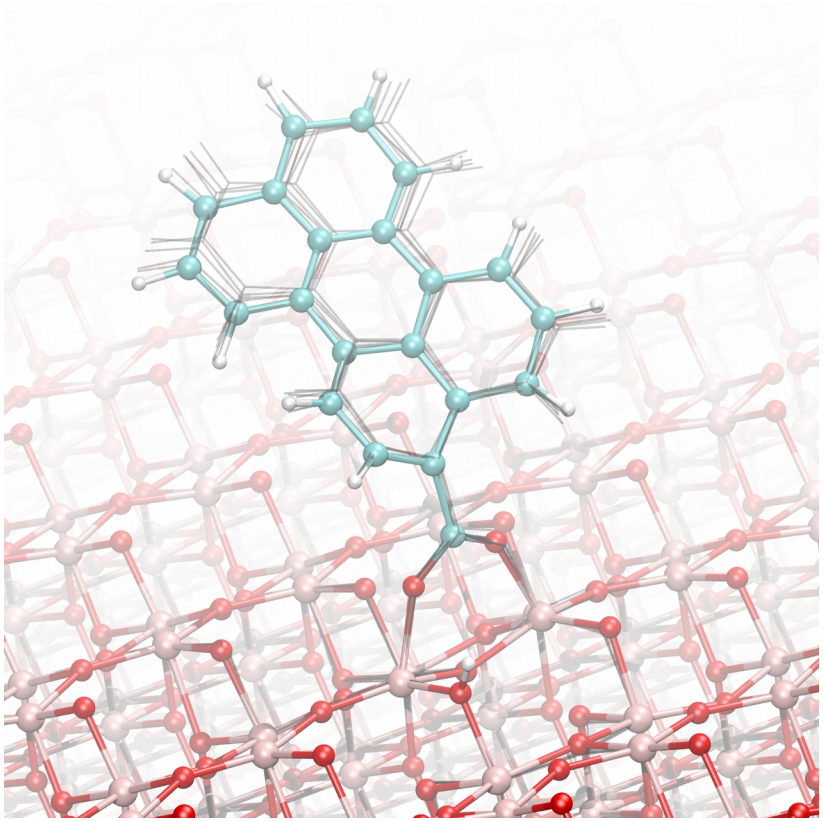
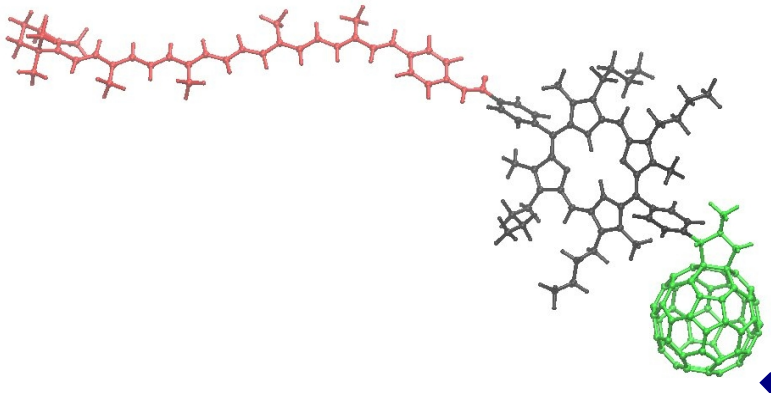
DynEMol Method

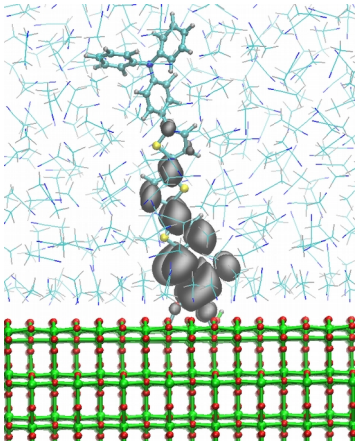
Dynamics of Electrons in Molecules
A Semi-empirical MO method for Large Scale Electronic Quantum Dynamics



DynEMol: tools for studying Dynamics of Electrons in Molecules.
https://sourceforge.net/projects/charge-transfer/

Thermodynamics X Quantum Dynamics Effects



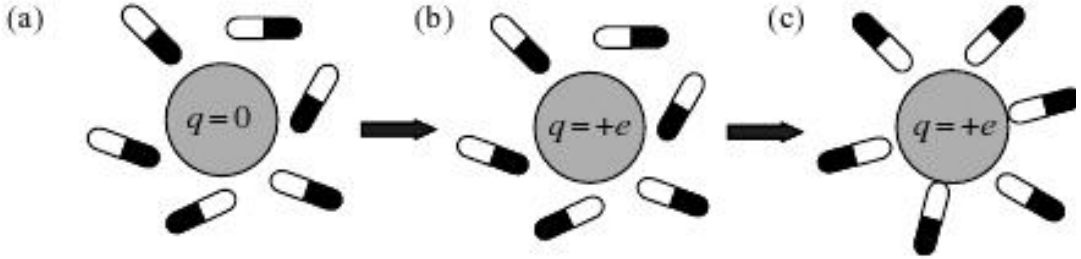


$$i\hbar\dot{\Psi} = \hat{H}\Psi$$

Strong electronic coupling

$$k_{ET} = Z_{ab}\exp\left\{-\frac{\left(\Delta G^0_{ab}+\lambda\right)^2}{4\lambda k_B T}\right\}$$

Marcus Theory
Thermodynamic driving force
Reorganization energy



DynEMol Method

Quantum-Classical separation in the spirit of Ehrenfest Dynamics:

$$i\hbar\frac{\partial}{\partial t}\left|\Psi(r;R,t)\right\rangle = \hat{H}_{el}(R(t))\left|\Psi(r;R,t)\right\rangle \ , \qquad \Psi(r;R,t) = \text{electronic wavepacket}$$

$$\begin{aligned}\dot{R} &= P/M \ , \\ \dot{P} &= -\nabla_R\langle\Psi(r;R,t)|V(r,R)|\Psi(r;R,t)\rangle_r \ ,\end{aligned}$$

$\hat{H}_{el}(R(t))$ is a hamiltonian on the electronic coordinates, which depends parametrically on the time-dependent nuclear positions.

$$\hat{H}_{el}(R(t)) = \hat{H}^{EHT} + \hat{H}^{El/Hl} + \hat{H}^{Pol} + \hat{H}^{Solvent}$$

$$\begin{aligned}\hat{H}^{EHT} &\equiv \text{extended Hückel theory} \\ \hat{H}^{El/Hl} &\equiv \text{electron-hole coupling} \\ \hat{H}^{Pol} &\equiv \text{intramolecular polarization} \\ \hat{H}^{Solvent} &\equiv \text{Solvent}\end{aligned}$$

short range (***SR***: EHT) + long range (***LR***: ElHl, Pol, Solvent) interactions:

$$\hat{H}_{el}(R(t)) = \hat{H}^{SR} + \hat{H}^{LR}$$

DynEMol Method

Extended Hückel theory to ***account for the chemical bonding***:

$$H_{ij}^{EHT}(R(t)) = \tfrac{1}{2} K_{ij} \;\; (h_i + h_j) \;\; S_{ij}(\vec{R}_p(t), \vec{R}_q(t))$$

$\{\mathrm{i}\} = \{\alpha, n\}$ designates the orbital α on the nth atom located at $\vec{R}_q$

Atomic Orbitals: Slater-type orbitals (STO)

$$f_i^{STO}(\vec{r} - \vec{R}(t)) = (\zeta_i)^{n+1/2} \sqrt{\frac{1}{(2n)!}} \; r^{n-1} \;\; \exp\left[-\zeta_i r\right] \;\; Y_{lm}(\theta, \varphi)$$

Overlap Matrix: $\begin{cases} S_{ij} = \delta_{ij} \;\; , & p = q \\ \\ S_{ij}(t) = \int f_i(\vec{r} - \vec{R}_p(t)) \;\; f_j(\vec{r} - \vec{R}_q(t)) \;\; d\vec{r} \;\; , & p \neq q \end{cases}$

$$\begin{aligned} Y_{ml} &= \text{Spherical Harmonics;} \\ K_{ij} &= \text{Wolfsberg-Helmoholz coupling parameter} \\ h_i, h_j &\approx \text{Valence State Ionization Potentials (VSIPs)} \\ \zeta &= \text{constant related to the effective charge of the nucleus} \end{aligned}$$

Sensitive to molecular geometry, short range couplings: cutoff = 10 Å.

DynEMol Method

Diabatic $\longleftrightarrow$ Adiabatic representation of the electronic wavefunctoin $\Psi(r; R, t)$

Diabatic (Atomic Orbital, AO) localized basis:

$$\Psi(t) = \sum_i c_i(t) f_i^{STO}(\vec{r} - \vec{R}(t)) \equiv \sum_i c_i(t) \left| i(t) \right\rangle$$

Adiabatic (Molecular Orbital, MO) delocalized basis:

$$\Psi(t) = \sum_\phi C_\phi(t) \left| \phi(t) \right\rangle$$

with,

$$\hat{H}_{el}(R_t) \left| \phi(R_t) \right\rangle = \varepsilon_\phi(R_t) \left| \phi(R_t) \right\rangle \ .$$

In the STO basis, the time-independent Schrödinger eigenvalue equation is

$$H(R_t) Q_\phi(R_t) = \varepsilon_\phi(R_t) S(R_t) Q_\phi(R_t)$$

with,

$$\left| \phi(t) \right\rangle = \sum_i Q_{i\phi} \left| i(t) \right\rangle$$

Diabatic (AO) $\longleftrightarrow$ Adiabatic (MO) basis transformation:

$$\hat{P}_{i \leftarrow \phi} = \sum_\phi \sum_{ij} \left| i \right\rangle \left(S^{-1} \right)_{ij} \langle i | \phi \rangle \langle \phi | = \sum_{i,\phi} Q_{i\phi} | i \rangle \langle \phi |$$

DynEMol Method

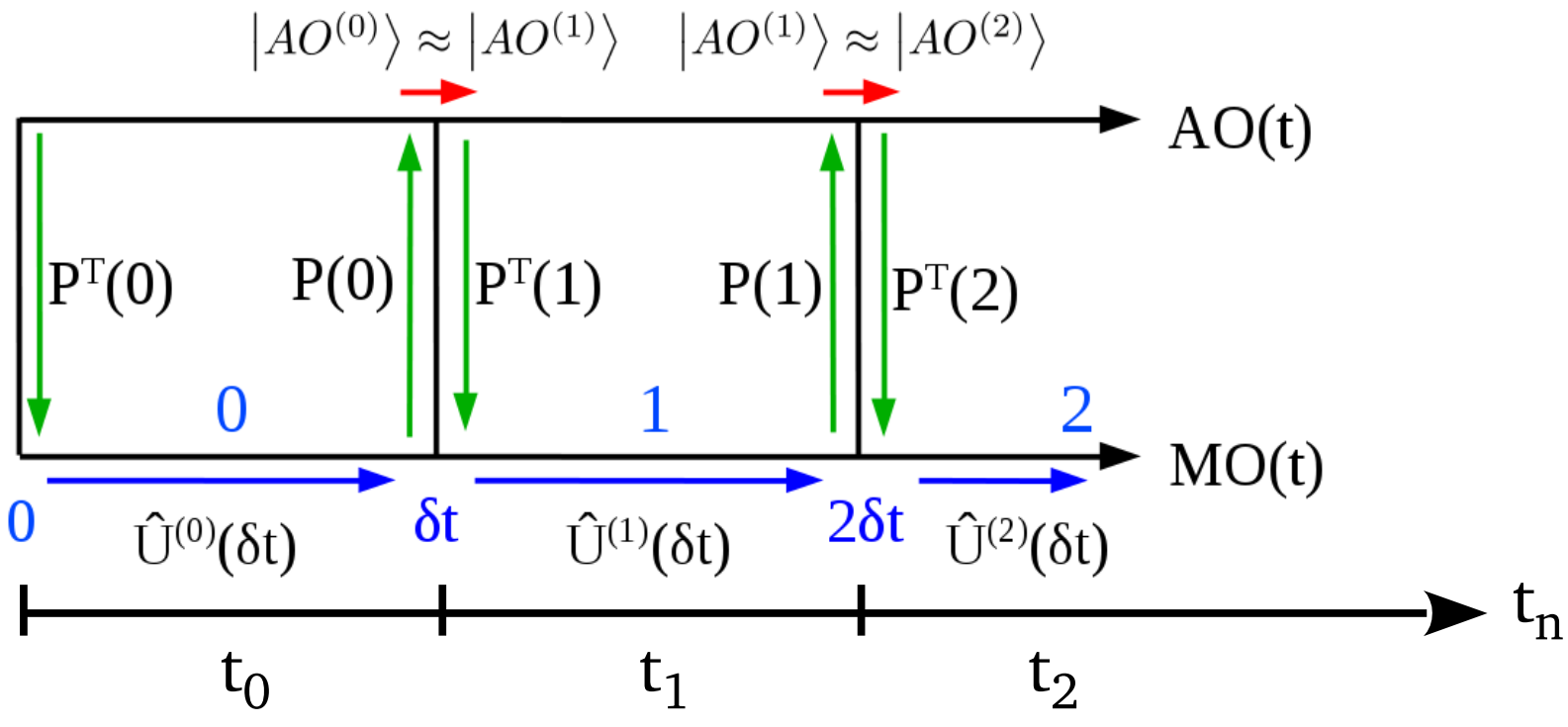
The time-dependent Schrödinger Equation (TDSE) in the Adiabatic (MO) basis set:

$$i\hbar\frac{\partial}{\partial t}\Psi(r;R,t) = \hat{H}_{el}\Psi(r;R,t)\ , \qquad \text{with} \quad |\Psi(t)\rangle = \sum_{\phi} C_{\phi}(t)\,|\phi(t)\rangle$$

Multiplying on the left by $\langle\gamma(t)|$ and integrating over $\mathbf{r}$ yields the electronic TDSE

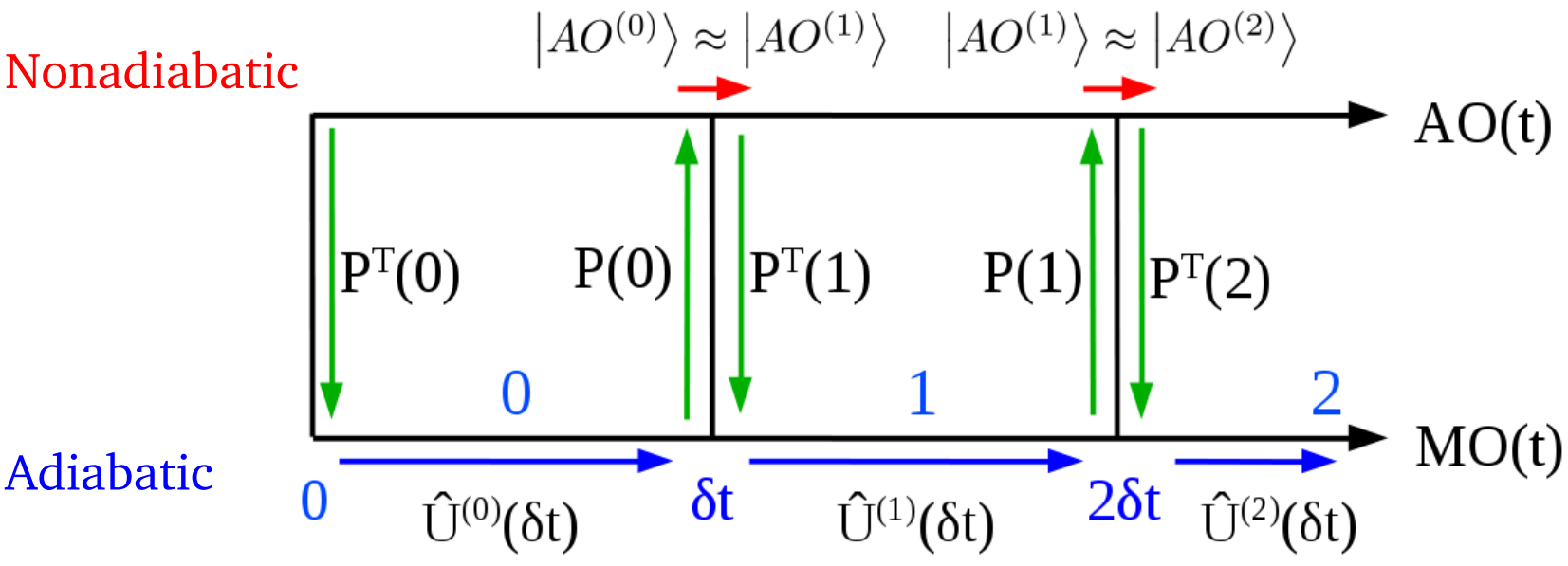
$$\frac{d}{dt}C_{\phi} + \sum_{\gamma} C_{\gamma}\langle\phi|\frac{d}{dt}\gamma\rangle + \frac{i}{\hbar}C_{\phi}E_{\phi} = 0\ .$$

To solve the TDSE numerically, the **time variable is discretized**: $\mathrm{t} \rightarrow t_n$



DynEMol Method

$$\frac{d}{dt}C_\phi + \sum_\gamma C_\gamma \langle\phi|\frac{d}{dt}\gamma\rangle + \frac{i}{\hbar}C_\phi E_\phi = 0\ .$$



The overall time propagator can be written as

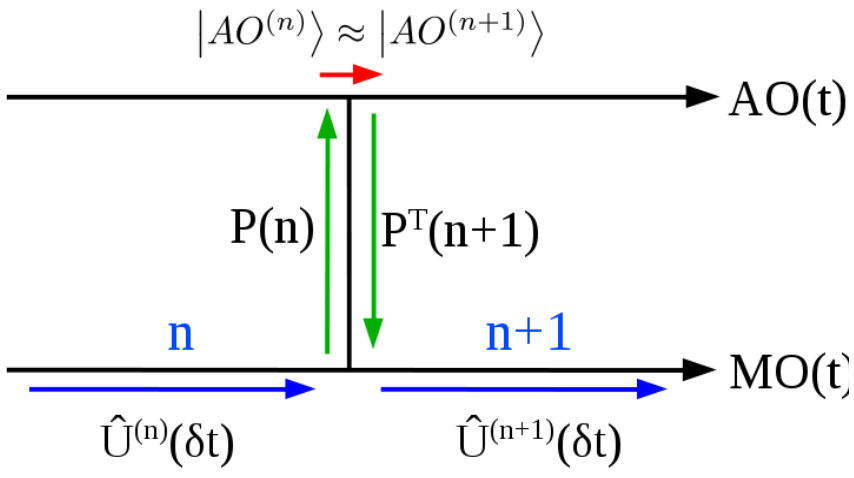
$$|\Psi(t+\delta t)\rangle = \hat{U}_{NA}(\delta t)\hat{U}_{AD}(\delta t)|\Psi(t)\rangle$$

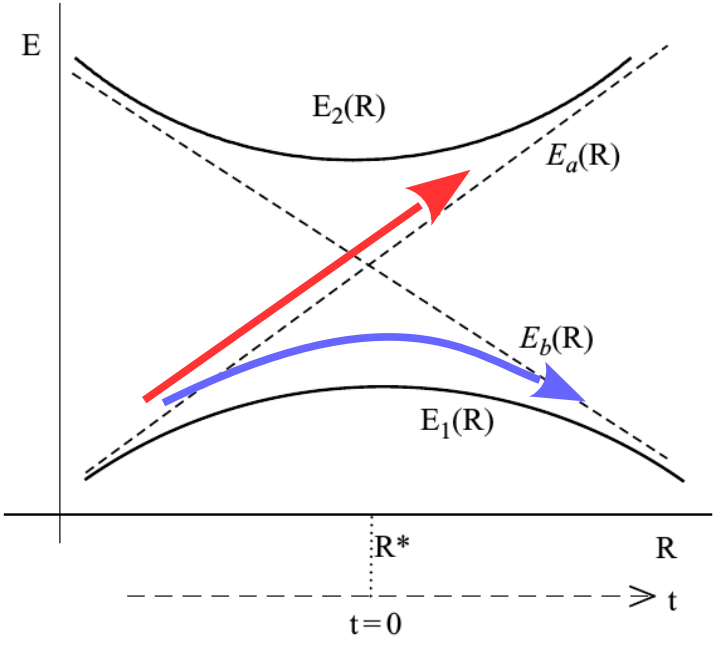
where $\hat{U}_{NA} = \left[\hat{P}^{(n+1)}\right]^T \left(\sum_{ij} |j^{(n+1)}\rangle (S^{-1})_{ji} \langle i^{(n)}|\right) \hat{P}^{(n)} \approx \left[\hat{P}^{(n+1)}\right]^T \hat{P}^{(n)}$

$$\hat{U}_{AD} = \exp\left[-\frac{i}{\hbar}\hat{H}_n \delta t\right], \qquad \text{with} \quad \hat{H}_{el}(t_n)\,|\phi(t_n)\rangle = \varepsilon_\phi(t_n)\,|\phi(t_n)\rangle$$

DynEMol Method

The nonadiabatic passage



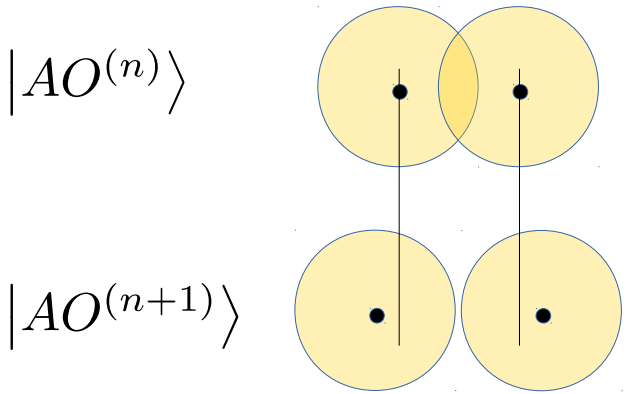


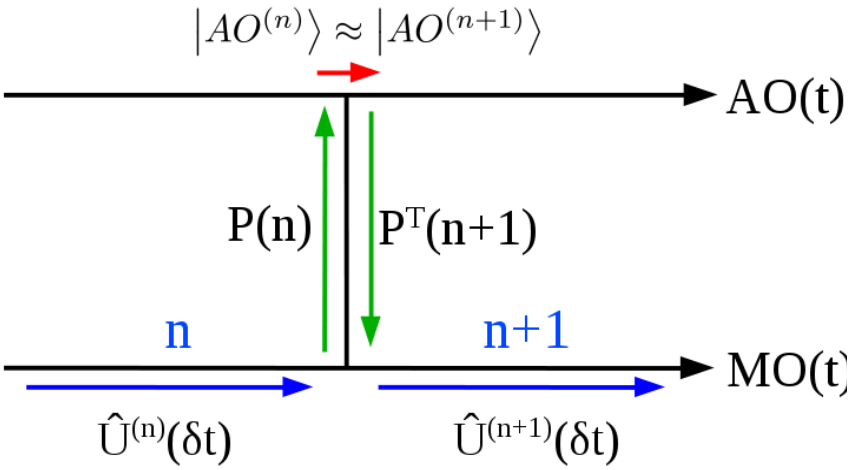
$$|\Psi(t+2\delta t)\rangle = \hat{U}_{AD}^{(n+1)}(\delta t)\ \hat{U}_{NA}(\delta t)\ \hat{U}_{AD}^{(n)}(\delta t)\ |\Psi(t)\rangle$$

$$= \exp\left[-\frac{i}{\hbar}\hat{H}_{n+1}\delta t\right]\ \left[\hat{P}^{(n+1)}\right]^T\ \hat{P}^{(n)}\ \exp\left[-\frac{i}{\hbar}\hat{H}_n\delta t\right]\ |\Psi(t)\rangle$$

DynEMol Method

The **quasi-static** approx. in the Diabatic basis: $\left|AO^{(n)}\right\rangle \approx \left|AO^{(n+1)}\right\rangle$





$$
\begin{aligned}
|i^{(n+1)}\rangle &\approx |i^{(n)}\rangle + \frac{d\vec{R}}{dt}\cdot\nabla_R|i^{(n)}\rangle\delta t \\
&\approx |i^{(n)}\rangle + (\vec{v}\delta t)\cdot\nabla_R|i^{(n)}\rangle
\end{aligned}
$$

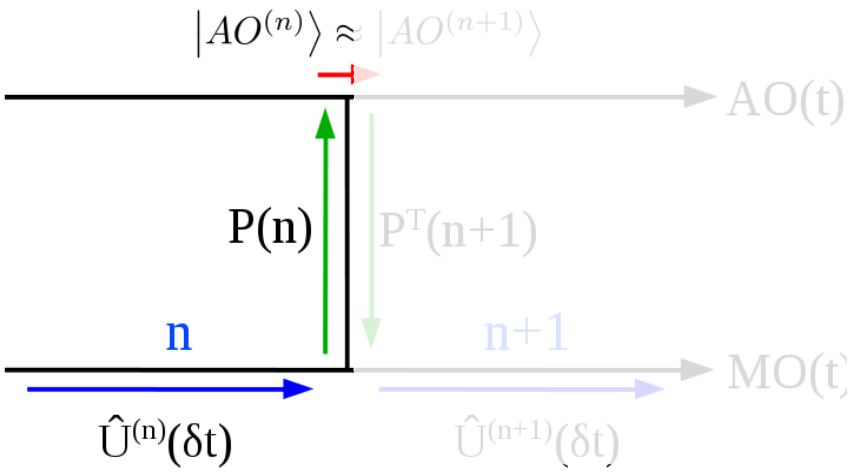
Consider a spherical STO, $f_i^{(n)}(\vec{r}-\vec{R}) = Ne^{-\zeta|\vec{r}-\vec{R}|}$

$$
|i^{(n+1)}\rangle \approx |i^{(n)}\rangle + \left(\vec{l}\cdot\zeta\frac{(\vec{r}-\vec{R})}{|\vec{r}-\vec{R}|}\right)|i^{(n)}\rangle = (1+l\zeta)\,|i^{(n)}\rangle\ ,
$$

$\vec{l} = \vec{v}\delta t$ is the nuclei displacement in the time-slice $\delta t \approx 0.05\ fs \implies l \ll 1$ Å

$\zeta \approx 1\ \text{Å}^{-1} \implies l\zeta \ll 1 \implies |i^{(n+1)}\rangle \approx |i^{(n)}\rangle$

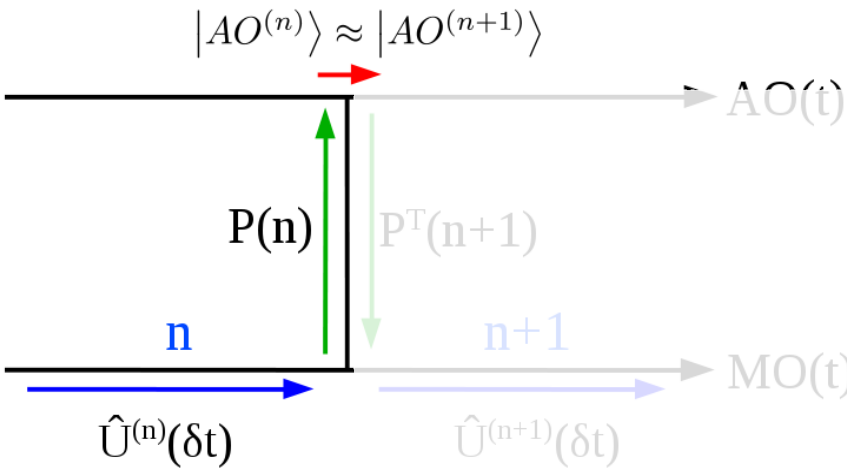
DynEMol Method: step-by-step



$$
\begin{aligned}
|\Psi(t+\delta t)\rangle &= \exp\left[-\frac{i}{\hbar}\hat{H}_n \delta t\right]|\Psi(0)\rangle \\
&= \sum_{\phi} C_{\phi}(\delta t)|\phi^{(n)}\rangle \\
&= \sum_{\phi} C_{\phi}(\delta t)\hat{P}^{(n)}|\phi^{(n)}\rangle \\
&= \sum_{i}\left(\sum_{\gamma} Q_{i\gamma}^{(n)} C_{\gamma}^{(n)}\right)|i^{(n)}\rangle = \sum_{i} A_i^{(n)}|i^{(n)}\rangle
\end{aligned}
$$

$$
\text{with,} \quad A_i^{(n)} = \left(\sum_{\gamma} Q_{i\gamma}^{(n)} C_{\gamma}^{(n)}\right)
$$

DynEMol Method: step-by-step



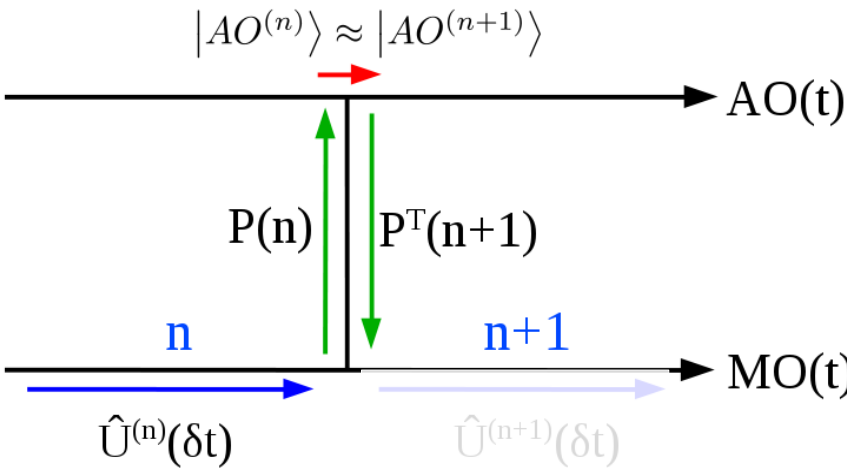
$$
\begin{aligned}
|\Psi(t+\delta t)\rangle &= \exp\left[-\frac{i}{\hbar}\hat{H}_n \delta t\right]|\Psi(0)\rangle \\
&= \sum_{\phi} C_{\phi}(\delta t)|\phi^{(n)}\rangle \\
&= \sum_{\phi} C_{\phi}(\delta t)\hat{P}^{(n)}|\phi^{(n)}\rangle \\
&= \sum_{i}\left(\sum_{\gamma} Q_{i\gamma}^{(n)} C_{\gamma}^{(n)}\right)|i^{(n)}\rangle = \sum_{i} A_i^{(n)}|i^{(n)}\rangle
\end{aligned}
$$

with, $A_i^{(n)} = \left(\sum_{\gamma} Q_{i\gamma}^{(n)} C_{\gamma}^{(n)}\right)$

The **quasi-static** approx. in the Diabatic basis:

$$|\Psi(t+\delta t)\rangle = \sum_i A_i|i^{(n)}\rangle = \sum_i A_i|i^{(n+1)}\rangle$$

DynEMol Method: step-by-step



with, $A_i^{(n)} = \left(\sum_\gamma Q_{i\gamma}^{(n)} C_\gamma^{(n)} \right)$

$$
\begin{aligned}
|\Psi(t+\delta t)\rangle &= \sum_i A_i^{(n)} \left[\hat{P}^{(n+1)}\right]^T |i^{(n+1)}\rangle \\
&= \sum_i A_i^{(n)} \sum_{j\phi} |\phi^{(n+1)}\rangle Q_{\phi j}^{(n+1)} \langle j^{(n+1)}|i^{(n+1)}\rangle \\
&= \sum_{i,j,\phi} A_i^{(n)} Q_{\phi j}^{(n+1)} S_{ji} |\phi^{(n+1)}\rangle \\
&= \sum_{\phi,\gamma} \left\{ \sum_{i,j} Q_{\phi j}^{(n+1)} S_{ji} Q_{i\gamma}^{(n)} \right\} C_\gamma^{(n)} |\phi^{(n+1)}\rangle \qquad \Omega_{\phi\gamma} \equiv \sum_{i,j} Q_{\phi j}^{(n+1)} S_{ji} Q_{i\gamma}^{(n)} \\
&= \sum_\phi \left\{ \sum_\gamma \Omega_{\phi\gamma} C_\gamma^{(n)} \right\} |\phi^{(n+1)}\rangle = \sum_\phi C_\phi^{(n+1)} |\phi^{(n+1)}\rangle
\end{aligned}
$$

where $C_\phi^{(n+1)} = \sum_\gamma \Omega_{\phi\gamma} C_\gamma^{(n)}$ and $\Omega_{\phi\gamma} = \langle \phi^{(n+1)} | \gamma^{(n)} \rangle$

DynEMol Method

The nonadiabatic scattering operator $\Omega_{\phi\gamma}$:

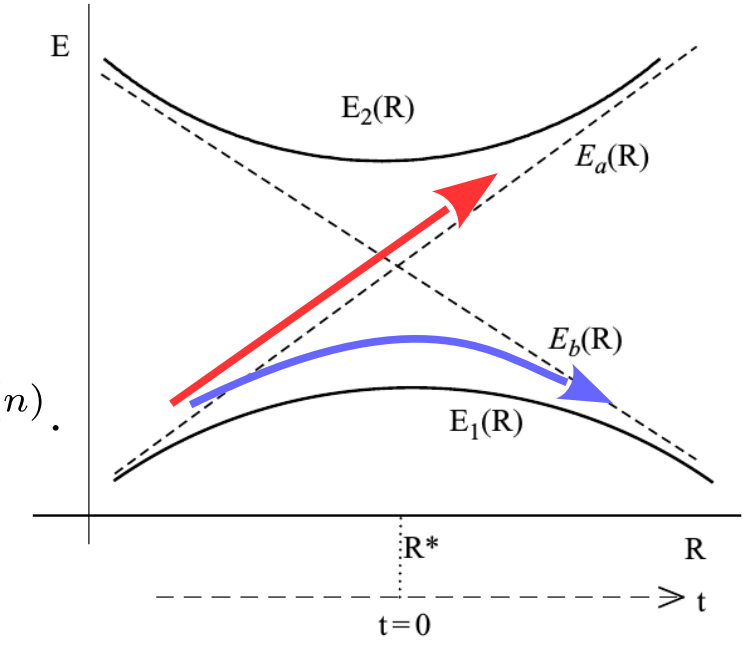
$$\Omega_{\phi\gamma} = \sum_{i,j} Q_{\phi j}^{(n+1)} S_{ji} Q_{i\gamma}^{(n)} = \langle \phi^{(n+1)} | \gamma^{(n)} \rangle$$

so that $C_\phi^{(n+1)} = \sum_\gamma \Omega_{\phi\gamma} C_\gamma^{(n)}$.

If the nuclei were fixed or barely moving ($\dot{R} \to 0$),

then $Q^{(n+1)} = Q^{(n)}$ and $\Omega_{\phi\gamma} = \delta_{\phi\gamma}$,

with the adiabatic coefficients $H_n Q^{(n)} = \varepsilon^{(n)} S^{(n)} Q^{(n)}$.



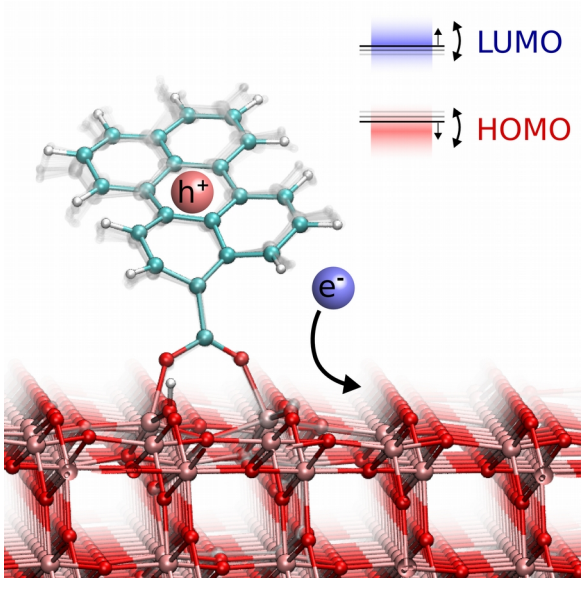
As the velocity of the nuclei increase, nonadiabatic transitions become possible:

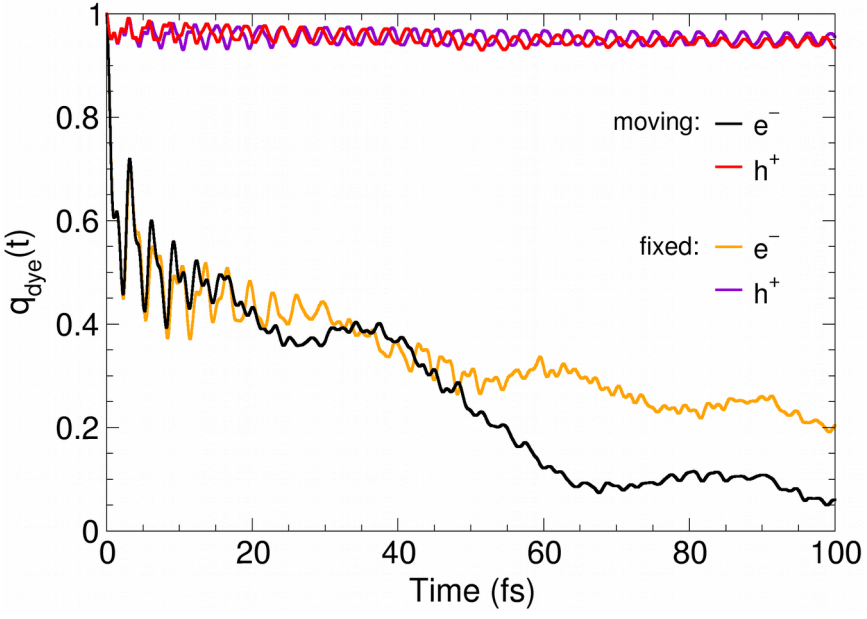
$$\langle \phi^{(n+1)} | \gamma^{(n)} \rangle \approx \delta_{\phi\gamma} + \sum_\varphi \langle \dot{\varphi}^{\ (n)} | \gamma^{(n)} \rangle \delta t$$

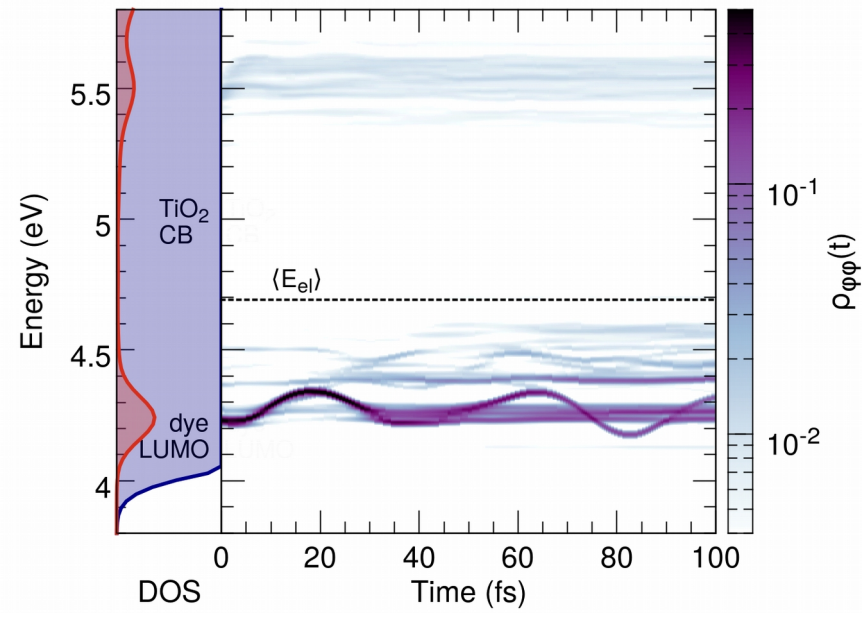
Thus we solve the ***TDSE for the electronic wavepacket***

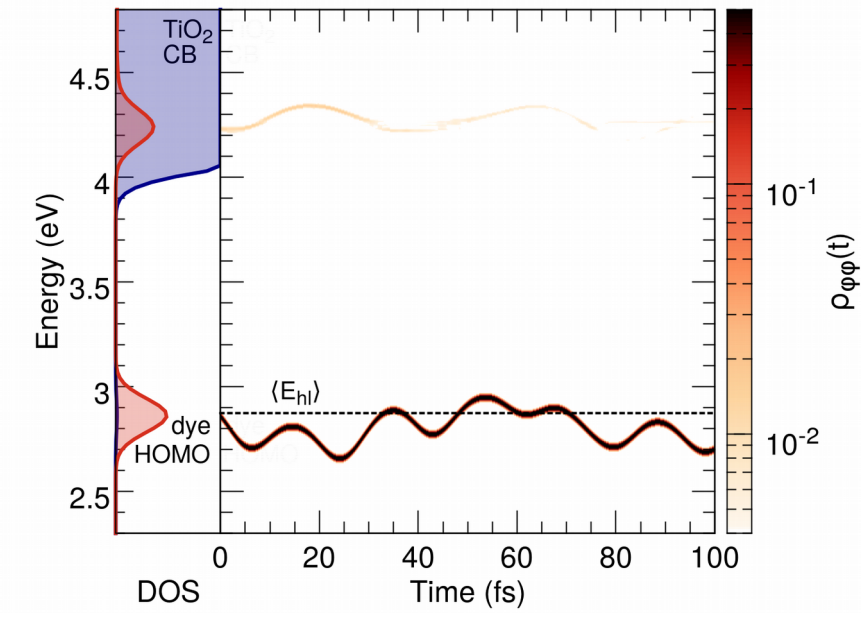
$$\frac{d}{dt} C_\phi + \sum_\gamma C_\gamma \langle \phi | \frac{d}{dt} \gamma \rangle + \frac{i}{\hbar} C_\phi E_\phi = 0 \ .$$

DynEMol Method: charge transfer









DynEMol Method: electron-nuclei coupling

Quantum-Classical separation in the spirit of Ehrenfest Dynamics:

$$i\hbar\frac{\partial}{\partial t}\left|\Psi(r;R,t)\right\rangle = \hat{H}_{el}(R(t))\left|\Psi(r;R,t)\right\rangle$$

$$\Downarrow$$

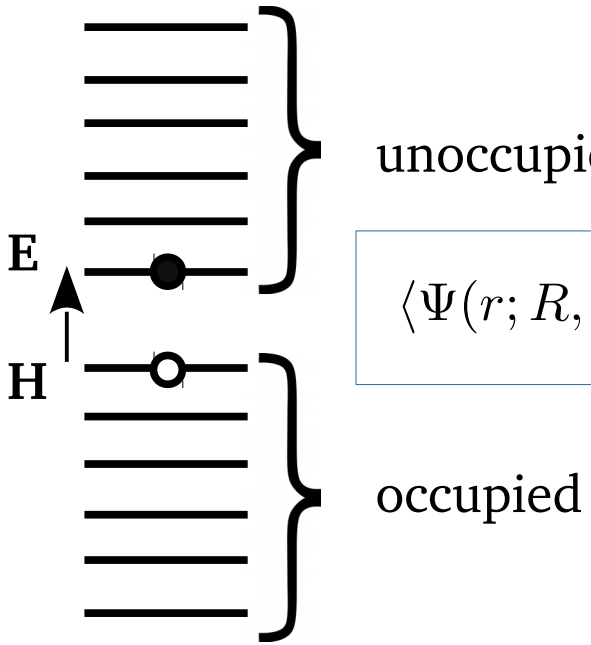
$$\frac{d}{dt}C_\phi + \sum_\gamma C_\gamma \langle\phi|\frac{d}{dt}\gamma\rangle + \frac{i}{\hbar}C_\phi E_\phi = 0$$

For the classical dynamics equations for the nuclei:

$$\begin{aligned}\dot{R} &= P/M\ , \\ \dot{P} &= -\nabla_R\langle\Psi(r;R,t)|V(r,R)|\Psi(r;R,t)\rangle_r\ ,\end{aligned}$$

DynEMol Method: electron-nuclei coupling

$$M\ddot{R} = -\nabla_R \langle \Psi(r;R,t)|V(r,R)|\Psi(r;R,t)\rangle_r$$



$$\langle \Psi(r;R,t)|V(r,R)|\Psi(r;R,t)\rangle_r \approx V_{GS}^{MM} + V_{EH}\left[\Psi^{el}(t), \Psi^{hl}(t)\right]$$

$$V_{GS}^{MM} = \sum_{bonds} K_b(R-R_o)^2 + \sum_{angles} K_\theta(\theta-\theta_o)^2 + \sum_{torsions}\sum_{n=0}^{5} C_n(cos\phi)^n$$

$$+ \sum_{i,j\neq i} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{R_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{R_{ij}}\right)^{6}\right] + \sum_{i,j\neq i}\frac{q_j q_i}{4\pi\epsilon_o R_{ij}}$$

with the GS-FF parameters: $K, R_0, K_\theta, \theta_0, C_n, \varepsilon_{ij}, \sigma_{ij}, q$

DynEMol Method: electron-nuclei coupling

$$\langle \Psi(r;R,t)|V(r,R)|\Psi(r;R,t)\rangle_r \approx V_{GS}^{MM} + V_{EH}\left[\Psi^{el}(t),\Psi^{hl}(t)\right]$$

$V_{EH}\left[\Psi^{el}(t),\Psi^{hl}(t)\right]$ is a functional of the excited electron-hole wavefunction:

$$V_{EH}\left[\Psi^{el}(t),\Psi^{hl}(t)\right] = Tr\left[\rho^{EH}\mathbf{H}\right] = \sum_{\varphi} E_{\varphi}\rho_{\varphi\varphi}^{EH} \ ,$$

where we define the electron-hole density matrix as $\boxed{\rho_{\phi\varphi}^{EH} = \rho_{\phi\varphi}^{el} - \rho_{\phi\varphi}^{hl}}$

with,

$$|\Psi^{el}\rangle\langle\Psi^{el}| = \sum_{\varphi\phi} B_{\varphi}B_{\phi}^{*}|\varphi\rangle\langle\phi| = \rho_{\phi\varphi}^{el}|\varphi\rangle\langle\phi|$$

$$|\Psi^{hl}\rangle\langle\Psi^{hl}| = \sum_{\varphi\phi} A_{\varphi}A_{\phi}^{*}|\varphi\rangle\langle\phi| = \rho_{\phi\varphi}^{hl}|\varphi\rangle\langle\phi|$$

The Hellmann-Feynman-Pulay force for the **extended Hückel hamiltonian**:

$$\mathbf{F}_N = -\nabla_N V_{EH}\left[\Psi^{el}(R,t),\Psi^{hl}(R,t)\right]$$

DynEMol Method

Deriving the nonadiabatic forces for the **extended Hückel hamiltonian**:

$$\mathbf{F}_n = -\nabla_N V_{EH}\left[\Psi^{el}(R,t), \Psi^{hl}(R,t)\right]$$

with the electron and hole wavepackets given by $|\Psi(t)\rangle = \sum_\phi C_\phi(t)\,|\phi(t)\rangle$

The time-dependent Schrödinger equation (TDSE) in the adiabatic basis is

$$\dot{C}_\phi + \sum_\varphi C_\varphi \langle\phi|\dot{\varphi}\rangle = \frac{-i}{\hbar} E_\phi C_\phi$$

In this case $E = \langle\Psi|\hat{H}(\{R\})|\Psi\rangle$ is no longer the variational energy. Therefore

$$\frac{dE}{dR_N} = \sum_\phi |C_\phi|^2 \frac{dE_\phi}{dR_N} + \sum_\phi E_\phi \left(\frac{dC_\phi^*}{dR_N} C_\phi + C_\phi^* \frac{dC_\phi}{dR_N}\right)$$

The first term on the **r.h.s.** is the **adiabatic** component of the force whereas the second term yields the **nonadiabatic** component of the force.

DynEMol Method

The **adiabatic** component of the force is calculated as follows:

For the time-independent Schrödinger equation, $\sum_j H_{ij} Q_j^\phi = \sum_j E_\phi S_{ij} Q_j^\phi$,

$$\frac{dE_\phi}{dR_N} = \frac{\partial E_\phi}{\partial R_N} = \frac{\partial}{\partial R_N} \langle \phi | \hat{H} | \phi \rangle = \frac{\partial}{\partial R_N} \sum_{i,j} Q_i^\phi \langle i | \hat{H} | j \rangle Q_j^\phi$$

The matrix elements of the extended Hückel hamiltonian are given by $H_{ij} = \xi_{ij} S_{ij}$ with $\xi_{ij} \equiv K_{ij}(h_i + h_j)/2$. They are independent of the coordinates $\mathbf{R}_N$.

Thus, making use of $\nabla_N \langle \phi | \phi \rangle = 0$ and $\sum_\beta H_{\alpha\beta} Q_\beta^\phi = \sum_\beta E_\phi S_{\alpha\beta} Q_\beta^\phi$, we get

$$\frac{\partial E_\phi}{\partial R_N} = \sum_{i,j} \frac{\partial}{\partial R_N} \left(Q_i^\phi \xi_{ij} S_{ij} Q_j^\phi \right) = \sum_{i,j} (\xi_{ij} - E^\phi) Q_i^\phi \left(\frac{\partial S_{ij}}{\partial R_N} \right) Q_j^\phi$$

The **adiabatic** component of the force acting on each atom is therefore

$$\sum_\phi |C_\phi|^2 \frac{dE_\phi}{dR_N} = \sum_\phi |C_\phi|^2 \frac{\partial \langle \phi | \hat{H} | \phi \rangle}{\partial R_N} = \sum_\phi |C_\phi|^2 \sum_{ij} (\xi_{ij} - E_\phi) Q_i^\phi \frac{\partial S_{ij}}{\partial R_N} Q_j^\phi$$

DynEMol Method

For the **nonadiabatic** component of the force we make use of the TDSE

$$\dot{C}_\phi + \sum_\varphi C_\varphi \langle \phi | \dot{\varphi} \rangle = \frac{-i}{\hbar} E_\phi C_\phi$$

to get

$$\sum_N \dot{\mathbf{R}}_n \cdot \sum_\phi E_\phi \nabla_N \left| C_\phi \right|^2 = - \sum_n \dot{\mathbf{R}}_N \cdot \sum_{\phi,\varphi}^{\phi \neq \varphi} C_\phi^* C_\varphi \left(E_\phi - E_\varphi \right) \mathbf{d}_{\phi\varphi}^N$$

and therefore

$$\sum_\phi E_\phi \left(\frac{dC_\phi^*}{dR_N} C_\phi + C_\phi^* \frac{dC_\phi}{dR_N} \right) = - \sum_{\phi,\varphi}^{\phi \neq \varphi} C_\phi^* C_\varphi \left(E_\phi - E_\varphi \right) \mathbf{d}_{\varphi\phi}^N$$

where $\mathbf{d}_{\varphi\phi}^N = \langle \phi | \nabla_{R_n} \varphi \rangle$ is the nonadiabatic coupling term. But we can also write

$$\mathbf{d}_{\varphi\phi}^N = \frac{\langle \phi | \nabla_N \hat{H} | \varphi \rangle}{E_\phi - E_\varphi} = \frac{\sum_{\alpha\beta} Q_\alpha^\phi Q_\beta^\varphi \langle \alpha | \nabla_N \hat{H} | \beta \rangle}{E_\phi - E_\varphi} \ ,$$

$$\sum_\phi E_\phi \left(\frac{dC_\phi^*}{dR_N} C_\phi + C_\phi^* \frac{dC_\phi}{dR_N} \right) = \sum_{\phi,\varphi}^{\phi \neq \varphi} C_\phi^* C_\varphi \langle \phi | \nabla_N \hat{H} | \varphi \rangle$$

with $\langle \alpha | \nabla_N \hat{H} | \beta \rangle = \nabla_N H_{\alpha\beta} - \langle \nabla_N \alpha | \hat{H} | \beta \rangle - \langle \alpha | \hat{H} | \nabla_N \beta \rangle$.

DynEMol Method

The Extended Hückel Hamiltonian ***operator*** is written as

$$\hat{H} = \sum_{ij} |i\rangle \sum_{kl} S_{ik}^{-1} H_{kl} S_{lj}^{-1} \langle j|$$

so that $\langle \alpha|\hat{H}|\beta\rangle = H_{\alpha\beta} = \xi_{\alpha\beta} S_{\alpha\beta}$. Therefore

$$\begin{aligned}
\sum_{\alpha\beta} Q_\alpha^\phi Q_\beta^\varphi \langle \alpha|\nabla_N \hat{H}|\beta\rangle &= \sum_{\alpha\beta} Q_\alpha^\phi Q_\beta^\varphi \nabla_N H_{\alpha\beta} \\
&- \sum_{\alpha\beta} Q_\alpha^\phi Q_\beta^\varphi \sum_{ia} \left\{ S_{ia}^{-1} H_{a\beta} \langle i|\nabla_N \alpha\rangle + H_{\alpha a} S_{ai}^{-1} \langle i|\nabla_N \beta\rangle \right\}
\end{aligned}$$

The generalized eigenvalue equation can be used to simplify the terms above

$$\begin{aligned}
\mathbf{H}\mathbf{Q}_\varphi &= E_\varphi \mathbf{S}\mathbf{Q}_\varphi \\
\mathbf{S}^{-1}\mathbf{H}\mathbf{Q}_\varphi &= E_\varphi \mathbf{Q}_\varphi \\
\sum_{a\beta} S_{ia}^{-1} H_{a\beta} Q_\beta^\varphi &= E_\varphi Q_i^\varphi
\end{aligned}$$

so that

$$\sum_{\alpha\beta} Q_\alpha^\phi Q_\beta^\varphi \langle \alpha|\nabla_N \hat{H}|\beta\rangle = \sum_{n\in N} \sum_{\forall\alpha} \left\{ Q_n^\phi Q_\alpha^\varphi \left(\xi_{n\alpha} - E_\varphi\right) + Q_\alpha^\phi Q_n^\varphi \left(\xi_{\alpha n} - E_\phi\right) \right\} \langle \alpha|\nabla_N f_n\rangle$$

DynEMol Method

The nonadiabatic component of the force can now be written in the analytical form

$$\sum_{\phi} E_{\phi} \nabla_{R_N} |C_{\phi}|^2 = \sum_{\varphi > \phi} 2\mathcal{R}\left(C_{\phi}^* C_{\varphi}\right) \times \sum_{n \in N} \sum_{\forall \alpha} \left\{ Q_n^{\phi} Q_{\alpha}^{\varphi} \left(\xi_{n\alpha} - E_{\varphi}\right) + Q_{\alpha}^{\phi} Q_n^{\varphi} \left(\xi_{\alpha n} - E_{\phi}\right) \right\} \langle \alpha | \nabla_N f_n \rangle \ .$$

Using the notation:

$\{\alpha\} \equiv \{a, A\}$: $f_{\alpha} \equiv f_a(\mathbf{r} - \mathbf{R}_A)$, for the atomic orbital a centered at atom A

$\{\nu\} \equiv \{n, N\}$: $f_{\nu} \equiv f_n(\mathbf{r} - \mathbf{R}_N)$, for the atomic orbital n centered at atom N

The total (AD + NA) on atom N, as due to $\Psi(r, R, t)$, is

$$\mathbf{F}_N = -2 \sum_{n \in N} \sum_{\forall \alpha} \langle f_a(\mathbf{r} - \mathbf{R}_A) | \nabla_N f_n(\mathbf{r} - \mathbf{R}_N) \rangle \left\{ \sum_{\phi} |C_{\phi}|^2 \left(\xi_{n\alpha} - E_{\phi}\right) Q_{\alpha}^{\phi} Q_n^{\phi} + \sum_{\varphi > \phi} \mathcal{R}\left(C_{\phi}^* C_{\varphi}\right) \left[Q_n^{\phi} Q_{\alpha}^{\varphi} \left(\xi_{n\alpha} - E_{\varphi}\right) + Q_{\alpha}^{\phi} Q_n^{\varphi} \left(\xi_{\alpha n} - E_{\phi}\right) \right] \right\} \ .$$

DynEMol Method

For the electron-hole excitation energy

$$V_{EH}\left[\Psi^{el}(t),\Psi^{hl}(t)\right] = Tr\left[\rho^{EH}\mathbf{H}\right] = \sum_{\varphi} E_{\varphi}\rho^{EH}_{\varphi\varphi} \ ,$$

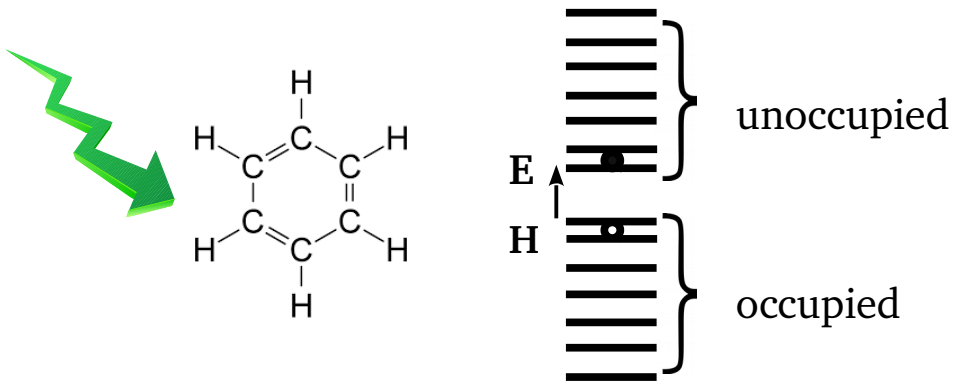
with the electron-hole density matrix as $\rho^{EH}_{\phi\varphi} = \rho^{el}_{\phi\varphi} - \rho^{hl}_{\phi\varphi}$

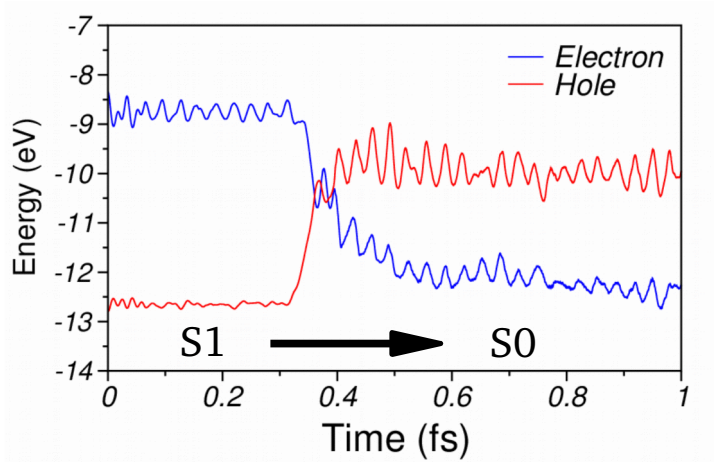
we write the complete Hellmann-Feynman-Pulay nonadiabtic force on atom N for the extended Hückel thoery (EHT) as

$$\begin{aligned}\mathbf{F}^{EH}_{N} &= -2\sum_{n\in N}\sum_{\forall\alpha}\langle f_a(\mathbf{r}-\mathbf{R}_A)|\nabla_N f_n(\mathbf{r}-\mathbf{R}_N)\rangle\left\{\sum_{\phi}\rho^{EH}_{\phi\phi}\left(\xi_{n\alpha}-E_{\phi}\right)Q^{\phi}_{\alpha}Q^{\phi}_{n}\right.\\ &+ \left.\sum_{\varphi>\phi}\mathcal{R}\left(\rho^{EH}_{\phi\varphi}\right)\left[Q^{\phi}_{n}Q^{\varphi}_{\alpha}\left(\xi_{n\alpha}-E_{\varphi}\right)+Q^{\phi}_{\alpha}Q^{\varphi}_{n}\left(\xi_{\alpha n}-E_{\phi}\right)\right]\right\} \ .\end{aligned}$$

DynEMol Method: Benzene NA relaxation dynamics

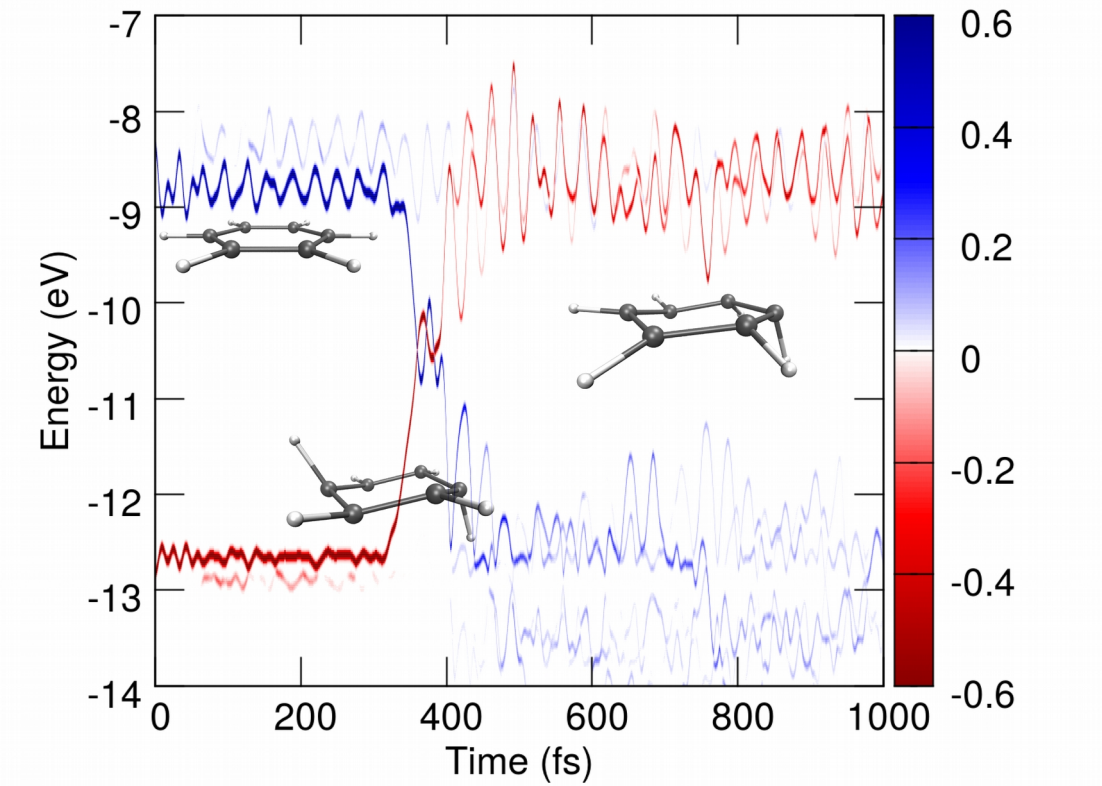
photoexcitation from the ground state planar minimum

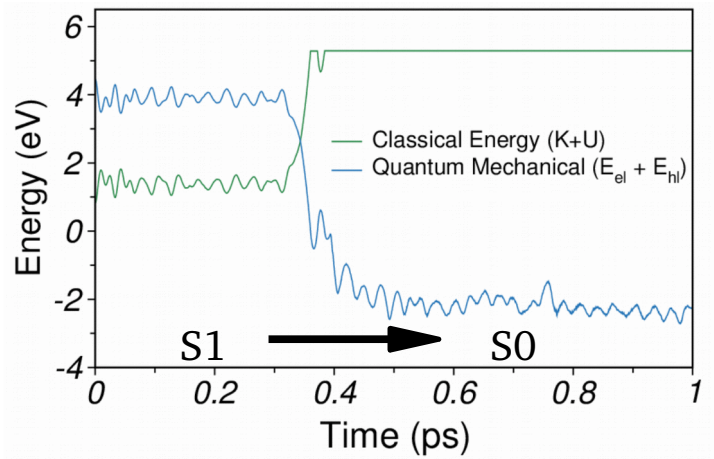


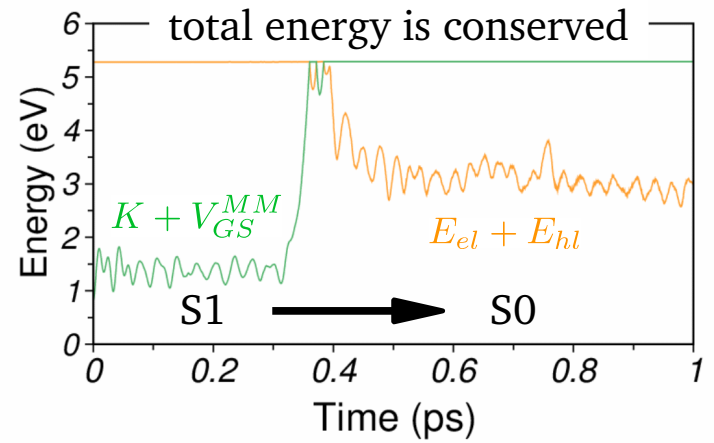


Electron-Hole density: $\rho^{EH}_{\varphi\varphi} = \rho^{el}_{\varphi\varphi} - \rho^{hl}_{\varphi\varphi}$

Molecular Orbital Occupations





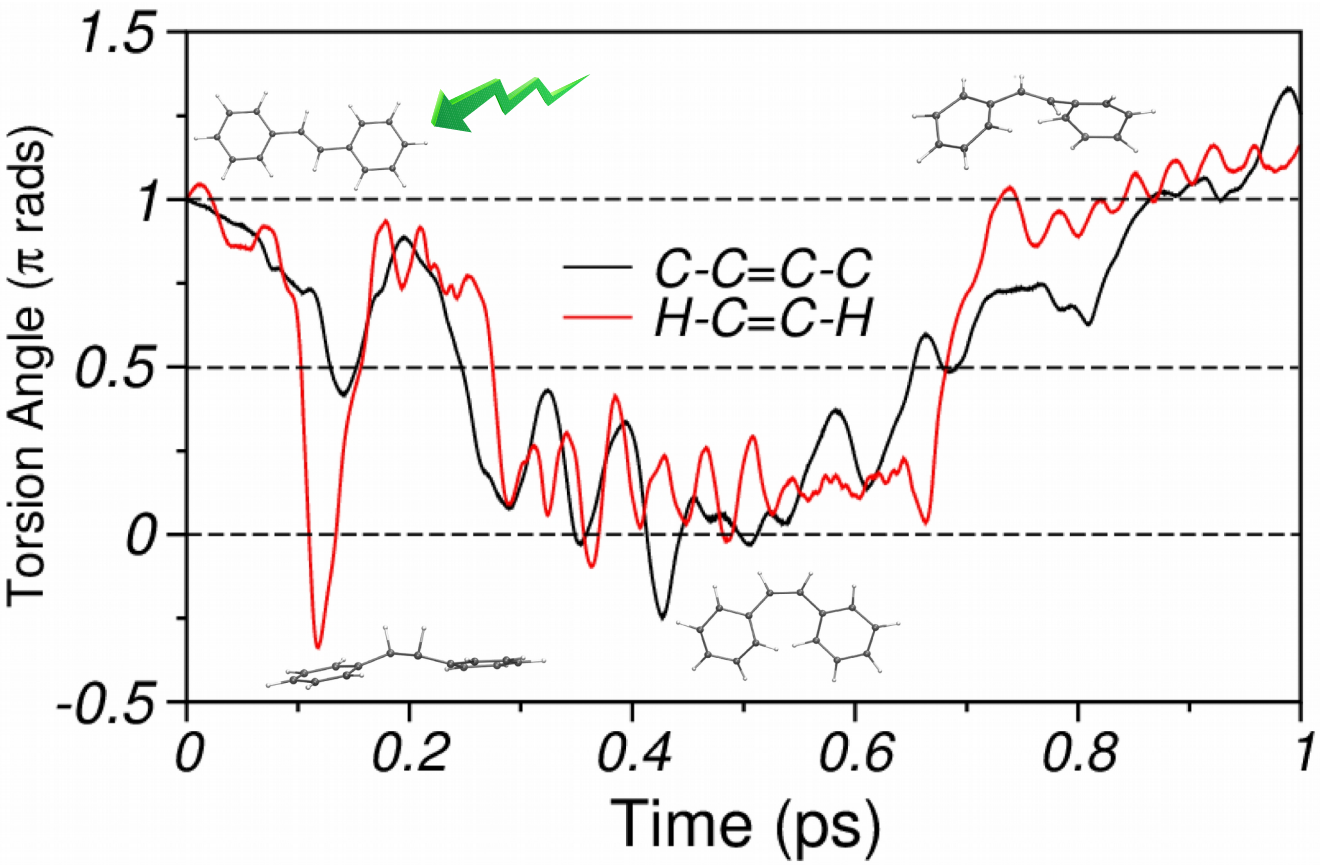


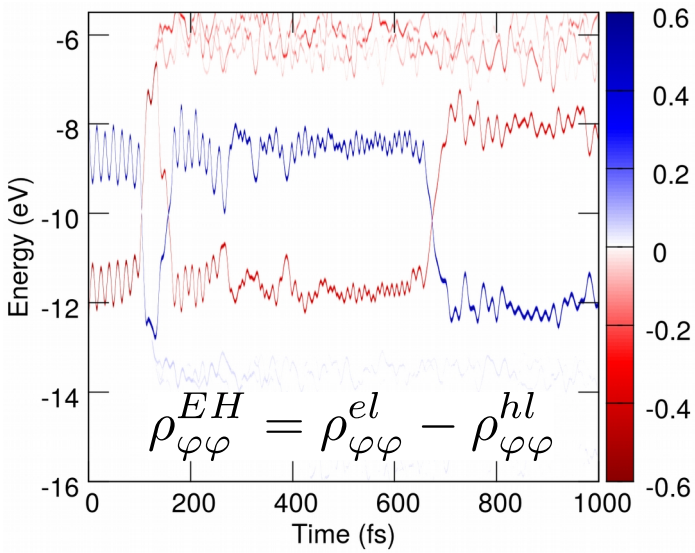
DynEMol Method: photoisomerization of *Stilbene*

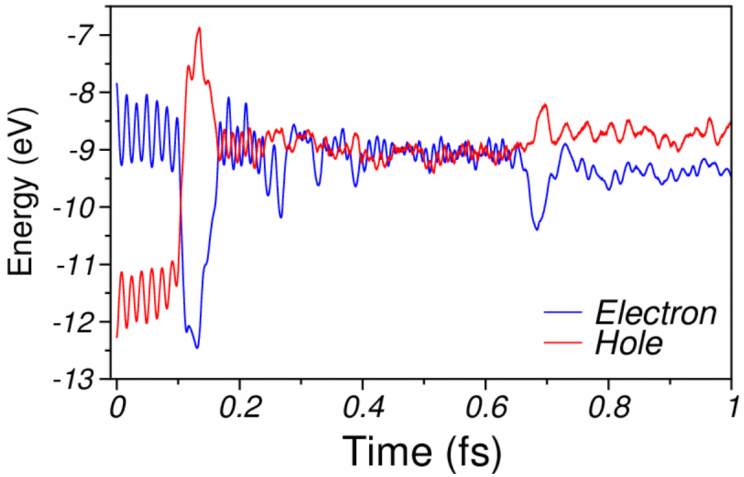
Concerted TRANS-CIS isomerization:

the trans→cis torsion of the *HC=CH* dihedral drives

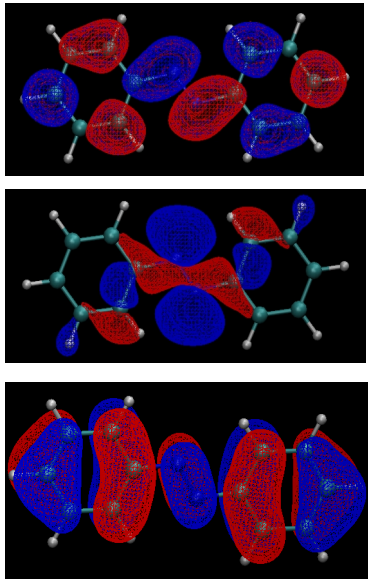
the *C-C=C-C* isomerization of the molecule







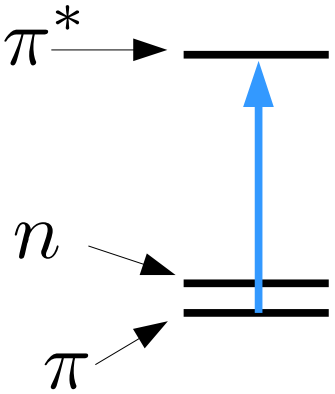
DynEMol Method: photoisomerization of *Azobenzene*

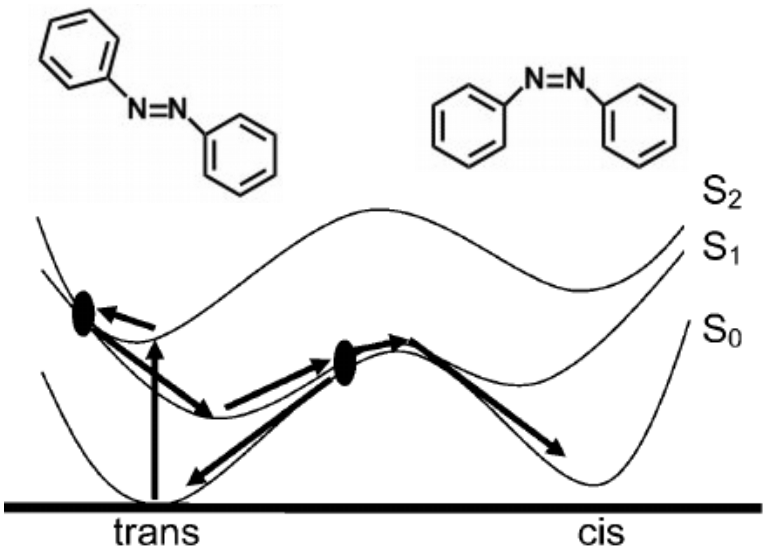


LUMO

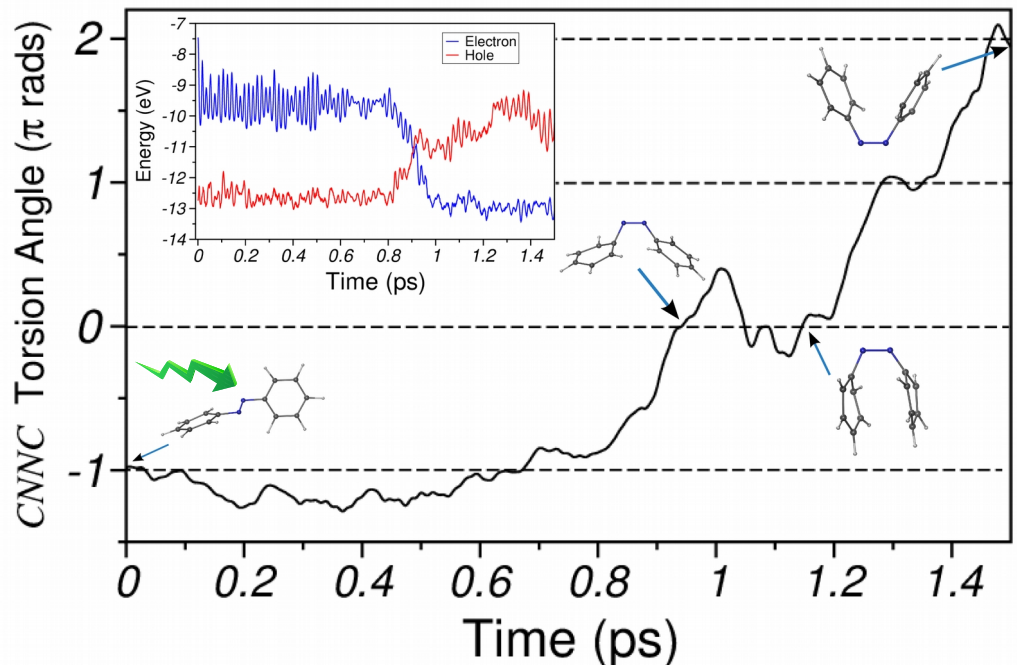
HOMO

HOMO-1

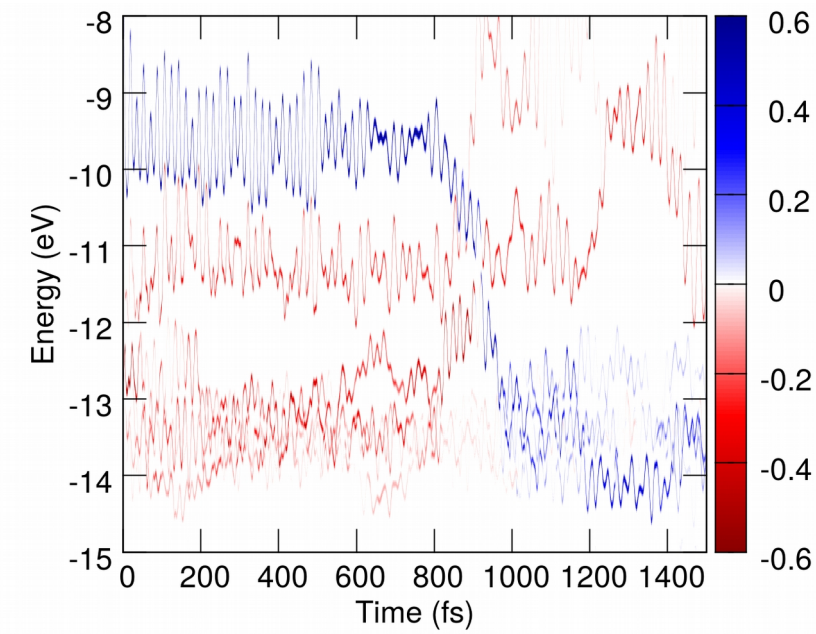




$\pi - \pi^* : \text{cis} \longrightarrow \text{trans}$

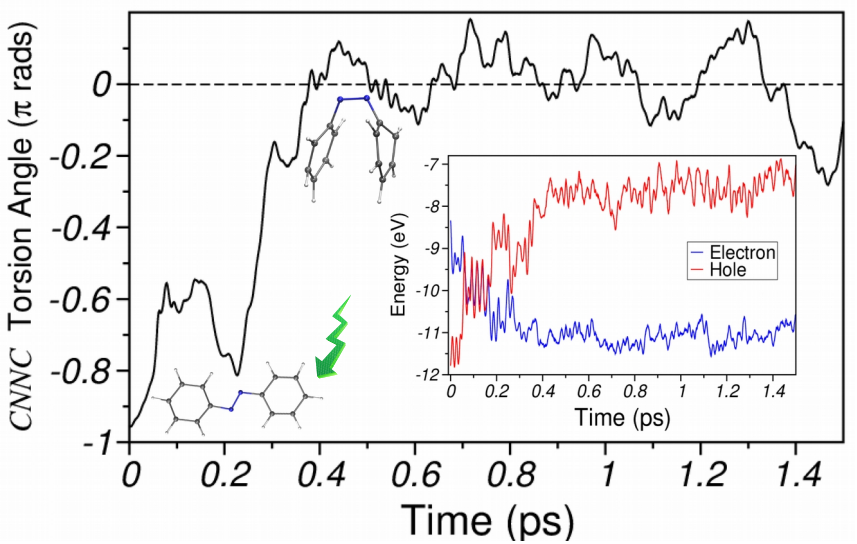


$$\rho^{EH}_{\varphi\varphi} = \rho^{el}_{\varphi\varphi} - \rho^{hl}_{\varphi\varphi}$$

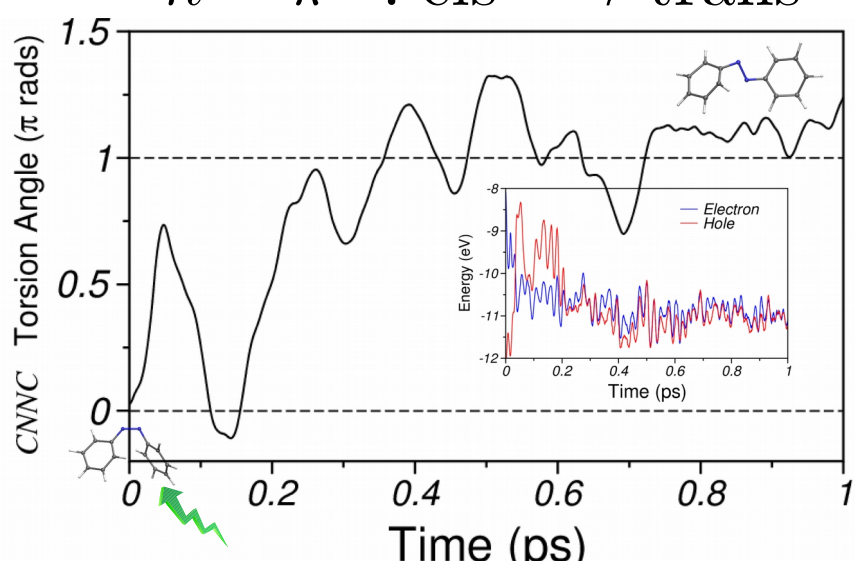


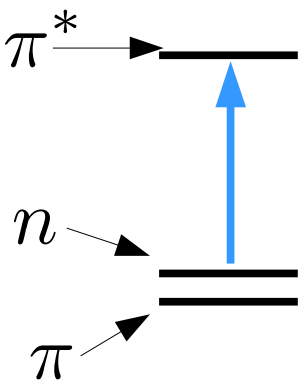
DynEMol Method: photoisomerization of *Azobenzene*

$n - \pi^* : \text{trans} \longrightarrow \text{cis}$

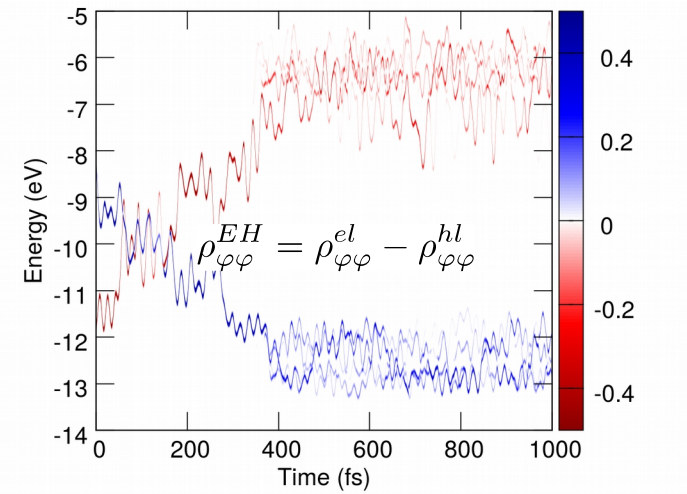


$n - \pi^* : \text{cis} \longrightarrow \text{trans}$

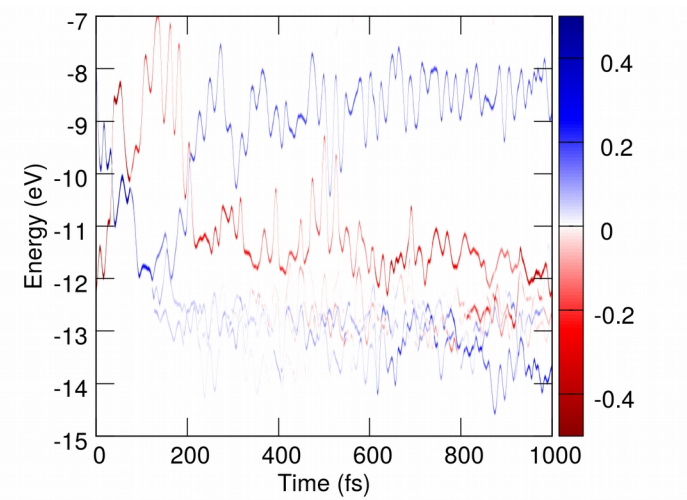




$\rho^{EH}_{\varphi\varphi} = \rho^{el}_{\varphi\varphi} - \rho^{hl}_{\varphi\varphi}$



$\rho^{EH}_{\varphi\varphi} = \rho^{el}_{\varphi\varphi} - \rho^{hl}_{\varphi\varphi}$



DynEMol Method:

Time-Dependent Self-Consistent Mean Field

Let us consider the ***direct electron-hole coupling.***
The hamiltonian of the ***e-h system*** is given by

$$\hat{H} = \hat{H}^{EHT}(\hat{r}_1) + \hat{H}^{EHT}(\hat{r}_2) + \hat{V}_{12}(\hat{r}_1, \hat{r}_2)$$

$$\begin{aligned} \hat{H}^{EHT} &\equiv \text{extended Hückel theory} \\ \hat{V}_{12} &\equiv e^2/|\vec{r}_1 - \vec{r}_2| \end{aligned}$$

Our ansatz is: $\Psi(r_1, r_2, t) = \phi_1(r_1, t)\chi_2(r_2, t)\ \exp\left[\frac{i}{\hbar}\alpha(t)\right]$

where $\alpha(t) = \int_0^t \varepsilon(t')dt'$ is an arbitrary phase factor

and $\varepsilon(t')$ is a function of time with dimensions of energy.

The total wavefunction satisfies the TDSE:

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

DynEMol Method:

Time-Dependent Self-Consistent Mean Field

Solving for the wavepacket ϕ_1 we get

$$i\hbar|\dot{\phi}_1\rangle = \left[\left\langle \hat{H}_2 \right\rangle_2 + \varepsilon - i\hbar\langle\chi_2|\dot{\chi}_2\rangle\right]|\phi_1\rangle + \left[\hat{H}_1 + \left\langle \hat{V}_{12} \right\rangle_2\right]|\phi_1\rangle \tag{1}$$

Solving for the wavepacket χ_2 we get

$$i\hbar|\dot{\chi}_2\rangle = \left[\left\langle \hat{H}_1 \right\rangle_1 + \varepsilon - i\hbar\langle\phi_1|\dot{\phi}_1\rangle\right]|\chi_2\rangle + \left[\hat{H}_2 + \left\langle \hat{V}_{12} \right\rangle_1\right]|\chi_2\rangle \tag{2}$$

Either of the above equations yield the contraint equation

$$\mathrm{i}\hbar\langle\phi_1|\dot{\phi}_1\rangle + i\hbar\langle\chi_2|\dot{\chi}_2\rangle - \varepsilon = E = \text{ constant}$$

where E is the total energy

$$E = \left\langle \hat{H}_1 \right\rangle_1 + \left\langle \hat{H}_2 \right\rangle_2 + \left\langle\left\langle \hat{V}_{12} \right\rangle\right\rangle$$

The gauge parameters $\langle\phi_1|\dot{\phi}_1\rangle$, $\langle\chi_2|\dot{\chi}_2\rangle$ and ε can be specified arbitrarily.

We chose them so that equations (1) and (2) are symmetric.

DynEMol Method:

Time-Dependent Self-Consistent Mean Field

Defining: $\quad i\hbar\langle\phi_1|\dot{\phi}_1\rangle = \left\langle \hat{H}_1 \right\rangle_1 + \varepsilon \ ,$

yields for equation (2)

$$\begin{aligned} i\hbar|\dot{\chi}_2\rangle &= \left[\left\langle \hat{H}_1 \right\rangle_1 + \varepsilon - i\hbar\langle\phi_1|\dot{\phi}_1\rangle\right]|\chi_2\rangle + \left[\hat{H}_2 + \left\langle \hat{V}_{12} \right\rangle_1\right]|\chi_2\rangle \\ &= \left[\hat{H}_2 + \left\langle \hat{V}_{12} \right\rangle_1\right]|\chi_2\rangle \end{aligned}$$

and for the constraint equation

$$\begin{aligned} i\hbar\langle\phi_1|\dot{\phi}_1\rangle + i\hbar\langle\chi_2|\dot{\chi}_2\rangle - \varepsilon &= \left\langle \hat{H}_1 \right\rangle_1 + \left\langle \hat{H}_2 \right\rangle_2 + \left\langle\left\langle \hat{V}_{12} \right\rangle\right\rangle \\ i\hbar\langle\chi_2|\dot{\chi}_2\rangle &= \left\langle \hat{H}_2 \right\rangle_2 + \left\langle\left\langle \hat{V}_{12} \right\rangle\right\rangle \end{aligned}$$

Thus, equation (1) becomes

$$\begin{aligned} i\hbar|\dot{\phi}_1\rangle &= \left[\left\langle \hat{H}_2 \right\rangle_2 + \varepsilon - i\hbar\langle\chi_2|\dot{\chi}_2\rangle\right]|\phi_1\rangle + \left[\hat{H}_1 + \left\langle \hat{V}_{12} \right\rangle_2\right]|\phi_1\rangle \\ &= \left[\varepsilon - \left\langle\left\langle \hat{V}_{12} \right\rangle\right\rangle\right]|\phi_1\rangle + \left[\hat{H}_1 + \left\langle \hat{V}_{12} \right\rangle_2\right]|\phi_1\rangle \\ &= \left[\hat{H}_1 + \left\langle \hat{V}_{12} \right\rangle_2\right]|\phi_1\rangle \end{aligned}$$

if we finally define: $\varepsilon \equiv \left\langle\left\langle \hat{V}_{12} \right\rangle\right\rangle \ .$

DynEMol Method:

Time-Dependent Self-Consistent Mean Field

Therefore, in summary, we have:

$$\Psi(r_1, r_2, t) = \phi_1(r_1, t)\chi_2(r_2, t)\ \exp\left[\frac{i}{\hbar}\alpha(t)\right] \qquad , \quad \alpha(t) = \int_0^t \varepsilon(t')dt'$$

$$\begin{aligned} i\hbar|\dot{\phi}_2\rangle &= \left[\hat{H}_1 + \left\langle \hat{V}_{12} \right\rangle_2\right]|\phi_1\rangle \\ i\hbar|\dot{\chi}_2\rangle &= \left[\hat{H}_2 + \left\langle \hat{V}_{12} \right\rangle_1\right]|\chi_2\rangle \\ \varepsilon(t) &= \left\langle\left\langle \hat{V}_{12} \right\rangle\right\rangle \end{aligned}$$

$|\Psi^{el}(t)\rangle = \sum_i C_i^{el}(t)|i(t)\rangle$ $\qquad$ $|\Psi^{hl}(t)\rangle = \sum_i C_i^{hl}(t)|i(t)\rangle$

$$\begin{aligned} \left\langle \hat{V}_{12} \right\rangle_2 &= [C_i^* C_j]^{el} \sum_{kl} [C_k^* C_l]^{hl} \langle ik|\frac{1}{|\vec{r}_1 - \vec{r}_2|}|jl\rangle \\ \left\langle \hat{V}_{12} \right\rangle_1 &= [C_i^* C_j]^{hl} \sum_{kl} [C_k^* C_l]^{el} \langle ik|\frac{1}{|\vec{r}_1 - \vec{r}_2|}|jl\rangle \\ \left\langle\left\langle \hat{V}_{12} \right\rangle\right\rangle &= \sum_{ij} [C_i^* C_j]^{el} \sum_{kl} [C_k^* C_l]^{hl} \langle ik|\frac{1}{|\vec{r}_1 - \vec{r}_2|}|jl\rangle \end{aligned}$$

DynEMol Method

Intramolecular Polarization Dynamics:

Charge-Induced polarization coupling $\sim \frac{1}{r^4}$

Induced Atomic Dipole Moment: $\vec{p}_i = \alpha_i \vec{E}_i$

$$\vec{E}_i = \sum_i \left(Q_j^{Hl} - Q_j^{El}\right) \frac{\vec{R}_i - \vec{R}_j}{|\vec{R}_i - \vec{R}_j|^3}$$

$$\alpha(r) = \alpha_0 \int_0^r f^2(1)$$