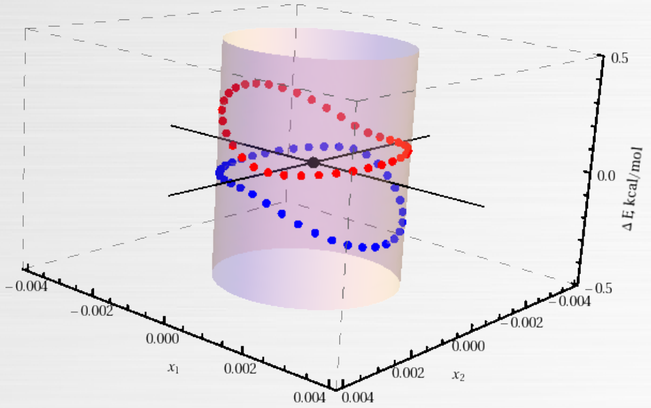
Maeda-Morokuma MECI optimization for TD-DFT

TD-DFT "BP vectors" from Maeda-Morokuma optimization

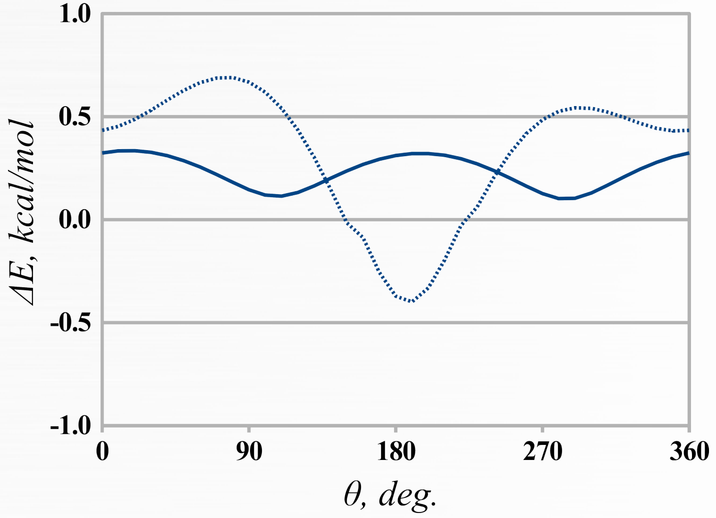
MECI geometries are surprisingly similar

Set up a loop within the BP around MECI and scan PES's

REKS PES profiles round a loop



S_1–S_0 energy gap (kcal/mol)



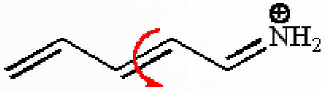
REKS – finite gap btw the PES's; proper conical intersection

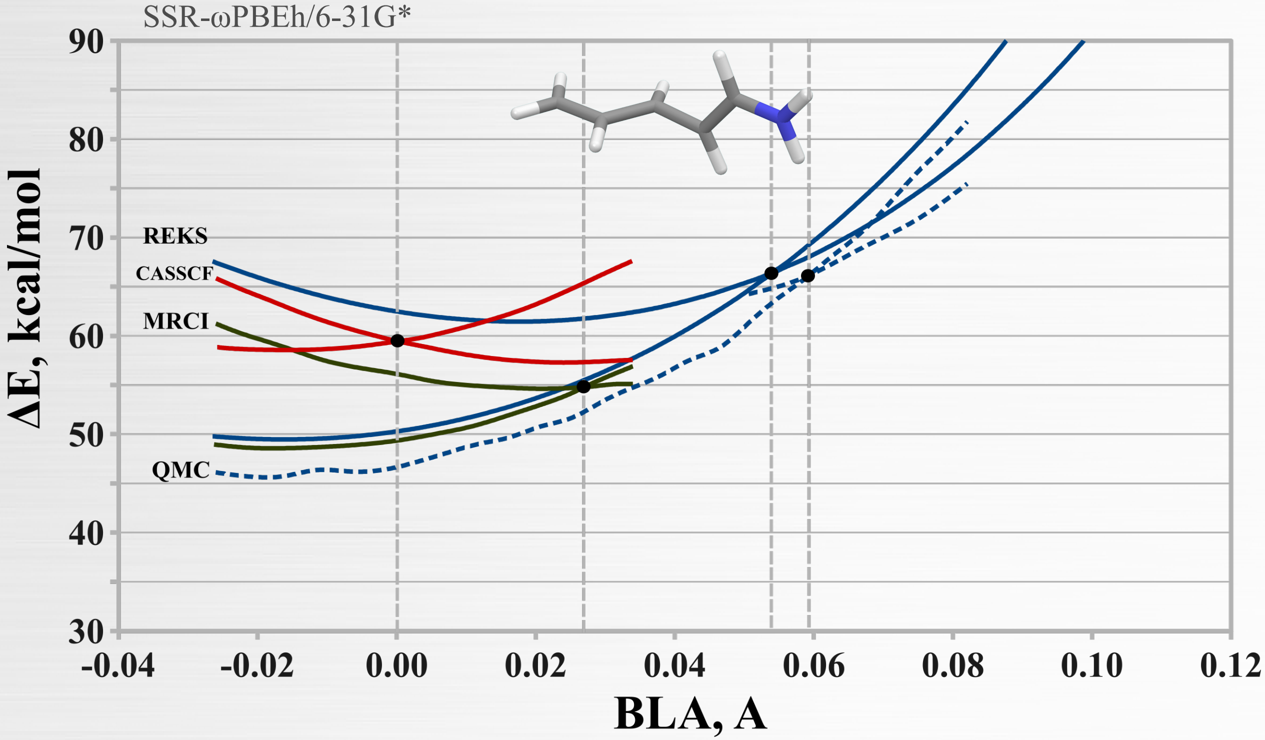
TD-DFT – crosses the zero line; not a conical, but linear intersection

Conical intersection in PSB3

PSB3 (penta-2,4-dieniminium) – a simple model of retinal chromophore

CI reached by bond length alternation (BLA) and torsion (Robb, Olivucci et al., 1997 – …)





CASSCF, MRCISD:

JCTC 8, 4069(2012)

QMC: JCTC 11, 992 (2015)

SI-SA-REKS and double excitations

Adiabatic LR-TD-DFT: no double excitations

SI-SA-REKS: easy to include them

3SI-2SA-REKS:

double excitation E_2^{DES} $C_2|\uparrow\downarrow\ -\rangle + C_1|-\ \uparrow\downarrow\rangle$

single excitation E_1^{OSS} $\frac{1}{\sqrt{2}}|\uparrow\ \downarrow\rangle - \frac{1}{\sqrt{2}}|\downarrow\ \uparrow\rangle$

ground state E_0^{PPS} $C_1|\uparrow\downarrow\ -\rangle - C_2|-\ \uparrow\downarrow\rangle$

$$\begin{pmatrix} E_0^{PPS} & \Delta_{01} & 0 \\ \Delta_{01} & E_1^{OSS} & \Delta_{12} \\ 0 & \Delta_{12} & E_2^{DES} \end{pmatrix}\begin{pmatrix} C_0 \\ C_1 \\ C_2 \end{pmatrix} = \begin{pmatrix} E_0^{SSR} & 0 & 0 \\ 0 & E_1^{SSR} & 0 \\ 0 & 0 & E_2^{SSR} \end{pmatrix}\begin{pmatrix} C_0 \\ C_1 \\ C_2 \end{pmatrix}$$

$$\Delta_{01} = \left(\sqrt{n_a} - \sqrt{n_b}\right)\varepsilon_{ab}$$

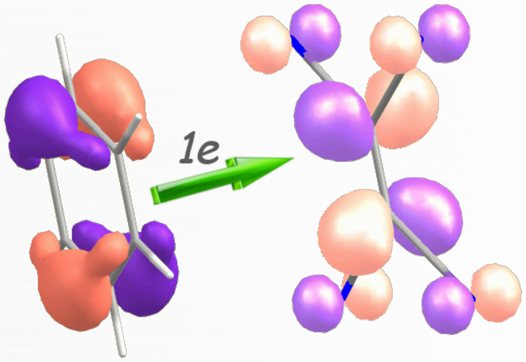
$$\Delta_{12} = \left(\sqrt{n_a} + \sqrt{n_b}\right)\varepsilon_{ab}$$

Can be derived by applying quasi-degenerate PT to a system of weakly interacting electrons and integrating w.r.t. coupling strength

Charge transfer excitations in D-A systems

Arene-TCNE complexes

HOMO → LUMO CT transition



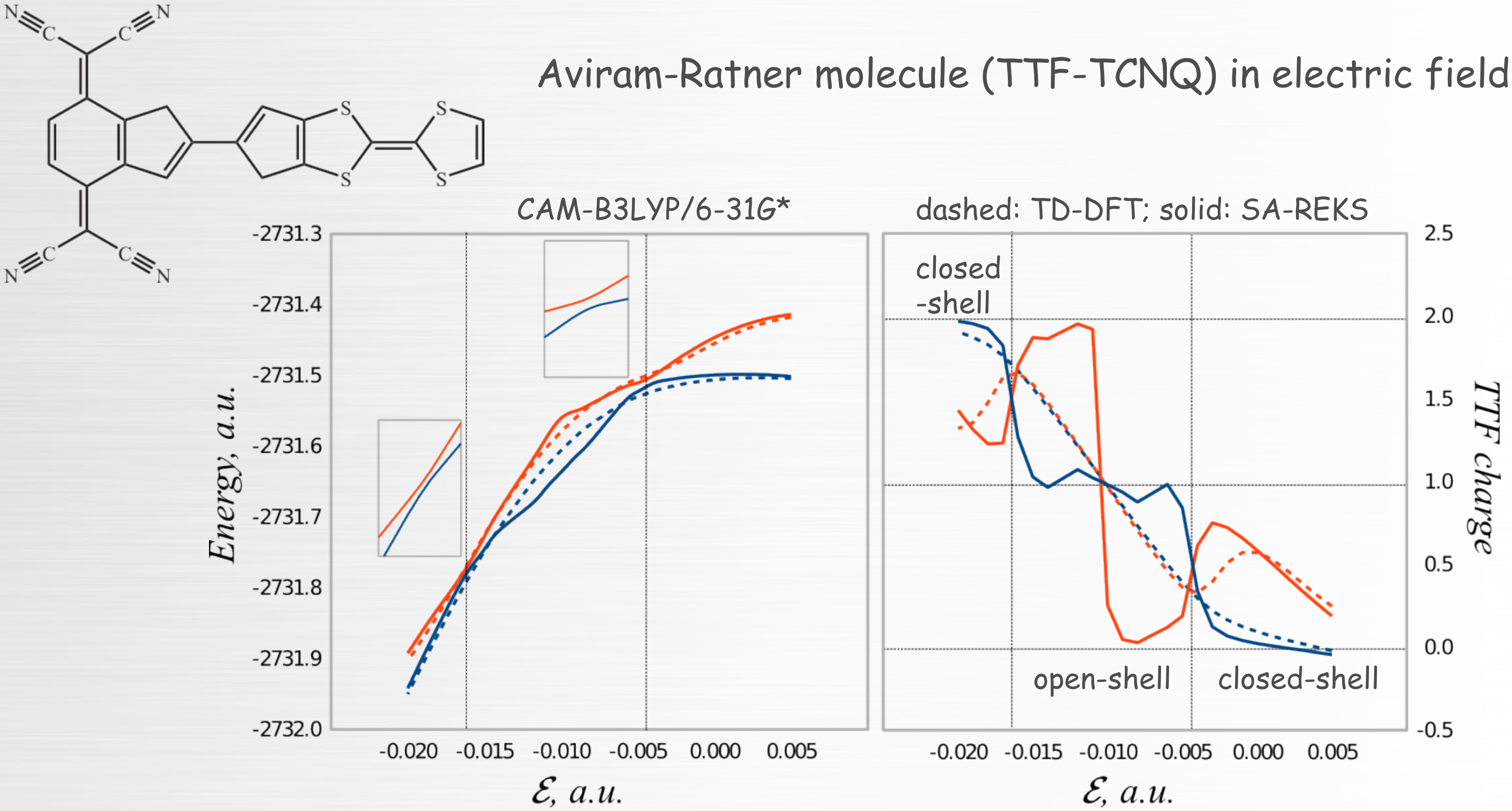
CT transition energies (eV) for a series of Ar-TCNE complexes

Arene	BLYP		B3LYP		CAM-B3LYP		Litr.	Exp.
	TD-DFT	SA-REKS	TD-DFT	SA-REKS	TD-DFT	SA-REKS		
benzene	1.54	3.53	2.06	3.70	3.03	3.68	3.80	**3.59**
tolyene	1.37	2.72	1.81	3.11	2.72	3.46	3.40	**3.36**
o-xylene	1.47	2.61	1.54	2.95	2.46	3.15	3.00	**3.15**
naphthalene	0.34	2.28	0.90	2.54	1.96	2.61	2.70	**2.60**
MAD	**2.00**	**0.39**	**1.60**	**0.16**	**0.63**	**0.05**	**0.13**	

MAD: mean absolute deviation
Litr.: Baer et al. JACS 131, 2818 (2009); tuned BNL functional
Exp.: Gas phase experimental excitation energies, JPC 76, 1982 (1972)

MF, JCP 141, 124123 (2014)

D-A systems: CT in ground and excited states



Aviram-Ratner molecule (TTF-TCNQ) in electric field

CAM-B3LYP/6-31G*

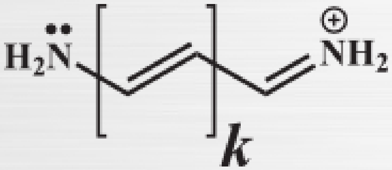
dashed: TD-DFT; solid: SA-REKS

SA-REKS: step-wise electron transfer in the ground state (correct)
wave-like electron transfer in the excited state

TD-DFT: continuous transfer of electron pair (incorrect)

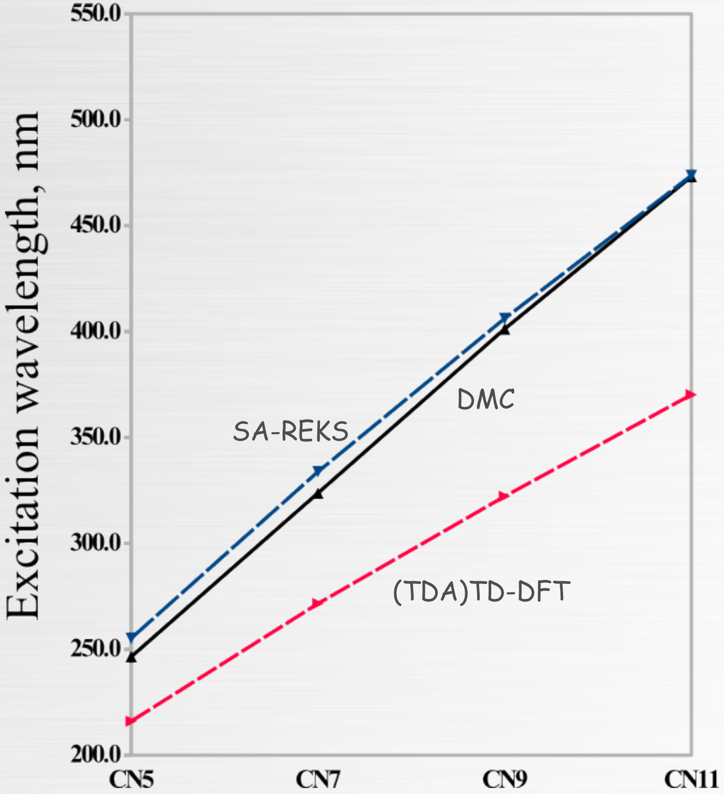
MF, JCP 141, 124123 (2014)

Lowest excitation energy of cyanine dyes



fluorescent dyes

used in biotechnology for labeling



Lowest excitation: vertical HOMO-LUMO transition

DMC: best theoretical *vertical* transitions

TD-DFT: yields large errors (~0.5 eV and more)

SA-REKS: yields accurate (~0.05 eV) excitation energies

SA-REKS: variational method

TD-DFT: linear response; insufficient orbital relaxation

Extension of SSR

SSR(2,2) is good for:

- dissociation of a single bond
- one-electron excitation
- crossing btw the ground and singly excited state
- description of S_1/S_0 photochemistry

Extension to bigger active space (M,N) is needed to:

- describe dissociation of multiple bond(s)
- describe several (singly) excited states
- describe multpily excited states (e.g., double excitations)
- describe crossing btw excited states
- S_n/S_m photochemistry

SSR(4,4); currently, testing stage:

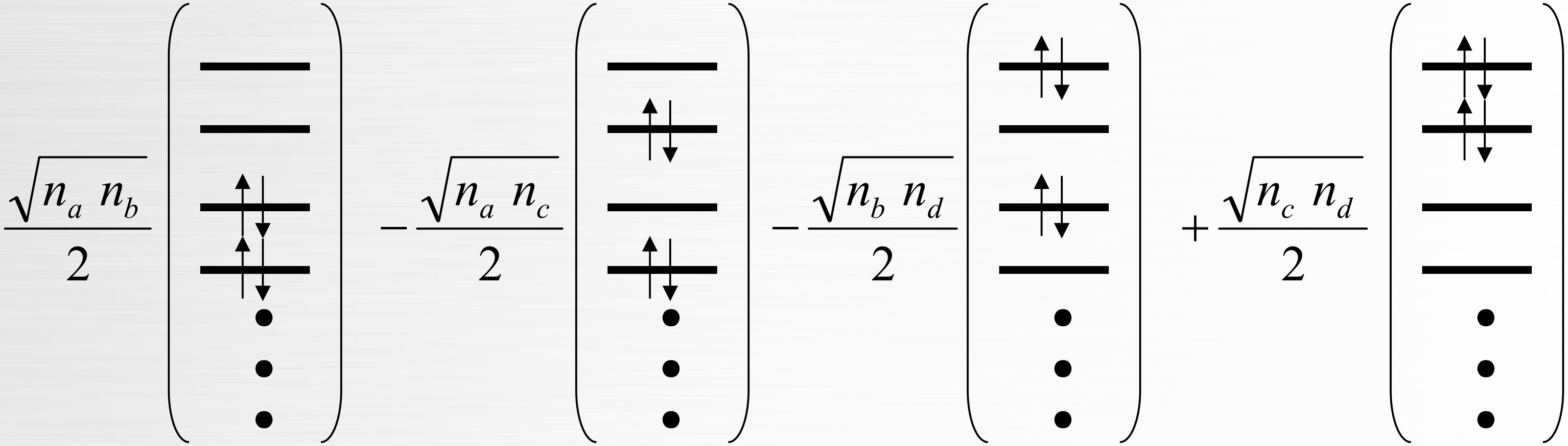
- correct double bond dissociation
- describe several excited states
- describe doubly excited states
- describe crossings btw the excited states

SI-SA-REKS(4,4); SSR(4,4)

SSR(4,4) employs GVB theory to derive the energies of the “diabatic” states

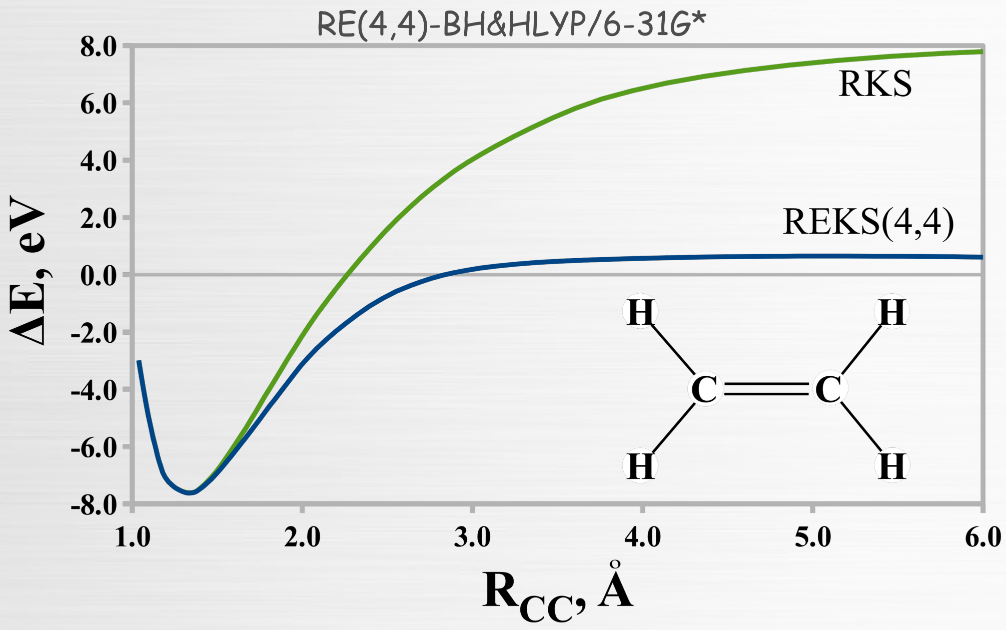
REKS(4,4) perfectly paired (PP) state; (a,d) and (b,c) GVB pairs

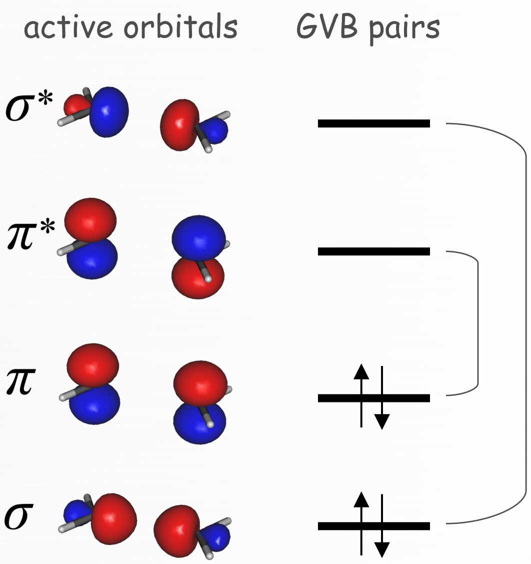
$$\Psi^{GVB-PP} = \hat{A}\left[\cdots \Phi_0^{NO}(1,2)\,\Phi_0^{NO}(3,4)\cdots\right] \qquad \Phi_0^{NO}(1,2) = \sqrt{\frac{n_a}{2}}\left|\phi_a\bar{\phi}_a\right\rangle - \sqrt{\frac{n_b}{2}}\left|\phi_b\bar{\phi}_b\right\rangle$$



$$E^{(4,4)} = \frac{n_a\, n_b}{4} E_{a\bar{a}b\bar{b}} + \frac{n_a\, n_c}{4} E_{a\bar{a}c\bar{c}} + \frac{n_b\, n_d}{4} E_{b\bar{b}d\bar{d}} + \frac{n_c\, n_d}{4} E^{\lambda}_{c\bar{c}d\bar{d}} - \left(n_a\, n_d\right)^{1/2} \Delta_{ad} - \left(n_b\, n_c\right)^{1/2} \Delta_{bc}$$

REKS(4,4): Double Bond Dissociation





- Considerable improvement over the standard KS DFT
- Flattens out at an incorrect diss. limit
  - missing open-shell configurations
  - can be improved through SSR procedure

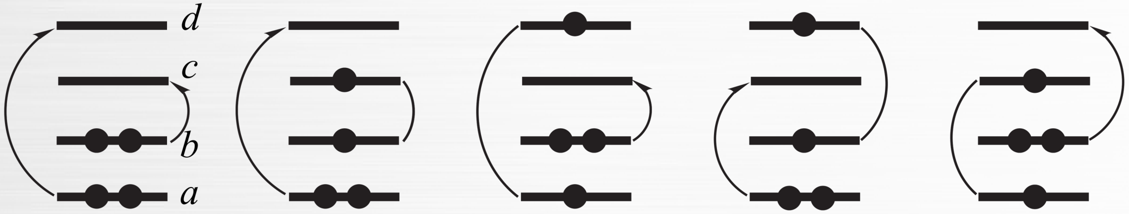
MF, T.J. Martínez, K. S. Kim, PCCP 18, 21040 (2016)
MF, F. Liu, K. S. Kim, T. J. Martínez, JCP 145, 244104 (2016)

SSR(4,4): Basic setup

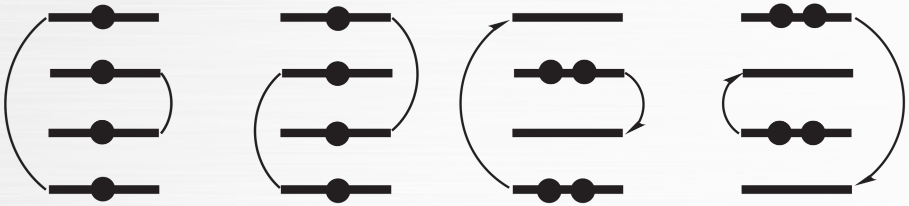
Configuration State Functions (spin-adapted) included in SSR(4,4)

perfectly paired

open-shell singlets (single excitations)



	PPS	OSS1	OSS2	OSS3	OSS4
K =	0	1	2	3	4



	DOSS	DSPS	DES1	DES2
K =	5	6	7	8

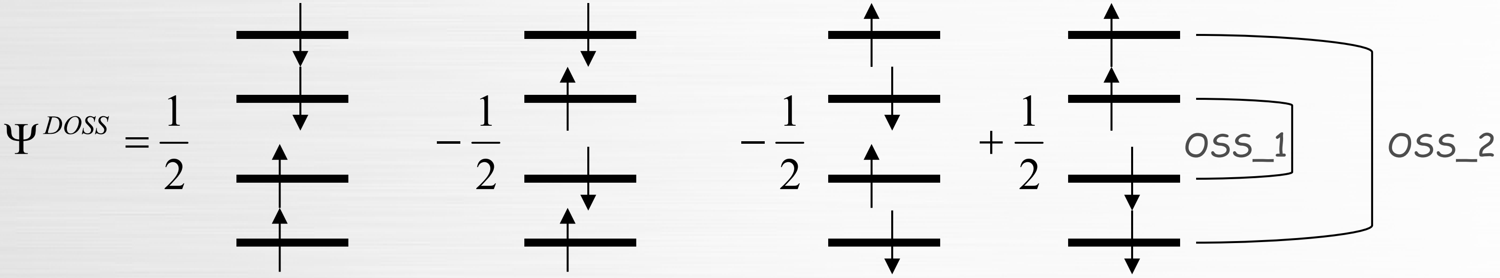
double open-shell singlet

doubly spin-polarized state

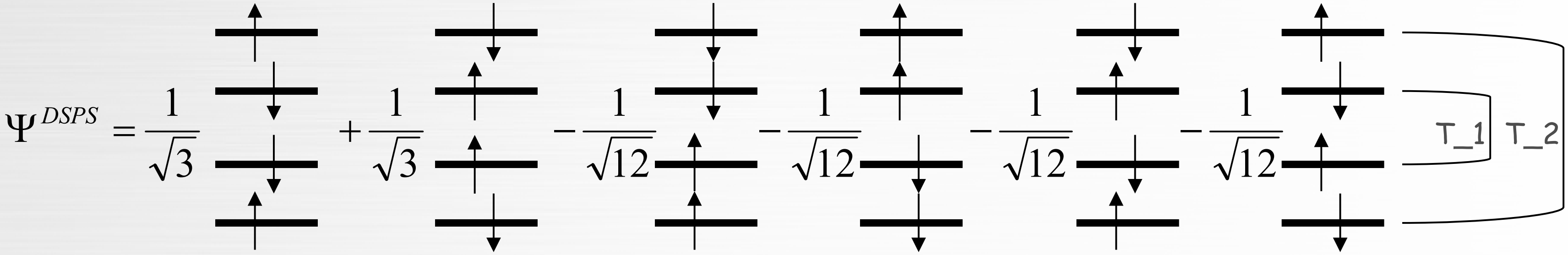
straight double excitations

Some explanations…

Double open-shell singlet (DOSS) state: $\Psi^{DOSS} = \hat{\mathcal{A}}\left[\cdots \Phi_1^{OSS}(1,2)\,\Phi_1^{OSS}(3,4)\cdots\right]$



Doubly spin-polarized state (DSPS); two triplets (GVB pairs) coupled to singlet



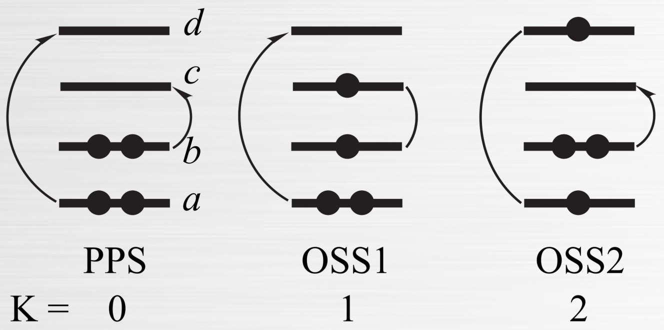
important for description of spin-polarization in strongly correlated molecules

SSR(4,4): Orbital Optimization

To include all 9 CSFs – too costly…

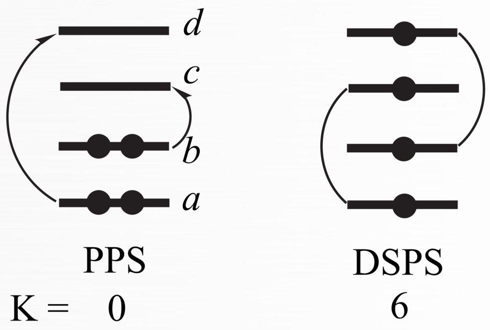
3-state SA-REKS(4,4)

$$E^{3SA} = \tfrac{1}{3} E_0^{PPS} + \tfrac{1}{3} E_1^{OSS1} + \tfrac{1}{3} E_2^{OSS2}$$



2-state SA-REKS(4,4)

$$E^{2SA} = \tfrac{1}{2} E_0^{PPS} + \tfrac{1}{2} E_6^{DSPS}$$



when single excitations are needed;
excitations of extended molecular systems

when double excitations are needed;
excitations of molecular dimers

Other setups also possible; can be implemented if need be…

SSR(4,4): How does it work…

1st: Optimize orbitals using 3SA-REKS(4,4) or 2SA-REKS(4,4)

$$E^{3SA} = (1-\omega_1-\omega_2)\,E_0^{PP} + \omega_1\, E_1^{OSS1} + \omega_2\, E_2^{OSS2} \qquad \text{or} \qquad E^{2SA} = (1-\omega_6)\,E_0^{PP} + \omega_6\, E_6^{DSPS}$$

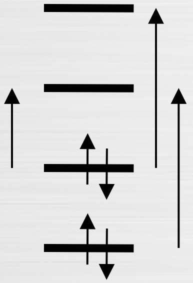
2nd: Build the secular equation in the space of 9 SSR(4,4) CSFs

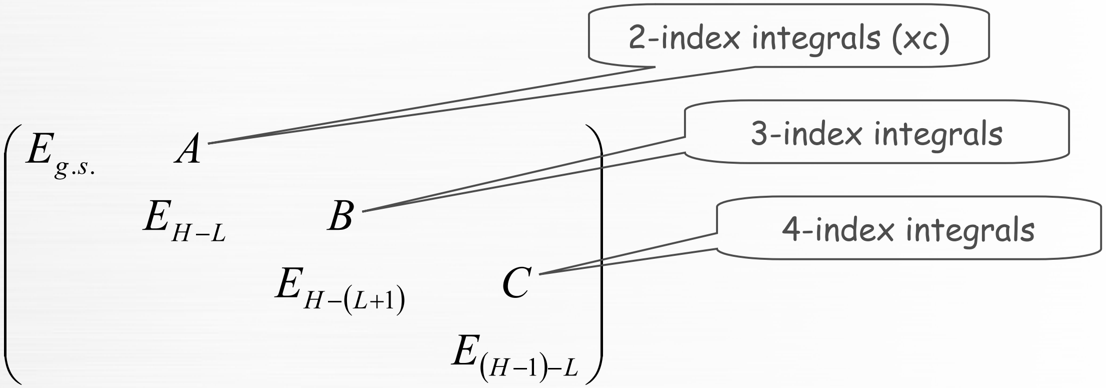
$$\begin{pmatrix} E_0^{PP} & h_{01} & h_{02} & \cdots \\ h_{01} & E_1^{OSS1} & h_{12} & \cdots \\ h_{02} & h_{12} & E_2^{OSS2} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \\ C_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} E_0^{SSR} & 0 & 0 & \cdots \\ 0 & E_1^{SSR} & 0 & \cdots \\ 0 & 0 & E_2^{SSR} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} C_0 \\ C_1 \\ C_2 \\ \vdots \end{pmatrix}$$

3rd: Solve the SSR(4,4) secular equation and analyze the results

JCP 145, 244104 (2016)
JCP 147, 064104 (2017)

SSR(4,4): Secular equation





$$\begin{pmatrix} E_{g.s.} & A & & \\ & E_{H-L} & B & \\ & & E_{H-(L+1)} & C \\ & & & E_{(H-1)-L} \end{pmatrix}$$

2-index integrals (xc)

3-index integrals

4-index integrals

2-index XC integrals $(ab|ba)=\frac{1}{2}\left(E[\ldots a\bar{b}]+E[\ldots\bar{a}b]-E[\ldots ab]-E[\ldots\bar{a}\bar{b}]\right)$

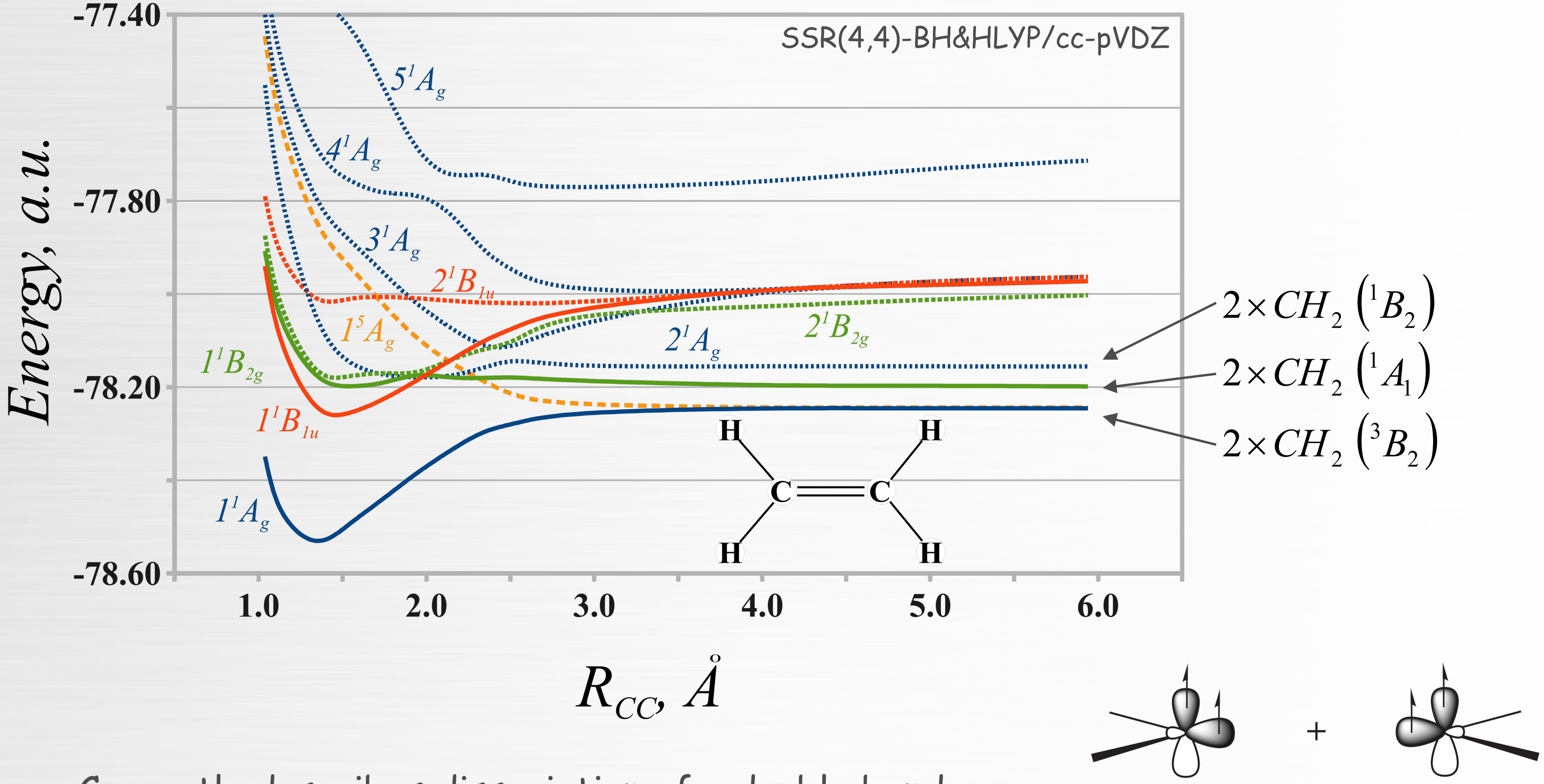
3-index XC integrals $(a\,b\,|\,b\,c)=\frac{1}{2}\left\langle \frac{\delta}{\delta\phi_b}\left(E_{a\bar{b}}-E_{ab}\right)\middle|\,\phi_c\right\rangle-\frac{1}{2}\left\langle \frac{\delta}{\delta\bar{\phi}_b}\left(E_{a\bar{b}}-E_{ab}\right)\middle|\,\bar{\phi}_c\right\rangle$

4-index XC integrals $(a\,d\,|\,b\,c)=\frac{1}{2}\left\langle \frac{\delta^2\left(E_{a\bar{b}}-E_{ab}\right)}{\delta\phi_a\,\delta\bar{\phi}_b}\middle|\,\bar{\phi}_d\,\phi_c\right\rangle$

All integrals transformed to energy differences;

convenient for λ-integration of the resulting energies

SSR(4,4): Double Bond Dissociation



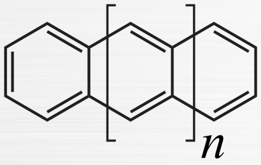
Correctly describes dissociation of a double bond

- recovers the ground state diss. limit
- recovers the excited states diss. limits

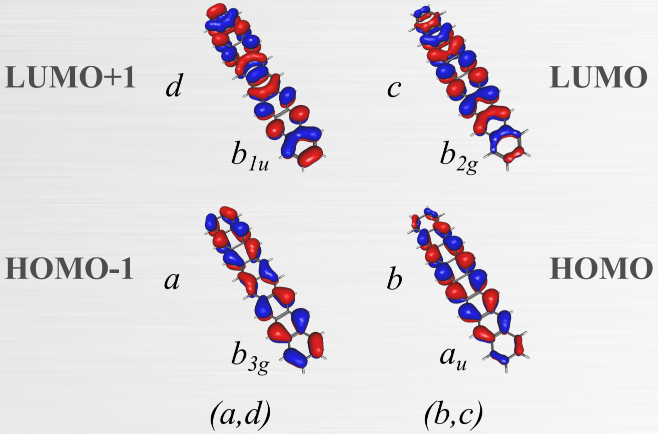
JCP 147, 064104 (2017)

SSR(4,4): Excitations in extended π-systems

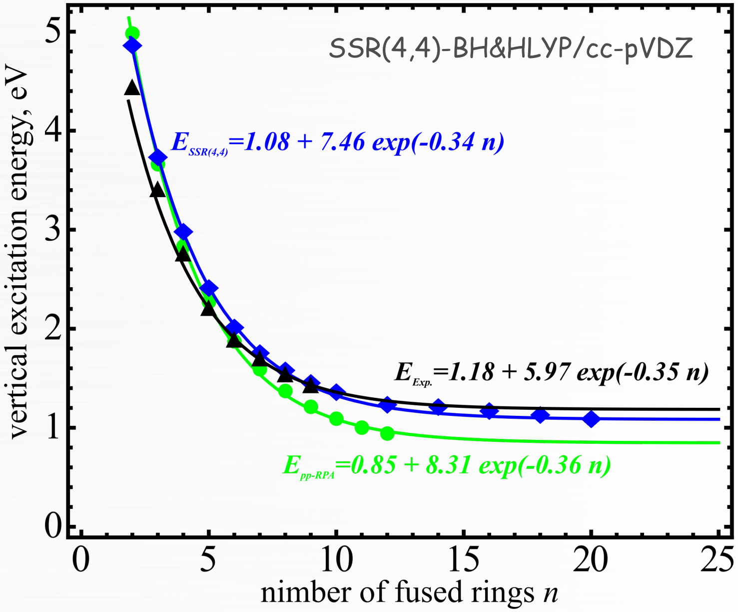
Polyacenes:



SSR(4,4) active space



Vertical excitation energy (eV)



SSR(4,4):

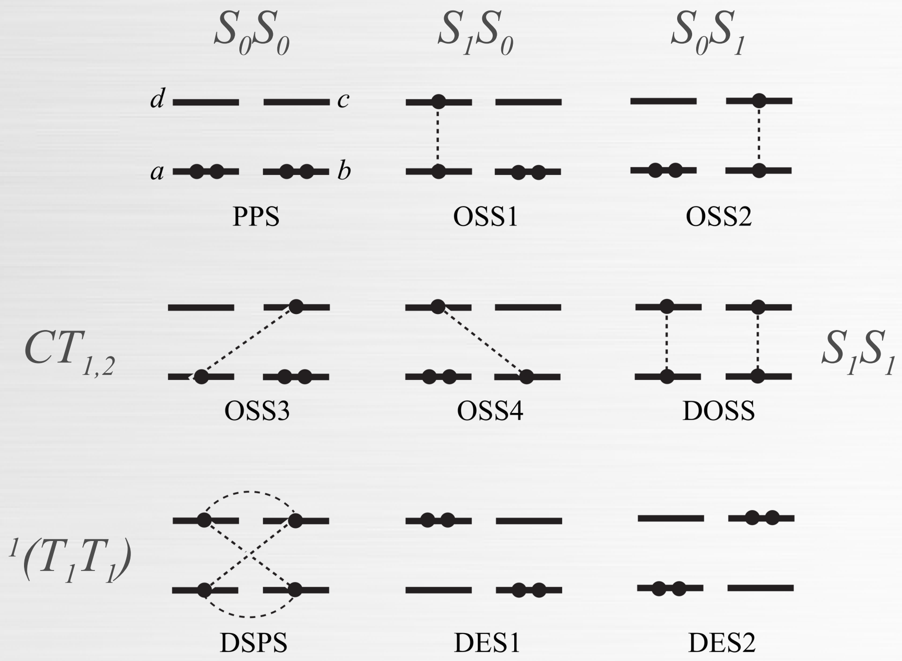
- yields very accurate vertical excitation energies
- considerably outperforms other methods, *e.g.*, pp-RPA

JCP 147, 064104 (2017)

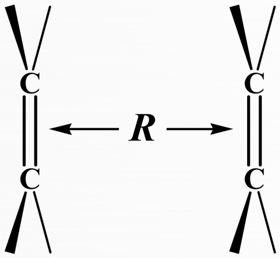
SSR(4,4): Molecular Dimers

SSR(4,4) CSFs for molecular dimers:

active orbitals localized on the fragments

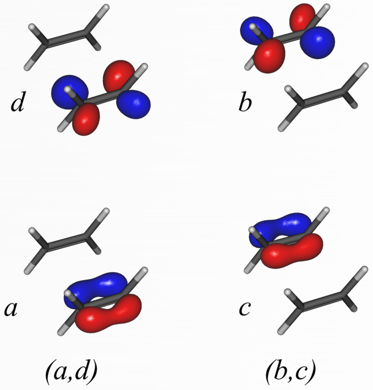


Example: ethylene dimer



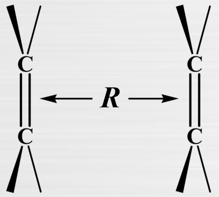
3SA-REKS(4,4) or 2SA-REKS(4,4)

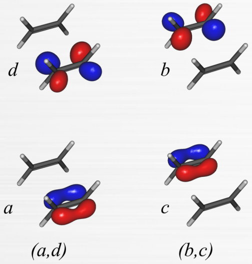
orbitals:



JCP 147, 064104 (2017)

SSR(4,4): Ethylene Dimer



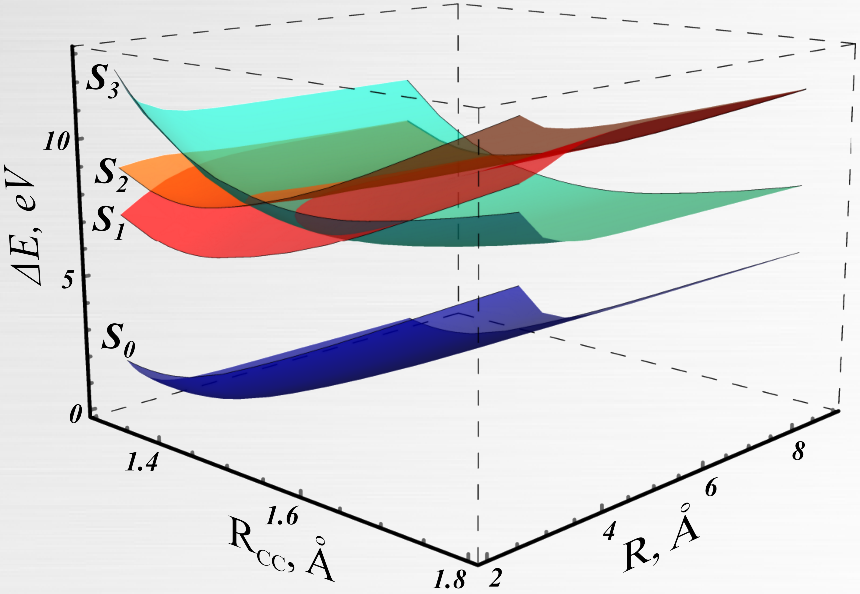


S_1, S_2 - local excitonic states

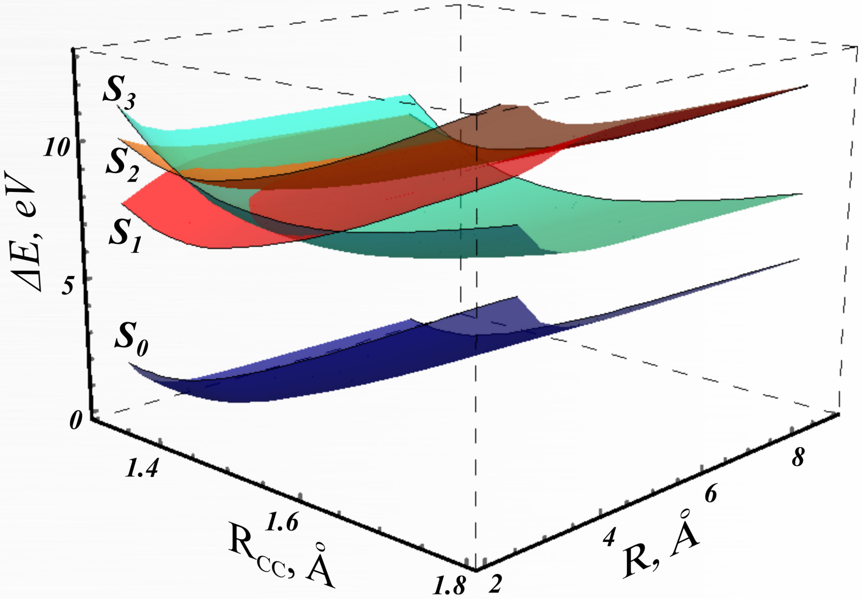
S_3 - multiexcitonic state $^1(T_1T_1)$

SSR(4,4)-BH&HLYP/cc-pVDZ

3SA-REKS(4,4) orbitals

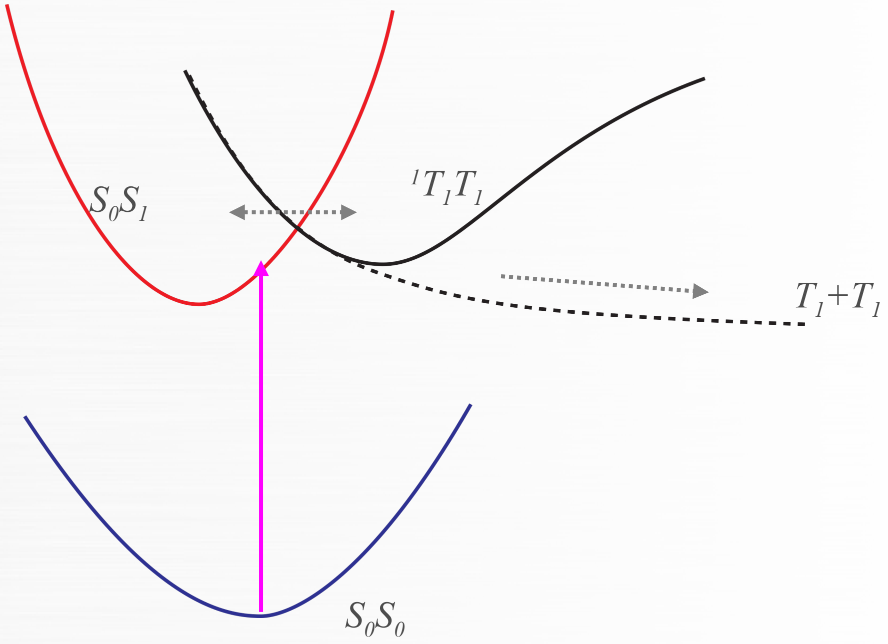


2SA-REKS(4,4) orbitals



JCP 147, 064104 (2017)

Singlet Exciton Fission

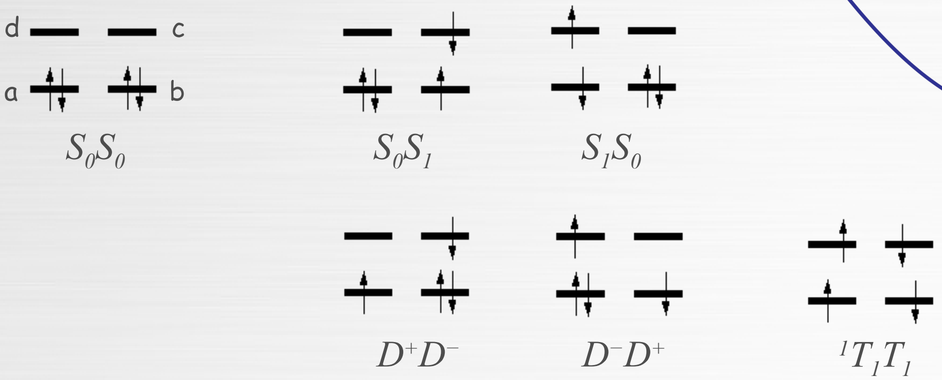


fission of singlet excited state
to 2 triplet excitons;
occurs in molecular crystals, solution, tethered dimers, etc.

2 pairs of charge carriers/photon

$$S_0S_0 \xrightarrow{h\nu} S_0S_1 \leftrightarrow {}^1T_1T_1 \rightarrow T_1 + T_1$$

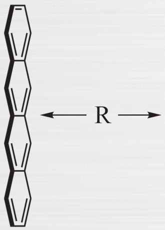
minimal model: dimer of chromophores



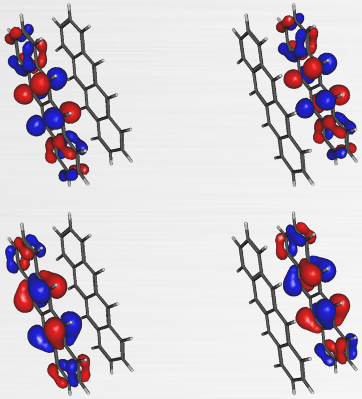
Strong (non-adiabatic) coupling btw LE and ME states – prerequisite for efficient SF

SSR(4,4): Tetracene and Pentacene Dimers

tetracene dimer's geometry

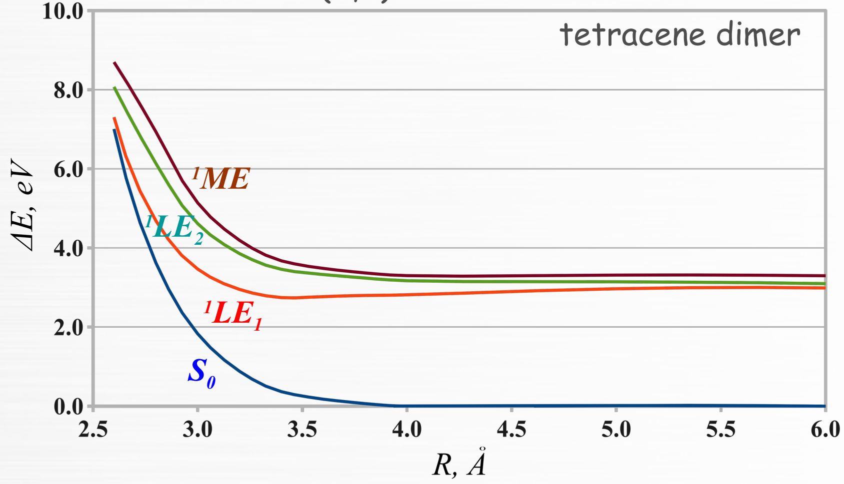


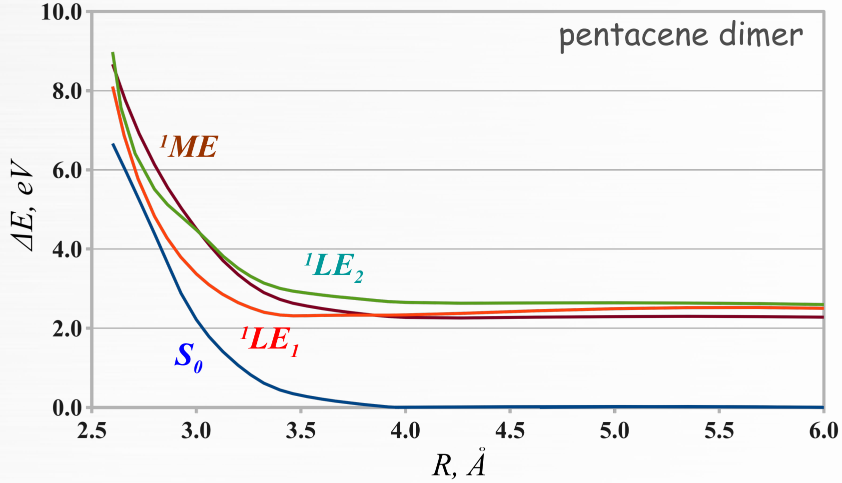
2SA-RE(4,4)-ωPBEh/6-31G*
active orbitals (tetracene)



(a,d) (b,c)

SSR(4,4)-ωPBEh/6-31G*





JCP 147, 064104 (2017)

REKS and eDFT for excited states

SSR: Variational approach to excited states

- Accurate description of photochemistry
    - light-induced rearrangements
        - molecular motors/switches
    - excitations of strongly correlated systems
        - bond dissociation/bond formation (photoreactions)
        - diradicals and open-shell species (molecular magnetism)
- Accurate description of extended conjugated systems
    - non-linear optics
    - photovoltaics
- Accurate description of charge transfer excitations
    - light harvesting (bio and synthetic)
    - photoelectrochemistry
    - molecular electronics (nanoelectronics)
- Description of observable properties
    - photoelectron spectra
    - band structure of extended systems

Ionization Energies and Photoelectron spectra

relaxed density matrix

Lagrangian

$$\frac{\partial E^X}{\partial \lambda} = tr\left(\mathbf{P}^X \mathbf{h}^\lambda\right) - \frac{1}{2} tr\left(\mathbf{W}^X \mathbf{S}^\lambda\right)$$

$$+ \sum_L \tilde{C}_L^X \frac{\partial' E_L^{2e}}{\partial \lambda} - \sum_L C_L^{SA} \sum_\sigma tr\left({}^X\mathbf{R}_L^\sigma \mathbf{T}_L^{\sigma,\lambda(2e)}\right)$$

Extended Koopmans' theorem (EKT):

$$\mathbf{W}^X \mathbf{C} = \mathbf{P}^X \mathbf{C}\mathbf{E}$$

Dyson's orbitals

ionization energies

EKT provides exact IPs (JCP 130, 194104 (2009))

ionization energy

PES signal: $I_{\text{PES}}(\text{eBE}) \propto \sum_{\text{p}}^{\text{orbitals}} \left|n_p\right|^2 \delta\left(\varepsilon_p - \text{eBE}\right)$ $\quad \left|n_p\right|^2 = \mathbf{C}_p \mathbf{C}_p^\dagger$

ionization probability

Summation over all ionization states; i.e., Dyson's orbitals

EKT/SSR formalism:

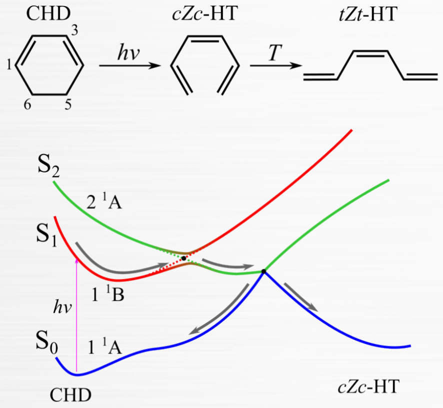
• Ionization energies:	JCTC 16, 4489-4504 (2020)
• Electron affinities:	J. Phys. Chem. A 124, 7795-7804 (2020)
• TRPES of CHD:	PCCP 22, 17567-17573 (2020)

TRPES: Ring Opening in Cyclohexadiene

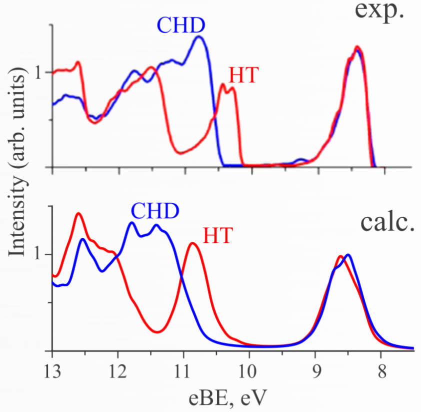
Dynamics characteristics

	CHD:HT	$\tau(S_1)$, fs
theor.	36:64	234±8
exp.	30:70	230±30
		170±80
		110–130

Mol. Phys. 117, 1128 (2019)

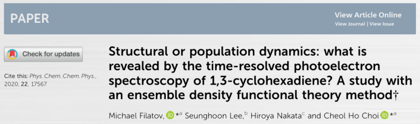


Static PE spectra



Intensity of TRPE signal:

$$I_{\mathrm{TRPES}}(\mathrm{eBE};t)\propto \sum_{K}^{\text{States}}\ \sum_{p}^{\text{orbitals}} N_K(t)\,\left|n_p(t)\right|^2\,\delta\big(\varepsilon_p(t)-\mathrm{eBE}\big)$$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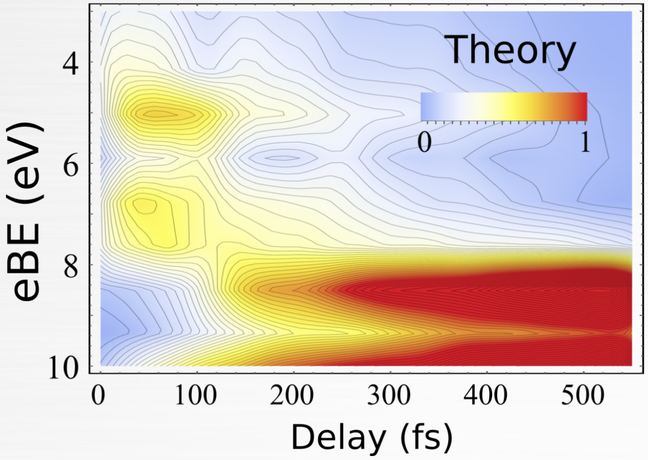
Cite this: Phys. Chem. Chem. Phys., 2020, 22, 17567

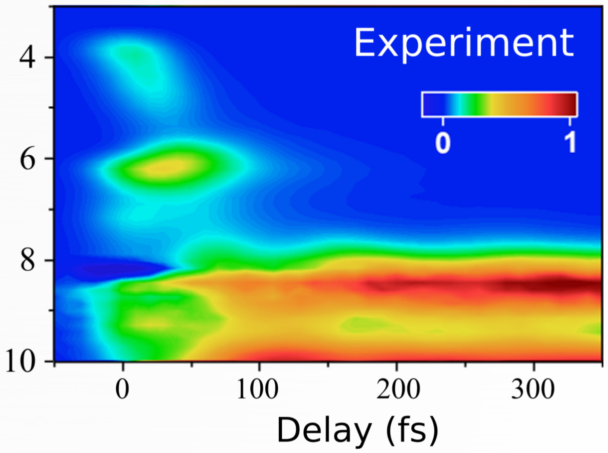
Structural or population dynamics: what is revealed by the time-resolved photoelectron spectroscopy of 1,3-cyclohexadiene? A study with an ensemble density functional theory method†

Michael Filatov, Seunghoon Lee, Hiroya Nakata and Cheol Ho Choi

PCCP. 22, 17567 (2020)

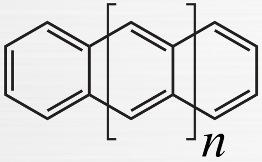
Karashima et al., JACS. 143, 8034 (2021)





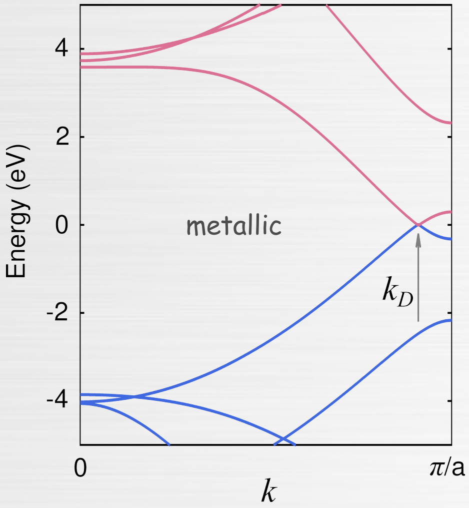
Band Structure of Polyacene

Polyacenes:

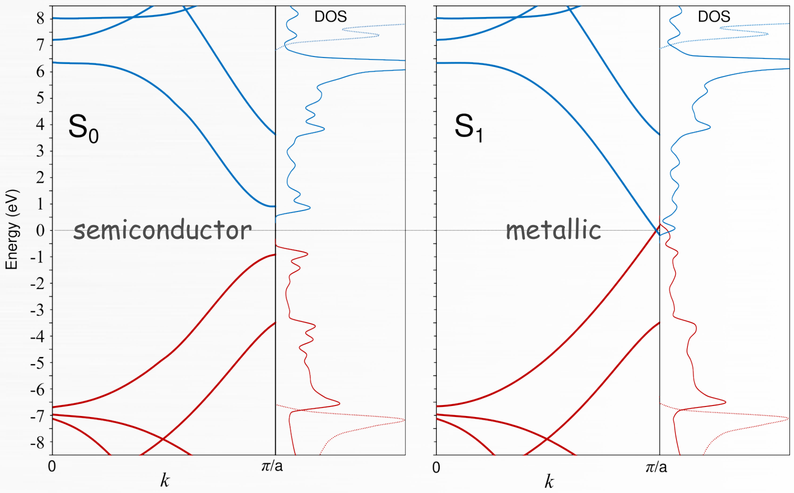


Bands dispersion from Dyson's orbitals of oligomers

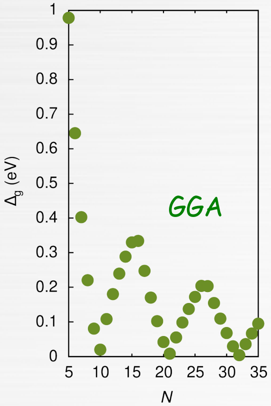
GGA/PBC calculations



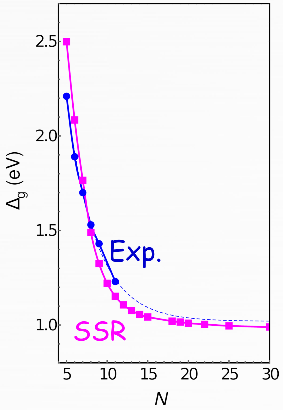
SSR/oligomer calculations



oscillatory optical gap!



Nat Commun 5, 5000 (2014)



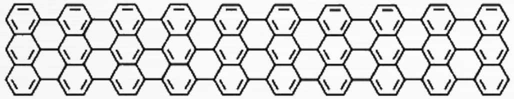
monotonic optical gap!

agrees with the experiment

Carbon Trends 7, 100146 (2022)

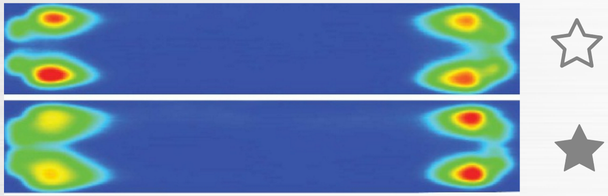
Band Structure of Graphene Nano-ribbons

7-atom-wide nano-ribbons



Experiment (STS)

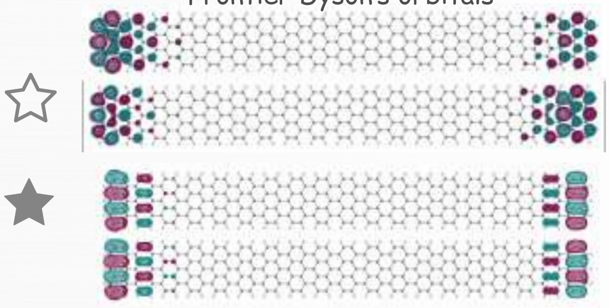
STS maps of empty and filled states



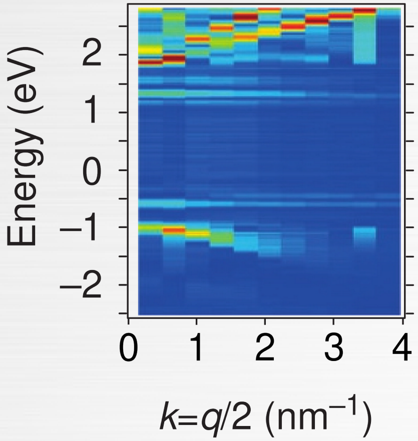
on NaCl surface

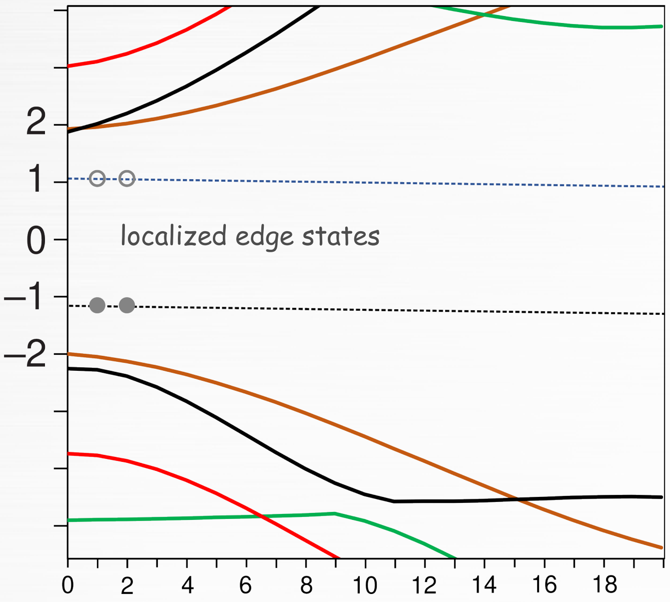
Calculation (SSR)

Frontier Dyson's orbitals



Occupied and empty bands from STS

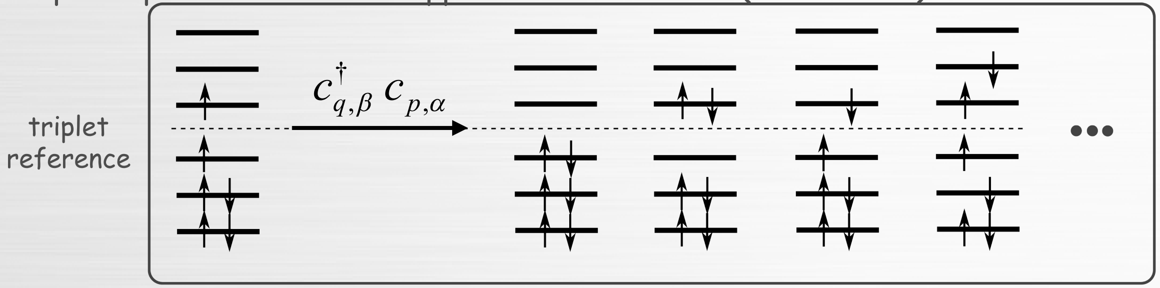




Nat Commun 7, 11507 (2016)

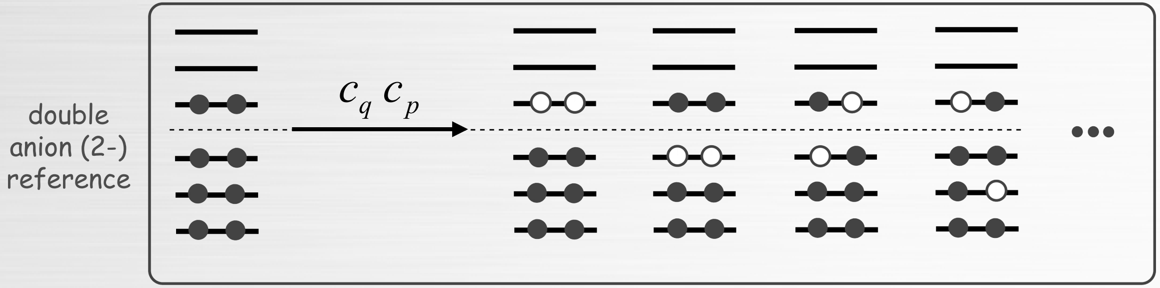
Alternatives

spin-flip Tamm-Dancoff Approximated TDDFT (SF-TDDFT)



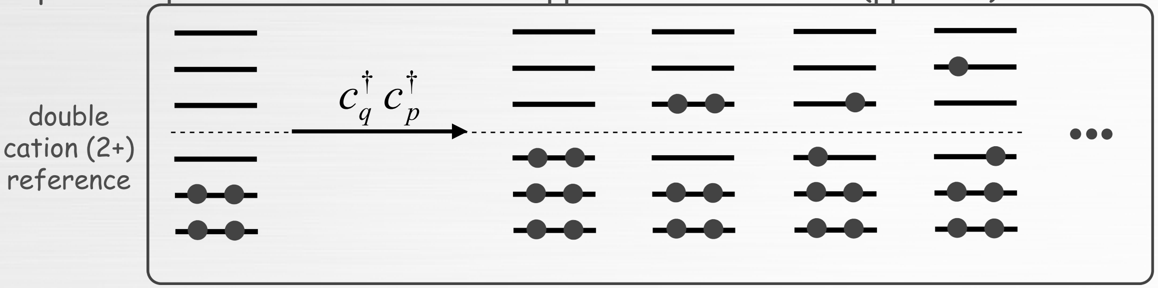
- spin-contamination (improvable)
  - mixed reference spin-flip
- single and double excitations only
  - no singlet fission
- non-uniqueness of reference state
  - multiple triplets may exist

hole-hole Tamm-Dancoff Approximated TDDFT (hh-TDA)



- charged reference state (2-)
- single and double excitations only
  - no singlet fission
- limited orbital adjustment
  - mixing with occupieds only

particle-particle Tamm-Dancoff Approximated TDDFT (pp-TDA)



- charged reference state (2+)
- single and double excitations only
  - no singlet fission
- limited orbital adjustment
  - mixing with virtuals only

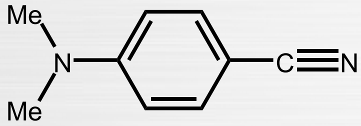
Total Energy non-Conservation in MRSF Dynamics

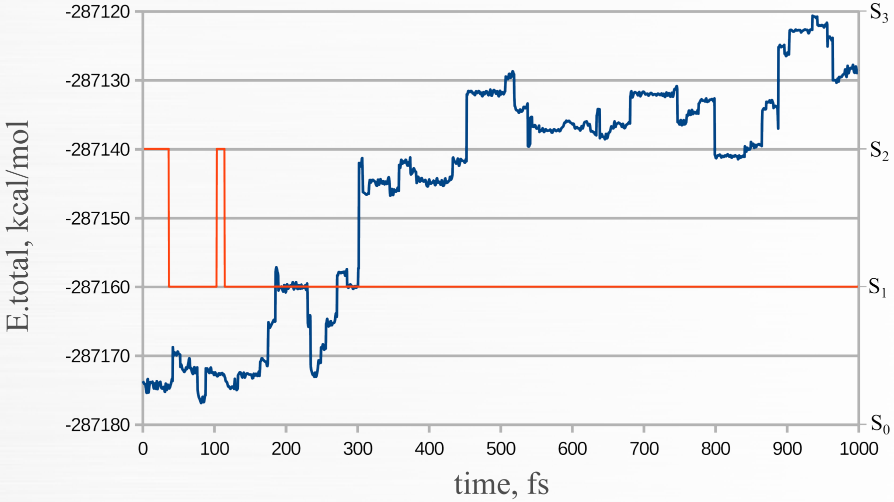
NAMD simulations MRSF-BH&HLYP/6-31G*

NVE ensemble

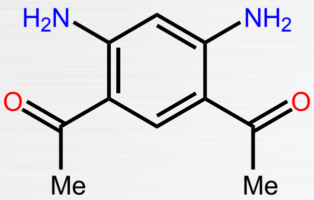
Total Energy = Nuclear KE + PES

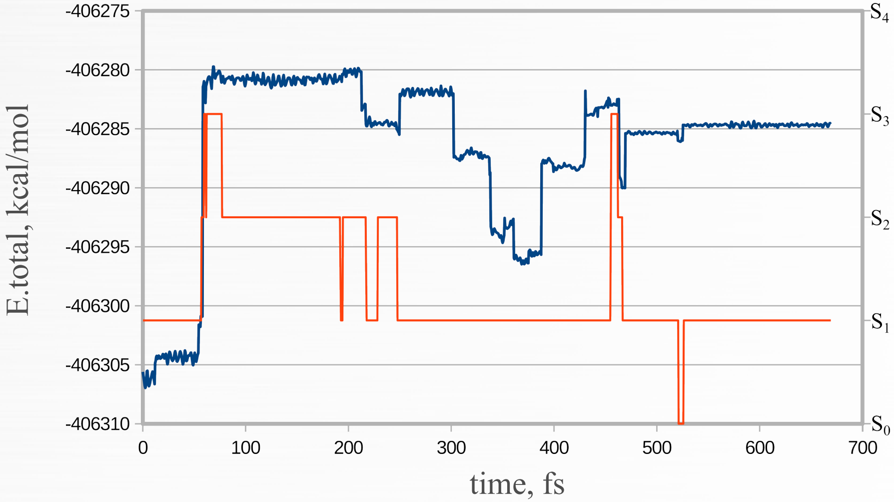
DMABN





m-DAPA





Energy jumps: Changing (triplet) reference state; cannot be cured easily

That was all!