Nonadiabatic Dynamics Beyond Standard TDDFT: A Finite-Temperature Perspective

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Non-adiabatic dynamics using TDDFT

Problem 1 (fundamental):
Wrong topolgy/topography of TDDFT around S_1-S_0 conical intersections

Levine et al. – Mol. Phys. **104** 1039 (2006)

Problem 2 (technical):
No SCF convergence around intersection

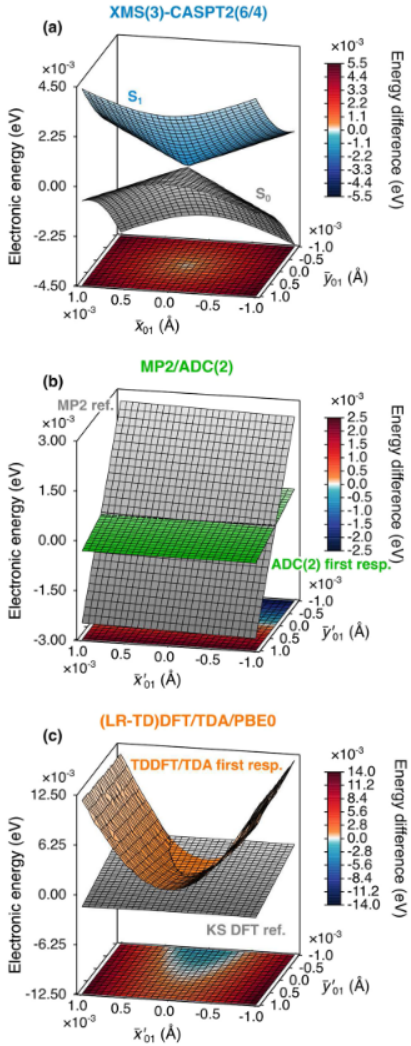
Some fixes:

`SF-TDDFT` Shao et al. – JCP **118** 4807 (2003)

`REKS` Filatov et al. – CPL **304** 429 (1999)

`CIC-TDA` Xu et al. – JCTC **21** 3600 (2025)

Formaldimine



Taylor et al. – JCP **159** 214115 (2023)

Ground state: Finite temperature (Mermin) DFT

- Mermin – Phys. Rev. **137** A1441 (1965)

One-to-one correspondence between external potential and the equilibrium electron density $n(r, t)$ at finite temperature

Free energy

$$\begin{aligned} F &= E - TS \\ &= E_{\text{FON-DFT}} + 2k_B T \sum_i \left[f_i \ln f_i + (1 - f_i) \ln(1 - f_i) \right], \end{aligned}$$

with orbital occupations $f_i = \left\{ 1 + \exp\left(\frac{\epsilon_i - \mu}{k_B T} \right) \right\}^{-1}$ and density $n(r, T) = \sum_i f_i \left| \psi_i(r) \right|^2$

Occupation smearing helps convergence around CI

[See also `TAO-DFT` (fictious temperature to model static correlation)

- Chai – JCP **136** 154104 (2012)]

Finite temperature TDDFT (FT-TDDFT)

- T. Yoshikawa, T. Doi, and H. Nakai – JCP **152** 244111 (2020)

$$\begin{pmatrix} \mathbf{A}^{FT} & \mathbf{B}^{FT} \\ \mathbf{B}^{FT} & \mathbf{A}^{FT} \end{pmatrix} \begin{pmatrix} \mathbf{X}^{FT} \\ \mathbf{Y}^{FT} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}^{FT} \\ \mathbf{Y}^{FT} \end{pmatrix},$$

$$\begin{aligned} A^{FT}_{pq,rs} &= \delta_{pr}\delta_{qs}(\epsilon_q - \epsilon_p) + f_p(1-f_q)K_{pq,rs} \qquad B^{FT}_{pq,rs} = f_p(1-f_q)K_{pq,sr} \\ X^{FT}_{pq} &= f_p(1-f_q)X_{pq} \qquad Y^{FT}_{pq} = f_p(1-f_q)Y_{pq} \quad (\text{for } \epsilon_q > \epsilon_p) \end{aligned}$$

Differs from Casida – Recent Advances in Density Functional Methods, Part I (1995)

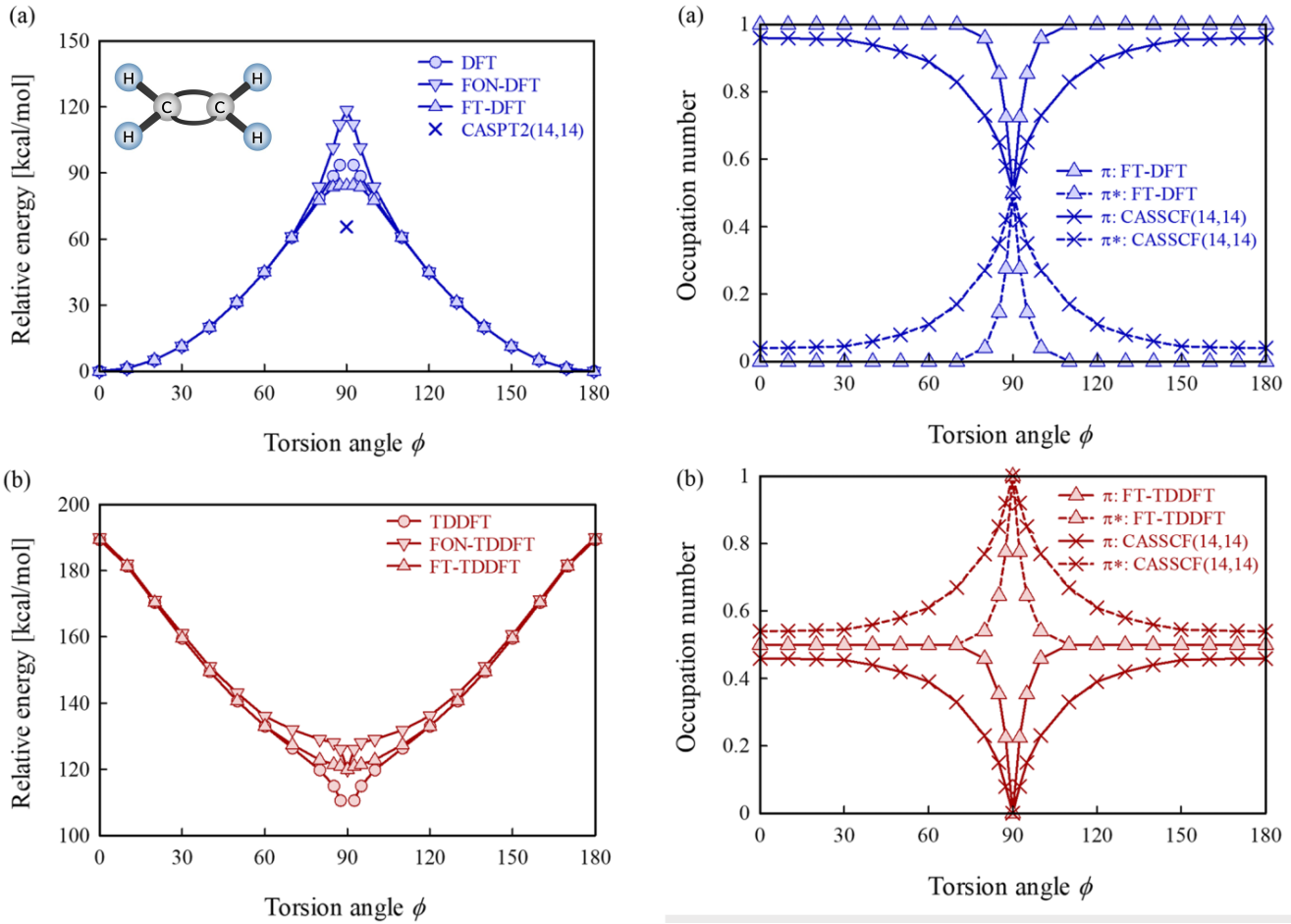
Occupations for excited state:

$$\tilde{f}_p = f_p + \frac{1}{2}\sum_{q(<p)}\left\{|X^{FT}_{qp}|^2 - |Y^{FT}_{qp}|^2\right\} - \frac{1}{2}\sum_{q(>p)}\left\{|X^{FT}_{pq}|^2 - |Y^{FT}_{pq}|^2\right\}$$

$$\Rightarrow F = E_{\text{FON-DFT}} + \omega + 2k_BT\sum_i\left[\tilde{f}_i \ln \tilde{f}_i + (1-\tilde{f}_i)\ln(1-\tilde{f}_i)\right]$$

Case study: Ethylene double bond rotation

- T. Yoshikawa, T. Doi, and H. Nakai – JCP **152** 244111 (2020)



Gap dependent temperature: $T = T_0 \operatorname{erfc}(\Delta E/(\Delta E_0)$

Excited state entropy revisited

T. Yoshikawa, T. Doi, and H. Nakai – JCP **152**

$$\tilde{f}_p = f_p + \frac{1}{2}\sum_{q(<p)}\left\{|X^{FT}_{qp}|^2 - |Y^{FT}_{qp}|^2\right\} - \frac{1}{2}\sum_{q(>p)}\left\{|X^{FT}_{pq}|^2 - |Y^{FT}_{pq}|^2\right\}$$

This work: Use relaxed 1-RDDM from TDDFT $\Delta\mathbf{P} = \mathbf{T} + \mathbf{Z}$

$$\begin{aligned} T_{ab\sigma} &= \frac{1}{2}\sum_i \{(X+Y)_{ia\sigma}(X+Y)_{ib\sigma} \\ &\quad +(X-Y)_{ia\sigma}(X-Y)_{ib\sigma} \\ T_{ij\sigma} &= -\frac{1}{2}\sum_a \{(X+Y)_{ia\sigma}(X+Y)_{ja\sigma} \\ &\quad +(X-Y)_{ia\sigma}(X-Y)_{ja\sigma} \end{aligned}$$

$$(\mathbf{A}+\mathbf{B})\,\mathbf{Z} = \mathbf{R}$$

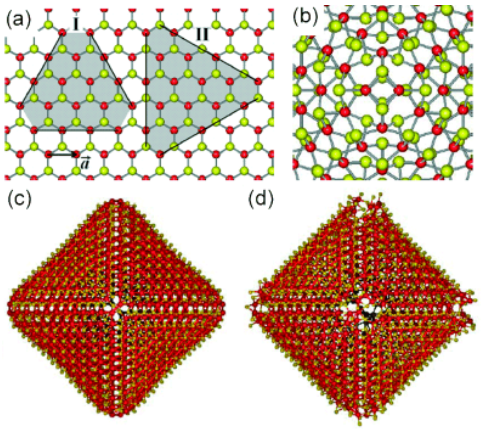
generalized to finite temperature.

Density functional based Tight-Binding (DFTB)

... is a simplified DFT method with additional approximations beyond the exchange-correlation functional.

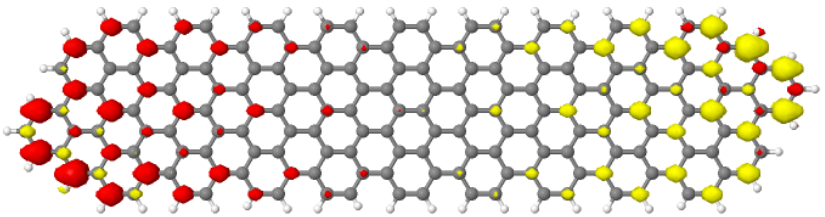
defects
large structures
many conformers
disordered systems
long MD

DFTB



DFTB-optimized structure of an $Mo_{576}S_{1140}$ fullerene (c), and the structure after an MD simulation at 300 K (d)

A.N. Enyashin et al. – Ang. Chem. Int. Ed. **46** 623 (2006)

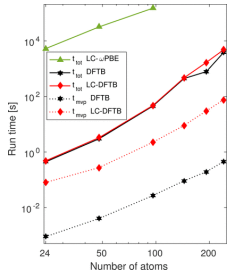


Spin-polarization of an armchair graphene nanoribbon with irregular edges

C.-A. Palma et al. – JPC Lett. **6** 3228 (2015)

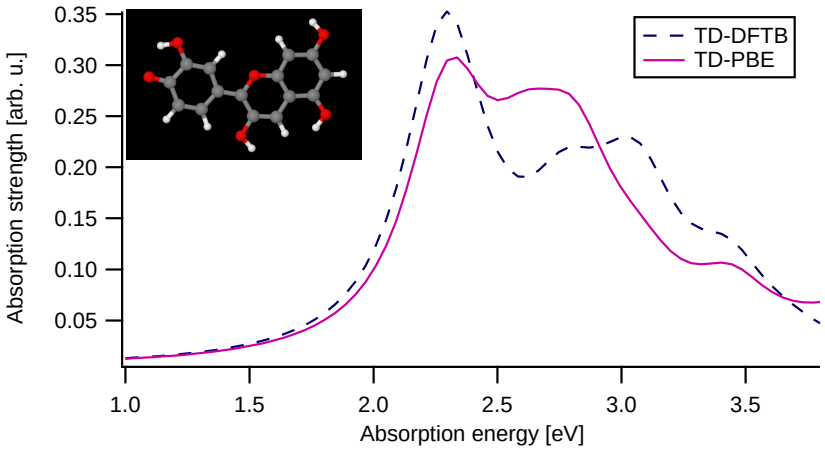
Time dependent DFTB --- TD-DFTB

$$i\frac{\partial}{\partial t}\phi_i(\vec{r},t) = H^{\mathrm{DFTB}}\phi_i(\vec{r},t)$$



Available implementations

- Casida PRB **63** 085108 (2001)
- Electron-ion dynamics EPJ D **35** 467 (2005)
- O(N) PRB **76** 045114 (2007)
- NAMD using Newton-X JCTC **13** 5846 (2017)
- Range-separated func. JCTC **13** 1737 (2017)
- NAMD using Sharc JCTC **20** 10602 (2024)



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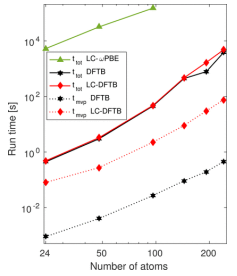

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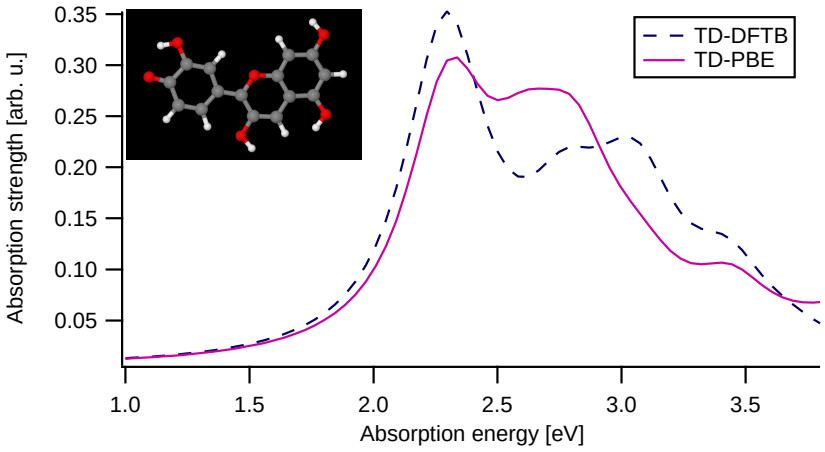
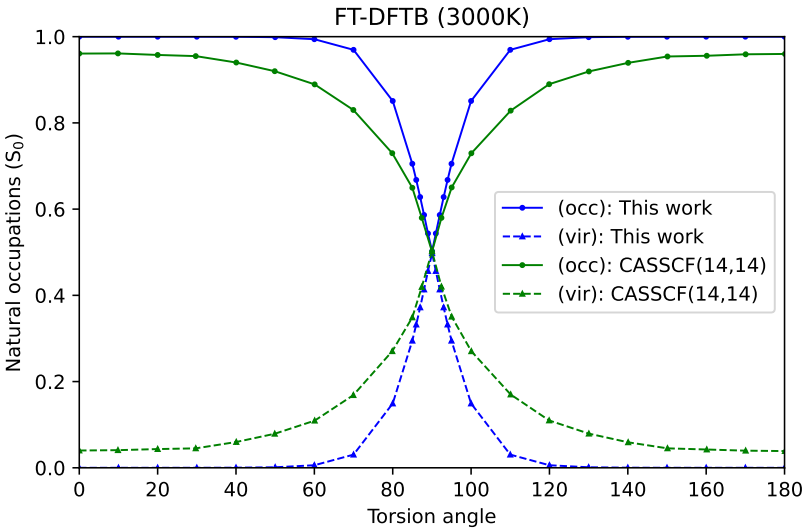


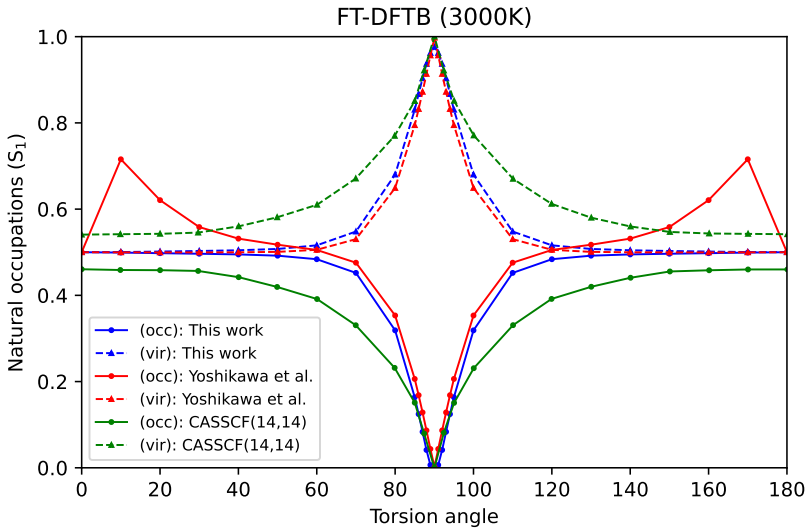
Standard deviation from experiment (eV)

	TD-DFTB	TD-PBE	TD-B3LYP	TD-PM3
Sing. (21 Com.)	0.34	0.38	0.29	0.54
Trip. (12 Com.)	0.28	0.22	0.25	1.02

F. Trani, G. Scalmani, G. Zheng, I. Carnimeo, M.J. Frisch, V. Barone – JCTC **7** 3304 (2011)

FT-DFTB: Case of ethylene





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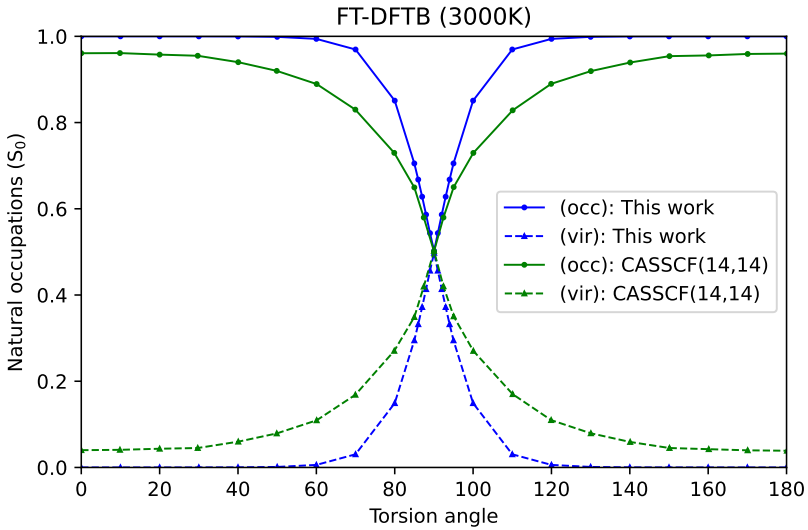

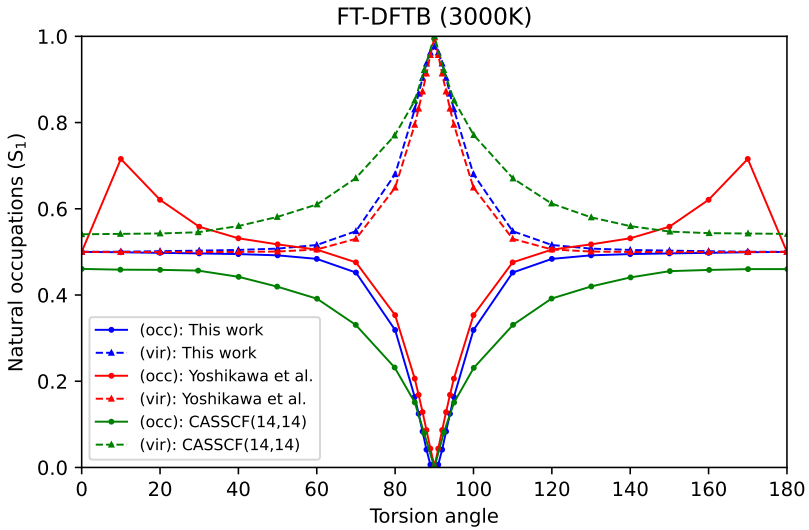

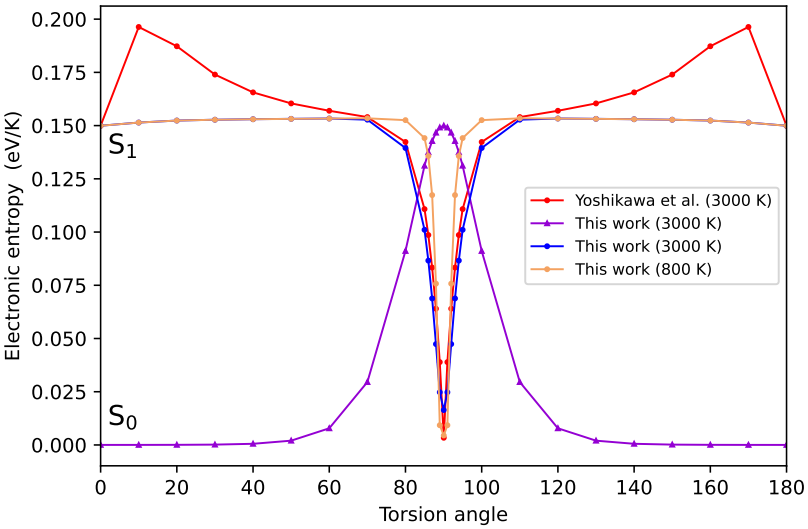

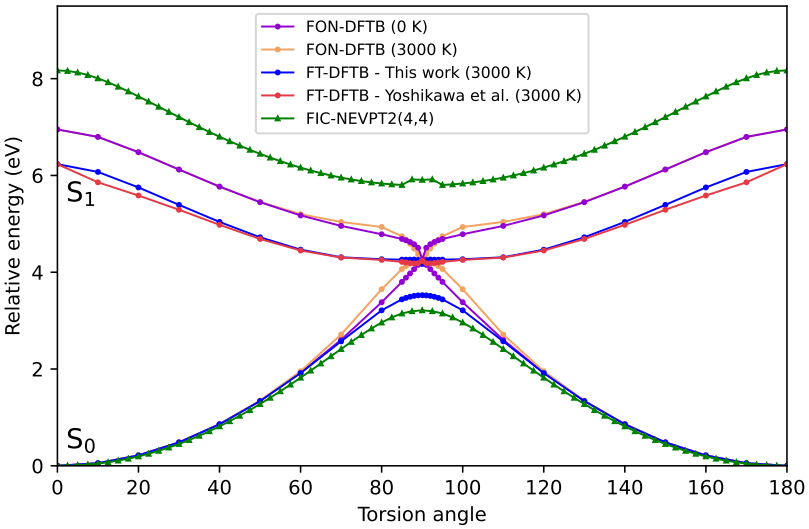

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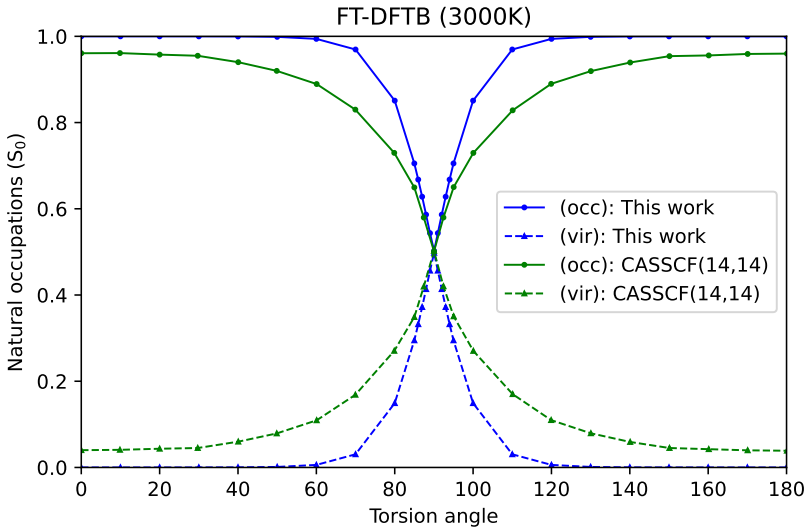

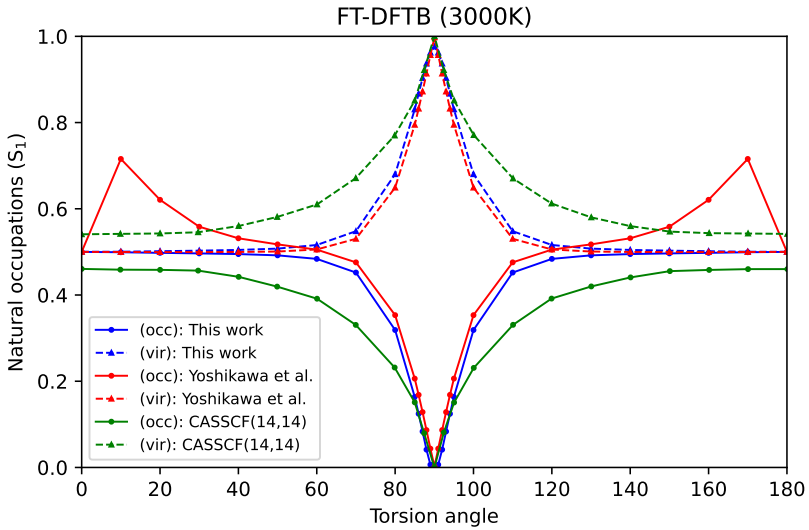

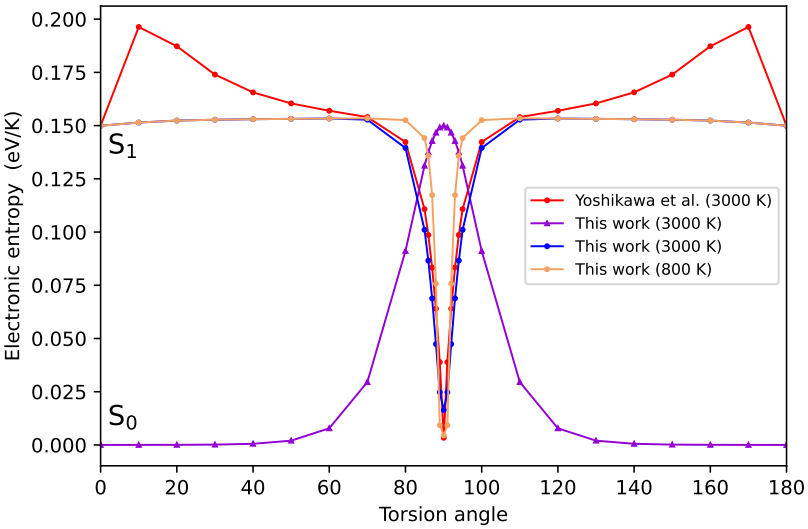

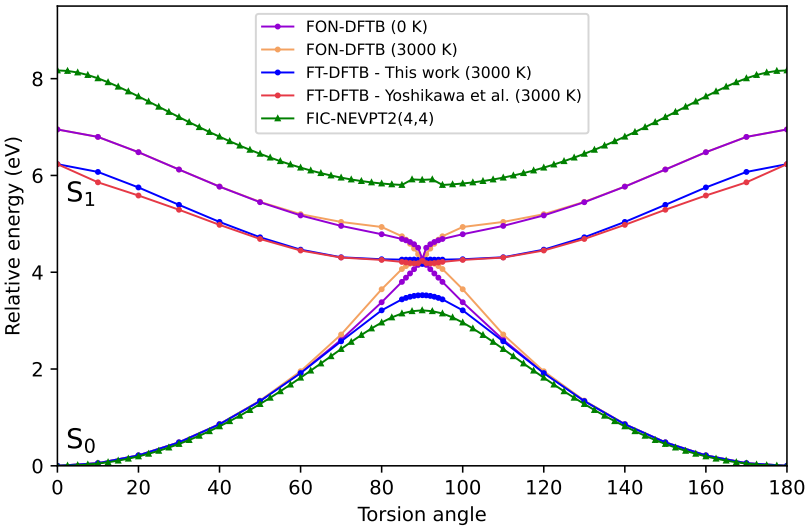

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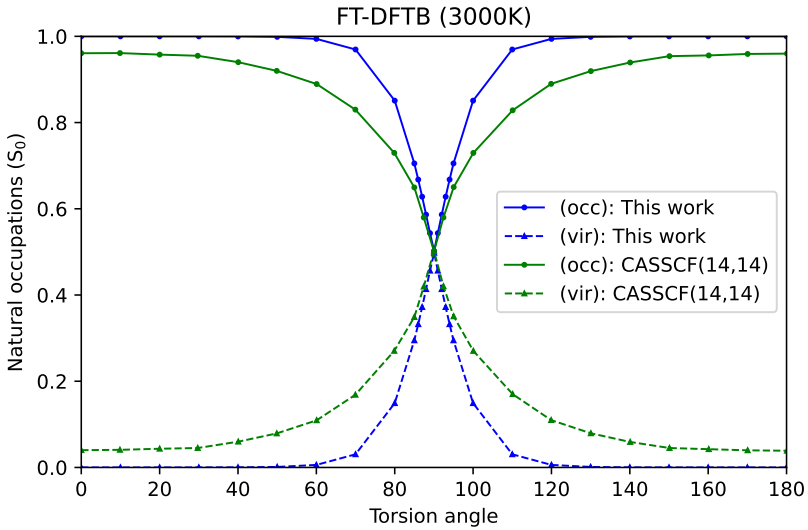

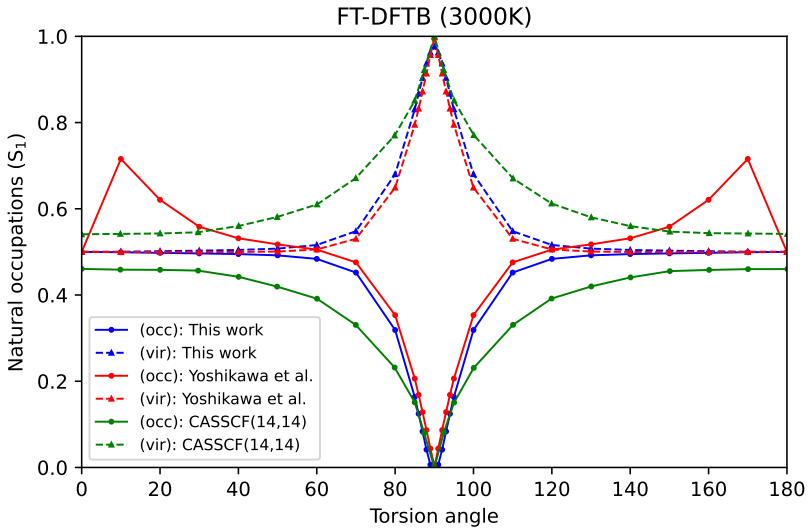

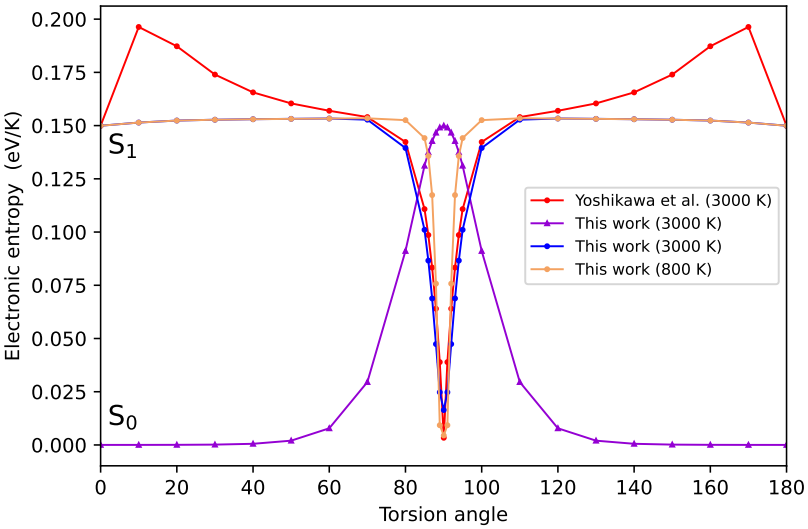

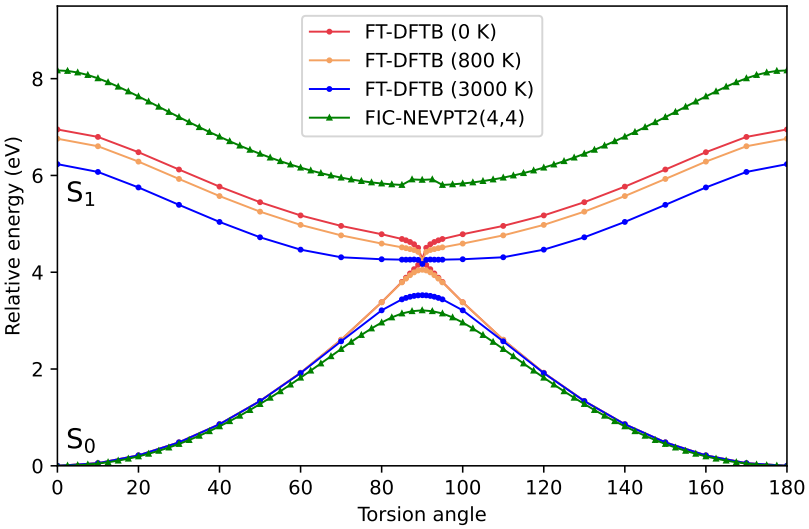

Entropy corrects wrong PES curvature and gap. Are there still CI?

Protonated Formaldimine S_1/S_0 branching space around CI

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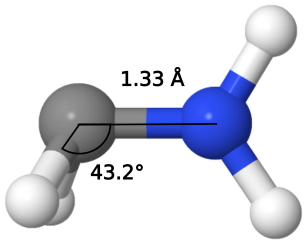
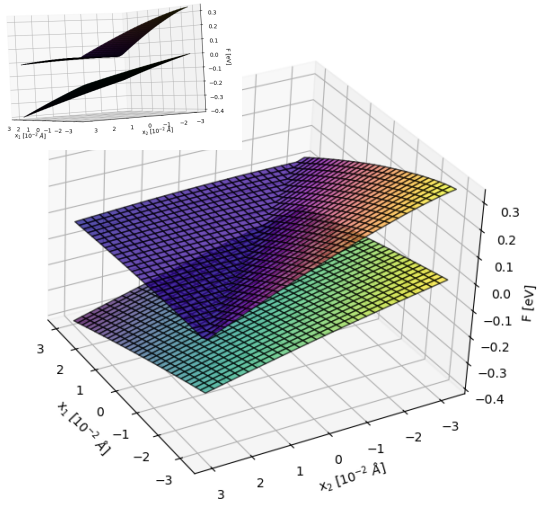
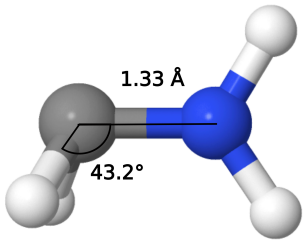


S_1/S_0 MECX



S_1 and S_0 PES

Protonated Formaldimine S_1/S_0 branching space around CI



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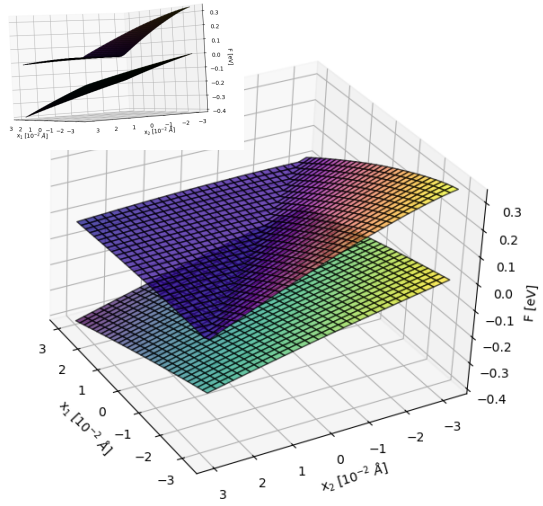

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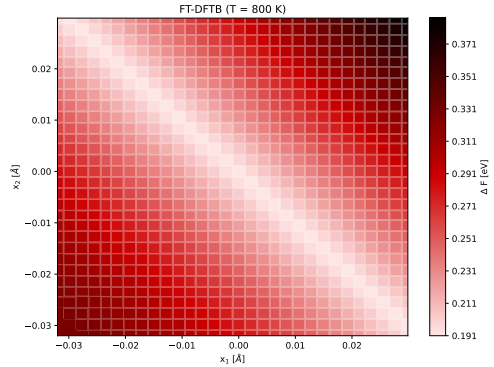
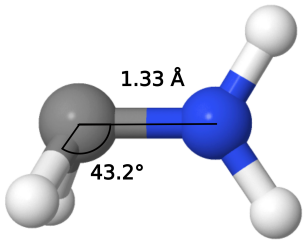


Protonated Formaldimine S_1/S_0 branching space around CI



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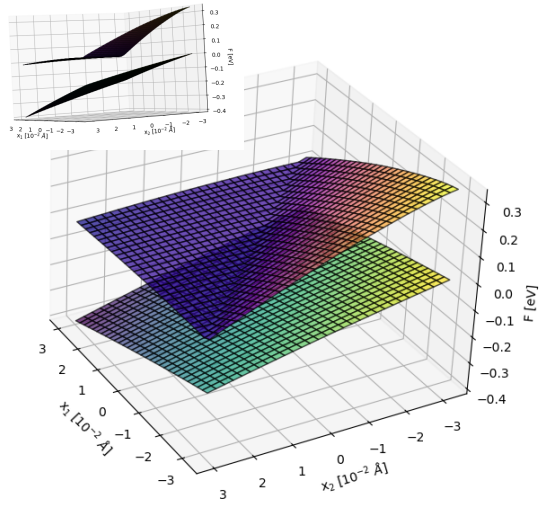
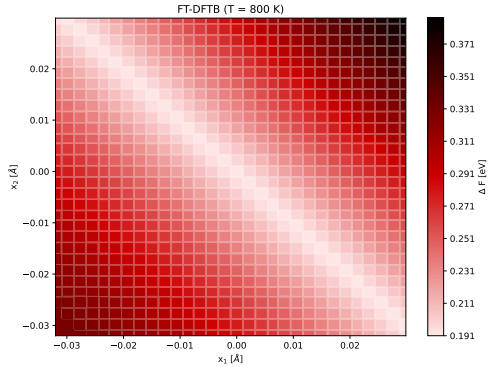
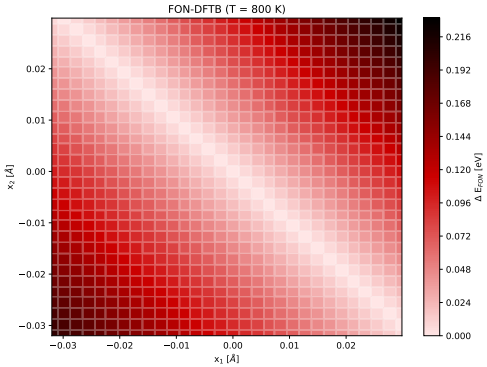
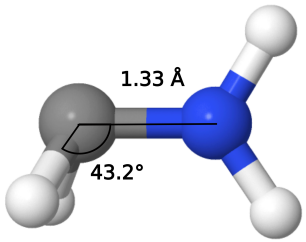


S_1 and S_0 PES





Protonated Formaldimine S_1/S_0 branching space around CI



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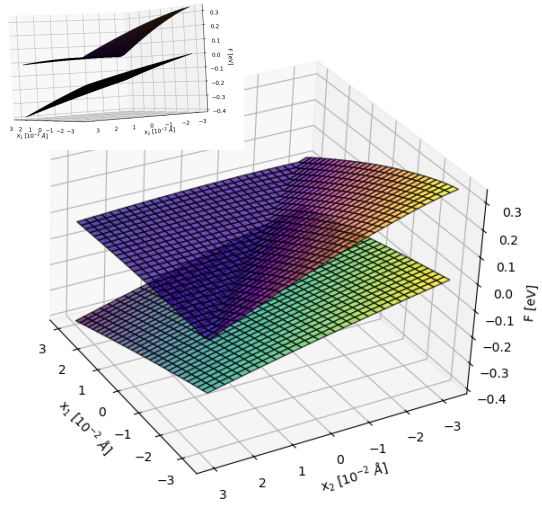

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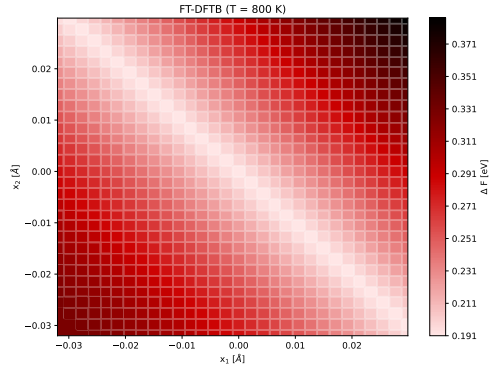

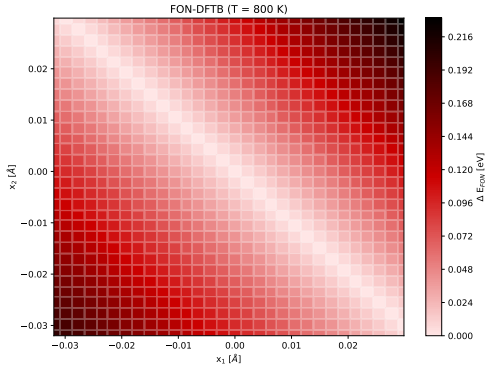

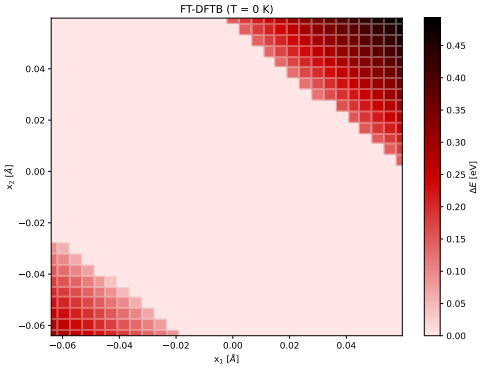

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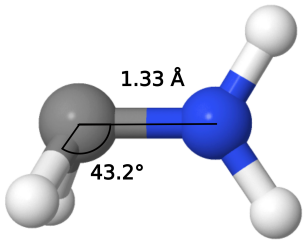

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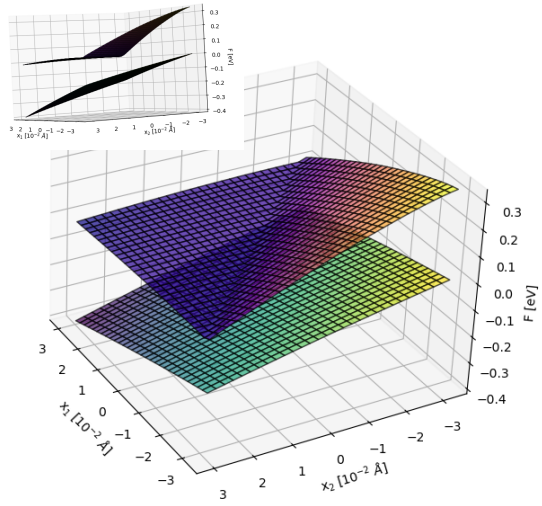
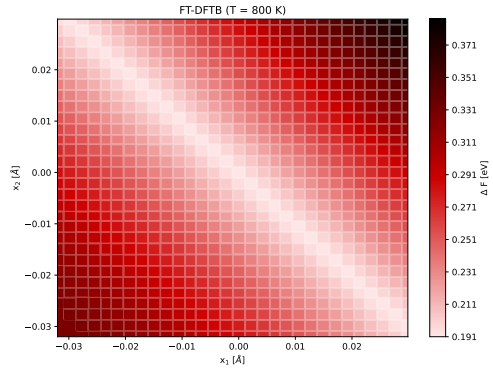
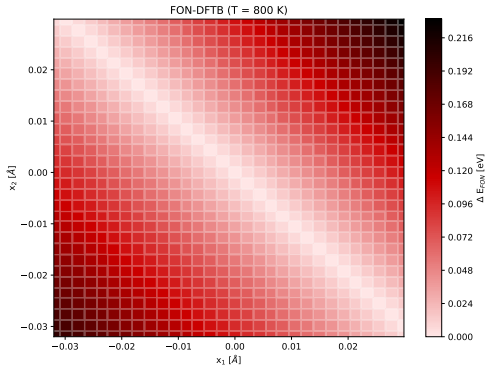
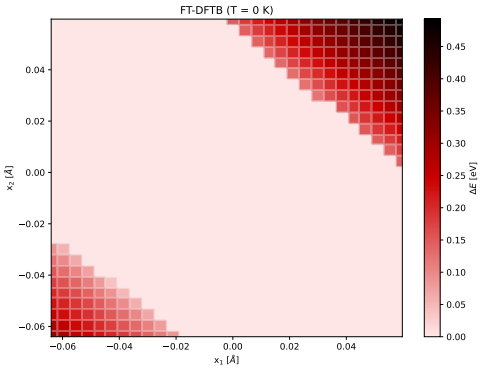


S_1 and S_0 PES

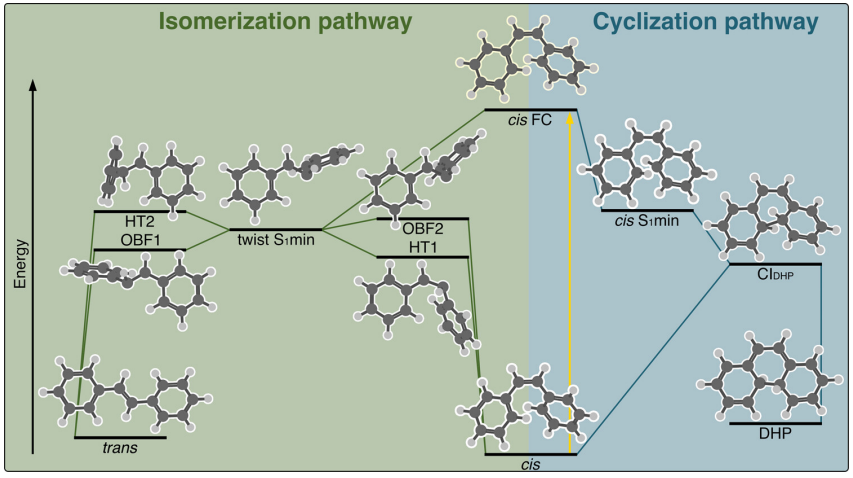






FON-DFTB CI has still wrong topology. No intersection for FT-DFTB

NAMD simulations on Stilbene

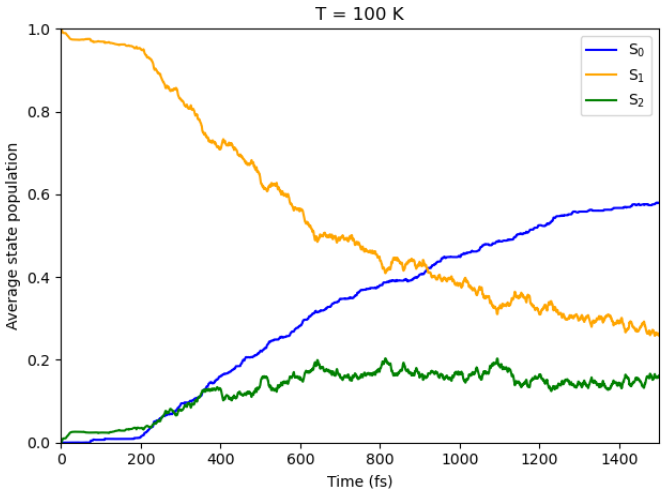


T. Jira et al. – JCTC **20** 10972 (2024)

NAMD parameters

- PyUnixMD - DFTB+ interface S. Lee et al. – J. Comp. Chem **42** 1755 (2021)
- FT-DFTB with `mio-1-1` Slater-Koster files
- Initial conditions from 5 ps BOMD at 200 K
- 500 trajectories of 1.5 ps length (Δt = 0.5 fs)
- Decoherence correction [Granucci/Persico – JCP **126** 134114 (2007)]
- Numerical forces, numerical NAC [from $(X+Y)^{FT}$]

Is the S_2 relevant for the $S_1 \rightarrow S_0$ decay?



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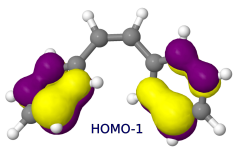
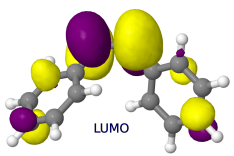
W.G. Han et al. – CPC **3** 167 (2002)





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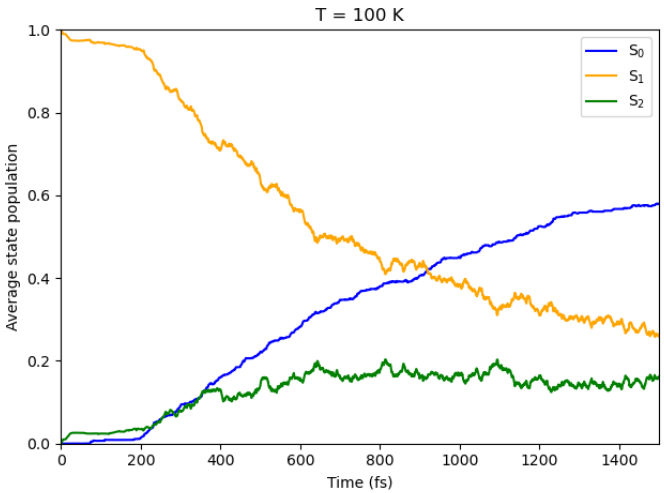
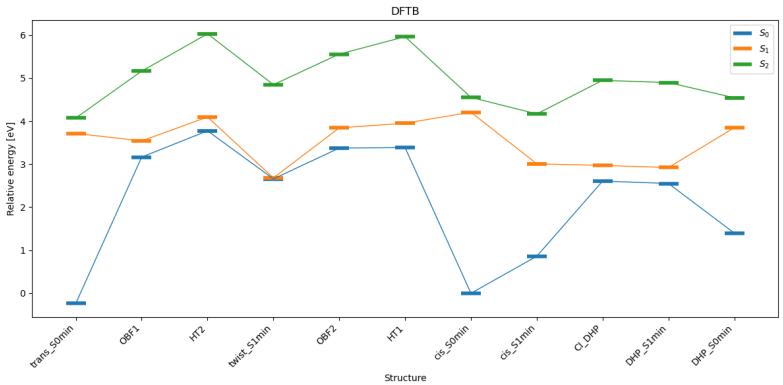


SA2-CASSCF(2,2)/SVP geometries



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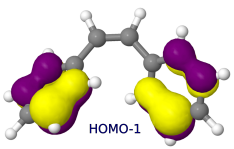

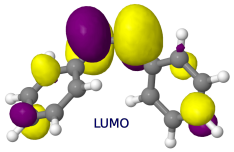

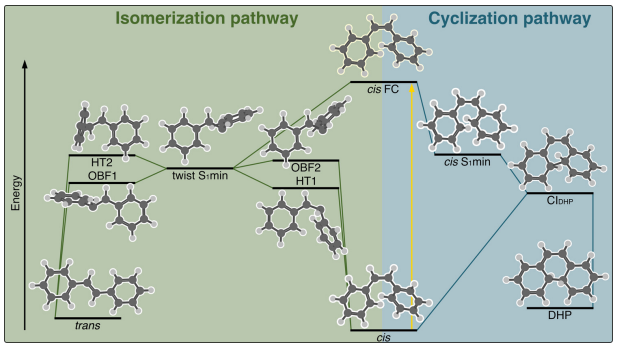

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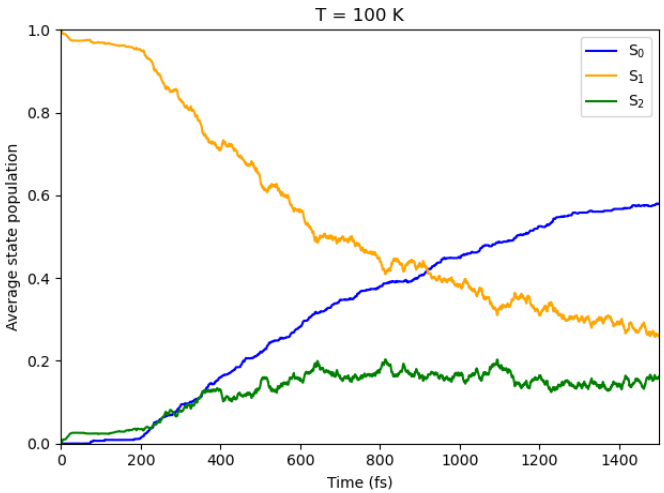

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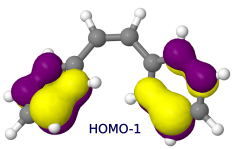

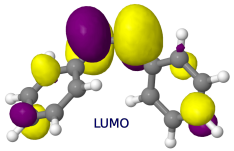

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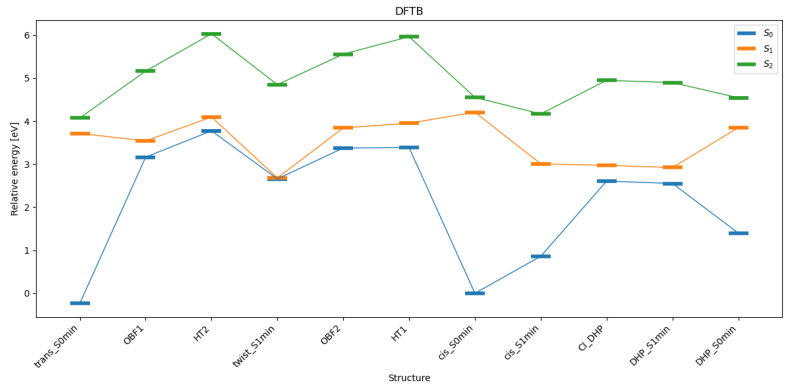

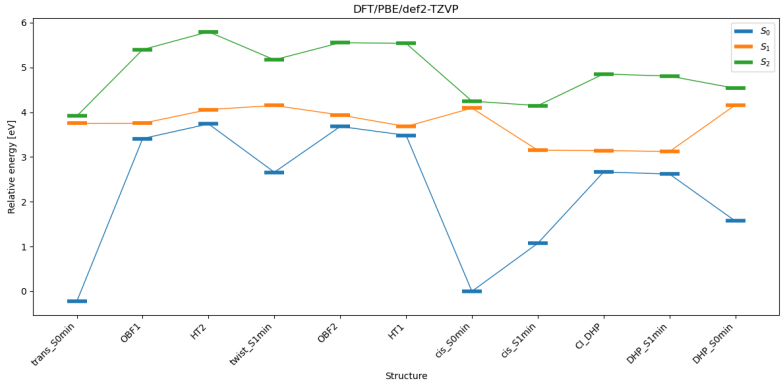

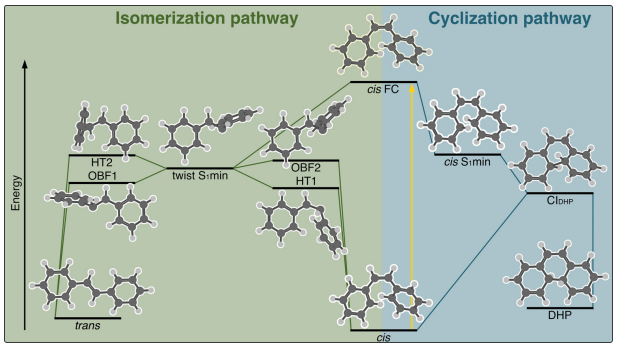

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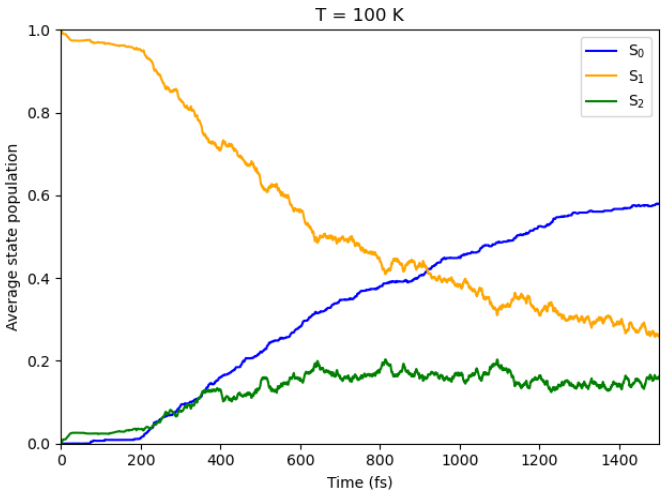

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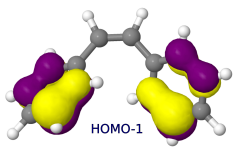

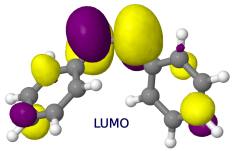

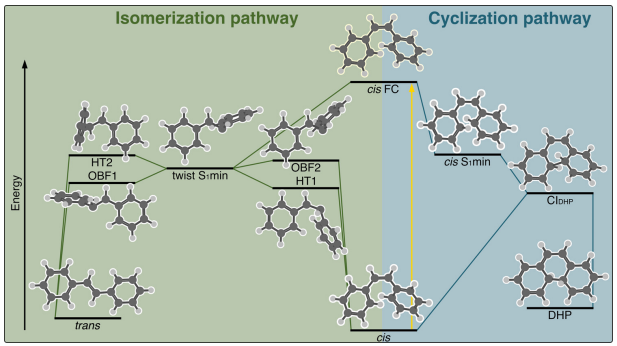

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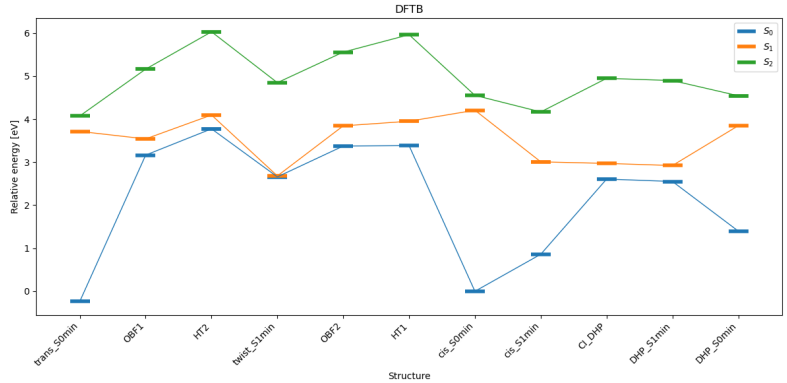

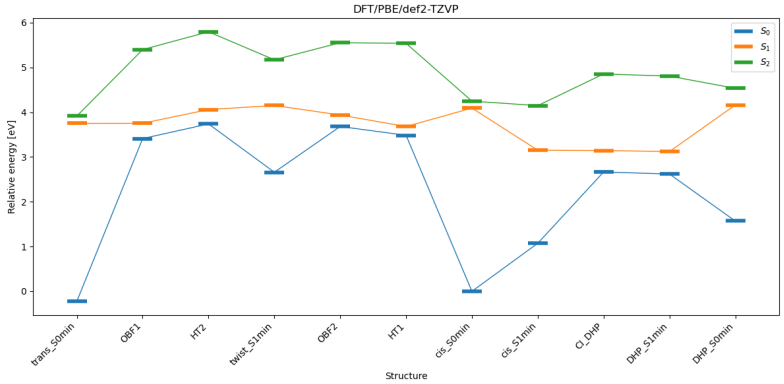

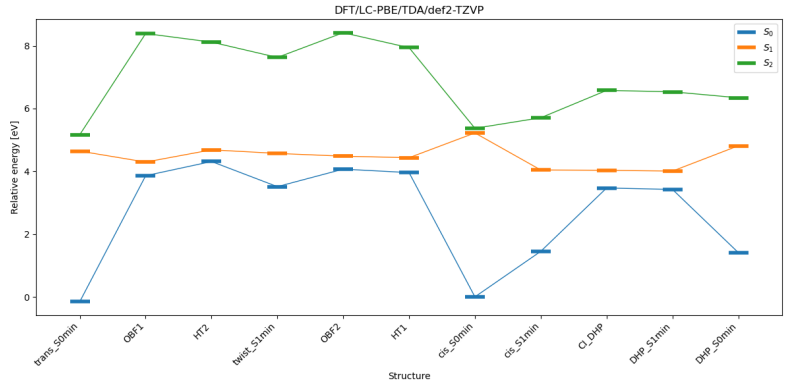

Temperature dependence of quantum yields

	ϕ_{cis}	ϕ_{trans}	ϕ_{DHP}	lifetime (fs)
experiment (solvents)	0.47-0.59	0.35-0.39	0.05-0.08	380-1650
OM3-MRCISD (LZSH)	0.48	0.52	0.00	321
SA2-CASSCF/SVP	0.29	0.68	0.03	360
XMS-SA3-CASPT2/cc-pVDZ	0.55	0.02	0.43	295
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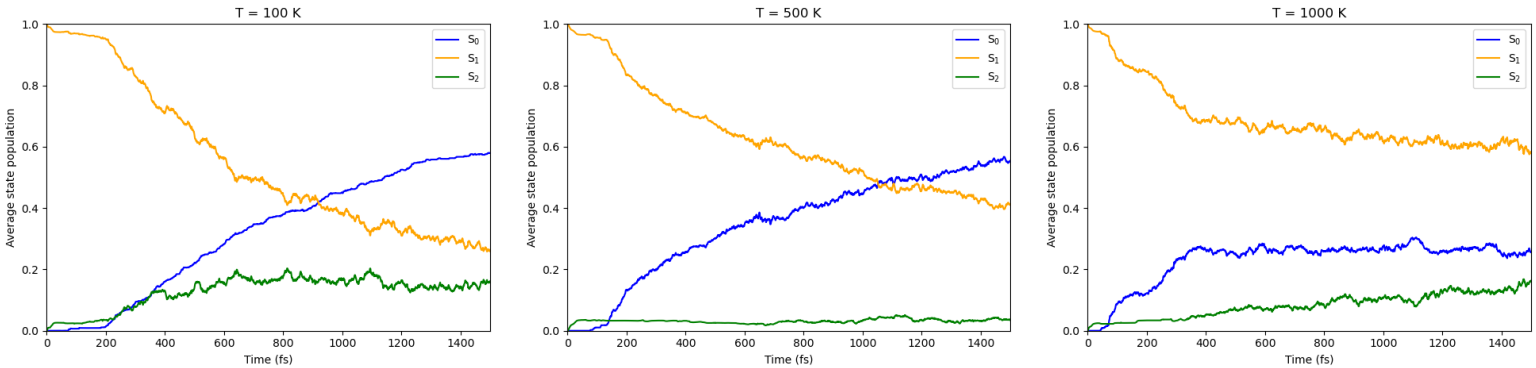
FT-DFTB (100 K)	0.49	0.37	0.14	
FT-DFTB (500 K)	0.59	0.38	0.03	
FT-DFTB (1000 K)	0.71	0.27	0.02	



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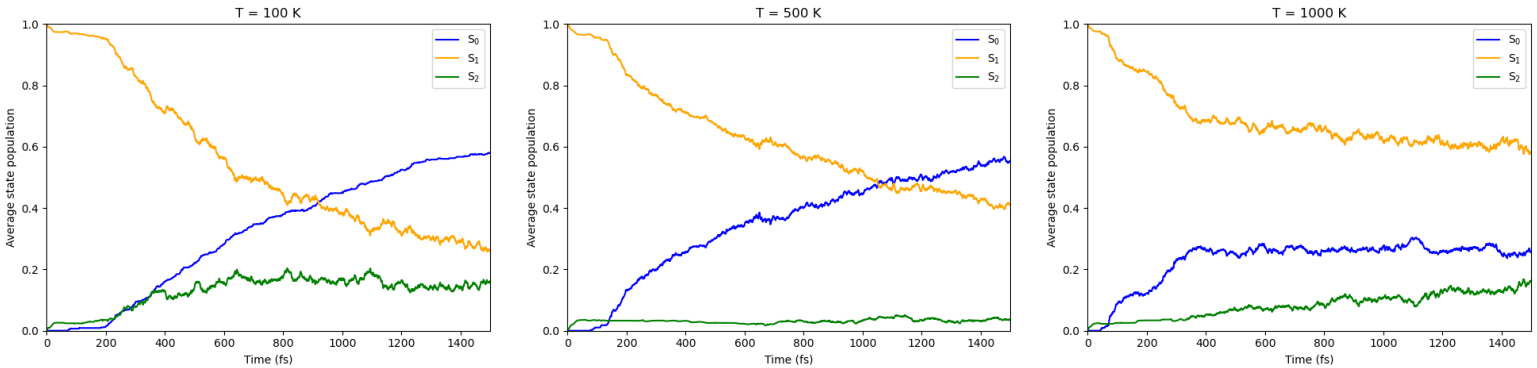

Higher T → flatter PES → lower velocity → lower NAC

Is forcing hops a valid approximation?

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FT-DFTB (100 K, ΔE_{fh} = 0.2 eV)	0.50	0.42	0.08	
FT-DFTB (100 K, ΔE_{fh} = 0.5 eV)	0.43	0.57	0.06	

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FT-DFTB (100 K, ΔE_{fh} = 0.5 eV)	0.43	0.57	0.06	

Simulations with forced hops do not converge

Conclusions

- FT-DFT and FT-TDDFT provide improved PES near degeneracy without SCF convergence problems

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Conclusions

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- New form of excited state entropy including orbital relaxation
- FT-DFT has still wrong topology of CI
- Analytical excited state forces difficult $\rightarrow$ automatic differentiation?
- Forced hops are not a well behaved approximation
- Which temperature to choose? $\rightarrow$ gap criteria