Ensemble Density Functional Theory Method for Non-Adiabatic Dynamics of Excited States

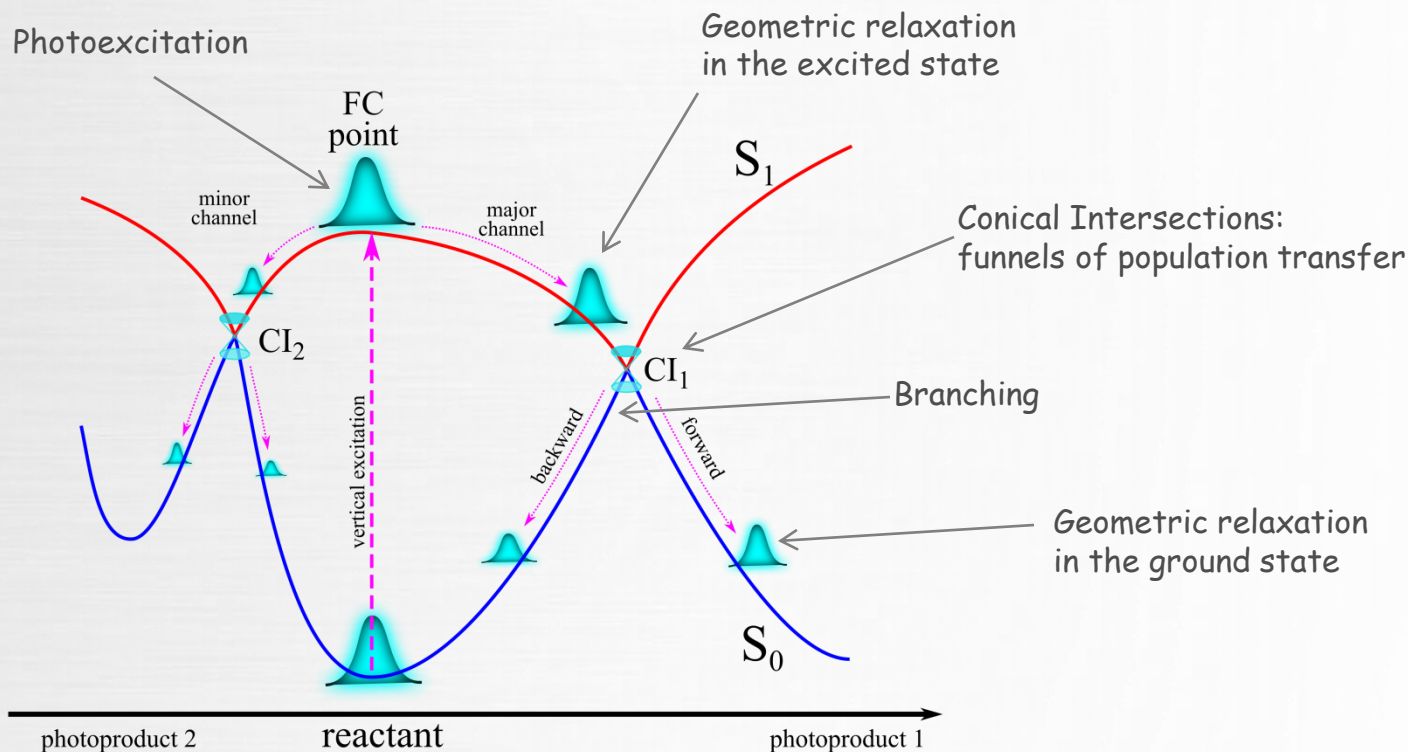*Michael Filatov*

SMU, Dallas (TX)

Virtual International Seminar on Theoretical Advancements, 24 May 2023

The Plan

- Motivation for this work
    - non-adiabatic dynamics of excited states
    - what QC methods are available
    - requirements for QC methods
- DFT/TDDFT vs ensemble DFT
    - advantages of eDFT
- Practical implementation of eDFT
    - REKS/SSR formalism
    - multi-configurational states
- Application of REKS/SSR to NAMD
    - technical aspects
    - results
    - TRPES and population dynamics
- Directions for further development
    - active space extension
    - automatic code generation
- Conclusions

Non-Adiabatic Molecular Dynamics (NAMD)

Ultrafast (~1-2 ps) transformations in excited states involving population and energy transfer

Photoexcitation

Geometric relaxation
in the excited state

FC
point

minor
channel

major
channel

S_1

Conical Intersections:
funnels of population transfer

CI_2

vertical excitation

CI_1

Branching

backward

forward

Geometric relaxation
in the ground state

S_0

photoproduct 2   reactant   photoproduct 1

Population transfer $S_k \to S_l$ mediated by nuclear motion; non-adiabatic coupling $\left\langle \Psi_l \left| \vec{\nabla} \Psi_k \right\rangle \right.$

Trajectory Surface-Hopping (TSH) Dynamics

Initial sampling $\rightarrow$ Classical EOM $\rightarrow$ Surface hopping $\rightarrow$ Final evaluation

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

sampling of the
Wigner function at T

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

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

probability
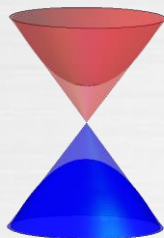depends on τ_{kl}

statistical averaging of
observables

Barbatti, WIREs, 1, 620 (2011)

NAC vector:

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

Energy

Surface hopping propagation

Reaction coordinate
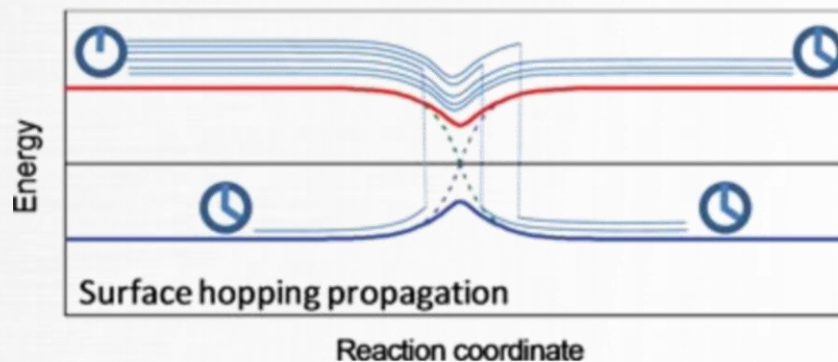
conical intersection

double cone topology

transition probability (Landau-Zener):

$$P(S_l \rightarrow S_k) = \exp\left[-\frac{\pi}{4\hbar} \cdot \frac{E_l - E_k}{\vec{v} \cdot \vec{\tau}_{kl}} \right]$$

QC Methods and Conical Intersections

CI topology matters (JCP, 155, 124111 (2021):

linear crossing yields wrong dynamics

correct topology	wrong topology
SA-CASSCF	SS-CASSCF
MS-CASPT2, XMS-CASPT2, XMCQDPT2	SS-CASPT2
MRCI(SD)	ADC(2), CC2
SF-TDDFT	TDDFT
	⋮
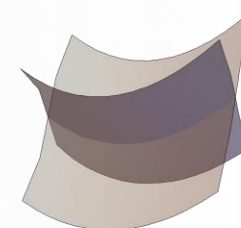
Many popular QC methods are inappropriate for NAMD simulations:

Levine, B. G et al. Conical intersections and double excitations in time-dependent density functional theory. *Mol. Phys.* **2006**, 104, 1039–1051

Nikiforov, A. et al. Assessment of approximate computational methods for conical intersections and branching plane vectors in organic molecules. *J. Chem. Phys.* **2014**, 141, 124122

Gozem, S. et al. On the Shape of Multireference, EOM-CC, and DFT Potential Energy Surfaces at a Conical Intersection. *J. Chem. Theory Comput.* **2014**, 10, 3074–3084

Tuna, D. et al. Assessment of Approximate Coupled-Cluster and Algebraic-Diagrammatic-Construction Methods for Ground- and Excited-State Reaction Paths and the Conical-Intersection Seam of a Retinal-Chromophore Model. *J. Chem. Theory Comput.* **2015**, 11, 5758–5781

DFT/TDDFT Formalism

DFT – ground state theory (H-K theorems)

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

Disadvantages of standard (spin-conserving, linear-response) TD-DFT:

- Limited class of excitations can be treated
  - no multiple (double, etc.) excitations

- No coupling btw the ground state and response (excited) 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

ensemble DFT: Alternative to KS DFT

	KS DFT	eDFT
Applicability:	ground state only	ground and excited states
V-representability:	assumed	rigorously proved
Non-interacting reference:	single-determinant; fixed occupations	multi-configurational; fractional occupations
Bond breaking:	brakes symmetry and/or wrong	doesn't brake symmetry
Excited states:	perturbational (response)	variational (ΔSCF) perturbational (response)
S_0/S_1 PES crossings (avoided and conical):	no	yes
multiple excitations:	no	yes

Ensemble DFT (eDFT)

Ground states:

S. M. Valone   (1980)
M. Levy   (1982)
E. H. Lieb   (1983)
H. & R. Englisch   (1984)

Any physical density can be mapped onto _ensemble_ density

$$\rho \Leftrightarrow \rho_{ens} = \sum_k w_k \, \rho_k \quad = \sum_p n_p \left| \phi_p(\vec{r}) \right|^2$$

Exact functional (E.H.Lieb):

$$F[\rho] = \sum_k w_k \, F[\rho_k]$$

Excited states:

Gross, Oliveira, Kohn (1988):   variational principle for ensembles of ground and excited states

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

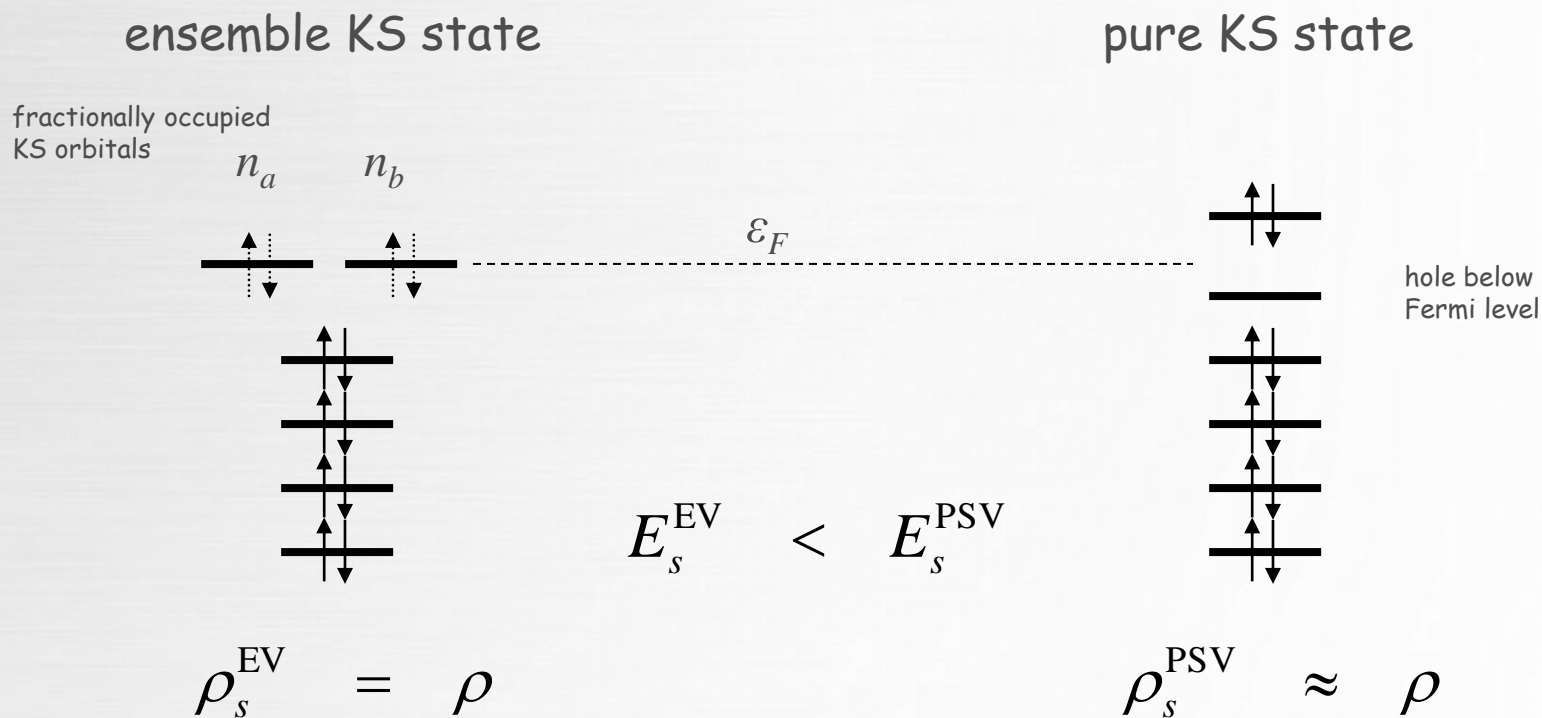basis for variational DFT of excited states

eDFT and fractional orbital occupations

E.-J. Baerends et al., (1998):　　　　　molecular systems H_2+H_2, C_2, CH_2

R. C. Morrison (2002):　　　　　　　Be-like atomic systems

ensemble KS state　　　　　　　　　　　　　　　pure KS state

fractionally occupied
KS orbitals

n_a　　　n_b

ε_F

hole below
Fermi level

$$E_s^{\text{EV}} \quad < \quad E_s^{\text{PSV}}$$

$$\rho_s^{\text{EV}} \quad = \quad \rho \qquad\qquad \rho_s^{\text{PSV}} \quad \approx \quad \rho$$

eDFT and non-dynamic correlation

Ullrich, Kohn (2001)
van Leeuwen (2003)

not all exact densities can be mapped onto single KS determinant

some need ensemble KS densities

exact density

mostly dynamic correlation

single KS det.

non-dynamic + dynamic

ensemble of KS dets.
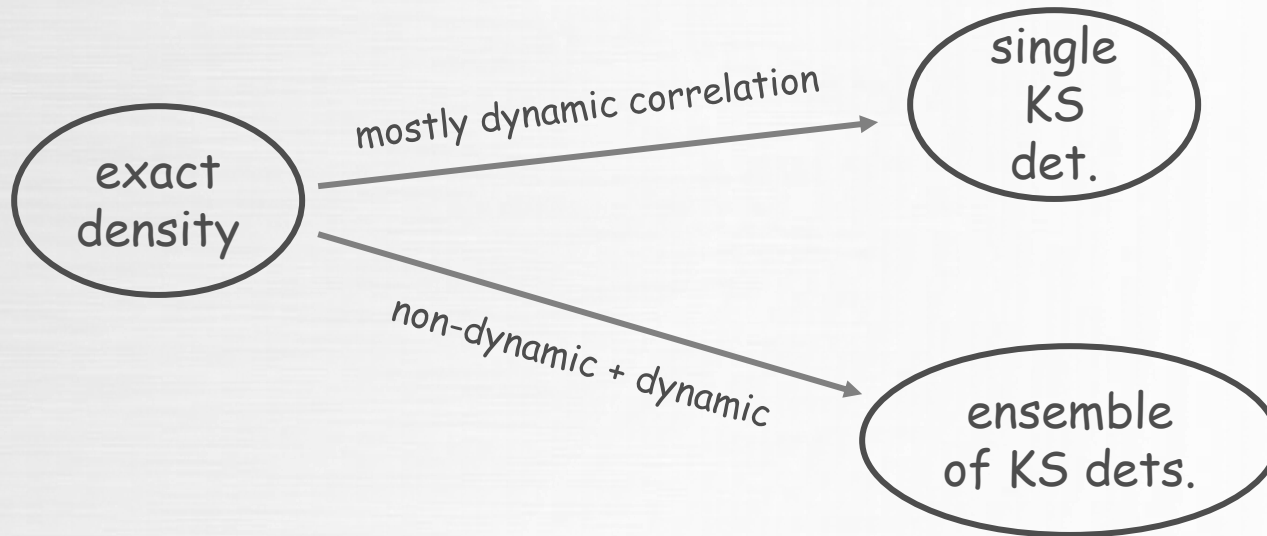
Non-dynamic correlation (WFT) $\rightarrow$ ensemble representation (DFT)

REKS Method: Practical Implementation of eDFT

What it is not: Not DFT-FON

$$E_{Hxc}^{DFT-FON}\left[\rho\right]= E_{Hxc}^{DFT}\left[\sum_p n_p \left|\phi_p\right|^2\right] \quad \left(+ \quad \text{correcting terms}\right)$$

critique: Averill, F.W.; Painter, G.S. Phys. Rev. B 46, 2498–2502 (1992)

What it is:

REKS: spin-restricted ensemble-referenced KS method

$$E_{Hxc}^{REKS}\left[\rho\right]= \sum_k w_k[n_p]\, E_{Hxc}^{approx.}\left[\rho_k\right]$$

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

- REKS energy functional is a weighted sum of energies of several configurations

- Obtained from mapping onto non-interacting ensemble KS reference state (adiabatic connection)

- Wavefunction theory (WFT) is used to derive energy expression at infinitesimal coupling strength λ

| $\lambda = 0$ ensemble reference | $\xrightarrow{\text{WFT}}$ | $\lambda \approx 0$ multi-reference state | $\xrightarrow{\lambda\text{-integration}}$ | $\lambda = 1$ REKS energy |

$$\hat{H}^{\lambda} = -\tfrac{1}{2}\sum_i \nabla_i^2 + \sum_i V_{ext}^{\lambda}(\vec{r}_i)+ \lambda \sum_{i<j} r_{ij}^{-1}$$
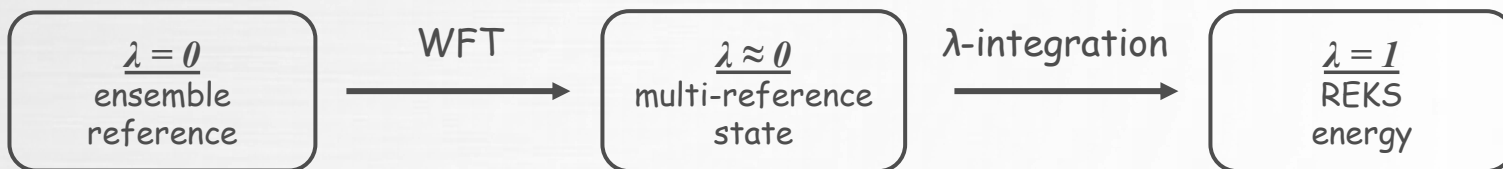
Adiabatic connection
J. Harris, R. O. Jones, J. Phys. F 4, 1170–1186 (1974)
J. Harris, Phys. Rev. A 29, 1648 (1984)

REKS Energy Functional

WFT:

$$E_0^\lambda = \sum_{i,j}^n C_{0,i}^\lambda C_{0,j}^\lambda \left\langle \Phi_i \left| \hat{H}^\lambda \right| \Phi_j \right\rangle$$
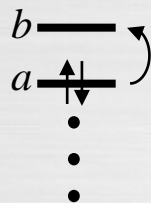
?

eDFT:

$$E_0^\lambda = \sum_k^n w_k^\lambda \, E^\lambda \left[\rho_k^\lambda \right]$$

Simplification: Use GVB wavefunctions (PPS: perfectly paired singlet)
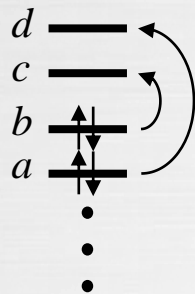in GVB, CI coeffs translate directly to FONs

REKS(2,2):

b ——

a ⬆⬇——

$$E^{(2,2)} = \frac{n_a}{2} E_{a\bar{a}} + \frac{n_b}{2} E_{b\bar{b}} + f(n_a, n_b) \Delta_{ab}$$

MF, S. Shaik, CPL 304, 429 (1999)
MF, S. Shaik, JCP 110, 116 (1999)

E is optimized w.r.t. the orbitals and FONs

REKS(4,4):

d ——
c ——
b ⬆——
a ⬆⬇——

$$E^{(4,4)} = \frac{n_a \, n_b}{4} E_{a\bar{a}b\bar{b}} + \frac{n_a \, n_c}{4} E_{a\bar{a}c\bar{c}} + \frac{n_b \, n_d}{4} E_{b\bar{b}d\bar{d}} + \frac{n_c \, n_d}{4} E_{c\bar{c}d\bar{d}} + f(n_a, n_d) \Delta_{ad} + f(n_b, n_c) \Delta_{bc}$$

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)

eDFT for excited states

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

eDFT: variational theory

GOK variational principle for ensembles (1988):

exact energies

$$\sum_k \omega_k \left\langle \Phi_k \left| \hat{H} \right| \Phi_k \right\rangle \geq \sum_k \omega_k \, E_k \; ; \qquad \sum_k \omega_k = 1$$

trial functions

Example: two-state problem (ground state and 1 excited state):

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

excitation energy: $\Delta E_{10} = \dfrac{E_{ens}(\omega) - E_0}{\omega} = \dfrac{E_1 - E_{ens}(\omega)}{1-\omega}$ explicit functional of states

$$\Delta E_{10} = \frac{d\,E_{ens}(\omega)}{d\omega}$$ implicit functional of states

State-Interaction State-Averaged REKS

GVB description is incomplete

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

REKS states – _diabatic states_ for GVB-like secular problem

$$
\begin{pmatrix} E_0^{PPS} & h_{01} & \cdots \\ h_{01} & E_1^{OSS} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}
\begin{pmatrix} a_0 \\ a_1 \\ \vdots \end{pmatrix}
=
\begin{pmatrix} E_0^{SSR} & 0 & \cdots \\ 0 & E_1^{SSR} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}
\begin{pmatrix} a_0 \\ a_1 \\ \vdots \end{pmatrix}
$$

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

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

Available setups:

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

SSR(4,4)
$$
E_{SA-REKS} = \tfrac{1}{3} E_0^{PPS} + \tfrac{1}{3} E_1^{OSS_1} + \tfrac{1}{3} E_2^{OSS_2}
$$

$$
E_{SA-REKS} = \tfrac{1}{2} E_0^{PPS} + \tfrac{1}{2} E_6^{DSPS}
$$

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

REKS/SSR Method: What's Available?

Analytical energy gradient; SA-REKS(2,2) & SSR(2,2) methods only (so far):

relaxed density matrix

Lagrangian

$$\frac{\partial E^X}{\partial \lambda} = tr\left(\mathbf{P}^X \mathbf{h}^\lambda\right) - \frac{1}{2} tr\left(\mathbf{W}^X \mathbf{S}^\lambda\right) + \sum_L \tilde{C}_L^X \frac{\partial' E_L^{2e}}{\partial \lambda} - \sum_L C_L^{SA} \sum_\sigma tr\left(^X \mathbf{R}_L^\sigma \mathbf{T}_L^{\sigma,\lambda(2e)}\right)$$

Non-Adiabatic Coupling Vector (SSR(2,2)):

$$\vec{\tau}_{01} = \frac{\left\langle S_0 \left| \vec{\nabla}\hat{H} \right| S_1 \right\rangle}{E_1 - E_0} = \frac{1}{E_1^{SSR} - E_0^{SSR}} \frac{a_{00} a_{01} \vec{\nabla}\left(E^{PPS} - E^{OSS}\right) + \vec{\nabla}h_{01}}{a_{00} a_{11} + a_{01} a_{10}}$$

Ionization Energies (via Extended Koopmans' Theorem):

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

Dyson's norm: $|n|^2 = \mathbf{C}^\dagger \mathbf{C}$ - probability of ionization

Dyson's orbitals

ionisation energies

gives access to TRPE spectra

REKS Method: Practical Implementation of eDFT

Characteristics of REKS/SSR methodology:

- Conforms with eDFT

- Employs ensemble non-interacting reference state

- Describes non-dynamic correlation in ground and excited states

  - correct <u>dissociation</u> of chemical bonds

  - <u>variational</u> excited states

  - correct <u>conical intersections</u> and avoided crossings

  - includes <u>multiple</u> (double, etc.) excitations

- Can be used with any density functional

- Computational cost: mean-field cost

Benchmarks: vertical excitation energies

MADs (eV) for 15 π-π* and n-π* transitions (w.r.t. 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

SSR and TD-DFT are equally good for simple molecules   JCP 141, 024112 (2014)

Bond dissociation and excited states

Lithium hydride: $1^1\Sigma^+$ and $2^1\Sigma^+$ states

SSR-ωPBEh/aug-cc-pVTZ
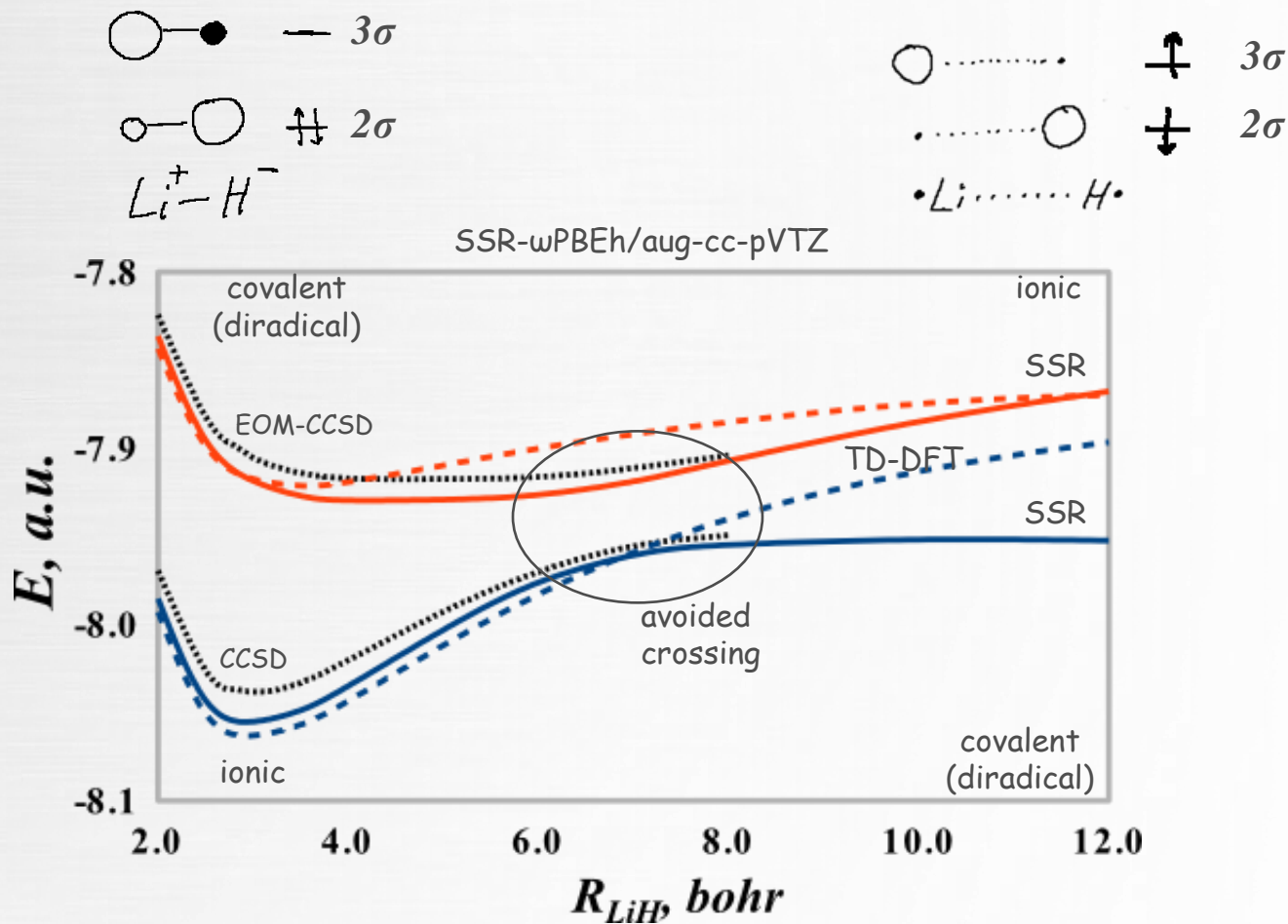
Conical intersections

PSB3 – a simple model of retinal chromophore
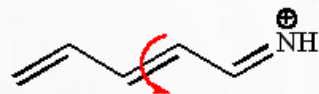
CI reached by bond length alternation (BLA) and torsion (Robb, Olivucci et al., 1997 – …)
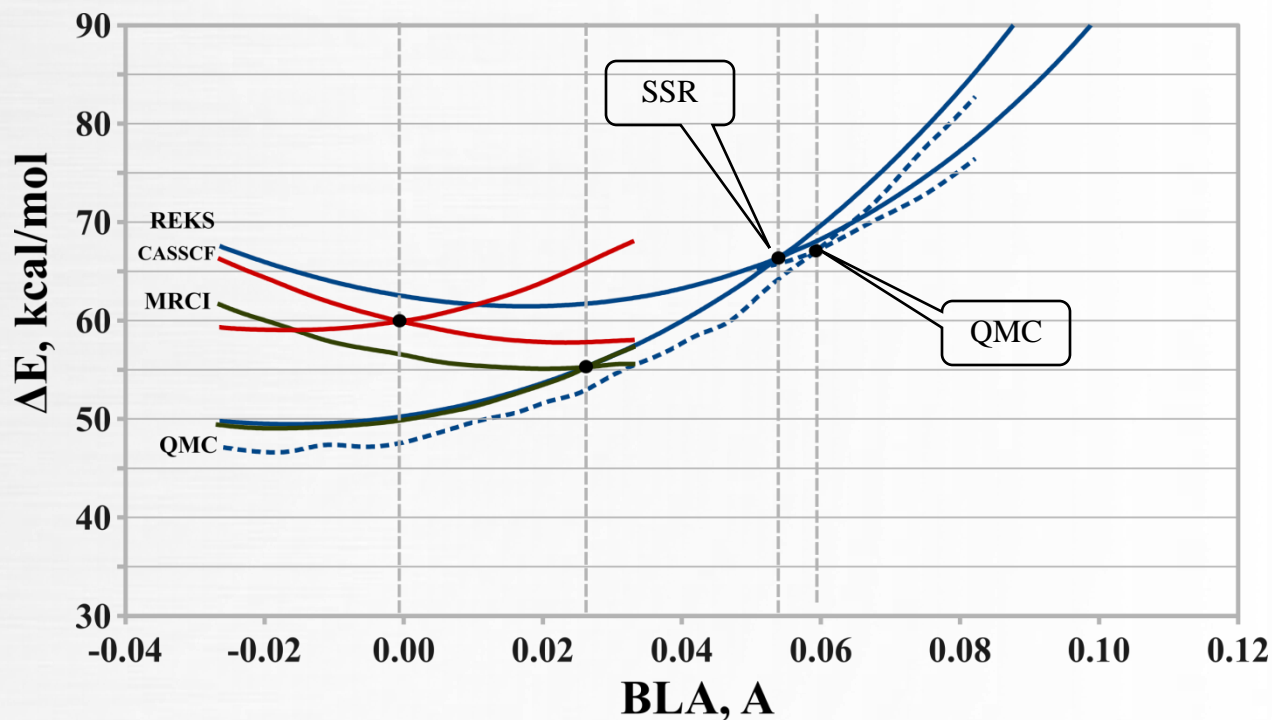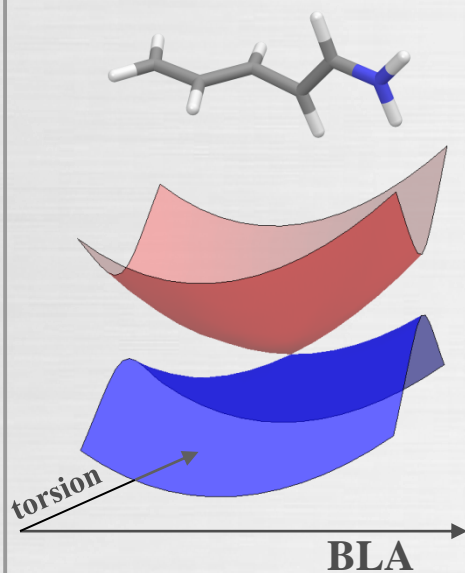
CASSCF, MRCISD: JCTC 8, 4069(2012)
QMC: JCTC 11, 992 (2015)
SSR: JCTC 14, 4499 (2018)

NAMD simulations of PSB3 photo-isomerization

Formalism: SSR + DISH-XF

decoherence induced surface
hopping from exact factorization

$cis:trans = 63:37$

18%

82%

MSPT2:   79:21
CASSCF: 54:46

$\tau(S_1) = 99 \pm 51$ fs
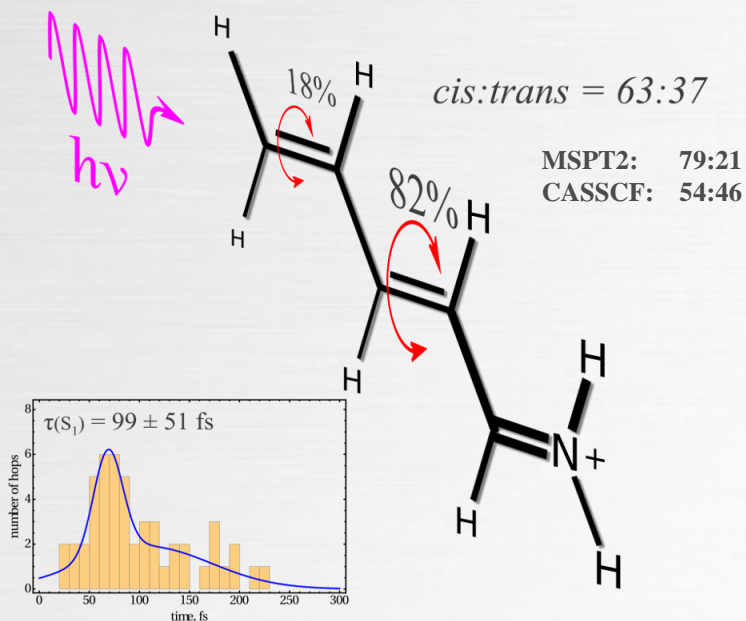
other works: 100 – 130 fs

Reaction channels:

	SSR	MSPT2	CASSCF
major channel	central C=C	central C=C	central C=C
minor channel	terminal C=C	terminal C=C	terminal C=N
major/ minor	82:18	89:11	78:22

SSR: JCTC 14, 4499 (2018)

MSPT2, CASSCF: JPC B 120, 1940 (2016)

NAMD simulations of PSB3 photo-isomerization

DISH-XF/SSR(2,2) simulations:

50 trajectories;

Wigner sampling at 300K; NVE ensemble;

time step 0.24 fs; duration 300 fs (1250 steps)

Population of S_1 (blue) and S_0 (red)

Total (el. + nuc.) energy conservation

$\sigma \sim 0.04$ kcal/mol
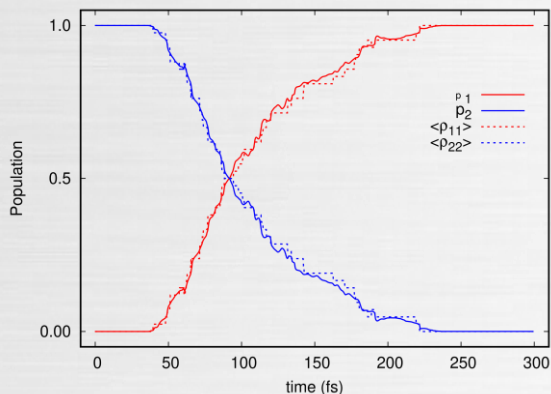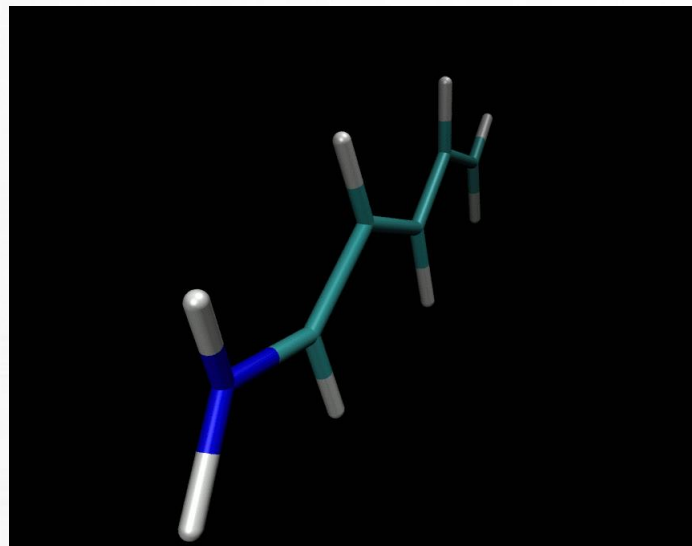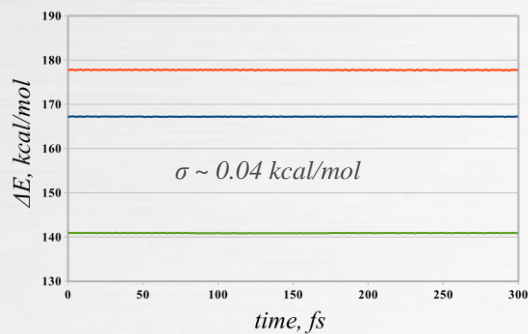
Sample trajectory:
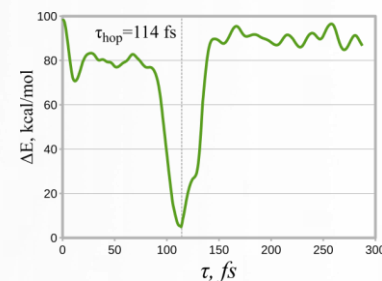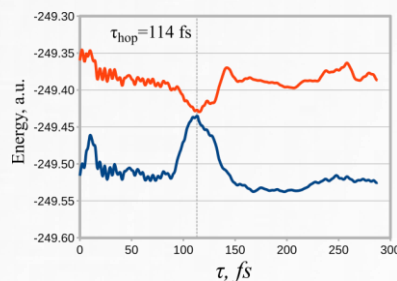
Normal Mode Analysis of the trajectories:

Forward (trans →cis): HOOP mode in sync with skeletal torsion modes

Backward (trans →trans): no synchronization

NAMD simulations of PSB3 photo-isomerization

DISH-XF/SSR(2,2) simulations:

50 trajectories;

Wigner sampling at 300K; NVE ensemble;

time step 0.24 fs; duration 300 fs (1250 steps)

Population of S_1 (blue) and S_0 (red)

Total (el. + nuc.) energy conservation

$\sigma \sim 0.04$ kcal/mol
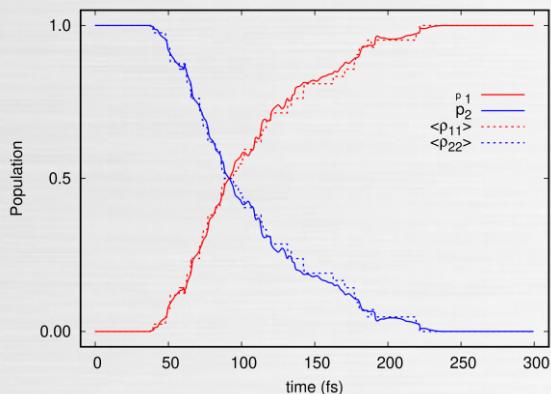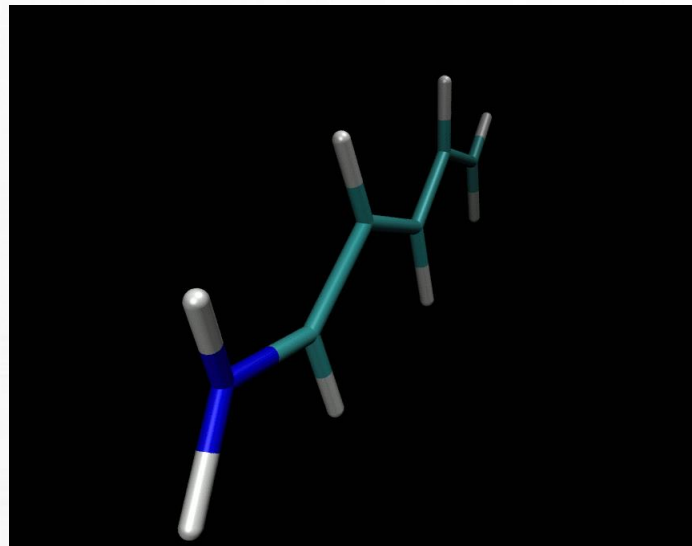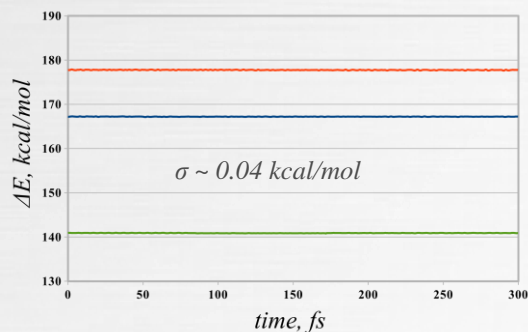
Sample trajectory:
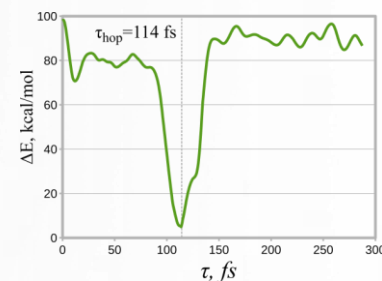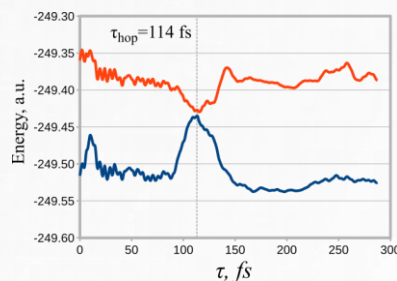
Normal Mode Analysis of the trajectories:

Forward (trans →cis): HOOP mode in sync with skeletal torsion modes

Backward (trans →trans): no synchronization

Other Applications of REKS/SSR

Rhodopsins/retinals

THE JOURNAL OF
PHYSICAL CHEMISTRY
Letters
Cite This: *J. Phys. Chem. Lett.* 2019, 10, 2862–2868   Letter   pubs.acs.org/JPCL

Nonadiabatic Photodynamics of Retinal Protonated Schiff Base in Channelrhodopsin 2

Ruibin Liang, Fang Liu, and Todd J. Martínez

JPCLett 10, 2862 (2019)

J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Cite This: *J. Am. Chem. Soc.* 2019, 141, 18193–18203   Article   pubs.acs.org/JACS

First-Principles Characterization of the Elusive I Fluorescent State and the Structural Evolution of Retinal Protonated Schiff Base in Bacteriorhodopsin

Jimmy K. Yu, Ruibin Liang, Fang Liu, and Todd J. Martínez

JACS 141, 18193 (2019)

J|A|C|S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS   Article
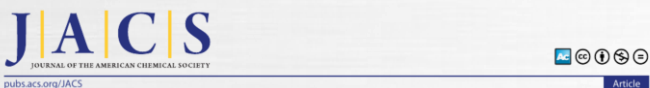
Electrostatic Control of Photoisomerization in Channelrhodopsin 2

Ruibin Liang, Jimmy K. Yu, Jan Meisner, Fang Liu, and Todd J. Martinez

JACS 143, 5425 (2021)

nature communications

Article   https://doi.org/10.1038/s41467-022-33993-4

On the fluorescence enhancement of arch neuronal optogenetic reporters

Received: 27 May 2022
Accepted: 7 October 2022
Published online: 28 October 2022

Leonardo Barneschi[1], Emanuele Marsili[1,2,7], Laura Pedraza-González[1,8], Daniele Padula[1], Luca De Vico[1], Danil Kaliakin[3], Alejandro Blanco-González[3], Nicolas Ferré[4], Miquel Huix-Rotllant[4], Michael Filatov[5] & Massimo Olivucci[1,3,6]

Nat. Comm. 13, 6432 (2022)

Other Applications of REKS/SSR

Light Driven Molecular Rotary Motors

THE JOURNAL OF PHYSICAL CHEMISTRY *Letters*

Letter

pubs.acs.org/JPCL

Computational Design of a Family of Light-Driven Rotary Molecular Motors with Improved Quantum Efficiency

Alexander Nikiforov,[†] Jose A. Gamez,[‡] Walter Thiel,[†] and Michael Filatov[#,‖,§]

JPCLett 7, 105 (2016)

THE JOURNAL OF PHYSICAL CHEMISTRY *Letters*

Letter

Cite This: *J. Phys. Chem. Lett.* 2018, 9, 4995−5001

pubs.acs.org/JPCL

Fulgides as Light-Driven Molecular Rotary Motors: Computational Design of a Prototype Compound

Michael Filatov,[*,†] Marco Paolino,[‡] Seung Kyu Min,[†] and Kwang S. Kim[†]

JPCLett 9, 4995 (2018)

ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Commun.,* 2019, 55, 5247

Received 11th March 2019,
Accepted 9th April 2019

DOI: 10.1039/c9cc01955c

Design and photoisomerization dynamics of a new family of synthetic 2-stroke light driven molecular rotary motors†

Michael Filatov,[*a] Marco Paolino,[b] Seung Kyu Min[c] and Cheol Ho Choi[a]

Chem. Comm. 55, 5247 (2019)

nature communications

Article

https://doi.org/10.1038/s41467-022-33695-x

Towards the engineering of a photon-only two-stroke rotary molecular motor

Received: 7 February 2022

Accepted: 27 September 2022

Published online: 28 October 2022

Michael Filatov(Gulak)[1], Marco Paolino[2], Robin Pierron[3], Andrea Cappelli[2], Gianluca Giorgi[2], Jérémie Léonard[3], Miquel Huix-Rotllant[4], Nicolas Ferré[4], Xuchun Yang[5], Danil Kaliakin[5], Alejandro Blanco-González[5] & Massimo Olivucci[2,5]

Nat. Comm. 13, 6433 (2022)

Design of a 2-stroke molecular motor

photon/heat
4-stroke motor

photon only
2-stroke motor
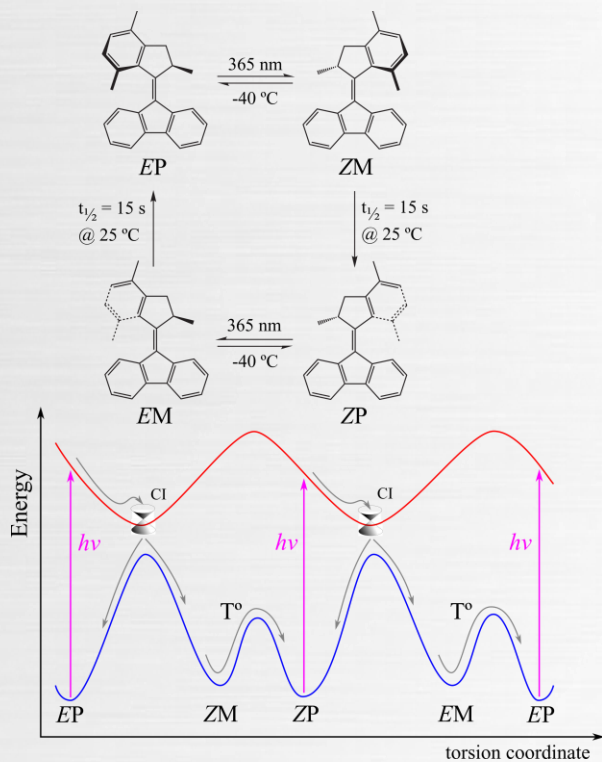
- temperature dependent
- interrupted rotation
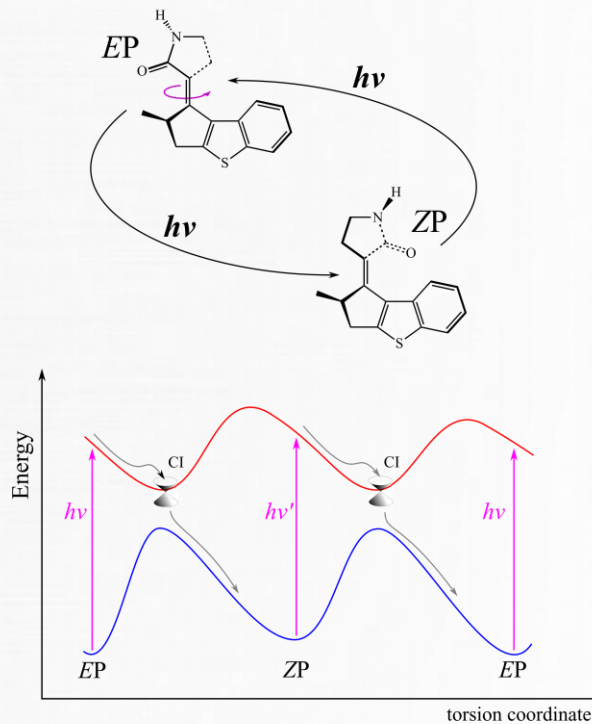
- temperature independent
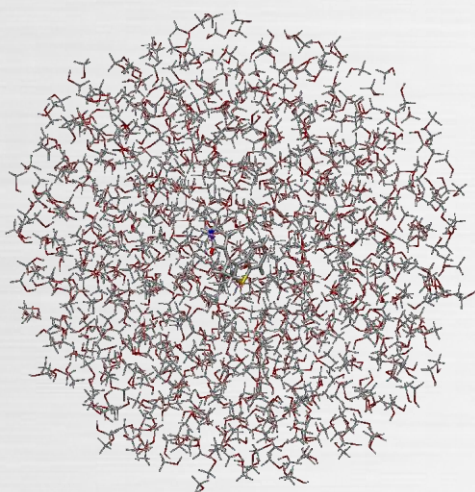- continuous rotation

Nat. Comm. 13, 6433 (2022)

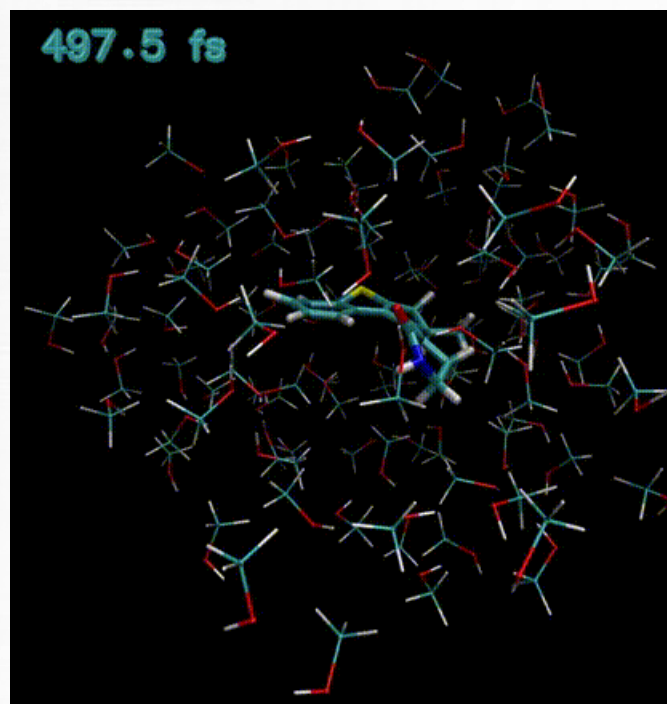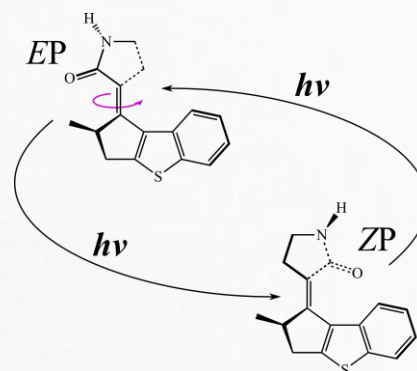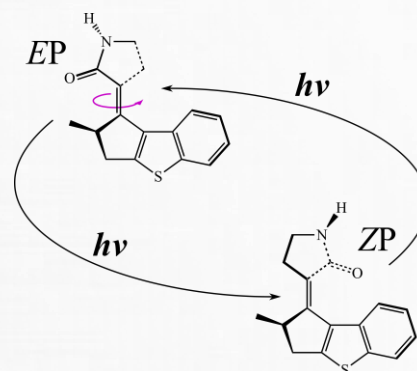# Design of a 2-stroke molecular motor

QM/MM NAMD simulations:

SSR(2,2)-BH&HLYP/6-31G* + Py-UNI-xMD + Tinker6.3

$906 \times$ MeOH + MTDP

$EP \rightarrow ZP$ photo-isomerization

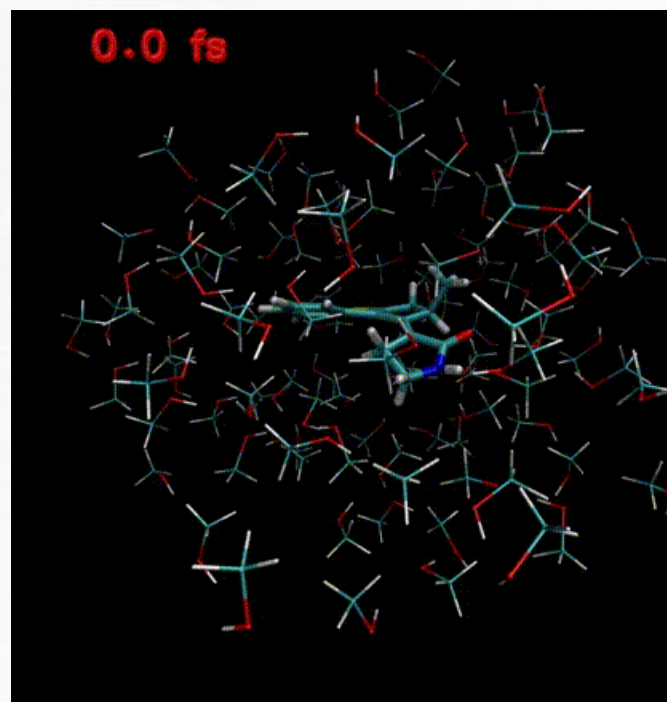|	theor.	exp.
$\tau(S_1)$, fs	523±69	~600
Φ_{iso}	0.33±0.09	0.25±0.05

Design of a 2-stroke molecular motor

QM/MM NAMD simulations:

SSR(2,2)-BH&HLYP/6-31G* + Py-UNI-xMD + Tinker6.3

906 × MeOH + MTDP

$EP \rightarrow ZP$ photo-isomerization

	theor.	exp.
$\tau(S_1)$, fs	523±69	~600
Φ_{iso}	0.33±0.09	0.25±0.05

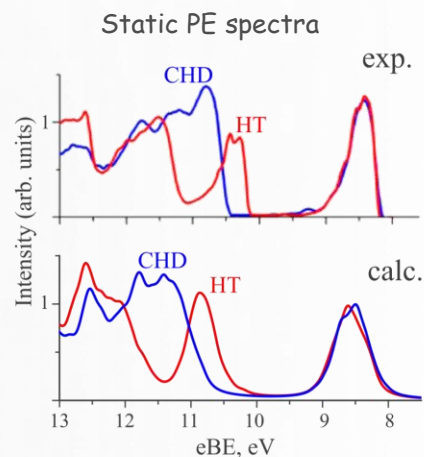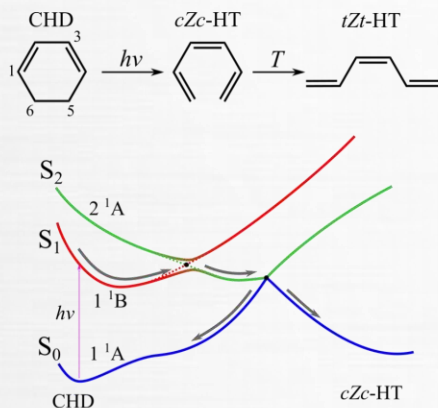# Ring Opening in Cyclohexadiene

Dynamics characteristics

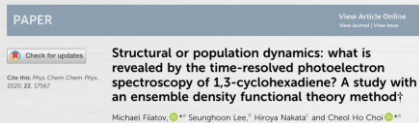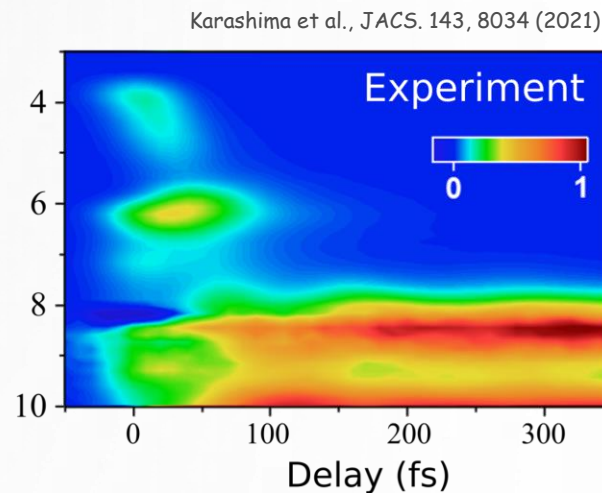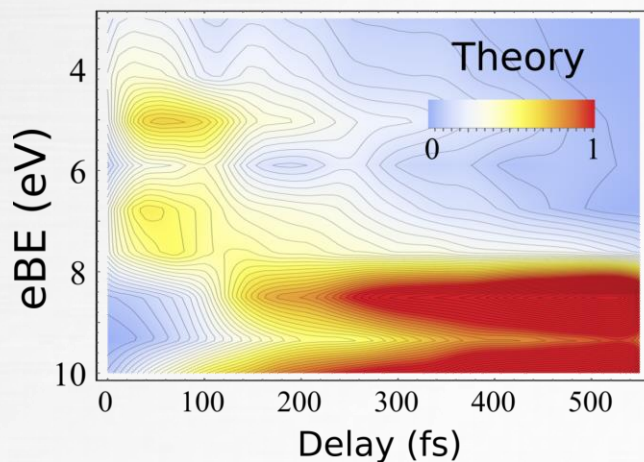|	CHD:HT	$\tau(S_1)$, fs
theor.	36:64	234±8
exp.	30:70	230±30
		170±80
		110–130

Mol. Phys. 117, 1128 (2019)

Intensity of TRPE signal:

Static PE spectra

$$I_{TRPES}\left(\text{eBE};t\right) \propto \sum_{K}^{\text{States}} \sum_{p}^{\text{orbitals}} N_K(t)\left|n_p(t)\right|^2 \delta\left(\varepsilon_p(t) - \text{eBE}\right)$$

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

PAPER

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†

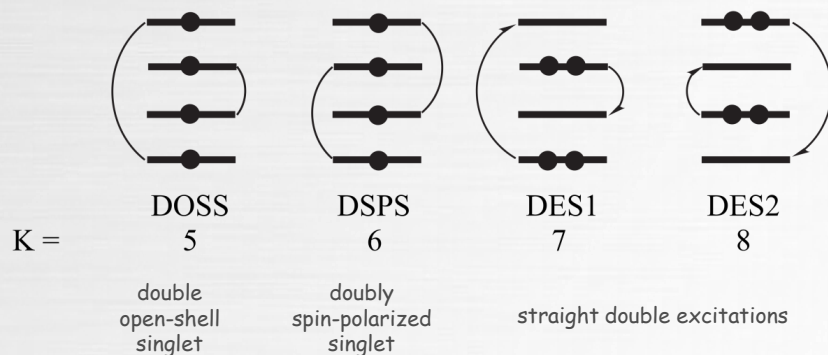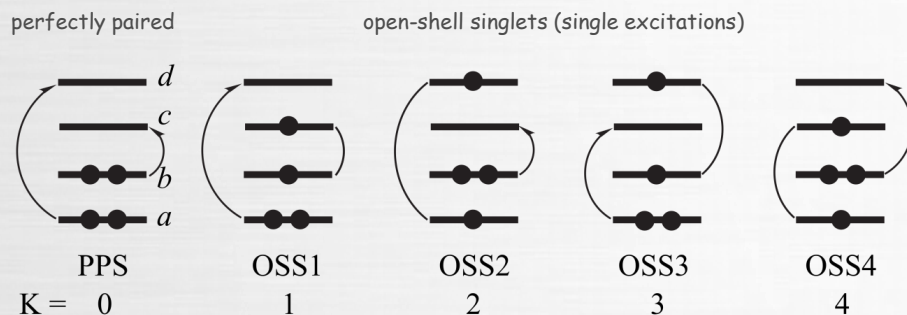Michael Filatov, Seunghoon Lee, Hiroya Nakata and Cheol Ho Choi

PCCP. 22, 17567 (2020)

Extension of Active Space: SSR(4,4)

Configurations (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 singlet

straight double excitations

Orbitals optimized for averaged state:
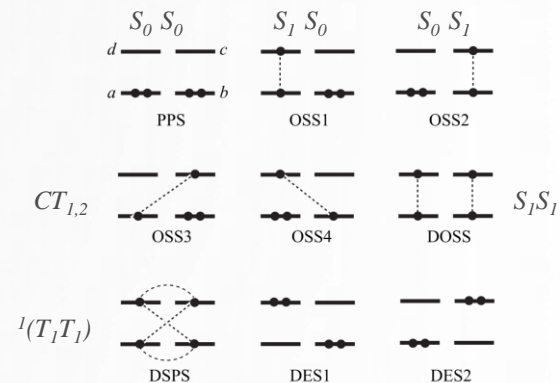
3SA = 0 + 1 + 2

2SA = 0 + 6

more states can be added as needed
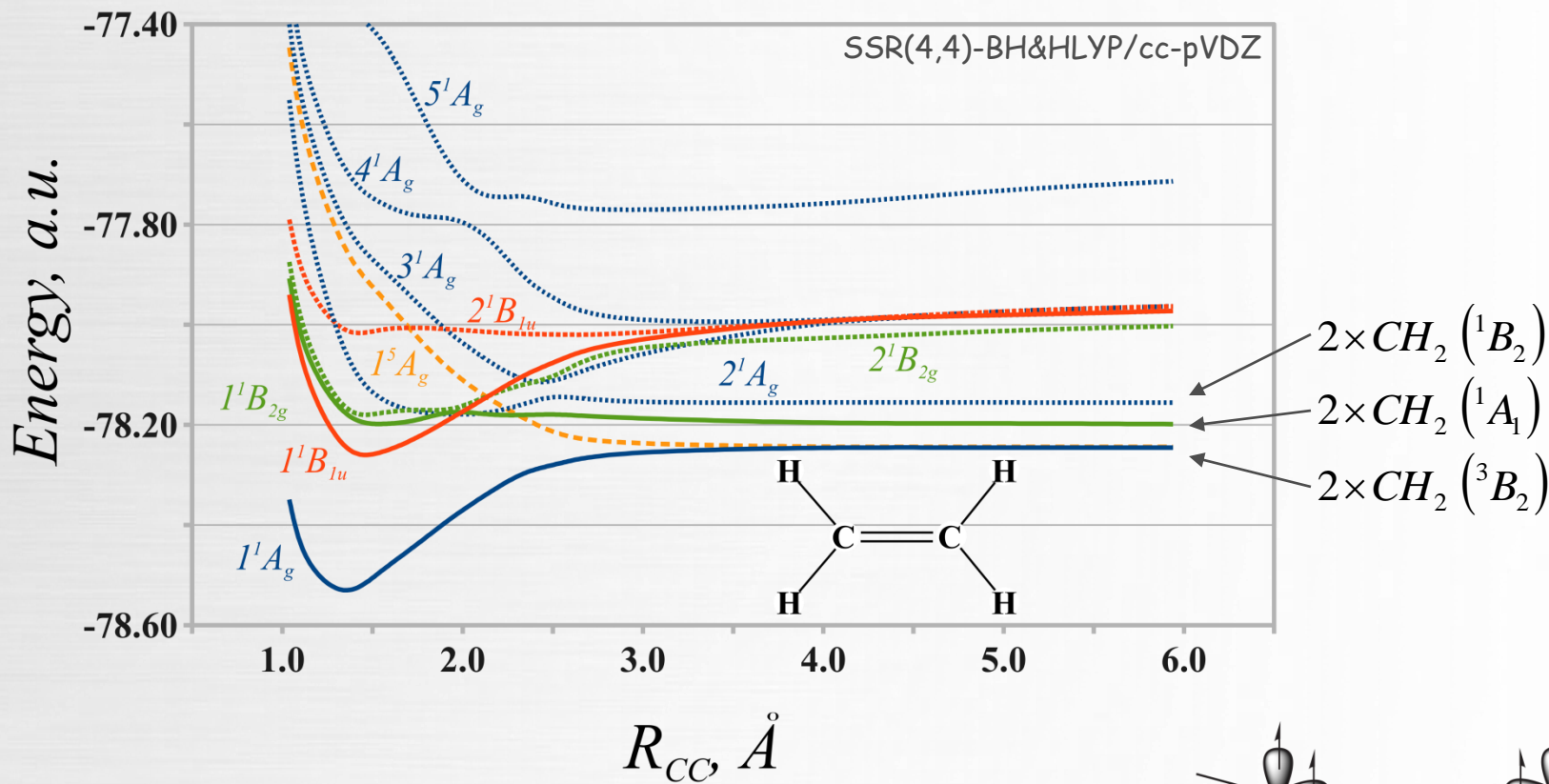
All configurations are included in state interaction (RCI)

Suitable for excitations in dimers:

$S_0 S_0$ $S_1 S_0$ $S_0 S_1$

PPS   OSS1   OSS2

$CT_{1,2}$ $S_1 S_1$

OSS3   OSS4   DOSS

$^1(T_1 T_1)$

DSPS   DES1   DES2

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

SSR(4,4): Double Bond Dissociation

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

5^1A_g

4^1A_g

3^1A_g

2^1B_{1u}

1^5A_g

1^1B_{2g}

1^1B_{1u}

1^1A_g

2^1B_{2g}

2^1A_g

$2 \times CH_2\left(^1B_2\right)$

$2 \times CH_2\left(^1A_1\right)$

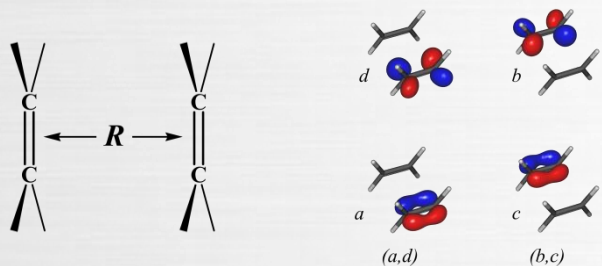$2 \times CH_2\left(^3B_2\right)$

Energy, a.u.

R_{CC}, Å

Correctly describes dissociation of a double bond

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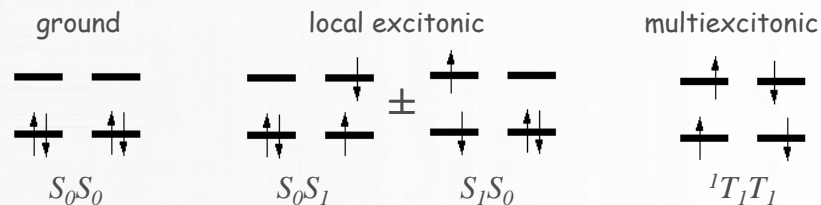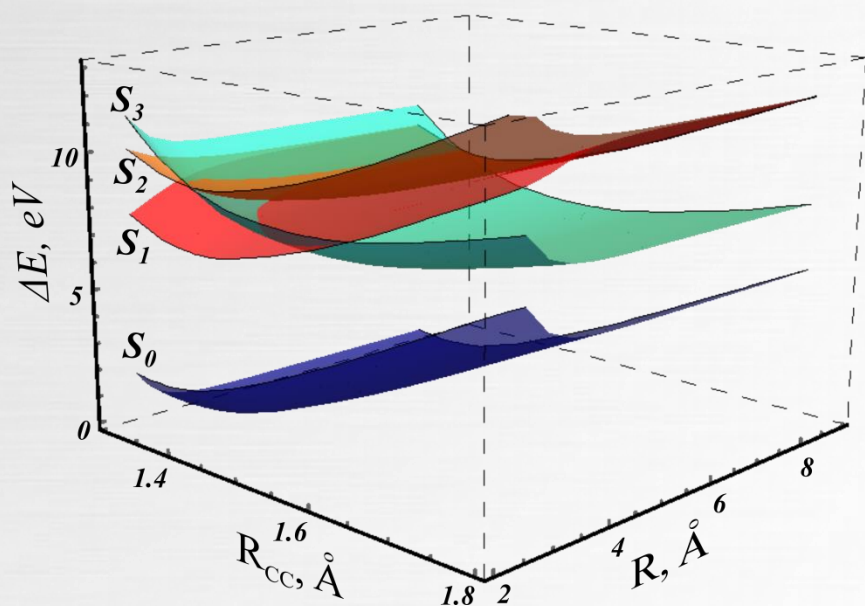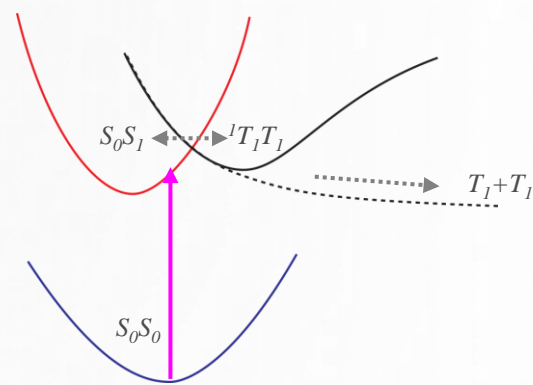- recovers the excited states diss. limits

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

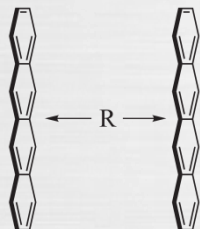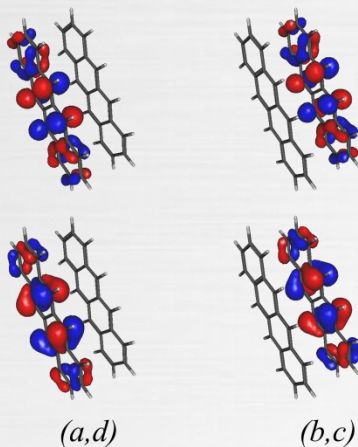ground   local excitonic   multiexcitonic

S_0S_0 S_0S_1 S_1S_0 $^1T_1T_1$

Singlet Exciton Fission

S_0S_1 $\longleftrightarrow$ $^1T_1T_1$ T_1+T_1

S_0S_0

Strong (non-adiabatic) LE/ME coupling – prerequisite for efficient SF

JCP 147, 064104 (2017)

tetracene dimer's geometry

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

(a,d)   *(b,c)*

SSR(4,4)-ωPBEh/6-31G*

tetracene dimer

^1ME
$^1LE_2$
$^1LE_1$
S_0

pentacene dimer

^1ME
$^1LE_2$
$^1LE_1$
S_0
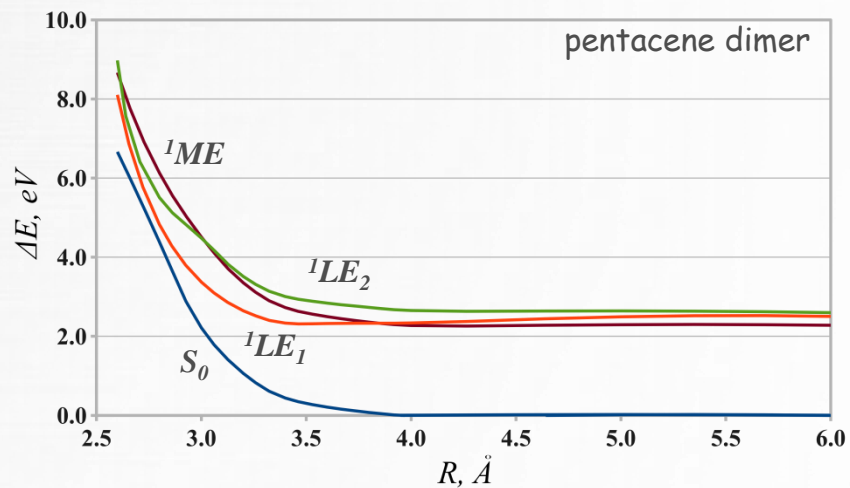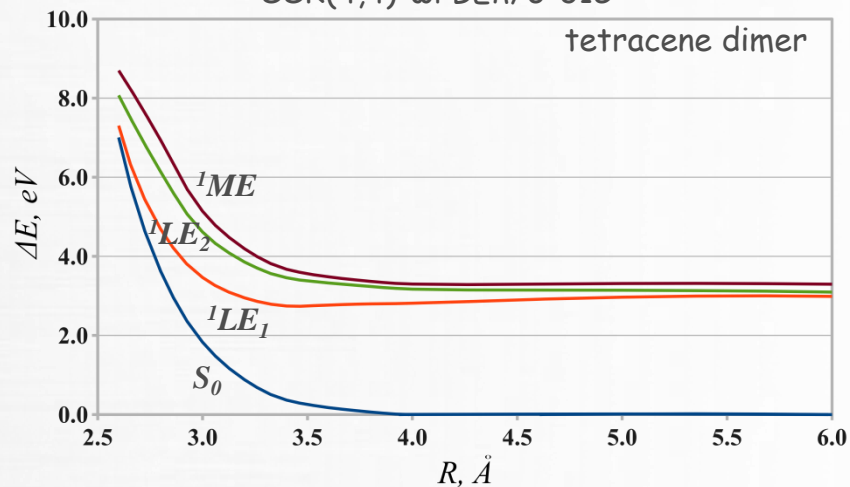
REKS/SSR: Extension to Arbitrary Active Space

REKS/SSR equations – easy to formalize

$$\begin{pmatrix} E_0 & h_{01} & h_{02} & \cdots \\ h_{01} & E_1 & h_{12} & \\ h_{02} & h_{12} & E_2 & \\ \vdots & & & \ddots \end{pmatrix}$$

Diagonal elements from GVB

$$\Psi^{GVB} = \hat{A}\left[\cdots \Phi_0^A(1,2)\Phi_0^B(3,4)\cdots\right] \quad ; A, B = PPS, OSS.$$

$$\Phi^{PPS}(1,2) = \sqrt{\frac{n_i}{2}}\left|\phi_i\,\bar{\phi}_i\right\rangle - \sqrt{\frac{n_p}{2}}\left|\phi_p\,\bar{\phi}_p\right\rangle \qquad \Phi^{OSS}(1,2) = \sqrt{\frac{1}{2}}\left|\phi_j\,\bar{\phi}_q\right\rangle + \sqrt{\frac{1}{2}}\left|\phi_j\,\bar{\phi}_q\right\rangle$$

Example:

$$E_X^{(N,N)} = \frac{n_i\,n_j\,n_k\cdots}{N}E_{i\bar{i}j\bar{j}k\bar{k}\cdots} + \frac{n_p\,n_j\,n_k\cdots}{N}E_{p\bar{p}j\bar{j}k\bar{k}\cdots} + \ldots + \frac{n_p\,n_q\,n_r\cdots}{N}E_{p\bar{p}q\bar{q}r\bar{r}\cdots} +$$

$$+ f(n_i,n_p)\Delta_{ip} + f(n_j,n_q)\Delta_{jq} + f(n_k,n_r)\Delta_{kr} + \ldots$$

Off-diagonal elements ~

$$\Delta_{ij} = E_{\bar{i}j} - E_{ij}$$ energy differences

$$\Delta_{ij,p} = \frac{1}{2}\left\langle \frac{\delta\Delta_{ij}}{\delta\phi_j}\,\middle|\,\phi_p\right\rangle - \frac{1}{2}\left\langle \frac{\delta\Delta_{ij}}{\delta\bar{\phi}_j}\,\middle|\,\bar{\phi}_p\right\rangle$$ Fock matrix differences

$$\Delta_{ij,pq} = \frac{1}{2}\left\langle \frac{\delta^2\Delta_{ij}}{\delta\phi_i\,\delta\bar{\phi}_j}\,\middle|\,\bar{\phi}_p\,\phi_q\right\rangle$$ XC kernel matrix differences

Computer Algebra Systems (CAS) can be used for automatic code generation

Conclusions

- Ensemble DFT
    - rigorous basis for multi-configurational DFT
    - describes strong non-dynamic correlation
    - variational excited states

- Practical implementation of eDFT
    - correct dissociation of chemical bonds
    - ground and excited states on the same footing
    - proper description of
        - conical intersections
        - avoided crossings
    - non-adiabatic dynamics
        - analytic gradients
        - analytic non-adiabatic couplings
        - time-resolved spectroscopic properties
    - excitations in multi-chromophoric systems
        - local excitonic and multi-excitonic states

- Directions for further REKS/SSR method development
    - automatic code generation for arbitrary active space
        - energies of individual states
        - analytic gradients and relaxed density matrices
        - observable properties
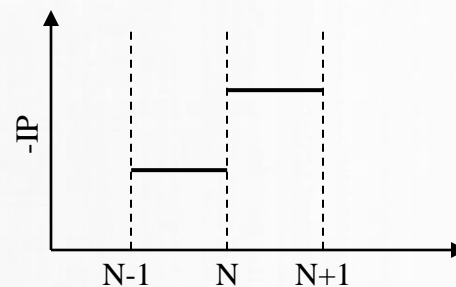
Thank you!

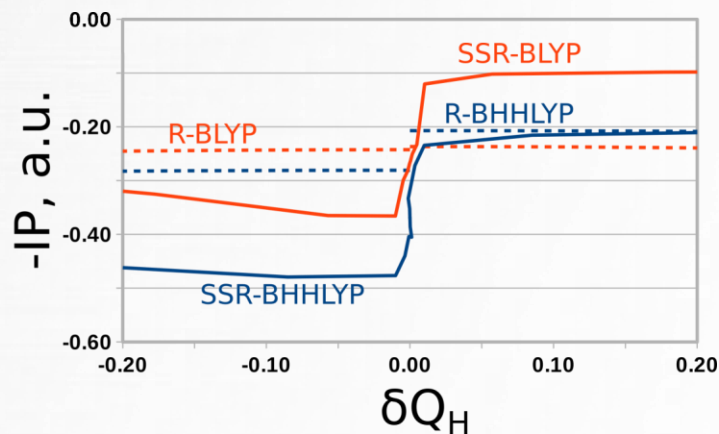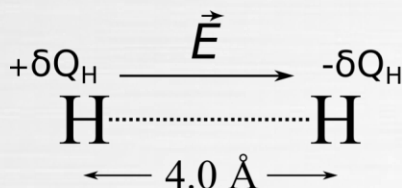# Derivative Discontinuity

The energy of an atom or a molecule should be piecewise linear as a function of the number of electrons N
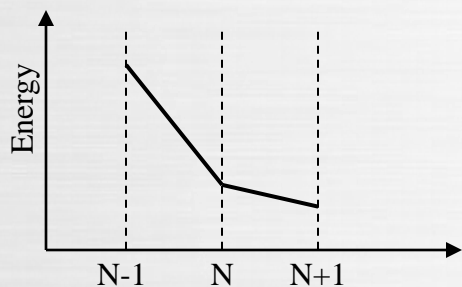
The ionization energy should have a step, when passing through an integer N
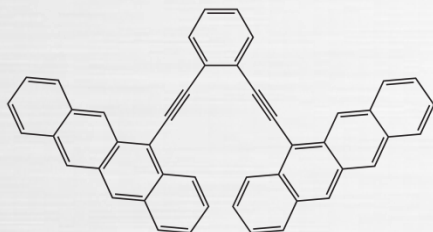Perdew, J.P., et al. Phys. Rev. Lett.49, 1691 (1982)

Stretched H2 in electric field; SSR(2,2) calculation; MF et al., J. Chem. Theory Comput. 16, 4489 (2020)

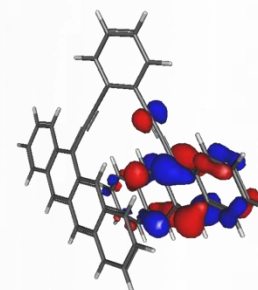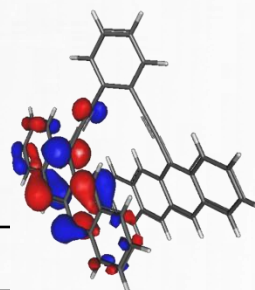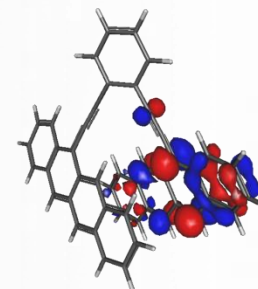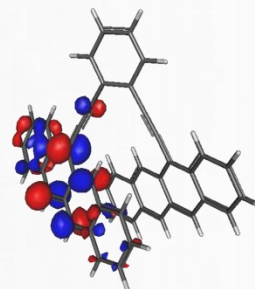# SSR(4,4): Synthetic tetracene dimer

ethynyl-tetracene dimer, BET-B

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

Korovina et al., JACS 138, 617 (2016)
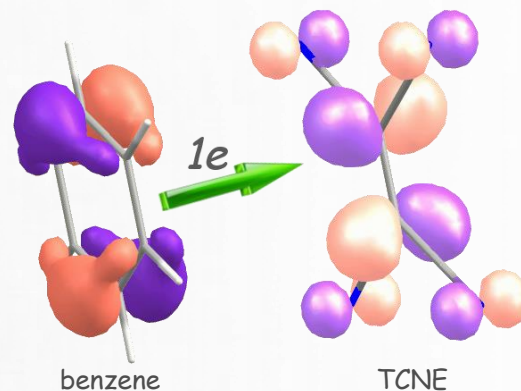
high efficiency of SF, ~152%

SSR(4,4)-ωPBEh/6-31G*

State	VEE, eV	composition
S_3	3.15	$0.1\ LE_1 + 0.1\ LE_2 + 0.78\ ME + 0.02\ CT$
S_2	3.08	$0.4\ LE_1 + 0.4\ LE_2 + 0.18\ ME + 0.02\ CT$
S_1	2.82	$0.5\ LE_1 + 0.5\ LE_2$
S_0	0	PP (closed-shell)

(a,d)   *(b,c)*

near degenerate and strongly
entangled LE and ME states

Charge transfer excitations

Arene-TCNE complexes (DA)

HOMO $\rightarrow$ LUMO CT transition

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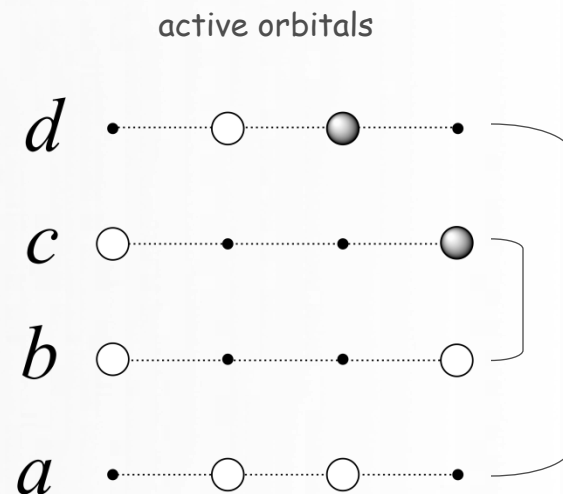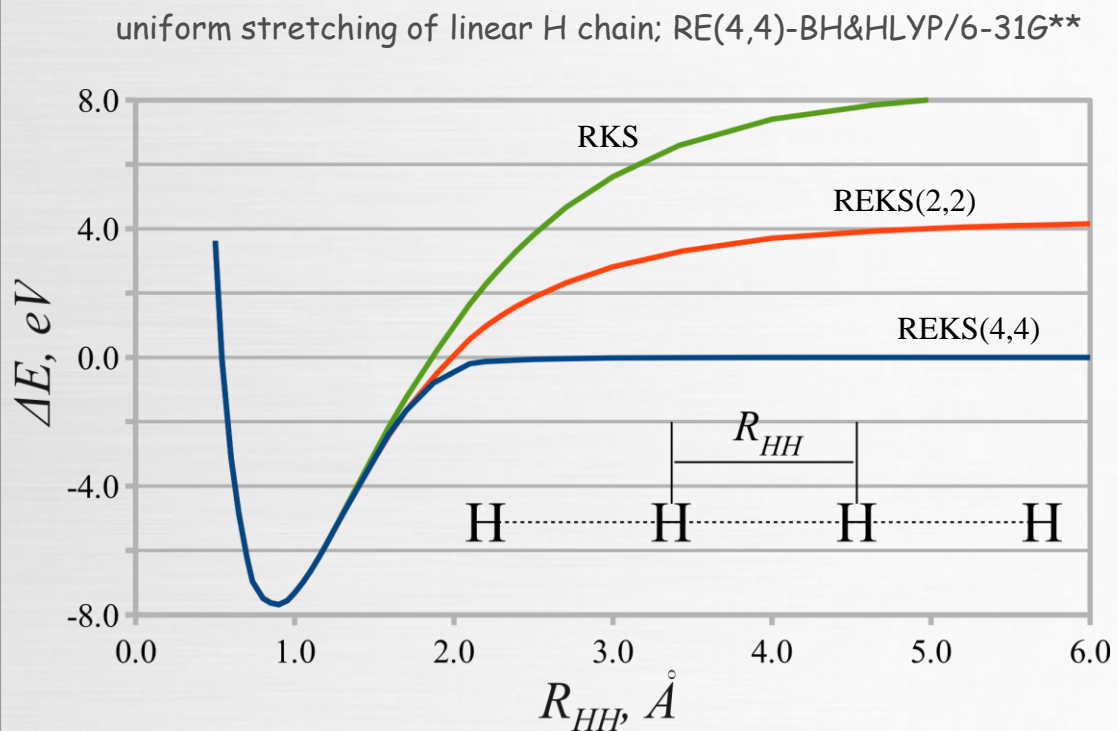
CT transition energies (eV) for a series of Ar-TCNE complexes

Arene	BLYP		B3LYP		CAM-B3LYP		Litr.	Exp.
	TD-DFT	SSR	TD-DFT	SSR	TD-DFT	SSR		
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
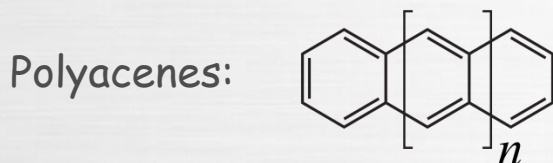Exp.: Gas phase experimental excitation energies, JPC 76, 1982 (1972)

JCP 141, 124123 (2014)

REKS(4,4): Dissociation of several single bonds

uniform stretching of linear H chain; RE(4,4)-BH&HLYP/6-31G**

active orbitals

size-consistent when dissociating into individual atoms (spin centers)

$$E^{(4,4)}\left(H_4\right)\Big|_{R\to\infty} = 4\,E(H)$$

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): Excitations in extended π-systems

Polyacenes:

SSR(4,4) active space

LUMO+1 d c LUMO

b_{1u} b_{2g}

HOMO-1 a b HOMO

b_{3g} a_u

(a,d)   *(b,c)*

Vertical excitation energy (eV)

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

$E_{SSR(4,4)}=1.08 + 7.46\ exp(-0.34\ n)$

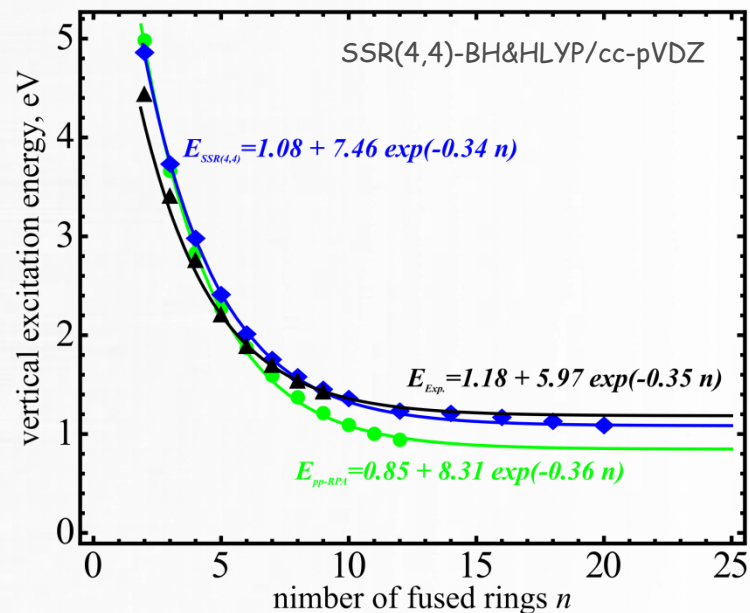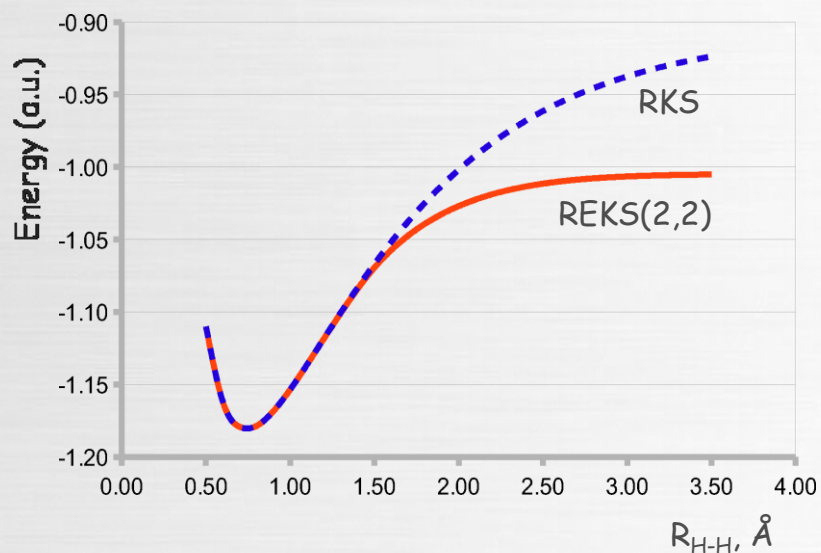$E_{Exp.}=1.18 + 5.97\ exp(-0.35\ n)$

$E_{pp\text{-}RPA}=0.85 + 8.31\ exp(-0.36\ n)$
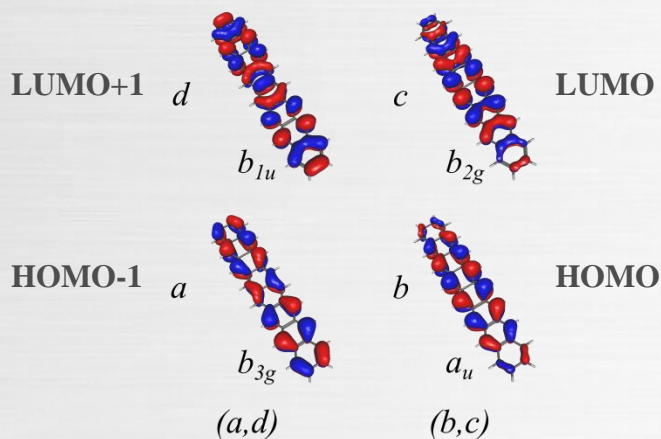
SSR(4,4):

- yields very accurate vertical excitation energies
- considerably outperforms other methods, *e.g.*, pp-RPA
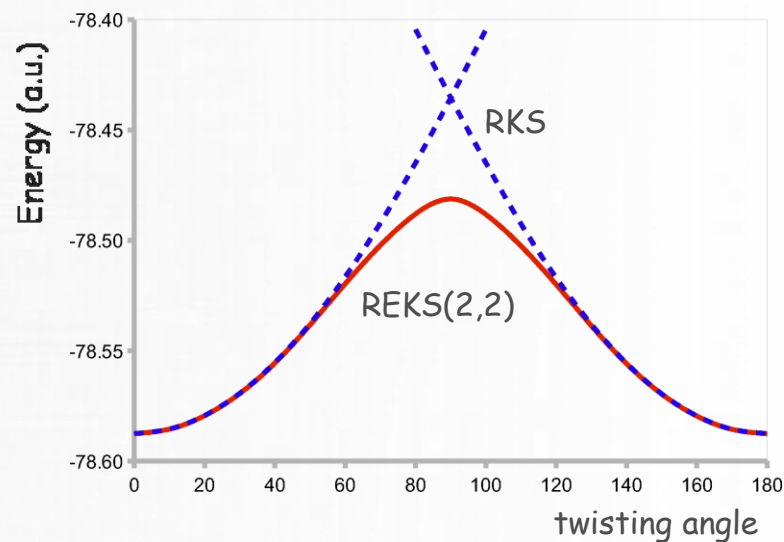
REKS(2,2): Bond dissociation

Bond stretching in H_2

Total energy at R_{H-H} = 0.741 Å

E^{RKS} = -1.1786 a.u.
E^{REKS} = -1.1786 a.u.

B3LYP/aug-cc-pVQZ

Twisting about double bond in C_2H_4

Total energy of planar ethylene

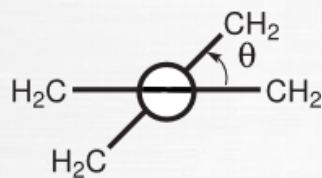E^{RKS} = -78.5874 a.u.
E^{REKS} = -78.5874 a.u.

B3LYP/6-31G*

Applications of REKS: Tetramethyleneethane diradical
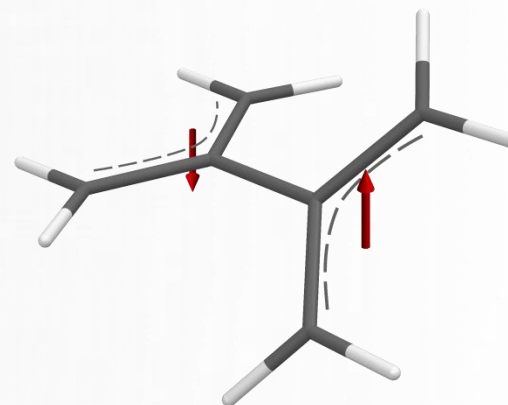
used in organic synthesis; as a ligand in metal complexes…
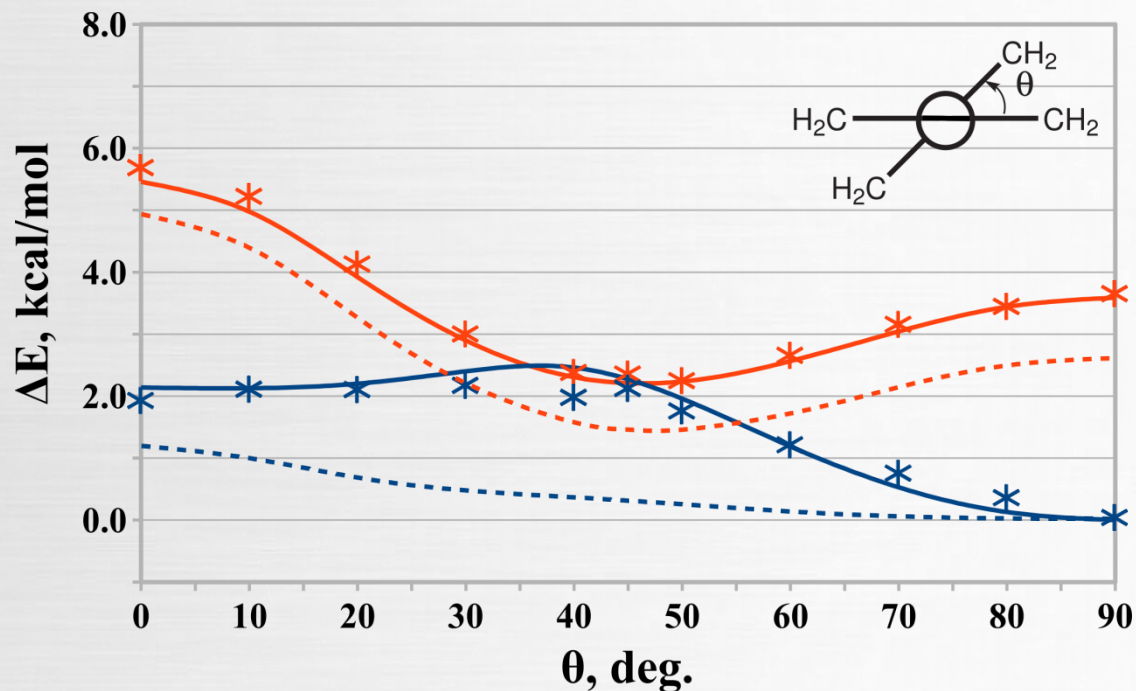
resonance structures

frontier orbitals

TME: singlet or triplet?

Matrix isolated TME: <u>triplet</u> EPR signal; linear CW plot   (Dowd, 1970, 1986)

NIPE spectroscopy (TME·⁻):   <u>singlet</u> below (ca. 3 kcal/mol) triplet   (Clifford et al., 1998)

Theory (CASSCF,CI, etc..):   <u>singlet</u> always below triplet   (Borden et al., 1987)

Applications of REKS: Tetramethyleneethane diradical

REKS: Filatov&Shaik, 1999

CASPT2: Caballol et al., 2000

QMC: Jordan et al., 2013
      Barborini&Coccia, 2015

<u>Singlet</u> is a global energy minimum

<u>Triplet</u> is *meta-stable* at intermediate θ (trapping, slow relaxation)

Reconciles theory and experiment (Lineberger&Borden, 2013)