ΔSCF for Efficient Nonadiabatic Molecular Dynamics in Condensed Phase Systems

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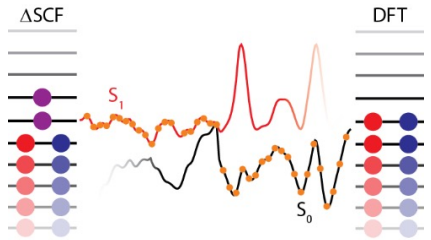
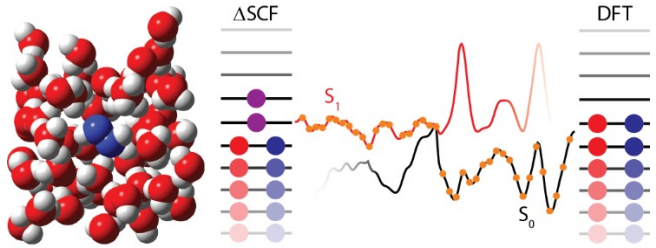


VISTA seminar, April 14, 2021

Outline

ΔSCF for Nonadiabatic Molecular Dynamics (NA-MD) in condensed phase systems



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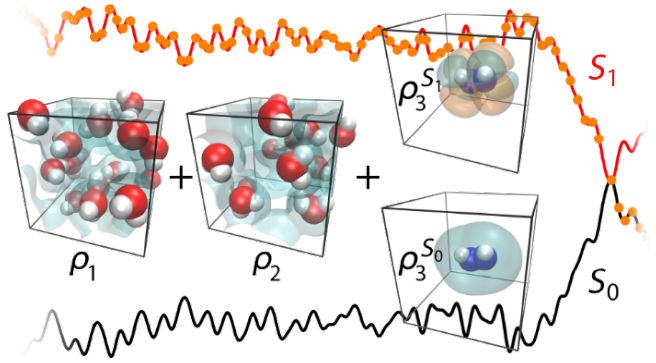
ΔSCF NA-MD with Subsystem Density Embedding (SDE)



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Motivation

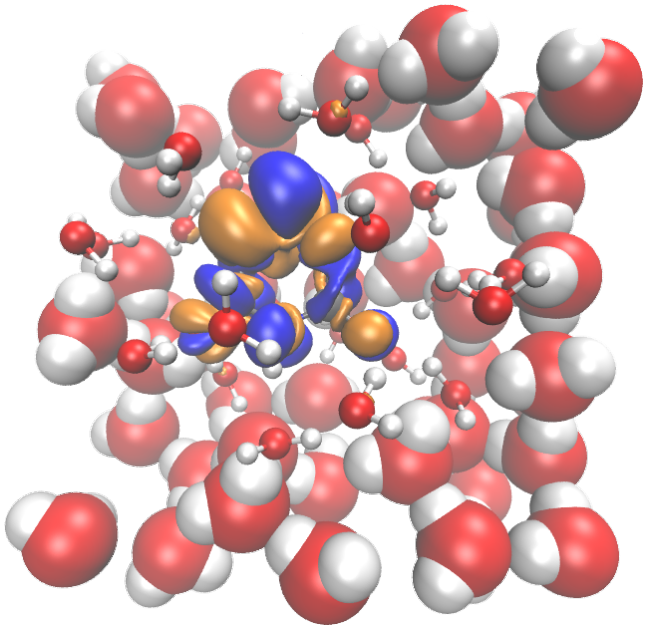
NA processes in condensed phase systems

- Trajectory Surface Hopping (TSH) NA-MD

Computationally challenging for all-atom simulations

Density Functional Theory (DFT) based methods

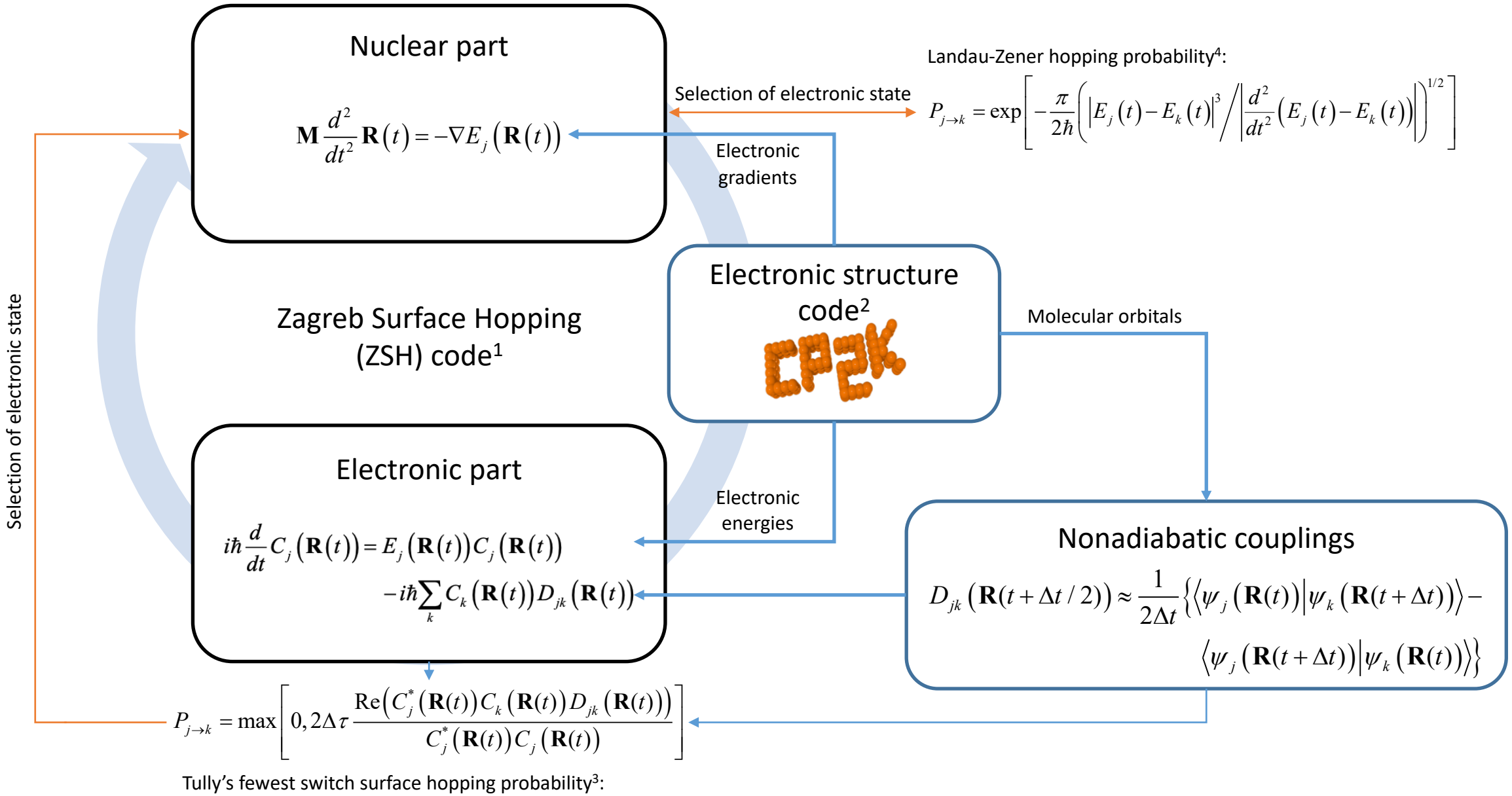
- Perturbative – Linear-Response (LR) Time-Dependent (TD) DFT
- Perturbative – Real-Time (RT) TD-DFT
- Variational – Delta Self-Consistent Field (ΔSCF)



Excited uracil in water

RT-TDDFT in our group: *J. Chem. Phys.* **194** (2018) 174108; *Chem. Phys.* **527** (2019) 110464; *J. Chem. Phys.* **151** (2019) 234110; *J. Chem. Theory Comput.* **17** (2021) 344

Trajectory Surface Hopping (TSH) NA-MD



1: ZSH code is available on the E-CAM software repository (www.e-cam2020.eu) 2: www.cp2k.org 3: *J. Chem. Phys.* **129** (2008) 164118 4: *Phys. Rev. A* **84** (2011) 014701

Delta Self-Consistent Field (ΔSCF) theory

Direct application of ground state DFT concepts to excited electronic states

$$|\Psi_0\rangle \Leftrightarrow \rho_0(\vec{r}) \Leftrightarrow V_{xc}^0[\rho_0]$$

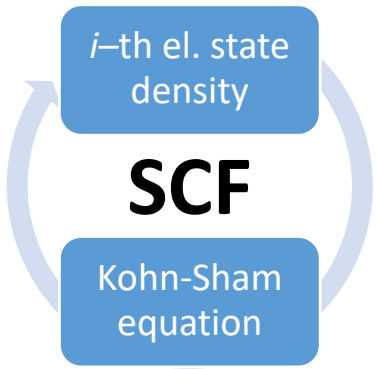
Ground electronic state

$$|\Psi_i\rangle \Leftrightarrow \rho_i(\vec{r}) \sim V_{xc}^0[\rho_i]$$

Excited *i*-th electronic state

Kohn-Sham (KS) DFT formulation

Optimize the electron density to match an excited state electron density



$$\rho_i(\vec{r}) = \sum_{\sigma=\{\alpha,\beta\}}^{j} n_{j\sigma}^{i} \left|\varphi_{j\sigma}^{i}(\vec{r})\right|^2 \quad \Leftrightarrow \quad \rho_i(\vec{r}) = \int \bar{\Psi}_i(\vec{r},\vec{r}_1,\ldots)\Psi_i(\vec{r},\vec{r}_1,\ldots)d\vec{r}_1\ldots$$

MO occupation number

KS molecular orbital (KS-MO)

$$E_i[\rho_i]$$

Variety of different ΔSCF density constructions and optimization flavors[1]

Multiplicity of excited electronic state

1: *J. Chem. Phys.* **120** (2004) 4593; *Phys. Rev. B* **78** (2008) 075441; *J. Phys. Chem. A* **112** (2008) 13164; *J. Chem. Phys.* **134** (2011) 054128; *J. Chem. Phys.* **139** (2013) 014708; *J. Chem. Theory Comput.* **16** (2020) 6968

ΔSCF singlet excited state

$$\mathrm{mod}\left(N_e, 2\right) = 0$$

Total number of electrons in system

$$\hat{S}_{\mathrm{tot}} \left|\Psi_i\right\rangle = 0$$

Total electron spin moment

$$\hat{S}_{\mathrm{tot},z} \left|\Psi_i\right\rangle = 0$$

Total electron spin moment projection

$$\rho_i\left(\vec{r}\right) = \rho_{i\alpha}\left(\vec{r}\right) + \rho_{i\beta}\left(\vec{r}\right)$$

$$\rho_{i\alpha}\left(\vec{r}\right) - \rho_{i\beta}\left(\vec{r}\right) = 0$$

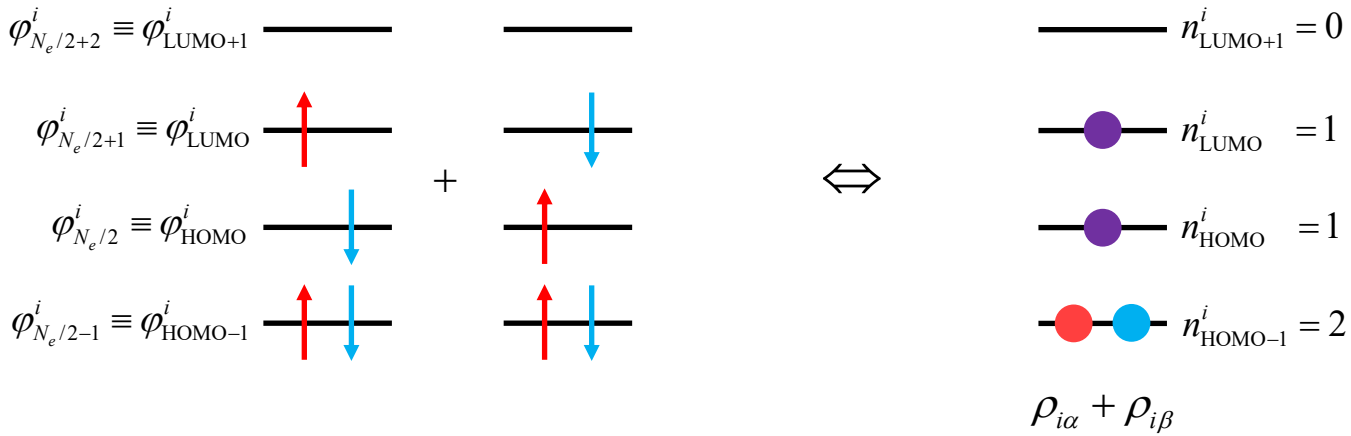
$$v_{\mathrm{xc}}\left[\rho_{i\alpha}, \rho_{i\beta}\right]$$

$$\varphi^i_{j\alpha}\left(\vec{r}\right) = \varphi^i_{j\beta}\left(\vec{r}\right)$$

Restricted (open) KS formulation

$$\left|\Psi_{\mathrm{S}i}\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\psi^i_{j\alpha\to a\alpha}\right\rangle + \left|\psi^i_{j\beta\to a\beta}\right\rangle \right)$$

Singlet excited state



$$\left|\psi^i_{j\alpha\to a\alpha}\right\rangle = \frac{1}{\sqrt{N_e}} \begin{vmatrix} \varphi^i_1(1)\alpha(1) & \cdots & \varphi^i_a(1)\alpha(1) & \cdots & \varphi^i_{N_e/2}(1)\beta(1) \\ \varphi^i_1(2)\alpha(2) & \cdots & \varphi^i_a(2)\alpha(2) & \cdots & \varphi^i_{N_e/2}(2)\beta(2) \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \varphi^i_1(N_e)\alpha(N_e) & \cdots & \varphi^i_a(N_e)\alpha(N_e) & \cdots & \varphi^i_{N_e/2}(N_e)\beta(N_e) \end{vmatrix}$$

Single excited Slater determinant

$$\left|\Psi_0\right\rangle = \frac{1}{\sqrt{N_e}} \begin{vmatrix} \varphi^0_1(1)\alpha(1) & \cdots & \varphi^0_j(1)\alpha(1) & \cdots & \varphi^0_{N_e/2}(1)\beta(1) \\ \varphi^0_1(2)\alpha(2) & \cdots & \varphi^0_j(2)\alpha(2) & \cdots & \varphi^0_{N_e/2}(2)\beta(2) \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \varphi^0_1(N_e)\alpha(N_e) & \cdots & \varphi^0_j(N_e)\alpha(N_e) & \cdots & \varphi^0_{N_e/2}(N_e)\beta(N_e) \end{vmatrix}$$

Ground electron state

ΔSCF implementation

Restricted KS with integer occupation numbers (2,1,0) ↔ Single-reference singlet excitation

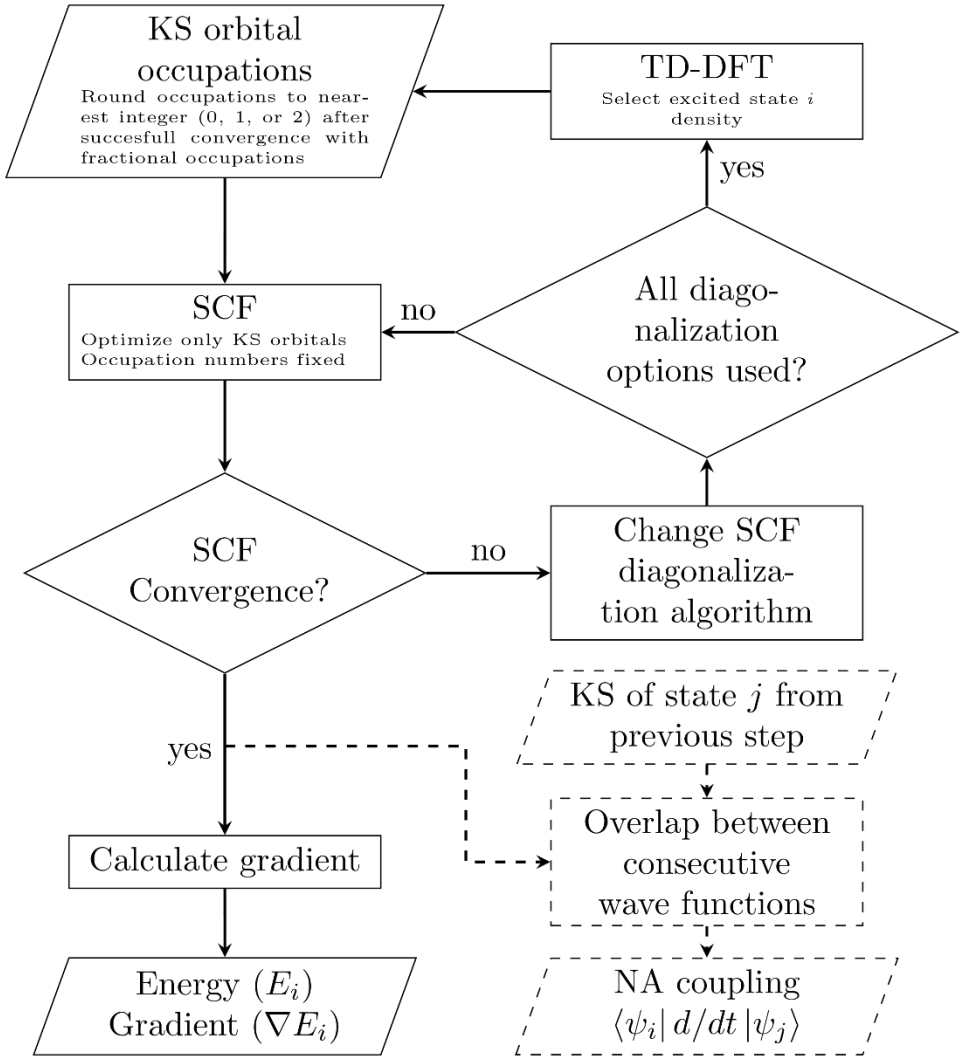
Elaborated SCF convergence procedure

Updating occupation numbers with TD-DFT

$$\left(n_j^i\right)' = n_j^i - \sum_a \left(X_{ja}^i\right)^2 \qquad \left(n_a^i\right)' = \sum_j \left(X_{ja}^i\right)^2$$

Tamm-Dancoff TD-DFT transition amplitudes

TD-DFT for initial occupation numbers and excited state verification



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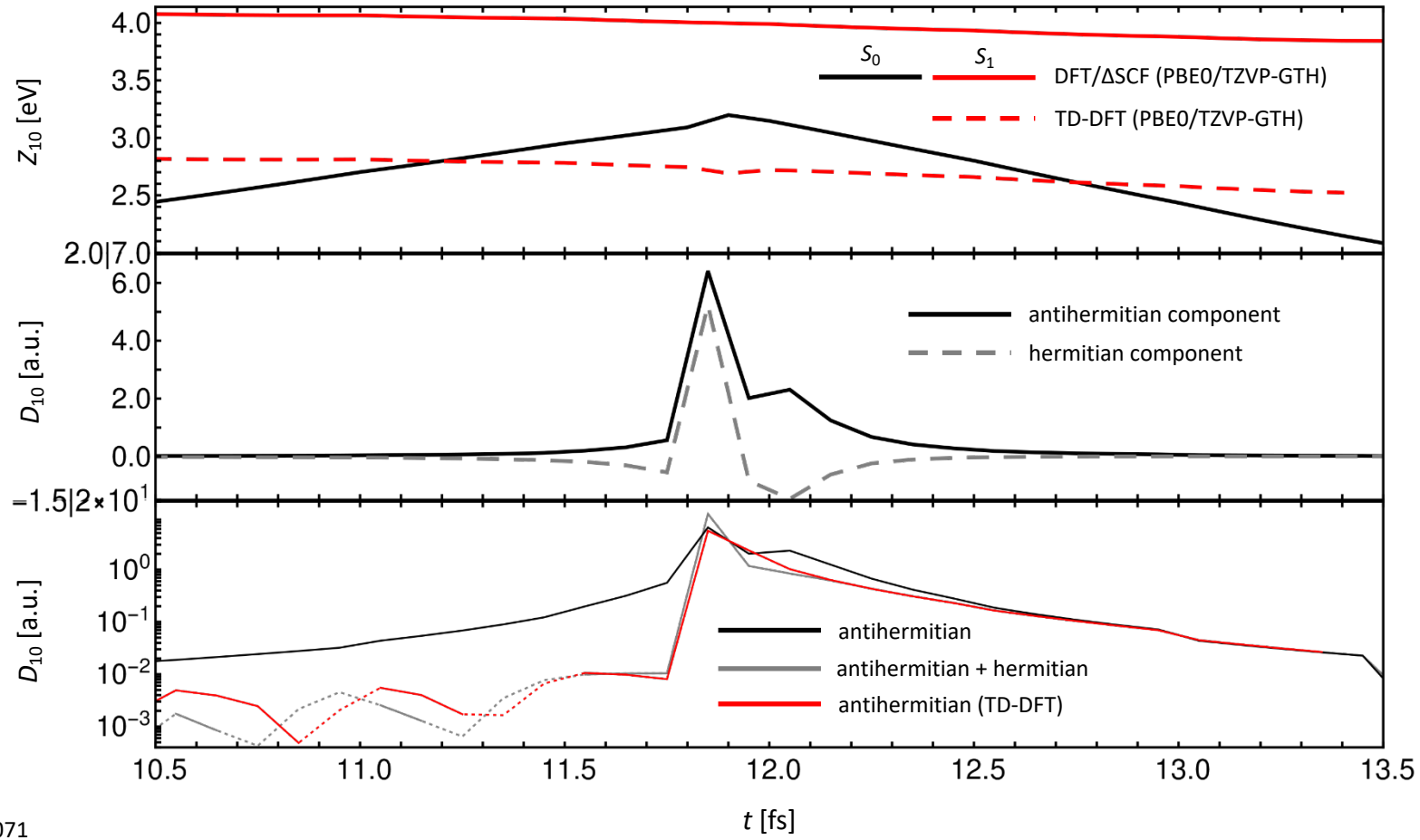
ΔSCF NA coupling

Nonorthogonality between KS MO of different excited electronic states $\left\langle \varphi_p^i \middle| \varphi_q^j \right\rangle \neq \delta_{pq}$

$$D'_{jk}\left(t+\Delta t/2\right) \approx \underbrace{\frac{1}{2\Delta t}\left\{\left\langle \Psi_j\left(t\right)\middle|\Psi_k\left(t+\Delta t\right)\right\rangle - \left\langle \Psi_j\left(t+\Delta t\right)\middle|\Psi_k\left(t\right)\right\rangle\right\}}_{\text{antihermitian}} + \underbrace{\frac{1}{2\Delta t}\left\{\left\langle \Psi_j\left(t+\Delta t\right)\middle|\Psi_k\left(t+\Delta t\right)\right\rangle - \left\langle \Psi_j\left(t\right)\middle|\Psi_k\left(t\right)\right\rangle\right\}}_{\text{hermitian}}$$



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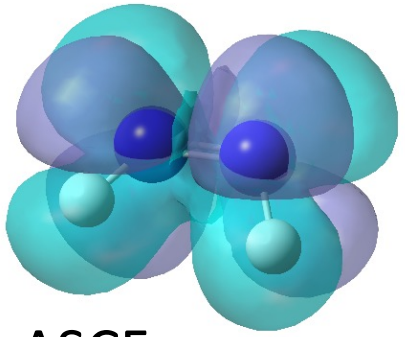
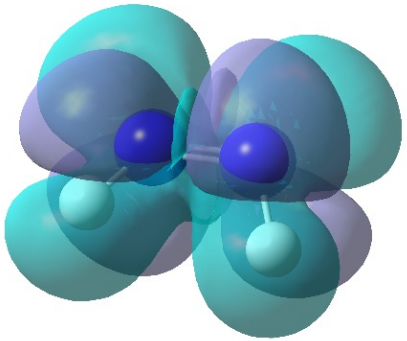
Systems - Diimide (N_2H_2)

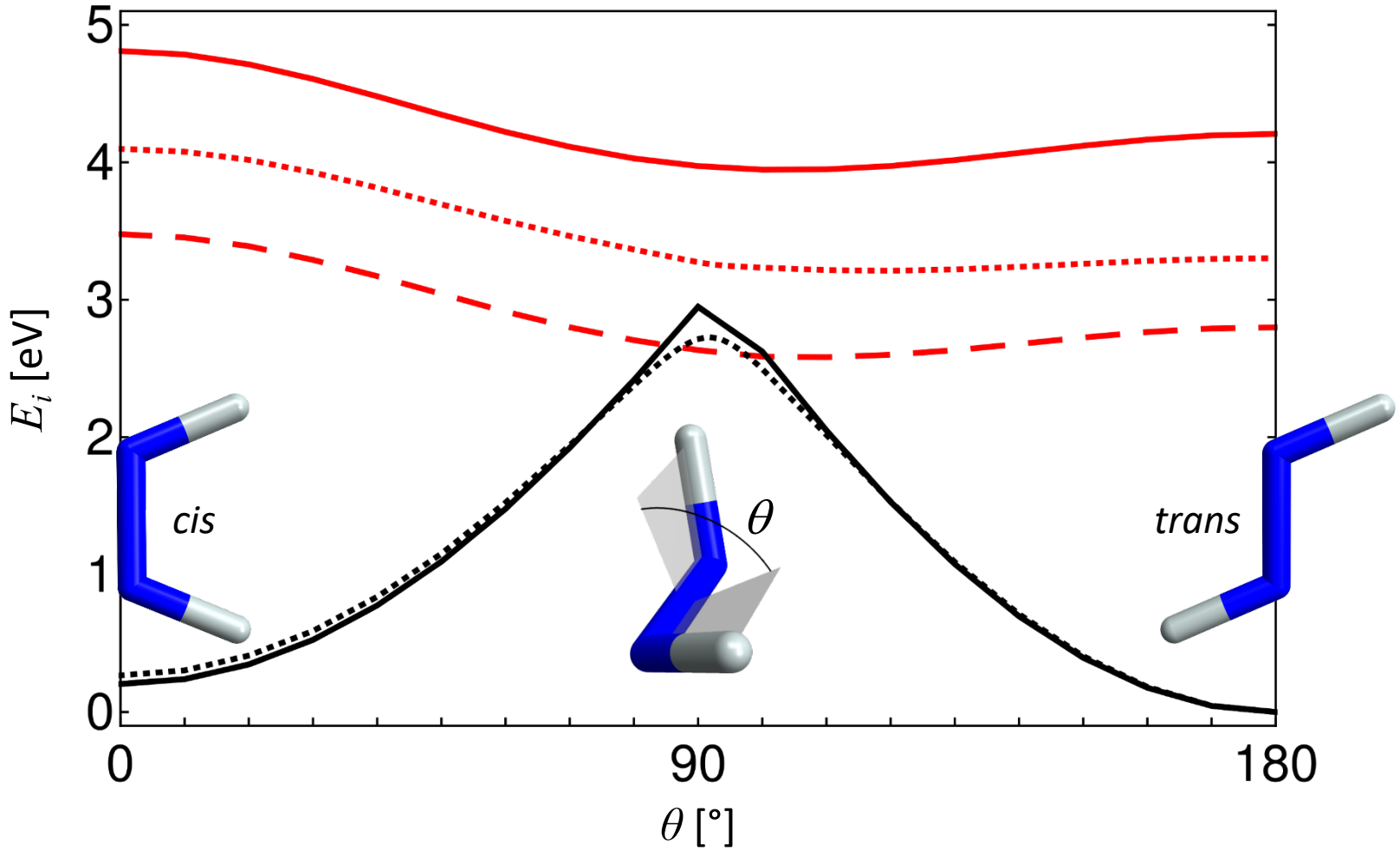
S_1: HOMO (n) → LUMO (π^*)



ΔSCF $\rho_{S1} - \rho_{S0}$



TD-DFT $\rho_{S1} - \rho_{S0}$



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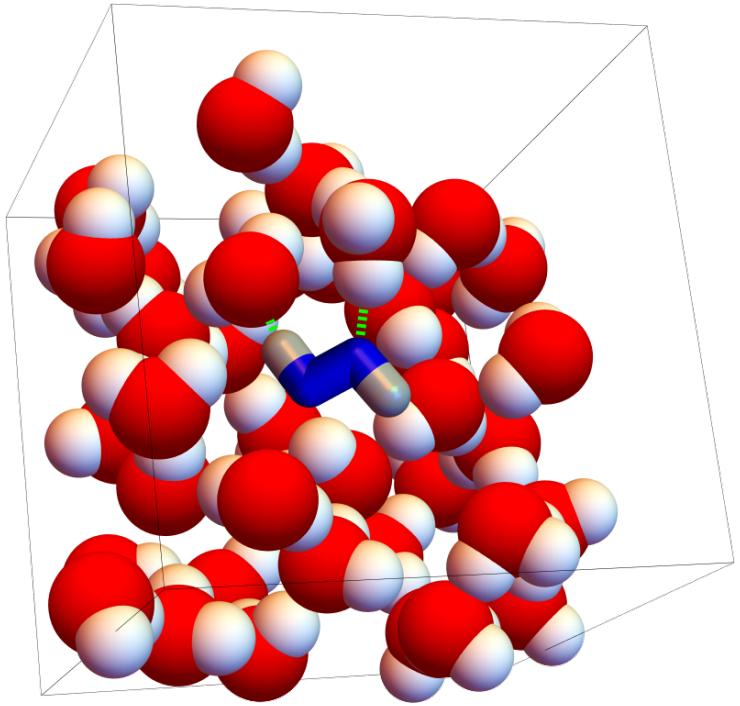
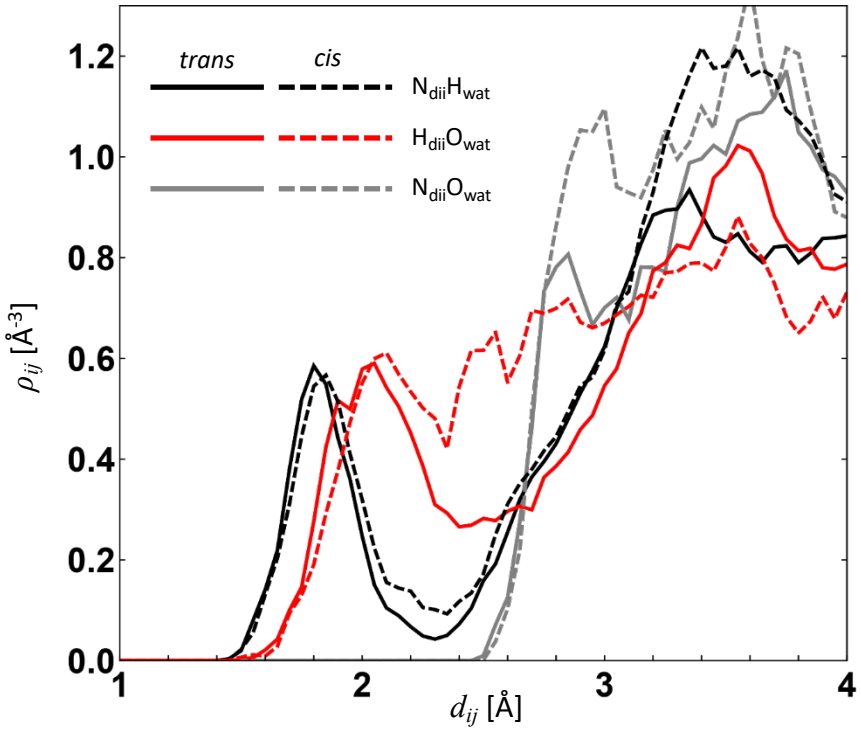
Systems - Diimide solvated in water

cis-diimide + 27 water molecules in a periodic box (8.987 Å)

trans-diimide + 62 water molecules in a periodic box (11.913 Å)





Vertical excitation to S_1 state: 4.45 ± 0.14 eV (solvated) vs. 4.46 ± 0.26 eV (vacuum)

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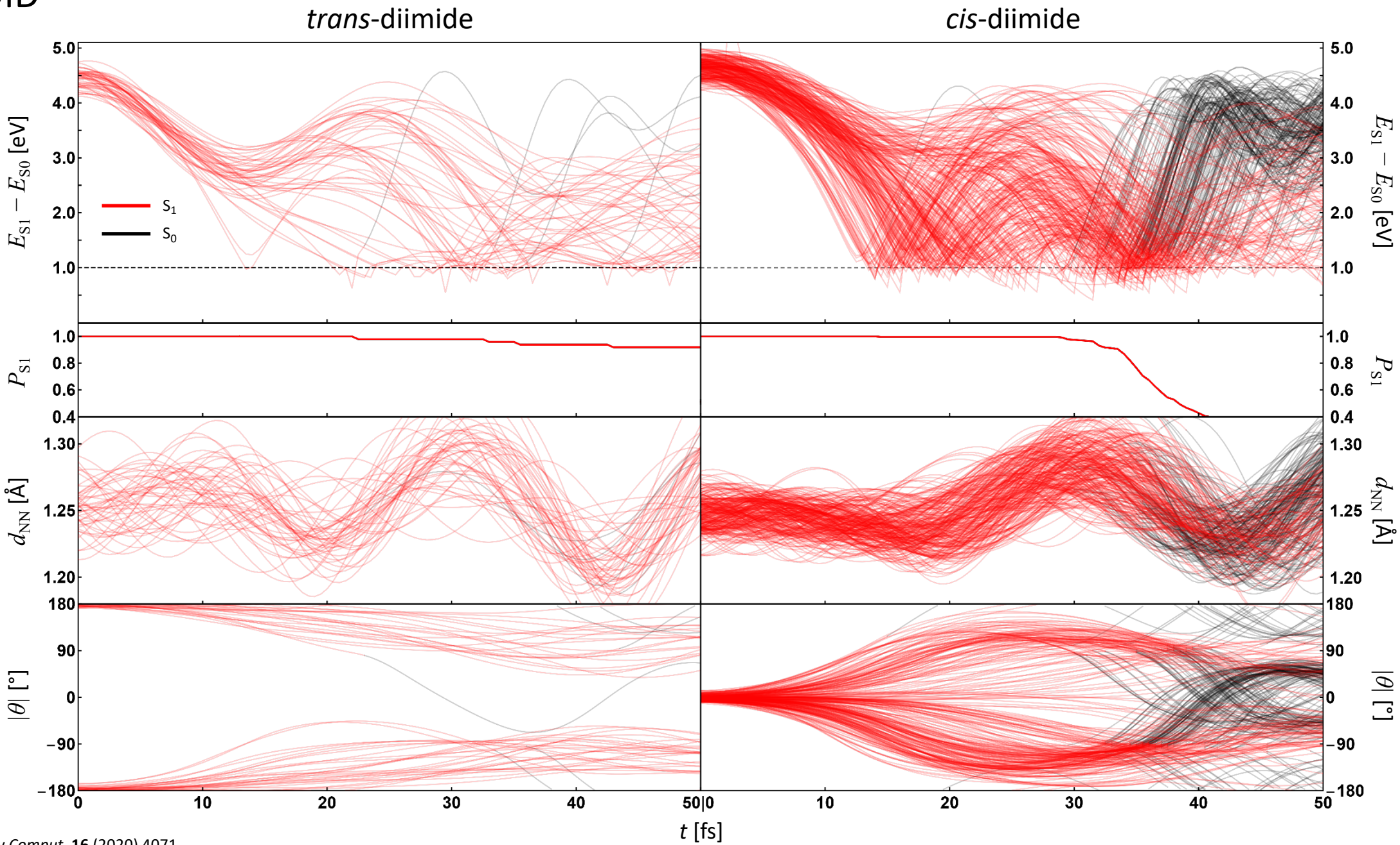
NA-MD



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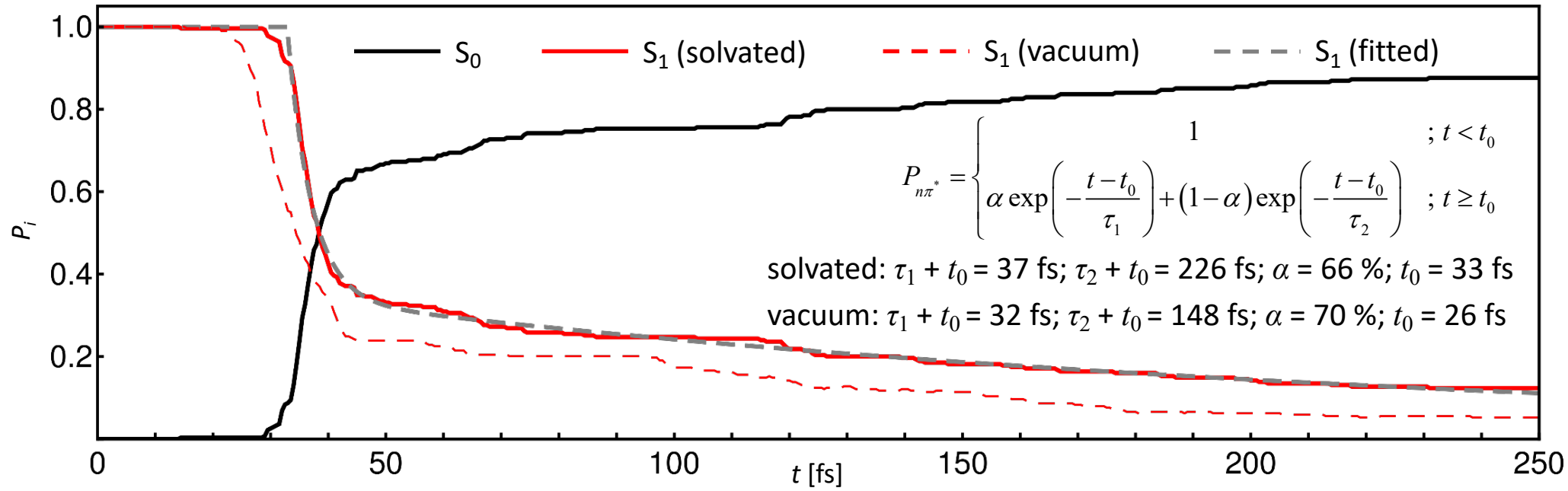
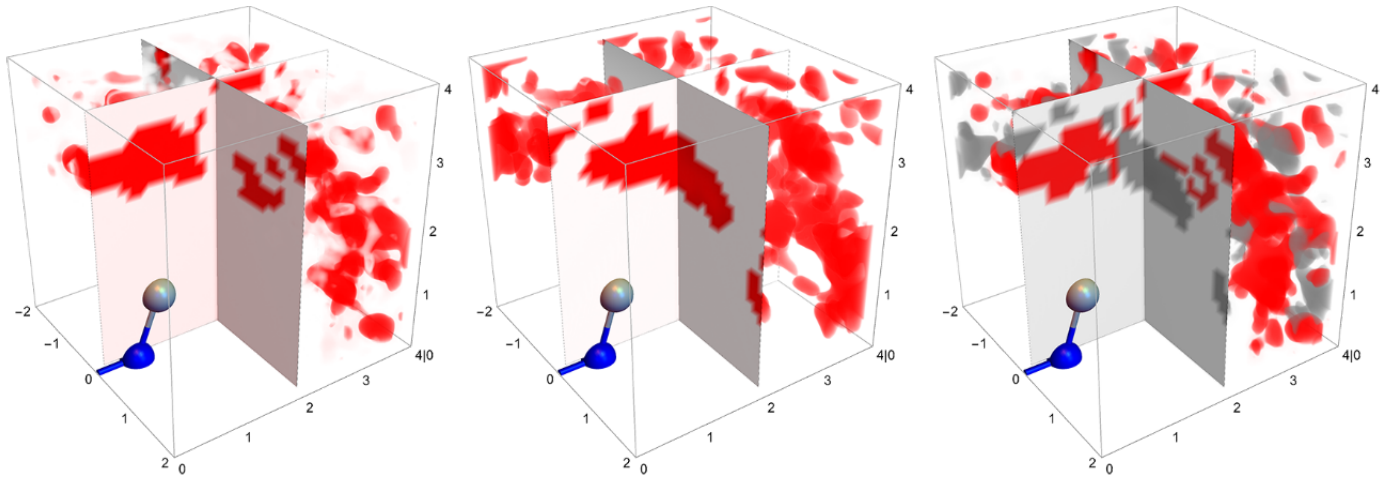
cis-diimide S_1 lifetimes



Solvated *trans*-diimide S_1 lifetimes appears longer



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ΔSCF with Subsystem Density Embedding (SDE)

Total electron density partitioned into subsystem electron densities

SDE[1] generalized to any stationary electronic state density

$$\rho^i_{total}(\vec{r}) = \sum_{s\in S}\rho^i_s(\vec{r}) = \sum_{s\in S}\sum_j n^i_{sj}\left|\varphi^i_{sj}(\vec{r})\right|^2$$

Total system electron density — Subsystem electron density

$$S = \bigcup_s S_s \qquad S_s \cap S_p = \varnothing \qquad \sum_{s\in S}\sum_j n^i_{sj} = N_{total}$$

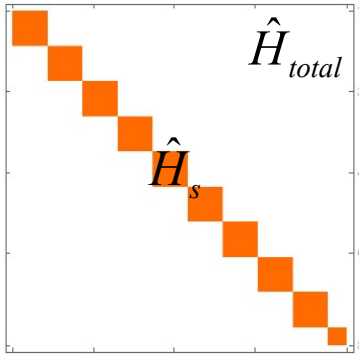
Total system number of electrons — Subsystem MO occupation numbers

$$E^i_{total}\left[\rho^i_{total}\right] = E_{ext}\left[\rho^i_{total}\right] + E_{Coul}\left[\rho^i_{total}\right] + E_{xc}\left[\rho^i_{total}\right] + E_{kin}\left[\rho^i_{total}\right] + \sum_{s\in S}\left(T\left[\{\varphi\}\right] - E_{kin}\left[\rho^i_s\right]\right)$$

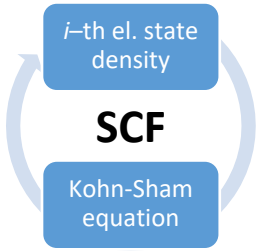
Total system electronic energy

$$\left\{-\frac{\hbar^2}{2}\nabla^2 + V_{KS}\left[\rho^i_{total}\right](\vec{r}) + V_{emb}\left[\rho^i_{total}, \rho^i_s\right](\vec{r})\right\}\varphi^i_{sj}(\vec{r}) = \varepsilon^i_{sj}\varphi^i_{sj}(\vec{r})$$

$$\left\langle \varphi^i_{sj} \middle| \varphi^{i'}_{s'j'} \right\rangle = \begin{cases} \delta_{ss'}\delta_{jj'}; & i = i' \\ \delta_{ss'}\delta_{jj'}S_{ii'}; & i \neq i' \end{cases}$$

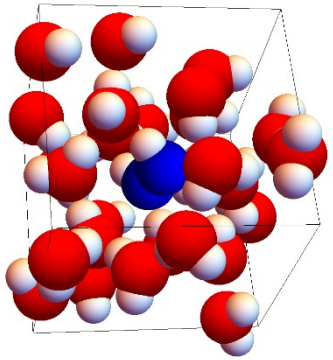


SCF applied simultaneously on all subsystems

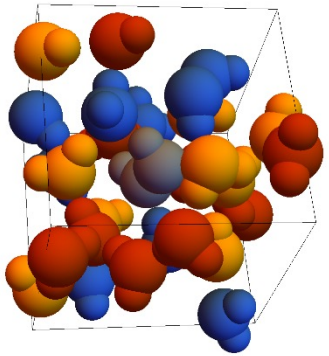


1: *J. Chem. Theory Comput.* **12** (2016) 3214

cis-diimide at the ΔSCF level with SDE

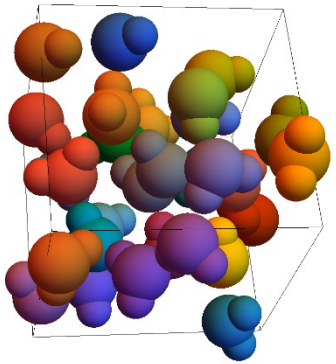


NE



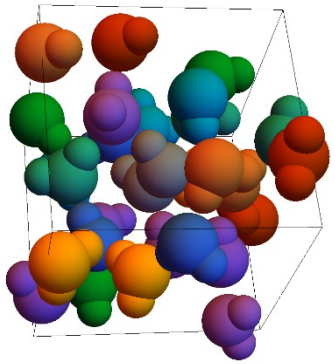
P3

3 subsystems
of 9 H_2O



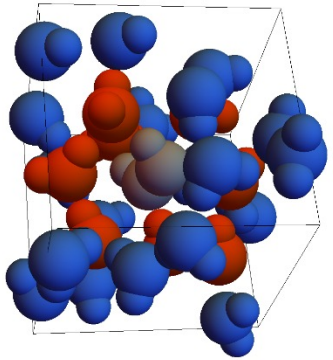
P9

9 subsystems
of 3 H_2O



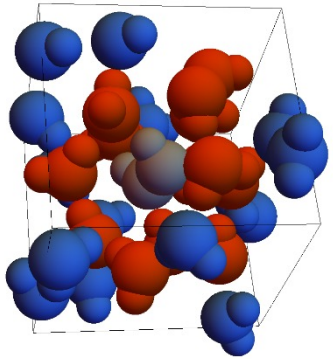
P27

27 subsystems
of 1 H_2O



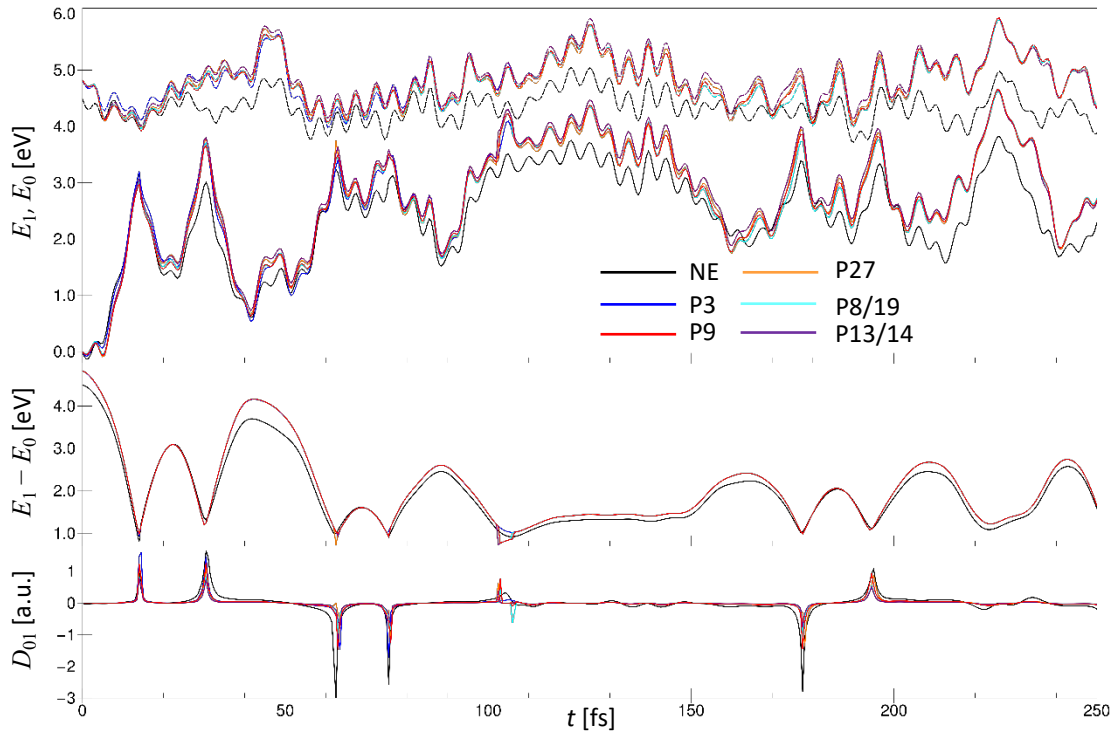
P8/19

Inner shell: 8 H_2O
Outer shell: 19 H_2O



P13/14

Inner shell: 13 H_2O
Outer shell: 14 H_2O



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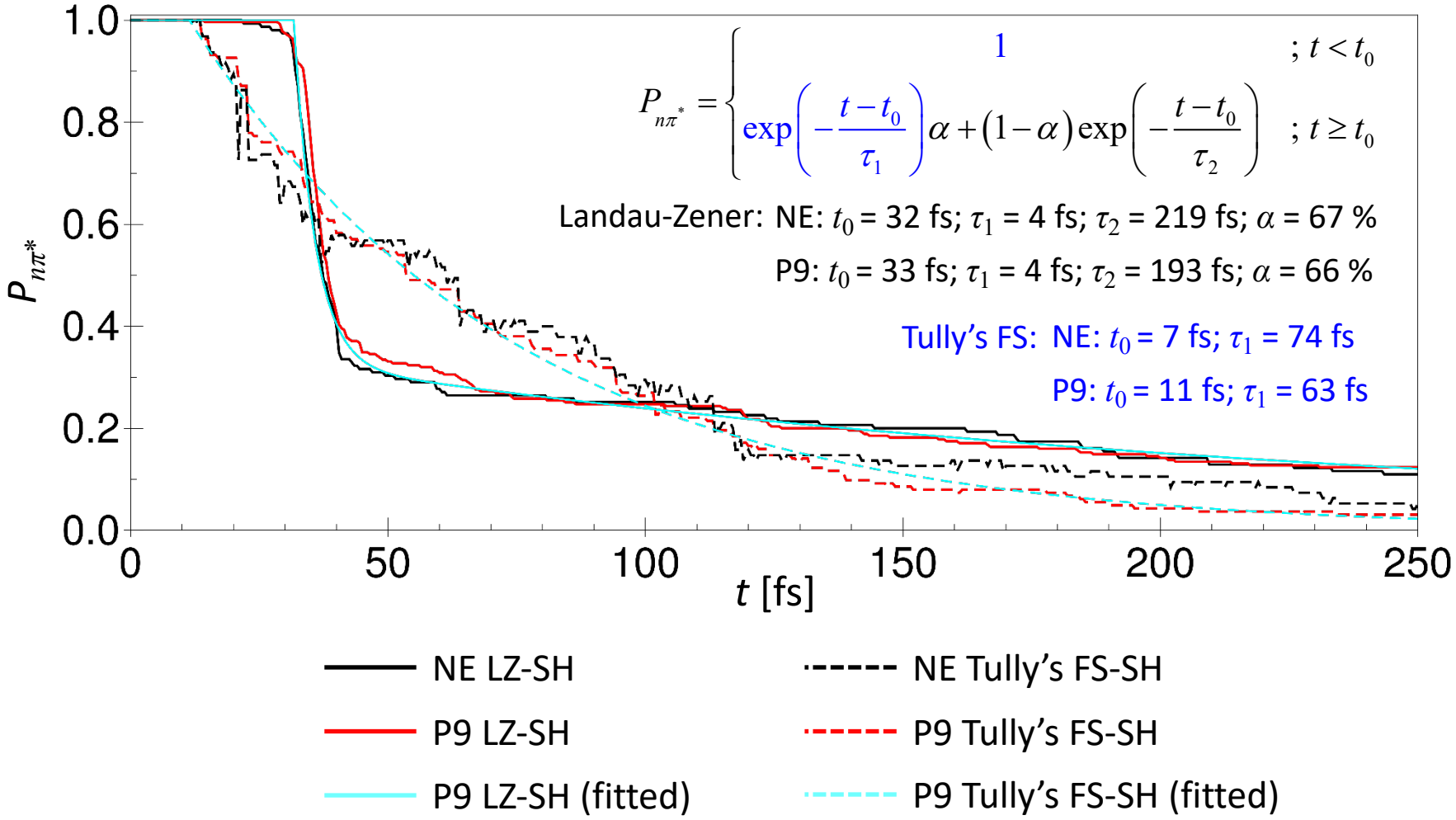
cis-diimide S_1 lifetime with SDE



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Conclusion and Outlook

Use of ΔSCF for description of singlet excited states

ΔSCF applied for NA-MD of condensed phase systems

ΔSCF can be significantly accelerated with SDE methods

Include spin-orbit coupling terms between singlet and triplet states at the ΔSCF level

Improve optimization algorithms for ΔSCF convergence

Generalized ΔSCF for any excited state multiplicity

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