

Excited-state direct orbital optimization for molecular dynamics simulations of photoinduced reactions

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Experimental collaborations



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$$a \cdot Dk + (1 - a) \cdot Is$$



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We need methods to robustly characterize **photoinduced dynamics in molecules and the response of the solvent** to assist ultrafast experiments (X-ray free electron lasers) and predict photoreactivity



Direct observation of coherent femtosecond solvent reorganization coupled to intramolecular electron transfer

Biasin et al. *Nat. Chem.* **13**, 343 (2021)



ARTICLE

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DOI: 10.1038/ncomms13678 OPEN

Atomistic characterization of the active-site solvation dynamics of a model photocatalyst

Driel et al. *Nat. Commun.* **7**, 13678 (2016)

How do we model **excited-state molecular dynamics in solution?**

$$i \frac{\partial}{\partial t} \Psi(\mathbf{R}, \mathbf{r}, t) = \hat{H} \Psi(\mathbf{R}, \mathbf{r}, t)$$

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \sum_i \chi_i(\mathbf{R}, t) \Phi_i(\mathbf{r}; \mathbf{R})$$

$$\hat{H}_e \Phi_i(\mathbf{r}; \mathbf{R}) = E_i(\mathbf{R}) \Phi_i(\mathbf{r}; \mathbf{R})$$

- **Quantum dynamics** \longrightarrow Few degrees of freedom, precomputed potential energy surfaces
- **Classical nuclear dynamics** \longrightarrow Hundreds of atoms (DFT), on-the-fly calculation of energy/forces

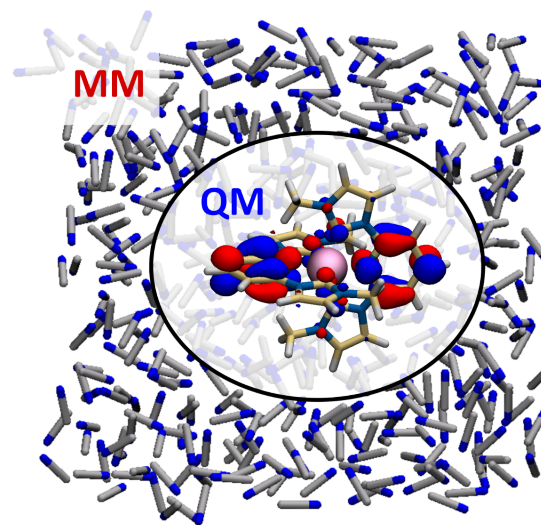
$$\ddot{\mathbf{R}}_\alpha = -\frac{\nabla_\alpha E_i}{M_\alpha}$$

Multiscale:

Quantum mechanics (bond breaking/formation)

Molecular mechanics (classical potentials)

$$\hat{H}_{\text{MM}} = \sum_{m,n>m} \left\{ \frac{q_m q_n}{R_{mn}} + 4\epsilon_{mn} \left[\left(\frac{\sigma_{mn}}{R_{mn}} \right)^{12} - \left(\frac{\sigma_{mn}}{R_{mn}} \right)^6 \right] \right\}$$



- I. Choice of electronic structure method for excited states

- II. QM/MM (solute-solvent) coupling?

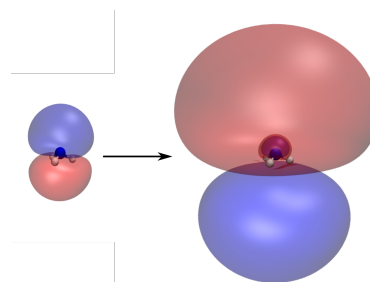
- III. Electronic dynamics?

I. Choice of electronic structure method for excited states

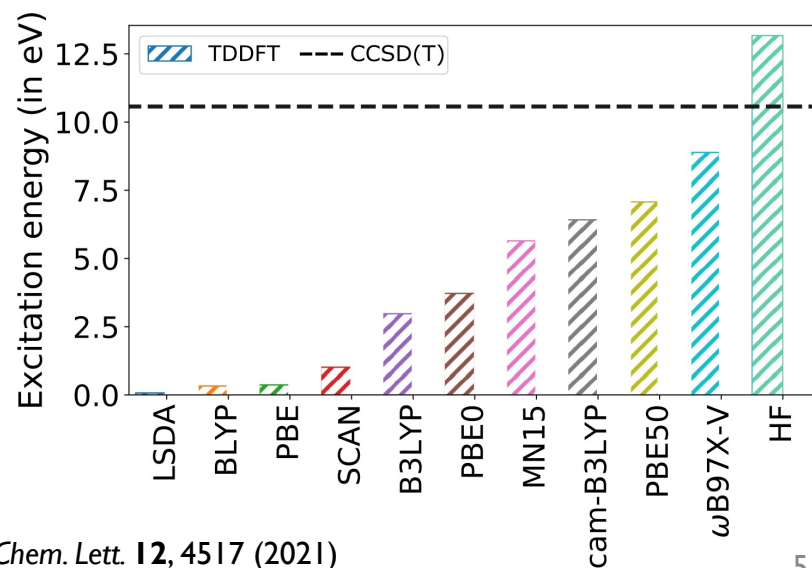
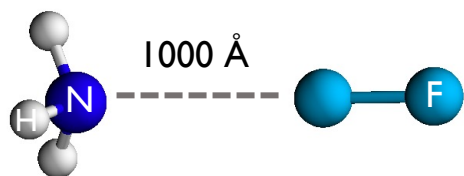
Common approach: linear-response time-dependent DFT (TDDFT)

- No **double excitations**, incorrect **conical intersections** between ground and excited states
Levine et al. *Mol. Phys.* **104**, 1039 (2006)

- Poor estimate of **Rydberg excitation energies**
Seidu et al. *J. Phys. Chem. A* **119**, 5107 (2015)



- **Long-range charge-transfer excitations** require the “right” amount of non-local exchange
Dreuw *J. Chem. Phys.* **119**, 2943 (2003)



I. Choice of electronic structure method for excited states

Alternative: **excited-state DFT (eDFT aka Δ SCF)**

Excited states \longrightarrow Generic **stationary points** of the energy density functional

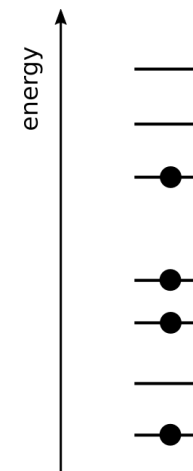
Ayers *Phys. Rev.A* **85**, 42518 (2012)

$$\hat{h}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

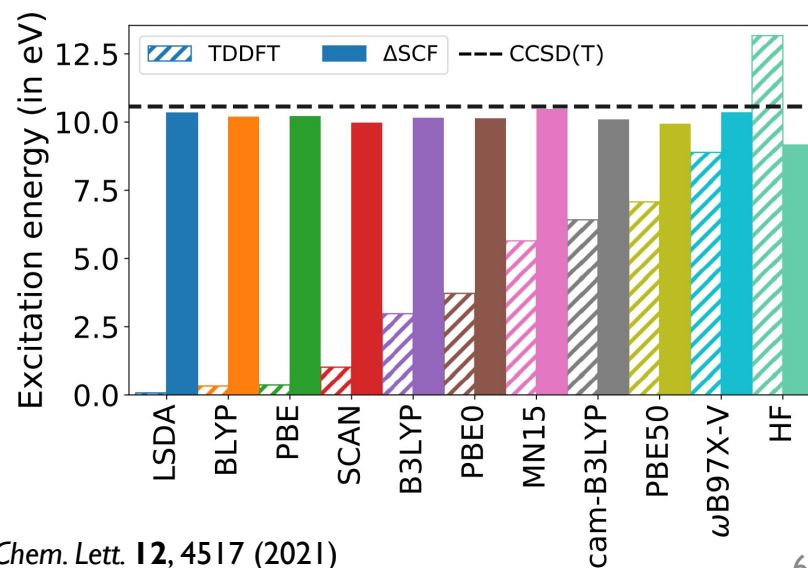
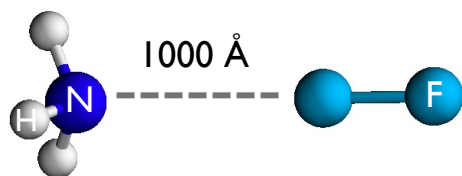
$$\hat{h} = -\frac{1}{2}\nabla^2 + \hat{v}_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \hat{v}_{\text{xc}}(\mathbf{r})$$

Approximations:

1. Ground-state xc functionals
2. Non-orthogonality

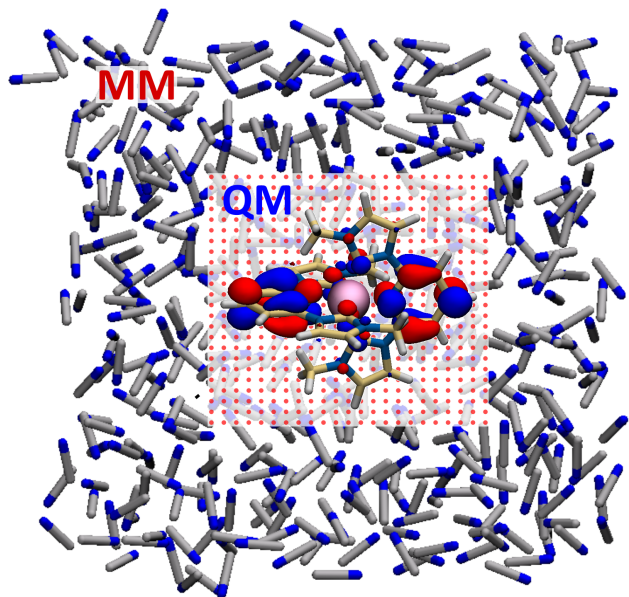


Variational \longrightarrow **Atomic forces** from Hellmann-Feynman theorem



II. QM/MM (solute-solvent) coupling?

QM/MM Electrostatic Embedding



$$\hat{H}_e^{\text{eff}} \Phi_i(\mathbf{r}; \mathbf{R}_\alpha, \mathbf{R}_m) = E_i(\mathbf{R}_\alpha, \mathbf{R}_m) \Phi_i(\mathbf{r}; \mathbf{R}_\alpha, \mathbf{R}_m)$$

$$\hat{H}_e^{\text{eff}} = \hat{H}_{\text{QM}} + \hat{H}_{\text{QM/MM}} + \hat{H}_{\text{MM}}$$

$$\hat{H}_{\text{QM/MM}} = - \sum_{i,m} \frac{q_m}{|\mathbf{r}_i - \mathbf{R}_m|} + \sum_{\alpha,m} \left\{ \frac{Z_\alpha q_m}{R_{\alpha m}} + 4\epsilon_{\alpha m} \left[\left(\frac{\sigma_{\alpha m}}{R_{\alpha m}} \right)^{12} - \left(\frac{\sigma_{\alpha m}}{R_{\alpha m}} \right)^6 \right] \right\}$$

Field et al. *J. Comput. Chem.* **11**, 700 (1990)

Implementation in **ASE** and **GPAW**

Dohn et al. *J. Chem. Theory Comput.* **13**, 6010 (2017)

Dohn *Int. J. Quantum Chem.* **120**, 26343 (2020)



Asmus O. Dohn



Elvar Ö. Jónsson

Slow (hundreds of fs - ps) orientational solvent response

Fast (fs) electronic solvent response \longrightarrow Polarizable Embedding

Jónsson et al. *J. Chem. Theory Comput.* **15**, 6562 (2019)

Dohn et al. *J. Chem. Theory Comput.* **15**, 6578 (2019)

III. Electronic dynamics?

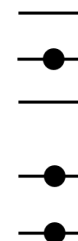
Born-Oppenheimer Molecular Dynamics (BOMD)

Single potential energy surface (electronic and nuclear dynamics do not affect each other)

Excited-state QM/MM BOMD calculation in practice

- Set GPAW calculator to use **orbital occupations to target an excited state**

```
>>> from gpaw.occupations import FixedOccupationNumbers
>>> f = [[1., 1., ..., 1., 0., 1., 0., ..., 0., 0.],
        [1., 1., ..., 1., 1., 0., 0., ..., 0., 0.]]
>>> qmcalc = GPAW(..., occupations=FixedOccupationNumbers(f))
```



- Choose **point charge model** for solvent (water/ACN in ASE)

```
>>> from ase.calculators.tip4p import TIP4P
>>> mmcalc = TIP4P()
```

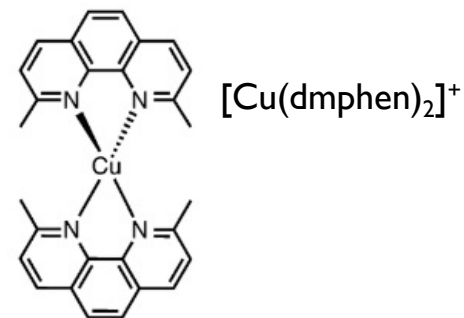
- Set up **EIQMMM calculator** with electrostatic embedding

```
>>> from ase.calculators.qmmm import EIQMMM, Embedding
>>> atoms.calc = EIQMMM(...,
                        qmcalc=qmcalc,
                        mmcalc=mmcalc,
                        embedding=Embedding(rc=0.02),
                        ...)
```

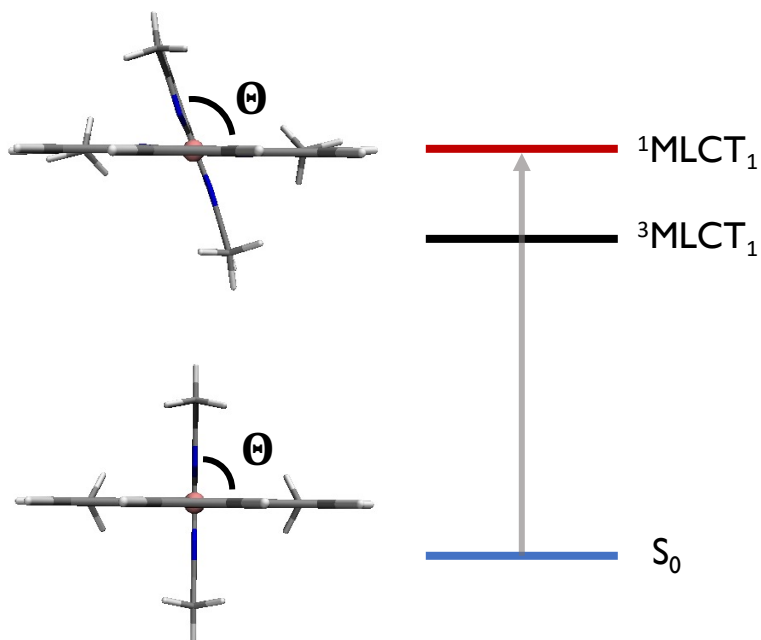
- Run MD

```
>>> from ase.md import VelocityVerlet
>>> md = VelocityVerlet(atoms, ...)
>>> md.run()
```

Dynamics of a copper complex photosensitizer



MLCT = metal-to-ligand charge transfer



Time scale of flattening in acetonitrile, time-resolved emission:

Shaw et al. *J. Am. Chem. Soc.* **129**, 2147–2160 (2007): 100 fs

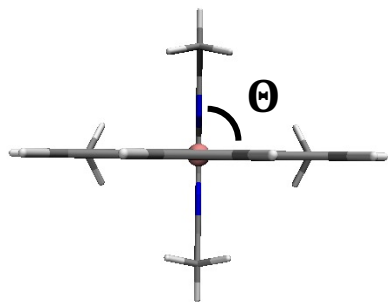
Iwamura *J. Am. Chem. Soc.* **129**, 5248 (2007): 340 fs

	BLYP, tzp(Cu)/dzp (LCAO)	Exp. ^a
$\Delta E(\text{GS} \rightarrow {}^1\text{MLCT}_1)$ (eV)	2.35 eV	2.25-2.29 eV

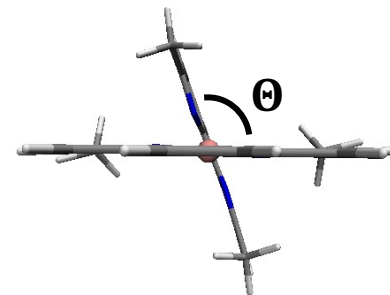
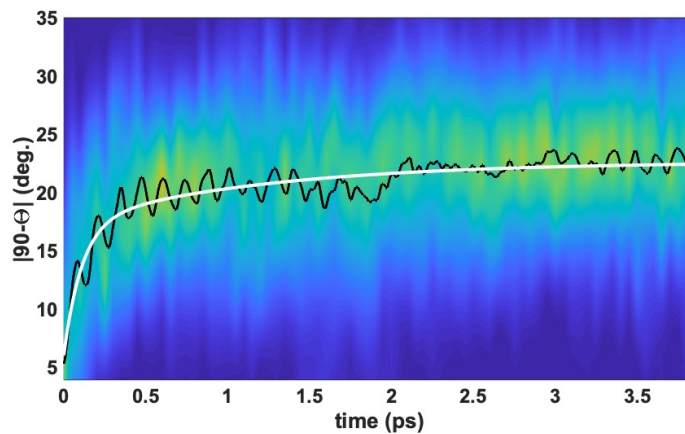
^aIwamura et al *J. Am. Chem. Soc.* **133**, 7728–7736 (2011)

48 QM/MM BOMD trajectories in ¹MLCT₁ state from 300 K equilibrium ground-state ensemble

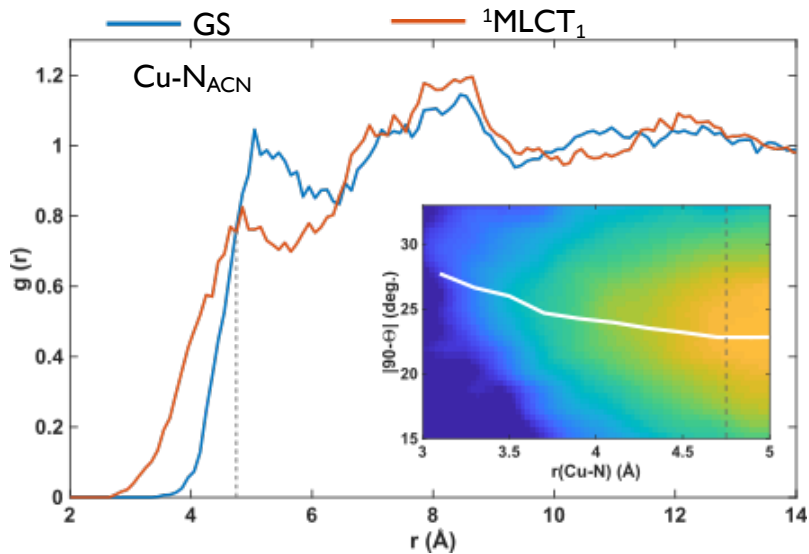
468 ACN molecules



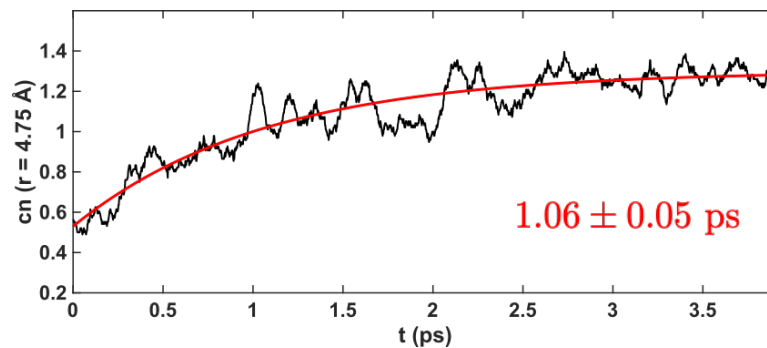
$$\tau_1 = 110 \pm 12 \text{ fs} \quad \tau_2 = 1.2 \pm 0.2 \text{ ps}$$



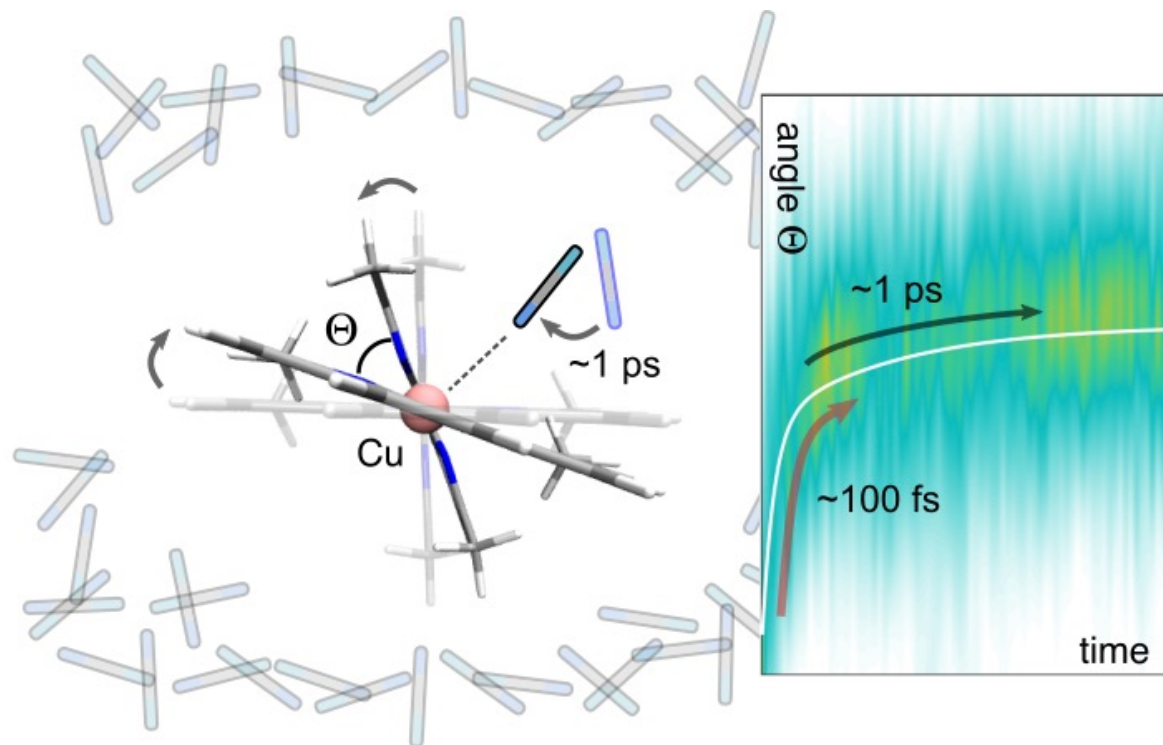
Equilibrium solute-solvent radial distribution functions



Time-dependent solute-solvent coordination number



Two-step concerted solute–solvent structural dynamics



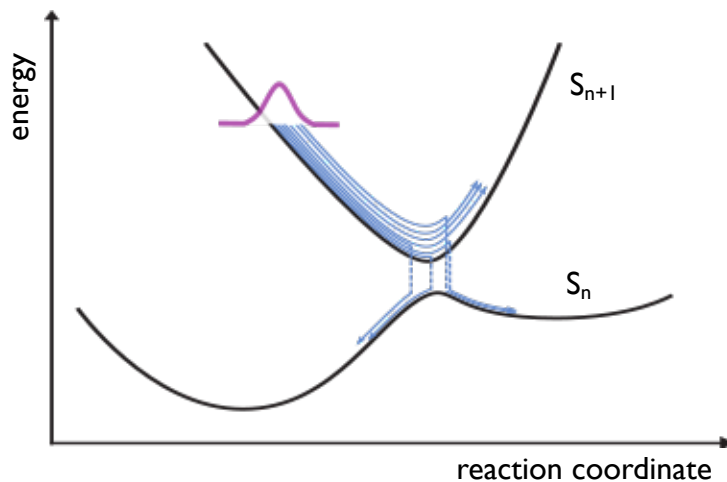
III. Electronic dynamics?

Born-Oppenheimer Molecular Dynamics (BOMD)

Single potential energy surface (electronic and nuclear dynamics do not affect each other)

Nonadiabatic Dynamics using mixed quantum-classical methods

- **Ehrenfest Dynamics** \longrightarrow Many states, single reaction path
- **Trajectory Surface Hopping** \longrightarrow Few states, multiple reaction paths

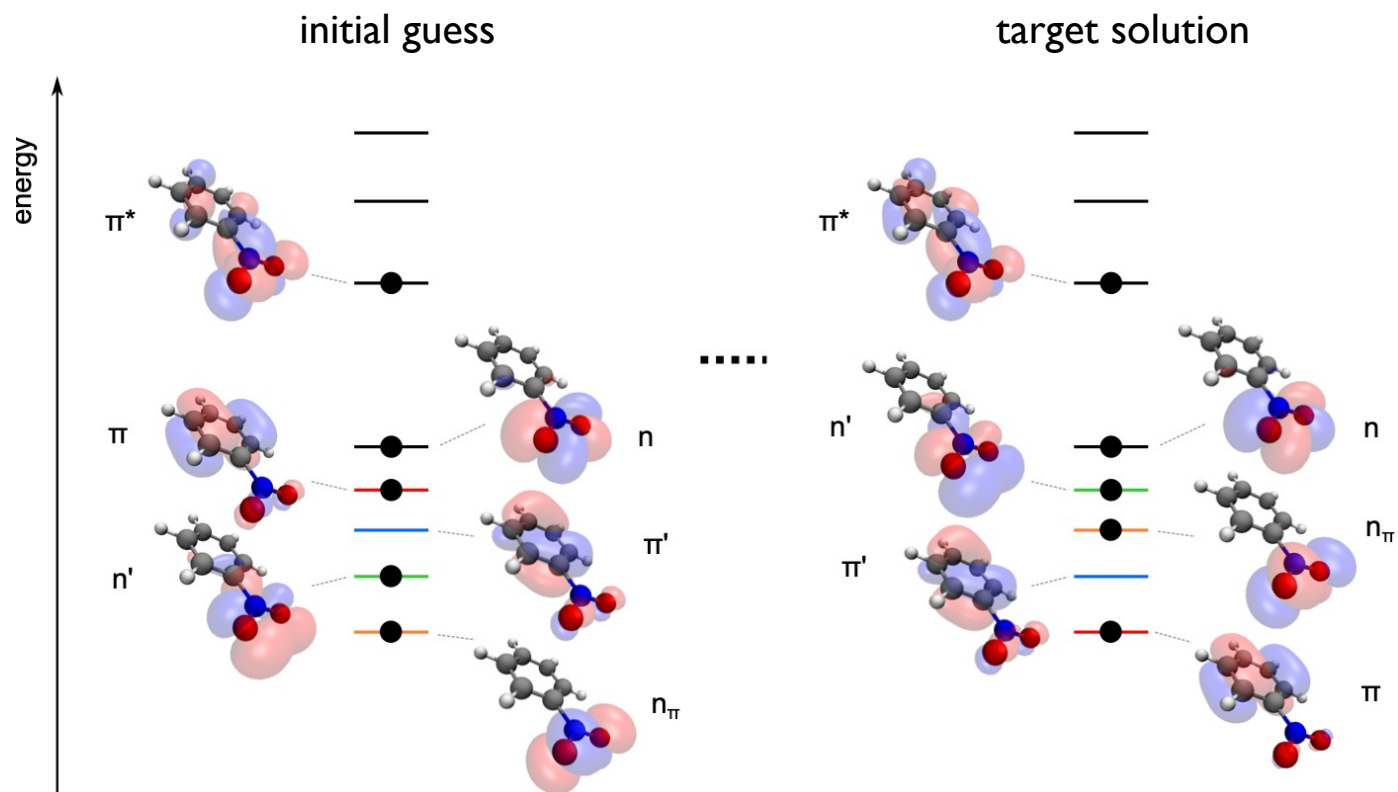


Need to consider **multiple potential energy surfaces and crossings**

Tully *J. Chem. Phys.* **93**, 1061 (1990)

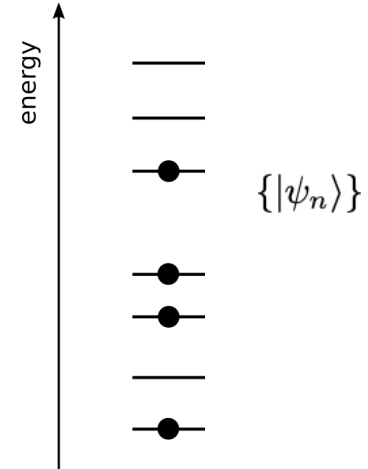
Fixed occupation numbers? Energy levels can change...

Nitrobenzene $A_1(\pi' \rightarrow \pi^*)$ excited state



Maximum Overlap Method (MOM)

- Choose N initial guess orbitals $\{|\psi_n\rangle\}$ (e.g. ground-state orbitals corresponding to non-Aufbau occupation of target excitation)
- At every SCF step k , occupy the orbitals $\{|\psi_m^{(k)}\rangle\}$ with the biggest weights P evaluated from the elements of the overlap matrix $O_{nm}^{(k)} = \langle \psi_n | \psi_m^{(k)} \rangle$:



➤ Method 1 $P_m^{(k)} = \max_n \left(|O_{nm}^{(k)}| \right)$ Dong et al. *J. Chem. Theory Comput.* **16**, 5635 (2020)

➤ Method 2 $P_m^{(k)} = \left(\sum_{n=1}^N |O_{nm}^{(k)}|^2 \right)^{1/2}$ Barca et al. *J. Chem. Theory Comput.* **14**, 1501 (2018)

$$O_{nm}^{(k)} = \langle \tilde{\psi}_n | \tilde{\psi}_m^{(k)} \rangle + \sum_{a, i_1, i_2} \langle \tilde{\psi}_n | \tilde{p}_{i_1}^a \rangle \left(\langle \phi_{i_1}^a | \phi_{i_2}^a \rangle - \langle \tilde{\phi}_{i_1}^a | \tilde{\phi}_{i_2}^a \rangle \right) \langle \tilde{p}_{i_2}^a | \tilde{\psi}_m^{(k)} \rangle \quad \text{FD/PW}$$

$$O_{nm}^{(k)} = \sum_{\mu\nu} c_{\mu n}^* S_{\mu\nu} c_{\nu m}^{(k)}, \quad S_{\mu\nu} = \langle \Phi_\mu | \Phi_\nu \rangle + \sum_{a, i_1, i_2} \langle \Phi_\mu | \tilde{p}_{i_1}^a \rangle \left(\langle \phi_{i_1}^a | \phi_{i_2}^a \rangle - \langle \tilde{\phi}_{i_1}^a | \tilde{\phi}_{i_2}^a \rangle \right) \langle \tilde{p}_{i_2}^a | \Phi_\nu \rangle \quad \text{LCAO}$$

Available in GPAW master: <https://wiki.fysik.dtu.dk/gpaw/documentation/mom/mom.html>

Levi, Ivanov & Jónsson *J. Chem. Theory Comput.* **16**, 6968 (2020)

Ivanov, Levi & Jónsson (2021), [arXiv:2102.06542v1](https://arxiv.org/abs/2102.06542v1)

MOM calculation in practice

- Perform ground-state calculation
- Create list of occupation numbers corresponding to target excitation (e.g. for HOMO→LUMO excitation swap occupation numbers between HOMO and LUMO ground-state orbitals):

```
>>> f = [[1., 1., ..., 1., 0., 1., 0., ..., 0., 0.],  
         [1., 1., ..., 1., 1., 0., 0., ..., 0., 0.]
```

- Prepare calculator for a MOM calculation (use class `gpaw.mom.OccupationsMOM`):

```
>>> from gpaw.mom import prepare_mom_calculation  
>>> mom.prepare_mom_calculation(calc, atoms, f, ...)
```

- Run excited-state calculation:

```
>>> atoms.get_potential_energy()
```

Available in GPAW master: <https://wiki.fysik.dtu.dk/gpaw/documentation/mom/mom.html>

Spin-polarized, PBE, sz+def2-TZVPD (**LCAO mode**)

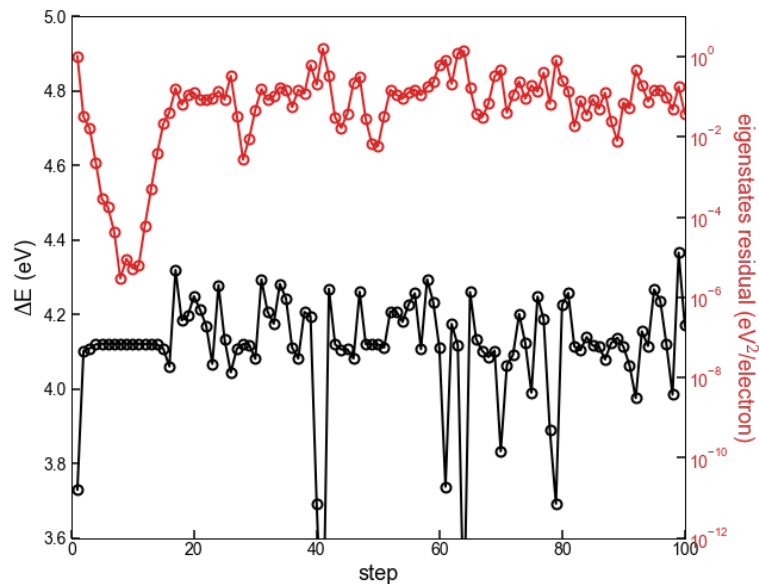
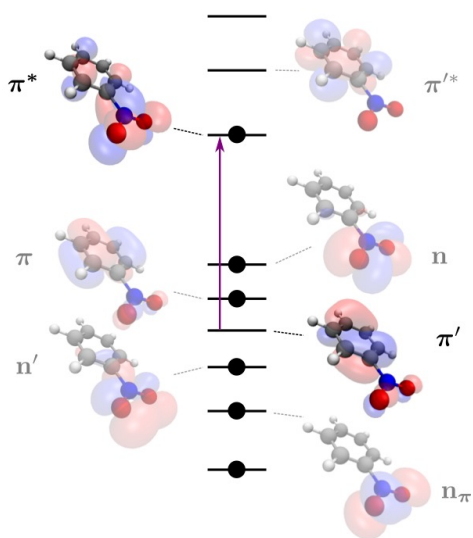
Direct diagonalization of Hamiltonian matrix (default LCAO eigensolver)

Pulay mixing of electron density (MixerSum, default in GPAW < 20.10.0)

Maximum Overlap Method

SCF-MOM

Nitrobenzene $A_1(\pi' \rightarrow \pi^*)$ excitation

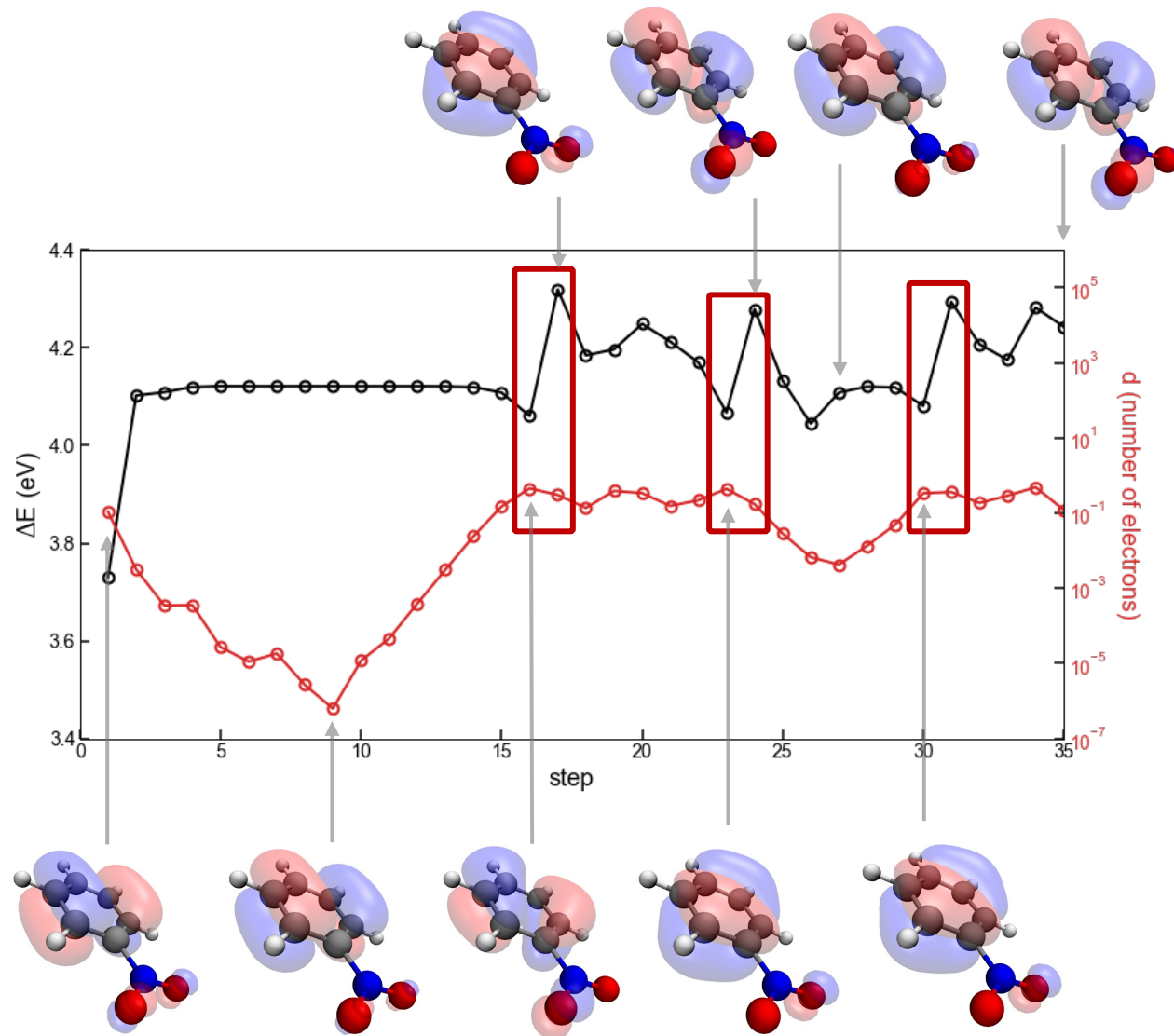


Mewes et al. *Phys. Chem. Chem. Phys.* **16**, 12393 (2014)

Hait & Head-Gordon *J. Chem. Theory Comput.* **16**, 1699 (2020)

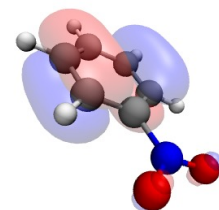
Carter-Fenk & Herbert *J. Chem. Theory Comput.* **16**, 5067 (2020)

MOM does not ensure convergence to a target solution!



Step	Idx π	$\langle \pi_{\text{targ}} \pi \rangle$	Idx π'	$\langle \pi_{\text{targ}} \pi' \rangle$
1	21	0.936	20	0.005
2	18	1.000	19	0.000
5	18	1.000	19	0.001
6	18	1.000	19	0.002
7	18	1.000	19	0.004
8	18	1.000	19	0.002
15	18	0.922	19	0.387
16	18	0.741	19	0.671
17	19	0.841	18	0.540
18	19	0.929	18	0.370
19	19	0.781	18	0.624
20	19	0.814	18	0.580
21	19	0.918	18	0.392
22	19	0.884	18	0.467
23	18	0.749	19	0.662
24	19	0.912	18	0.404
25	19	0.984	18	0.166
26	19	0.991	18	0.054
27	18	0.999	19	0.052
28	18	0.993	19	0.116
29	18	0.975	19	0.221
30	18	0.815	19	0.579
31	19	0.804	18	0.594
32	19	0.903	18	0.429
33	19	0.842	18	0.538
34	19	0.720	18	0.694
35	19	0.936	18	0.343

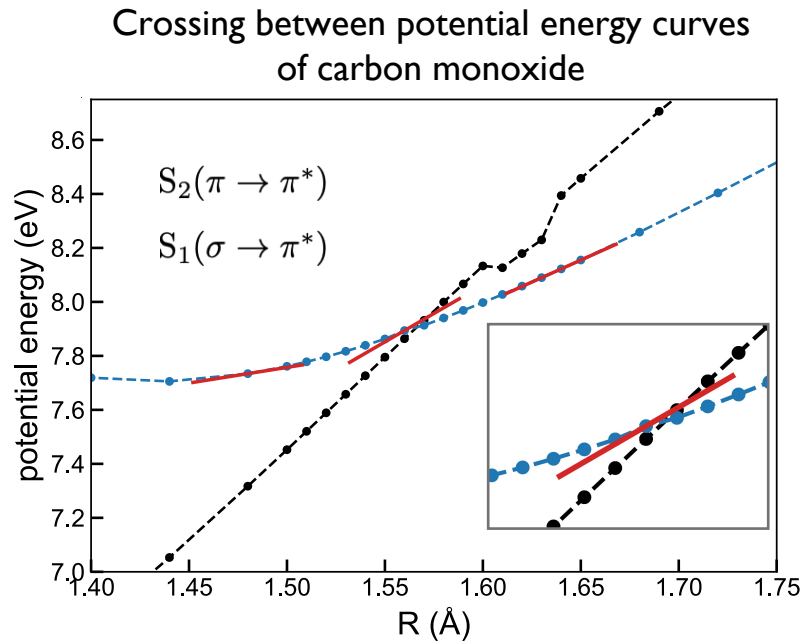
Target π orbital:



Distance from target solution:
$$d^{(k)} = N_e - \sum_{ij} \left| \langle \psi_i^{\text{targ}} | \psi_j^{(k)} \rangle \right|^2$$

Convergence can be improved by changing the density mixing or using a smearing of the occupation numbers

Not optimal...



Gaussian smearing of hole and excited electron

$$f_l(\epsilon_l) = 1 - s_i(\epsilon_l) \quad f_m(\epsilon_m) = s_a(\epsilon_m)$$

$$s_{i|a}(\epsilon_{l|m}) = \frac{1}{A_{i|a}} \exp \left[-\frac{(\epsilon_{l|m} - \epsilon_{i|a})^2}{2\sigma^2} \right]$$

Levi, Ivanov & Jónsson *J. Chem. Theory Comput.* **16**, 6968 (2020)

Direct Orbital Optimization (DO)



Aleksei V. Ivanov

$$\psi'_n(\mathbf{r}) = \sum_n U_{nm} \psi_m(\mathbf{r}) \quad \text{Exponential transformation: } U = e^\theta, \quad \theta = -\theta^\dagger$$

Quasi-Newton unconstrained optimization: $\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} - \mathbf{B}^{(k)} \mathbf{g}^{(k)}$, $\mathbf{B} = \mathbf{H}^{-1}$

Ivanov et al. *Comput. Phys. Commun.* 108047 (2021)

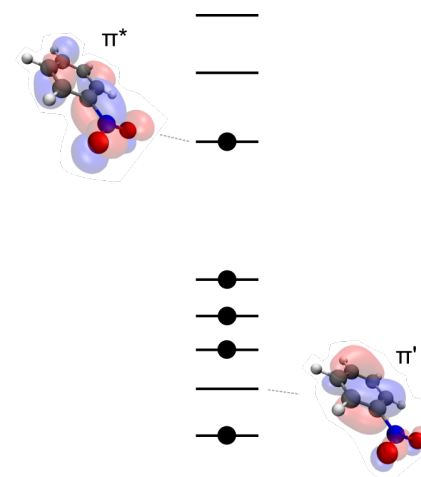
Van Voorhis & Head-Gordon *Mol. Phys.* **100**, 1713 (2002)

Hutter et al. *Chem. Phys.* **101**, 3862 (1994)

Most DO algorithms perform energy minimization (ground state), but **excited states are often saddle points!**

$$H_{ijlm} \equiv \left. \frac{\partial^2 E}{\partial \theta_{ij} \partial \theta_{lm}} \right|_{\theta=0} \approx \left. \frac{\frac{\partial E}{\partial \theta_{ij}}(\theta_{lm} + \varepsilon) - \frac{\partial E}{\partial \theta_{ij}}(\theta_{lm} - \varepsilon)}{2\varepsilon} \right|_{\theta=0}$$

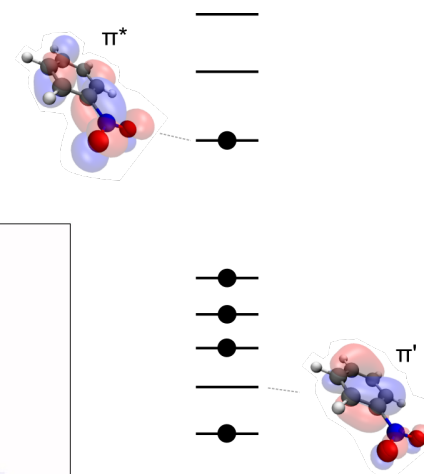
$$\mathbf{LHL}^{-1} = \begin{pmatrix} -6.7 & 0 & 0 & 0 & 0 & \dots & 0 \\ 0 & -3.4 & 0 & 0 & 0 & \dots & 0 \\ 0 & 0 & -2.2 & 0 & 0 & \dots & 0 \\ 0 & 0 & 0 & -0.5 & 0 & \dots & 0 \\ 0 & 0 & 0 & 0 & 0.0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \dots & 60.0 \end{pmatrix} \text{ eV}$$



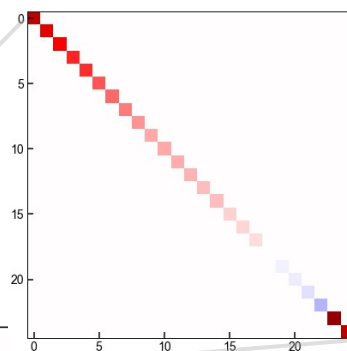
4th order saddle point

- Initial inverse Hessian (or **preconditioner**) that estimates directions of negative curvature

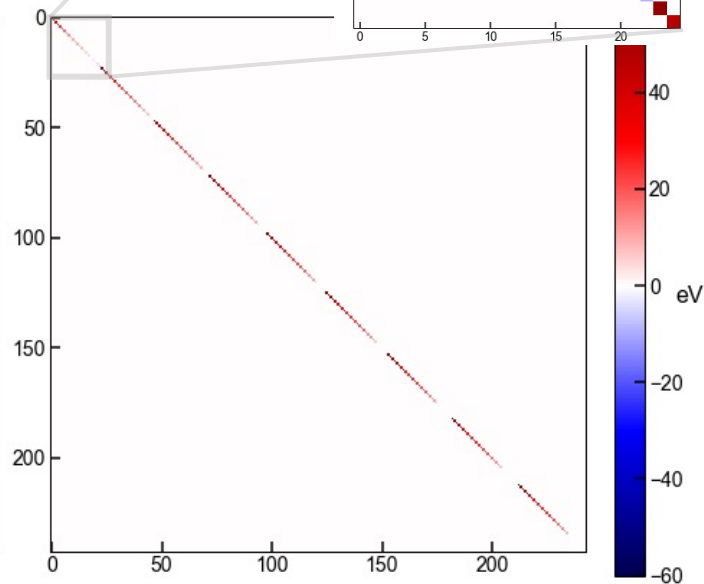
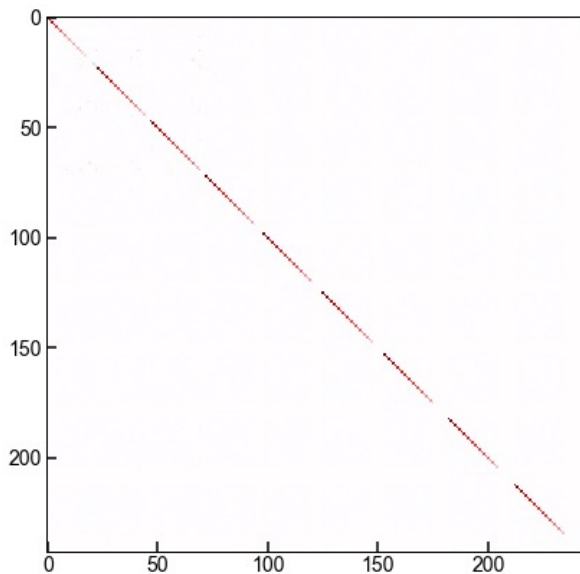
$$B_{ij}^0 = -\frac{1}{2(\epsilon_i - \epsilon_j)(f_i - f_j)}$$



Approximate analytical Hessian



Numerical Hessian



- Initial inverse Hessian (or **preconditioner**) that estimates directions of negative curvature

$$B_{ij}^0 = -\frac{1}{2(\epsilon_i - \epsilon_j)(f_i - f_j)}$$

- **Limited-memory symmetric rank-one (L-SR1)** Hessian update that can develop negative eigenvalues (new)

- **Maximum Overlap Method**

DO-MOM

Implementation in FD/PW: previous talk (Aleksei V. Ivanov)

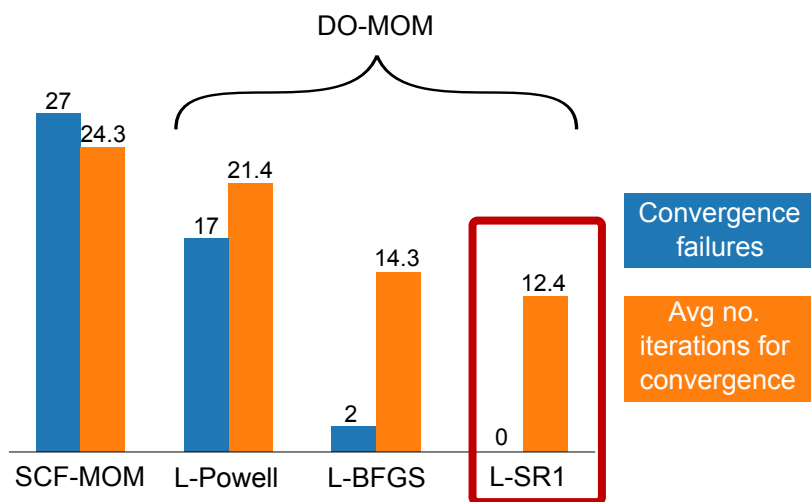
Implementation in LCAO:
$$o_{\mu n} = \sum_{m=1}^M c_{\mu m} [e^{\theta}]_{mn}$$

Only one parameter (max step length): If $\|\Delta \mathbf{x}^{(k)}\| \geq p_{\max}$ set $\Delta \mathbf{x}^{(k)} \leftarrow \frac{p_{\max}}{\|\Delta \mathbf{x}^{(k)}\|} \Delta \mathbf{x}^{(k)}$

p_{\max} of 0.20 usually good compromise between stability and speed

Levi, Ivanov & Jónsson *J. Chem. Theory Comput.* **16**, 6968 (2020)

Levi, Ivanov & Jonsson *Faraday Discuss.* **224**, 448 (2020)



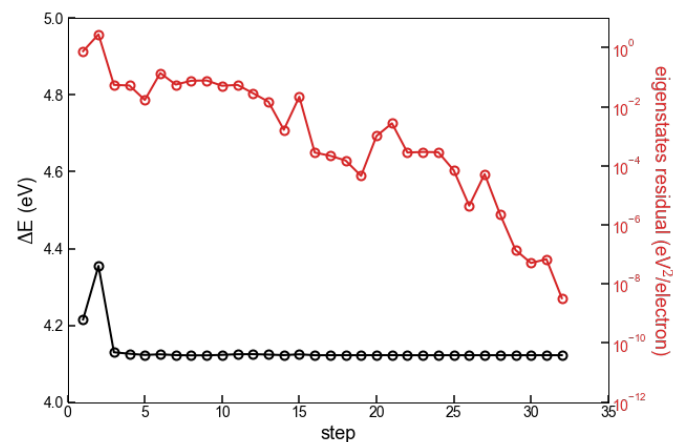
89 excited states

21 small and medium size molecules

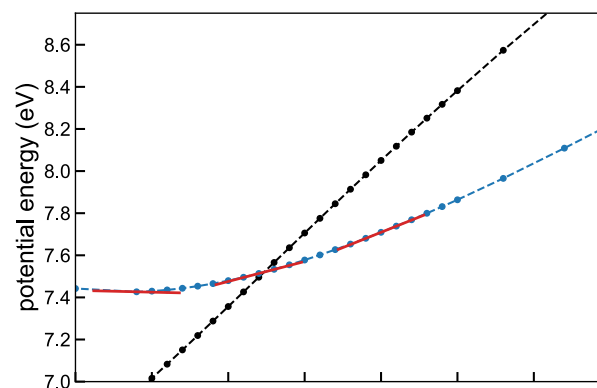
(Loos et al. J. Chem. Theory Comput. **14**, 4360 (2018))

Spin-polarized, PBE, sz+aug-cc-pVDZ

Nitrobenzene $A_1(\pi' \rightarrow \pi^*)$ excitation

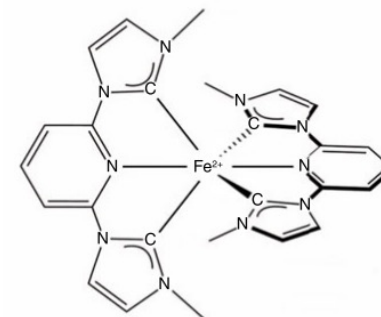


Crossing between potential energy curves of carbon monoxide



Levi, Ivanov & Jónsson J. Chem. Theory Comput. **16**, 6968 (2020)

Potential energy curves of an iron carbene photosensitizer

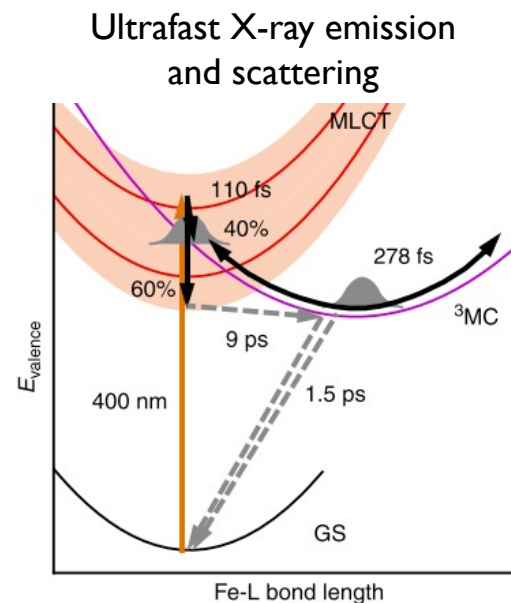
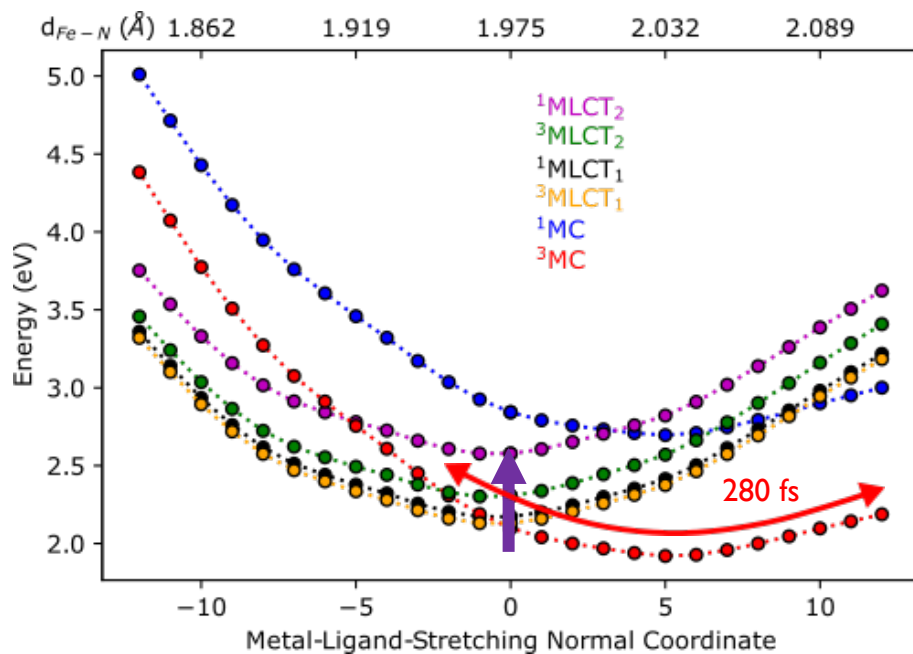


[Fe(bmip)₂]²⁺

	BLYP, FD mode	Exp. (acetonitrile) ^{a,b}
$\Delta E(\text{GS} \rightarrow {}^1\text{MLCT}_2)$ (eV)	2.57	2.71
$T({}^3\text{MC})$ (fs)	280	278

^aY. Liu *et al.*, Chem. Commun. **49**, 6412 2013

^bKunnus *et al.* Nat. Commun. **11**, 634 2020

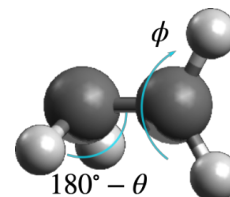


Kunnus *et al.* Nat. Commun. **11**, 634 2020

Ivanov, Levi & Jónsson (2021), [arXiv:2102.06542v1](https://arxiv.org/abs/2102.06542v1)

Geometries from Pápai *et al.* J. Phys. Chem. Lett. **7**, 2009, 2016

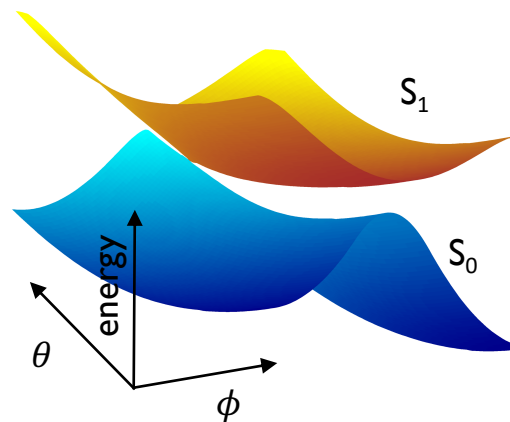
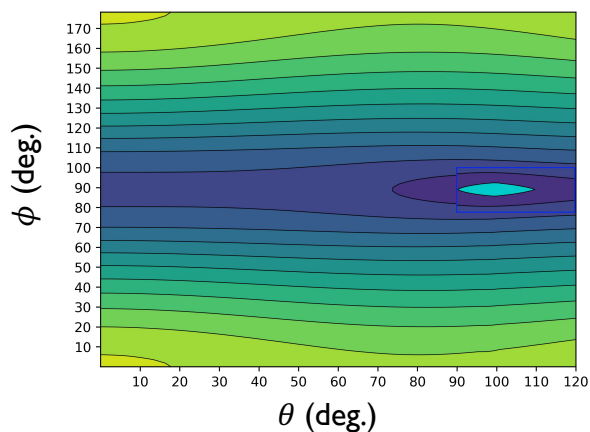
Calculation of a conical intersection in ethylene



ϕ : torsion
 θ : pyramidalization

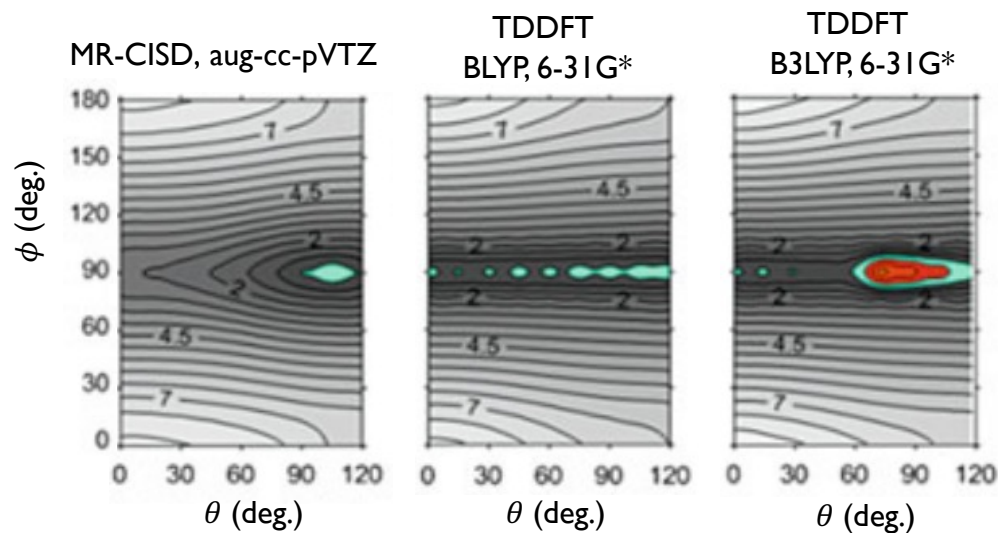
S_1 - S_0 energy gap (eV)

Spin-polarized, PBE, sz+aug-cc-pVDZ



Yorick L. A. Schmerwitz

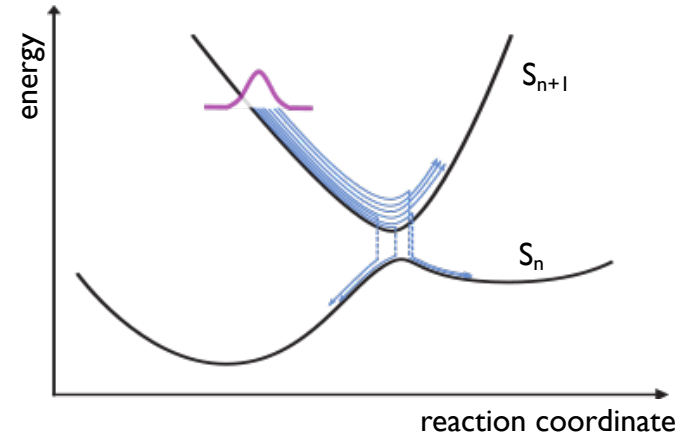
Poster 2



Ongoing...

- Implementation of **Trajectory Surface Hopping** in ASE/GPAW

$$i \frac{\partial}{\partial t} a_i = \sum_j \left(E_j - i \langle \Psi_i | \nabla_{\mathbf{R}} | \Psi_j \rangle \cdot \frac{\partial \mathbf{R}}{\partial t} \right) a_j$$



➤ Propagation of electronic amplitudes \longrightarrow ASE

➤ Calculation of **nonadiabatic couplings** \longrightarrow GPAW

- Scalar couplings (numerically) $\langle \Psi_i | \nabla_{\mathbf{R}} | \Psi_j \rangle \cdot \frac{\partial \mathbf{R}}{\partial t} = \left\langle \Psi_i \left| \frac{\partial}{\partial t} \right| \Psi_j \right\rangle$
- Vectorial couplings (analytically) $\langle \Psi_i | \nabla_{\mathbf{R}} | \Psi_j \rangle$



Yorick L. A. Schmerwitz
Poster 2

- Assessment of direct orbital optimization in nonadiabatic molecular dynamics simulations

Thank you for your attention!