



Aalto University
School of Science

NON-ADIABATIC MOLECULAR DYNAMICS

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General references:

D. Marx and J. Hutter, *Ab Initio Molecular dynamics*, Cambridge 2009
www.theochem.ruhr-uni-bochum.de/research/marx/marx.pdf

C.A. Ullrich, *Time-Dependent Density-Functional Theory*, Oxford 2012

Electronic structure calculations with the GPAW code, 21-23 May 2013

Non-adiabatic processes

Born-Oppenheimer approximation of momentarily clamped nuclei and instantaneously adjusting electron states is not valid in many important processes

EXAMPLES:

- Dynamics of molecules after photon absorption, e.g. isomerization of the visual chromophore 11-cis-retinal (modeled by protonated formalimine CH_2NH_2^+)
- Charge injection from a dye molecule into TiO_2 in dye-sensitized (Grätzel) solar cells
- Excited state evolution of a protected gold cluster (Ari)
- Transmission of energetic ions through solids (Ari)

Ab-initio molecular dynamics

Quantum mechanical system of nuclei and electrons

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}, t) = i \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) \quad \hat{H} \text{ time-independent Hamiltonian}$$

$\Psi(\mathbf{r}, \mathbf{R}, t)$ Total (electrons + nuclei) wavefunction

$$\begin{aligned} \hat{H} &= \sum_{j=1}^{N_e} -\frac{\nabla_{\mathbf{r}_j}^2}{2} + \frac{1}{2} \sum_{j,k;j \neq k}^{N_e} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} + \sum_{j=1}^{N_n} -\frac{\nabla_{\mathbf{R}_j}^2}{2M_j} + \frac{1}{2} \sum_{j,k;j \neq k}^{N_e} \frac{Z_j Z_k}{|\mathbf{R}_j - \mathbf{R}_k|} - \sum_{j=1}^{N_e} \sum_{k=1}^{N_n} \frac{Z_k}{|\mathbf{r}_j - \mathbf{R}_k|} \\ &= [\hat{T}_e + \hat{W}_{ee}] + [\hat{T}_n + \hat{W}_{nn}] + \hat{W}_{en} \end{aligned}$$

Consider: electrons generate a potential on which nuclei move
→ Ab-initio MD with classical nuclei and QM electronic structure

Born-Oppenheimer approximation

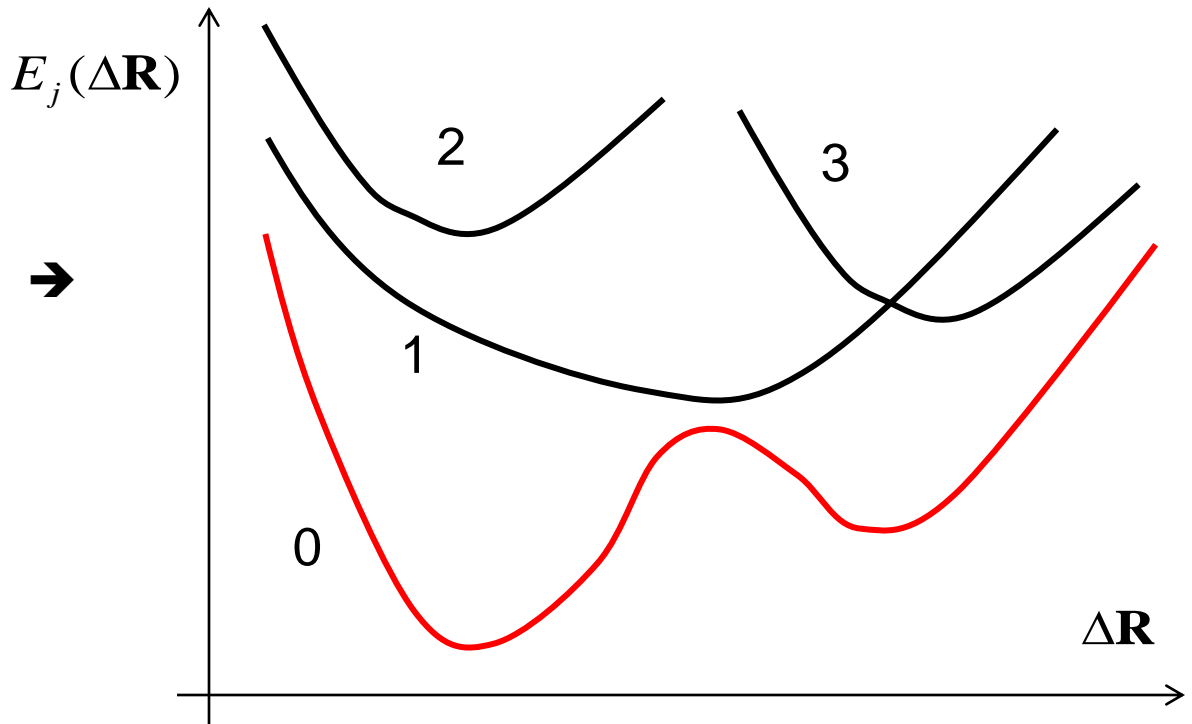
$M_I \gg 1 \Rightarrow$ Clamped nuclei

$$\hat{H}_{BO}(\mathbf{r}; \mathbf{R}) = \sum_{j=1}^{N_e} -\frac{\nabla_{\mathbf{r}_j}}{2} + \frac{1}{2} \sum_{j,k;j \neq k}^{N_e} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} + \frac{1}{2} \sum_{j,k;j \neq k}^{N_e} \frac{Z_j Z_k}{|\mathbf{R}_j - \mathbf{R}_k|} - \sum_{j=1}^{N_e} \sum_{k=1}^{N_n} \frac{Z_k}{|\mathbf{r}_j - \mathbf{R}_k|} = \hat{T}_e + \hat{W}_{ee} + \hat{W}_{nn} + \hat{W}_{en}$$

$$\hat{H}_{BO}(\mathbf{r}; \mathbf{R})\Phi_j(\mathbf{r}; \mathbf{R}) = E_j(\mathbf{R})\Phi_j(\mathbf{r}; \mathbf{R}) \quad (\mathbf{r}; \text{ are variables, } ; \mathbf{R}) \text{ are parameters}$$

→ Adiabatic potential energy surfaces $E_i(\mathbf{R})$

DFT (ground state)
TDDFT (excited states)
Post Hartree-Fock methods



Towards electron-nucleus dynamics

Born - Huang Ansatz for the electron - nucleus wavefunction : $\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{l=0}^{\infty} \Phi_l(\mathbf{r}; \mathbf{R}) \Omega_l(\mathbf{R}, t)$

$\Phi_l(\mathbf{r}; \mathbf{R})$ are a complete set of static electronic basis functions

$$\langle \Phi_l | \Phi_k \rangle = \delta_{l,k}$$

Nuclear $\Omega_l(\mathbf{R}, t)$ act as time - dependent expansion coefficients

$$\hat{H}_{BO}(\mathbf{r}; \mathbf{R}) \Phi_j(\mathbf{r}; \mathbf{R}) = E_j(\mathbf{R}) \Phi_j(\mathbf{r}; \mathbf{R})$$

Add the ansatz into the time - dependent Schrödinger equation

$$\hat{H} \Psi(\mathbf{r}, \mathbf{R}, t) = i \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) \quad \hat{H} \sum_{l=0}^{\infty} \Phi_l(\mathbf{r}; \mathbf{R}) \Omega_l(\mathbf{R}, t) = i \frac{\partial}{\partial t} \sum_{l=0}^{\infty} \Phi_l(\mathbf{r}; \mathbf{R}) \Omega_l(\mathbf{R}, t)$$

Left multiplication by $\Phi_k^*(\mathbf{r}; \mathbf{R})$, integration over \mathbf{r}

$$(\hat{H} = \hat{H}_{BO} + \hat{T}_n)$$

$$\sum_{l=0}^{\infty} \int d\mathbf{r} \Phi_k^*(\mathbf{r}; \mathbf{R}) \hat{H} \Phi_l(\mathbf{r}; \mathbf{R}) \Omega_l(\mathbf{R}, t) = i \frac{\partial}{\partial t} \Omega_l(\mathbf{R}, t) \sum_{l=0}^{\infty} \int d\mathbf{r} \Phi_k^*(\mathbf{r}; \mathbf{R}) \Phi_l(\mathbf{r}; \mathbf{R})$$

$$\left[\sum_{j=1}^{N_n} -\frac{\nabla_{\mathbf{R}_j}^2}{2M_j} + E_k(\mathbf{R}) \right] \Omega_k(\mathbf{R}, t) + \sum_{l=0}^{\infty} D_{kl} \Omega_l(\mathbf{R}, t) = i \frac{\partial}{\partial t} \Omega_k(\mathbf{R}, t)$$

Non - adiabatic coupling terms : D_{kl}

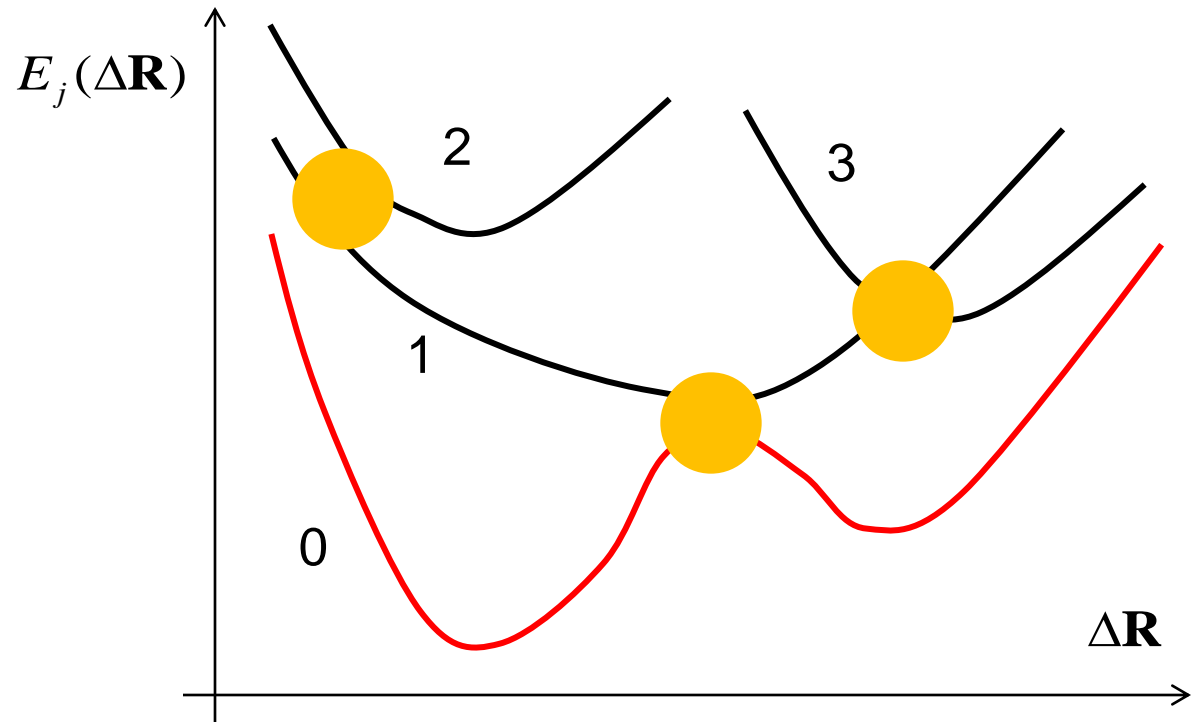
EQUATION FOR THE NUCLEAR TIME-DEPENDENT $\Omega_k(\mathbf{R}, t)$

$$\left[\sum_{j=1}^{N_n} -\frac{\nabla_{\mathbf{R}_j}^2}{2M_j} + E_k(\mathbf{R}) \right] \Omega_k(\mathbf{R}, t) + \sum_{l=0}^{\infty} D_{kl} \Omega_l(\mathbf{R}, t) = i \frac{\partial}{\partial t} \Omega_k(\mathbf{R}, t)$$

$E_k(\mathbf{R})$ is the PES for nuclei

NON-ADIABATIC COUPLING TERMS IN BORN-HUANG ANSATZ:

$$D_{kl} = \int d\mathbf{r} \Phi_k^*(\mathbf{r}; \mathbf{R}) \left[-\sum_{j=1}^{N_n} \frac{\nabla_{\mathbf{R}_j}^2}{2M_j} \right] \Phi_l(\mathbf{r}; \mathbf{R}) + \sum_{j=1}^{N_n} \frac{1}{M_j} \left\{ \int d\mathbf{r} \Phi_k^*(\mathbf{r}; \mathbf{R}) \left[-i\nabla_{\mathbf{R}_j} \right] \Phi_l(\mathbf{r}; \mathbf{R}) \right\} \left[-i\nabla_{\mathbf{R}_j} \right]$$



Further

Neglecting all diagonal and off - diagonal coupling terms D_{kl}

⇒ BORN - OPPENHEIMER APPROXIMATION

$$\left[\sum_{j=1}^{N_n} -\frac{\nabla_{\mathbf{R}_j}^2}{2M_j} + E_k(\mathbf{R}) \right] \Omega_k(\mathbf{R}, t) = i \frac{\partial}{\partial t} \Omega_k(\mathbf{R}, t)$$

⇒ Ground - state dynamics or dynamics far from coupled electronic states

Towards classical dynamics of nuclei (Now we need to write \hbar)

$$\left[\sum_{j=1}^{N_n} -\frac{\hbar^2 \nabla_{\mathbf{R}_j}^2}{2M_j} + E_k(\mathbf{R}) \right] \Omega_k(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \Omega_k(\mathbf{R}, t) \quad \text{Complex valued } \Omega_k(\mathbf{R}, t)$$

$$\text{Polar expansion : } \Omega_k(\mathbf{R}, t) = A_k(\mathbf{R}, t) \exp\left[\frac{i}{\hbar} S_k(\mathbf{R}, t)\right]$$

Insert, separate imaginary and real parts:

$$\frac{\partial S_k}{\partial t} = \sum_{j=1}^{N_n} \frac{\hbar^2 \nabla_{\mathbf{R}_j}^2 A_k}{2M_j A_k} - \sum_{j=1}^{N_n} \frac{(\nabla_{\mathbf{R}_j} S_k)^2}{2M_j} - E_k$$
$$\frac{\partial A_k}{\partial t} = - \sum_{j=1}^{N_n} \frac{(\nabla_{\mathbf{R}_j} S_k)(\nabla_{\mathbf{R}_j} A_k)}{M_j} - \sum_{j=1}^{N_n} \frac{A_k \nabla_{\mathbf{R}_j}^2 S_k}{2M_j}$$

HOME WORK

No approximations beyond the BO one

Classical limit of the real part when $\hbar \rightarrow 0$

$$\frac{\partial S_k}{\partial t} = - \sum_{j=1}^{N_n} \frac{(\nabla_{\mathbf{R}_j} S_k)^2}{2M_j} - E_k$$

Hamilton - Jacobi equation of the classical mechanics

S_k is the classical action for a particle:

$$S_k(t) = \int_{t_0}^t L(t') dt' = \int_{t_0}^t [E_{kin}(t') - E_{pot}(t')] dt'$$

HOME WORK

Hamiltonian mechanics, momentum of nucleus i : $\nabla_{\mathbf{R}_i} S_k = \mathbf{p}_i^k = M_i \mathbf{v}_i^k$

Take the $\nabla_{\mathbf{R}_i}$ gradient of the Hamilton - Jacobi equation, use $\nabla_{\mathbf{R}_i} S_k / M_i = \mathbf{v}_i^k$

\Rightarrow

$$M_i \frac{d}{dt} \mathbf{v}_i^k = -\nabla_{\mathbf{R}_i} E_k$$

Classical dynamics for nuclei on the PES E_k

Born-Oppenheimer (adiabatic) molecular dynamics

Time - dependent Schrödinger equation of the electron - nucleus system:

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}, t) = i \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) \quad ; \quad \hat{H}(\mathbf{r}; \mathbf{R}) = \hat{T}_e + \hat{W}_{ee} + \hat{T}_n + \hat{W}_{nn} + \hat{W}_{en}$$

Born - Huang Ansatz: $\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{l=0}^{\infty} \Phi_l(\mathbf{r}; \mathbf{R}) \Omega_l(\mathbf{R}, t)$

with

$$\underline{\hat{H}_{BO}(\mathbf{r}; \mathbf{R}) \Phi_l(\mathbf{r}; \mathbf{R}) = E_l(\mathbf{R}) \Phi_l(\mathbf{r}; \mathbf{R})} \quad ; \quad \hat{H}_{BO}(\mathbf{r}; \mathbf{R}) = \hat{T}_e + \hat{W}_{ee} + \hat{W}_{nn} + \hat{W}_{en}$$

Born - Oppenheimer approximation : omission of nonadiabatic coupling terms

On the classical limit for nuclei with $E_k(\mathbf{R})$ as the potential:

$$\underline{M_i \ddot{\mathbf{R}}_i^k = -\nabla_{\mathbf{R}_i} E_k(\mathbf{R})}$$

Ehrenfest (non-adiabatic) molecular dynamics

Time - dependent Schrödinger equation of the electron - nucleus system:

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}, t) = i \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) \quad ; \quad \hat{H}(\mathbf{r}; \mathbf{R}) = \hat{T}_e + \hat{W}_{ee} + \hat{T}_n + \hat{W}_{nn} + \hat{W}_{en}$$

$$\text{Ehrenfest Ansatz: } \Psi(\mathbf{r}, \mathbf{R}, t) = \Phi(\mathbf{r}; \mathbf{R}, t) \Omega(\mathbf{R}, t) \exp \left[i \int_{t_0}^t \langle \hat{H}_{el}(t') \rangle dt' \right]$$

Time - dependent electronic part $\Phi(\mathbf{r}; t)$ phase factor for convenience

See also A.Abedi, N.T.Maitra, and E.K.U.Gross, PRL **105**, 123002 (2010)

$$\langle \hat{H}_{el}(t) \rangle = \int d\mathbf{r} \int d\mathbf{R} \Phi^*(\mathbf{r}; \mathbf{R}, t) \Omega^*(\mathbf{R}, t) \hat{H}_{el}(t) \Phi(\mathbf{r}; \mathbf{R}, t) \Omega(\mathbf{R}, t)$$

$$\hat{H}_{el}(t) = \hat{T}_e + V_e(t) + \hat{W}_{ee} + \hat{W}_{nn} + \hat{W}_{en} = \hat{H}_{BO}(\mathbf{r}; \mathbf{R}) + V_e(t) \quad ; \quad V_e(t) \text{ is an external potential,}$$

e.g. , laserfield

Towards Ehrenfest dynamics

HOME WORK

Following the derivation of the Born-Oppenheimer dynamics:

- Ehrenfest ansatz for the total wavefunction into the time-dependent Schrödinger equation
- Obtain time evolution equations for electronic and nuclear wavefunctions
- Transform nuclear wavefunction into a polar form and insert it to the time evolution equation for nuclei
- Take the classical limit \rightarrow Hamilton-Jacobi equation
- Take the gradient of the HJ equation \rightarrow a Newton equation of motion for nuclei with an average potential
- Take the classical limit for nuclei in the time evolution equation for electron states \rightarrow electronic time-dependent Schrödinger equation

Ehrenfest dynamics equations

$$i \frac{\partial}{\partial t} \Phi(\mathbf{r}; \mathbf{R}, t) = \widehat{H}_{el}(\mathbf{r}; \mathbf{R}) \Phi(\mathbf{r}; \mathbf{R}, t)$$

Proper time - evolution of the electron system (within TDDFT)

$$M_i \ddot{\mathbf{R}}_i = -\nabla_{\mathbf{R}_i} \langle \widehat{H}_{el}(\mathbf{r}; \mathbf{R}) \rangle$$

More developed algorithm

$\Phi(\mathbf{r}; \mathbf{R}, t)$ and $\widehat{H}_{el}(\mathbf{r}; \mathbf{R})$ depend parametrically on $\mathbf{R} \Rightarrow$ feedback between electronic and nuclear degrees of freedom

Classical time evolution of nuclei with the potential given by the average $\langle \widehat{H}_{el}(\mathbf{r}; \mathbf{R}) \rangle$ at time t but a small time step $O(1 \text{ as})$ dictated by electrons needed in discretization

Born-Oppenheimer dynamics

$$\widehat{H}_{el}(\mathbf{r}; \mathbf{R}) \Phi_l(\mathbf{r}; \mathbf{R}) = E_k(\mathbf{R}) \Phi_k(\mathbf{r}; \mathbf{R})$$

$$M_i \ddot{\mathbf{R}}_i^k = -\nabla_{\mathbf{R}_i} E_k(\mathbf{R}) = -\nabla_{\mathbf{R}_i} \langle \Phi_k | \widehat{H}_{el} | \Phi_k \rangle$$

Time - independent Schrödinger equation

Simple algorithm

The proper time - evaluation of electron states is not calculated and the dynamics is dictated by nuclei \Rightarrow A longer time step $O(1 \text{ fs})$ can be used

Mixing of electronic states in Ehrenfest dynamics

$$i \frac{\partial}{\partial t} \Phi(\mathbf{r}; \mathbf{R}, t) = \hat{H}_{el}(\mathbf{r}; \mathbf{R}) \Phi(\mathbf{r}; \mathbf{R}, t)$$
$$M_i \ddot{\mathbf{R}}_i = -\nabla_{\mathbf{R}_i} \langle \hat{H}_{el}(\mathbf{r}; \mathbf{R}) \rangle$$

⇒

$$i \dot{c}_k(t) = c_k(t) E_k(\mathbf{R}) - i \sum_l c_l(t) D_{kl}$$
$$M_i \ddot{\mathbf{R}}_i = -\nabla_{\mathbf{R}_i} \sum_k |c_k(t)|^2 E_k(\mathbf{R})$$

Expansion in adiabatic states $\hat{H}_{el}(\mathbf{r}; \mathbf{R})$

$$\Phi(\mathbf{r}; \mathbf{R}, t) = \sum_{l=0}^{\infty} c_l(t) \Phi_l(\mathbf{r}; \mathbf{R})$$

Time dependence now in $\{c_l(t)\}$,

$|c_l(t)|^2$ is the population of state l

Non-adiabatic effects:

Coupling of adiabatic states due to the nuclei dynamics

Mean-field like treatment

Coupling constants between adiabatic electronic states in Ehrenfest ansatz:

$$D_{kl} = \langle \Phi_k | \frac{\partial}{\partial t} | \Phi_l \rangle = \langle \Phi_k | \frac{\partial \mathbf{R}}{\partial t} \frac{\partial}{\partial \mathbf{R}} | \Phi_l \rangle = \dot{\mathbf{R}} \cdot \langle \Phi_k | \nabla_{\mathbf{R}} | \Phi_l \rangle = \dot{\mathbf{R}} \cdot \mathbf{d}_{kl}$$

Nuclear dynamics with a mean-field potential

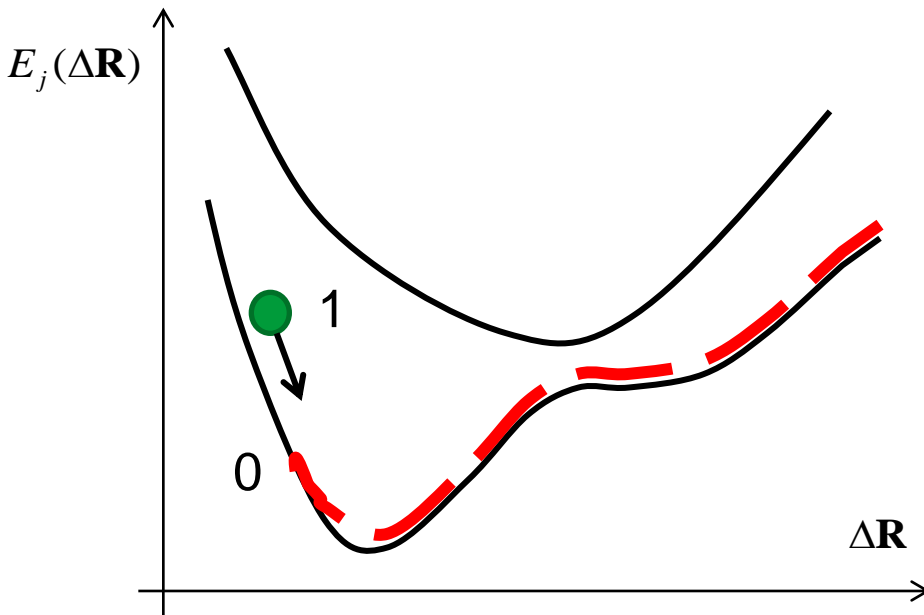
$$\hat{H}_{el}(\mathbf{r}; \mathbf{R})\Phi_l(\mathbf{r}; \mathbf{R}) = E_k(\mathbf{R})\Phi_k(\mathbf{r}; \mathbf{R})$$

$$M_i \ddot{\mathbf{R}}_i^k = -\nabla_{\mathbf{R}_i} E_k(\mathbf{R}) = -\nabla_{\mathbf{R}_i} \langle \Phi_k | \hat{H}_{el} | \Phi_k \rangle$$

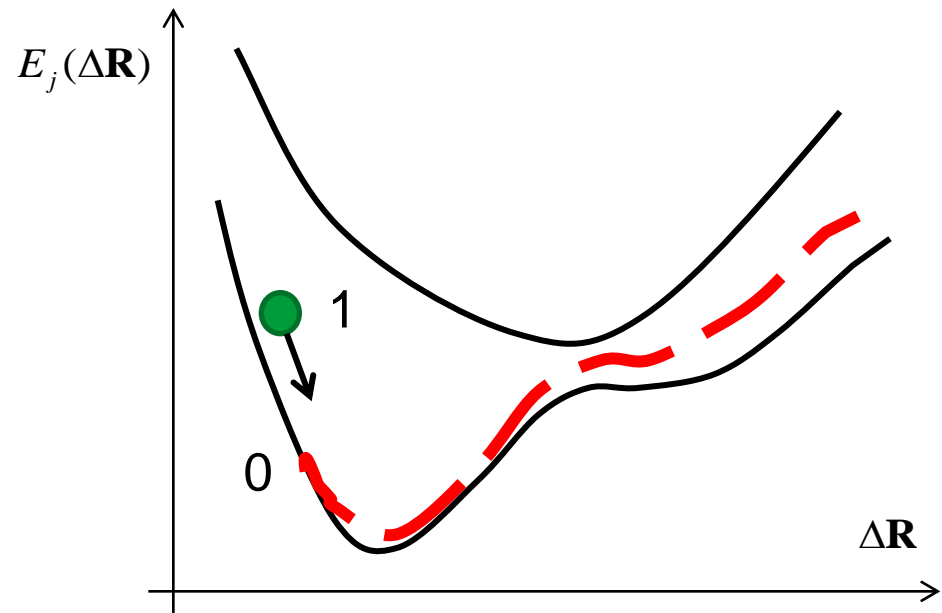
$$i\dot{c}_k(t) = c_k(t)E_k(\mathbf{R}) - i\sum_l c_l(t)D_{kl}$$

$$M_i \ddot{\mathbf{R}}_i = -\nabla_{\mathbf{R}_i} \sum_k |c_k(t)|^2 E_k(\mathbf{R})$$

Born-Oppenheimer



Ehrenfest



Ehrenfest dynamics with an atomic-position dependent basis

Ari Ojanperä et al., J. Chem. Phys. **136**, 144103 (2012).

Propagating Kohn-Sham single-electron states: $\varphi_n(\mathbf{r}; \mathbf{R}, t) = \sum_{k=0}^{\infty} c_{n,k}(t) \chi_k(\mathbf{r}; \mathbf{R})$

Analogously to the above treatment for nonadiabatic mixing $\left(\Phi(\mathbf{r}; \mathbf{R}, t) = \sum_{l=0}^{\infty} c_l(t) \Phi_l(\mathbf{r}; \mathbf{R}) \right)$:

$$i\mathbf{S}\dot{\mathbf{c}}_n(t) = (\mathbf{H} - i\dot{\mathbf{R}} \cdot \mathbf{d}) \mathbf{c}_n(t) \quad ; \quad S_{kl} = \langle \chi_k | \chi_l \rangle \quad ; \quad H_{kl} = \langle \chi_k | \hat{H}_{KS} | \chi_l \rangle \quad ; \quad d_{kl} = \langle \chi_k | \nabla_{\mathbf{R}} | \chi_l \rangle$$

Classical dynamics of nuclei $M_i \ddot{\mathbf{R}}_i = \mathbf{F}_i$ needs energy-conserving forces:

$$\mathbf{F}_i = - \frac{dE_{el}}{d\mathbf{R}_i} = - \frac{\partial E_{el}}{\partial \mathbf{R}_i} - \sum_n \left[\frac{\partial E_{el}}{\partial \mathbf{c}_n} \frac{d\mathbf{c}_n}{d\mathbf{R}_i} + c.c. \right] = \dots = - \frac{\partial E_{el}}{\partial \mathbf{R}_i} + \sum_n f_n \mathbf{c}_n^* (\mathbf{H} \mathbf{S}^{-1} \mathbf{d}_i + c.c.) \mathbf{c}_n \quad ;$$

$f_n =$ occupation of KS-state φ_n

$E_{el}[\rho; \mathbf{R}] = T_s[\rho] + E_{ext}[\rho; \mathbf{R}] + E_H[\rho] + E_{xc}[\rho] =$ total nonadiabatic electron energy

\mathbf{F}_i contains: Hellmann-Feynman force + Pulay corrections + terms due to nonadiabaticity

Position-dependent basis: The expressions for \mathbf{F}_i (non-adiabatic) and \mathbf{F}_i (ground state) are different

Ehrenfest dynamics within the Projector Augmented-Wave (PAW) method

Ari Ojanperä et al., J. Chem. Phys. **136**, 144103 (2012).



PAW formalism :

$$\varphi_n = \hat{T} \tilde{\varphi}_n = \left[1 + \sum_{\mathbf{R}_j, k} \left(\left| \phi_k^{\mathbf{R}_j} \right\rangle - \left| \tilde{\phi}_k^{\mathbf{R}_j} \right\rangle \right) \left\langle p_k^{\mathbf{R}_j} \right| \right] \tilde{\varphi}_n \quad \varphi_n = \text{all electron wf} \quad ; \quad \tilde{\varphi}_n = \text{PAW pseudo wf}$$

Atomic-position dependent partial waves $\left| \phi_k^{\mathbf{R}_j} \right\rangle$, $\left| \tilde{\phi}_k^{\mathbf{R}_j} \right\rangle$ and projectors $\left\langle p_k^{\mathbf{R}_j} \right|$

\Rightarrow

$$i\tilde{S} \frac{\partial \tilde{\varphi}_n}{\partial t} = (\tilde{H} + \tilde{P}) \tilde{\varphi}_n \quad \tilde{P} = -i\hat{T}^t \frac{\partial \hat{T}}{\partial t} = -i\dot{\mathbf{R}} \cdot \hat{\mathbf{d}}$$

$$M_i \ddot{\mathbf{R}}_i = \mathbf{F}_{\mathbf{R}_i}$$

$$\tilde{S} = \hat{T}^t \hat{T} \quad ; \quad \tilde{H} = \hat{T}^t \hat{H}_{KS} \hat{T} \quad ; \quad \text{Operator } \hat{\mathbf{d}} = \hat{\mathbf{d}} \left[\left| \phi_k^{\mathbf{R}_j} \right\rangle, \left| \tilde{\phi}_k^{\mathbf{R}_j} \right\rangle, \left\langle p_k^{\mathbf{R}_j} \right| \right] = \dots$$

$$\mathbf{F}_{\mathbf{R}_i} = -\frac{\partial E_{el}^{PAW}}{\partial \mathbf{R}_i} + \sum_n f_n \left\langle \tilde{\varphi}_n \left| \left(\tilde{H} \tilde{S}^{-1} \mathbf{d}_i + c.c. \right) \tilde{\varphi}_n \right\rangle = \dots$$

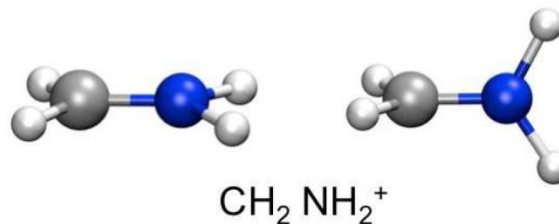
For details, see JCP **136**, 144103 (2012)

Ehrenfest dynamics within the Projector Augmented-Wave (PAW) method

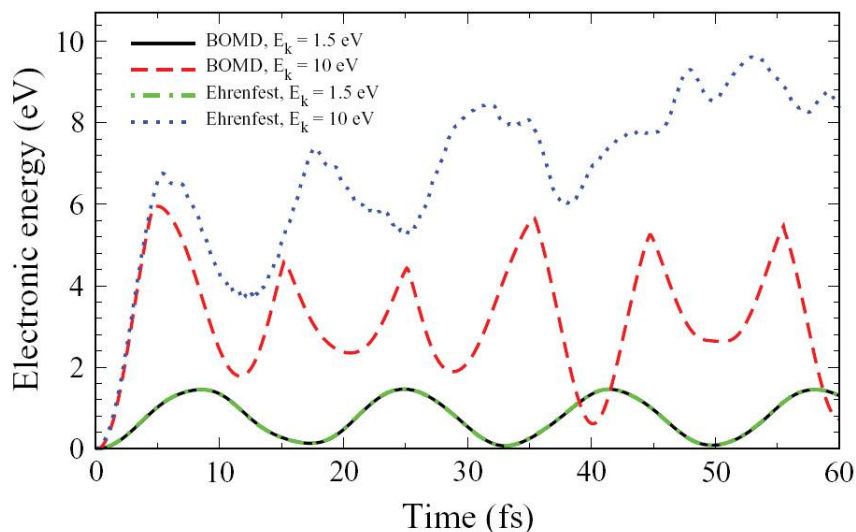
A. Ojanperä et al., J. Chem. Phys. **136**, 144103 (2012).



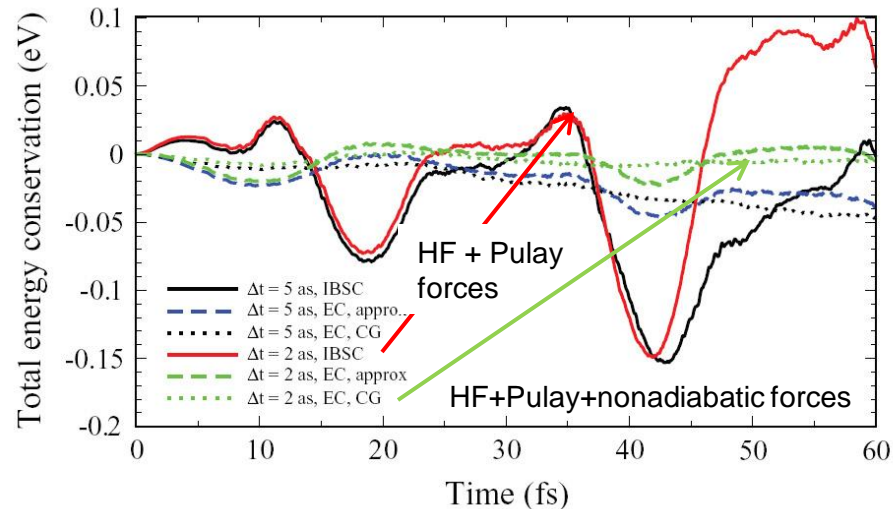
Torsional rotation of protonated formalimine



Rotational excitation energy

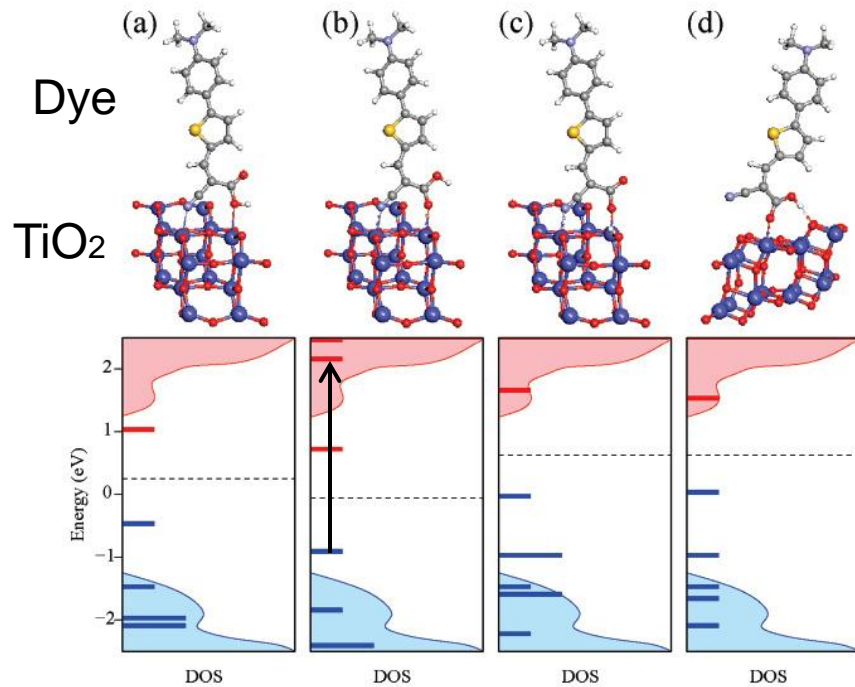


See also Tapavicza et al. PRL **98**, 023001 (2007),
Li et al. JCP **123**, 084106 (2005)



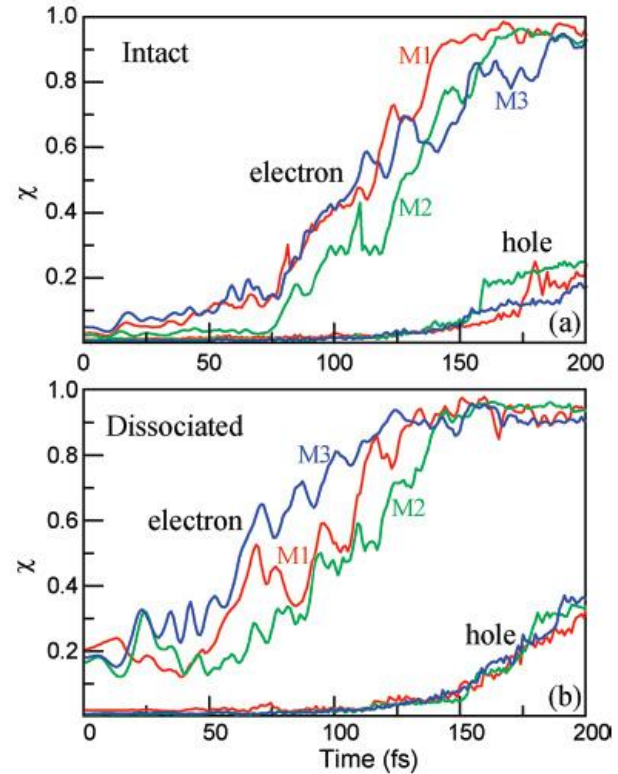
Electron and hole dynamics in dye-sensitized solar cells

S. Meng and E. Kaxiras, Nano Letters **10**, 1238 (2010).



Separation of the electron and hole
Effect of dye species, size, binding, surface defects

Electrons and holes injected into TiO₂



Ehrenfest dynamics, Summary

WORKS WELL when:

- A single trajectory in the nuclear dynamics is dominant
- Ultrafast processes and initial stages of an excitation before any significant amount of level crossings
- A large number of similar electronic excitations are involved
- dynamics is governed by an average force (e.g. metals)

LIMITED when

- Branching of ionic trajectories or excited states involve multiple paths
- **SURFACE HOPPING METHODS**

NOTE ALSO

- TDDFT implementations rely on the TDDFT excited state description
- Need for benchmarking

NOTE FURTHER

- For a time-dependent basis, the energy conserving force contains terms due to non-adiabatic couplings