Why go beyond Ehrenfest? Two-way energy transfer between electrons and ions

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Summary

- The coupled electron-nuclear system
- The Ehrenfest theorem
- The Ehrenfest approximation
- Why is the Ehrenfest approximation nonadiabatic?
- Two reasons for going beyond Ehrenfest
- Considerations:
  - Heating rates
  - Model systems
- Survey of approaches to the problem

Comments and notation

- ‘Nuclei’ and ‘ions’ are synonymous
- Use
  - I,J to label ions (nuclei) with coordinates $\mathbf{R}_I$,
  - i,j to label electrons with coordinates $\mathbf{r}_\mathrm{i}$,
  - n,m to label adiabatic electronic states
- Will not discuss how to solve the electronic part of the problem – assume we have some good (or at least adequate) way of doing this

The Ehrenfest theorem: general case

For any quantum system with a Hamiltonian of the form

$$\hat{H} = \sum_I \frac{\hat{P}^2}{2M_I} + V(\{\hat{\mathbf{R}}_I\}, \hat{O})$$

Any other operators commuting with **P** and **R**

the *exact* Heisenberg equations of motion are

$$\partial_t \hat{\mathbf{R}}_I = \frac{\mathrm{i}}{\hbar}[\hat{H}, \mathbf{R}_I] = \frac{\hat{\mathbf{P}}_I}{M_I}$$

$$\partial_t \hat{\mathbf{P}}_I = \frac{\mathrm{i}}{\hbar}[\hat{H}, \mathbf{P}_I] = -\nabla_{\mathbf{R}_I} V$$

This gives rise to *exact* equations for the corresponding expectation values:

$$\partial_t \langle \hat{\mathbf{R}}_I \rangle = \frac{\langle \hat{\mathbf{P}}_I \rangle}{M_I} \qquad \partial_t \langle \hat{\mathbf{P}}_I \rangle = -\langle \nabla_{\mathbf{R}_I} V \rangle$$

where the expectation values are defined using the full density operator of the system:

$$\langle \hat{O} \rangle = \mathrm{Tr}[\hat{\rho}\hat{O}]$$

(can be evaluated in any representation – Schrödinger, Heisenberg or interaction)

The Ehrenfest theorem: electrons and nuclei

For a non-relativistic system of interacting electrons and nuclei, we have

$$\hat{H} = \hat{H}_{\mathrm{e}} + \hat{H}_{\mathrm{ion}} + \hat{H}_{\mathrm{e-ion}} = \hat{T}_{\mathrm{e}} + \hat{T}_{\mathrm{ion}} + \hat{V}(\hat{\mathbf{r}}, \hat{\mathbf{R}})$$

$$\hat{H}_{\mathrm{e}} = \hat{T}_e + \hat{V}_{\mathrm{e-e}} = \sum_i \frac{\hat{p}_i^2}{2m_i} + \frac{e^2}{4\pi\epsilon_0} \sum_{i>j} \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|}$$

$$\hat{H}_{\mathrm{ion}} = \hat{T}_{\mathrm{ion}} + \hat{V}_{\mathrm{ion}} = \sum_I \frac{\hat{P}_I^2}{2M_I} + \frac{e^2}{4\pi\epsilon_0} \sum_{I>J} \frac{Z_I Z_J}{|\hat{\mathbf{R}}_I - \hat{\mathbf{R}}_J|}$$

$$\hat{H}_{\mathrm{e-ion}} = \hat{V}_{\mathrm{e-ion}} = \frac{-e^2}{4\pi\epsilon_0} \sum_{i,J} \frac{Z_J}{|\hat{\mathbf{r}}_i - \hat{\mathbf{R}}_J|}$$

$$V(\mathbf{r}, \mathbf{R}) = \hat{V}_{\mathrm{e-ion}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\mathrm{e-e}}(\mathbf{r}) + \hat{V}_{\mathrm{ion}}(\mathbf{R})$$

The exact Ehrenfest equations for the nuclei become

Force operator on nucleus I, evaluated in the full electron-nuclear quantum state

$$\partial_t \langle \hat{\mathbf{R}}_I \rangle = \frac{\langle \hat{\mathbf{P}}_I \rangle}{M_I}$$

$$\partial_t \langle \hat{\mathbf{P}}_I \rangle = -\langle \nabla_{\mathbf{R}_I} V \rangle = -\langle \nabla_{\mathbf{R}_I} (\hat{V}_{\mathrm{e-ion}} + \hat{V}_{\mathrm{ion}}) \rangle \equiv \langle \hat{\mathbf{F}}_I \rangle$$

For operators acting on the ions only $\langle \hat{O} \rangle = \mathrm{Tr}[\hat{\rho}_{\mathrm{ion}} \hat{O}]$

with the nuclear density operator $\hat{\rho}_{\mathrm{ion}} = \mathrm{Tr}_{\mathrm{e}}[\hat{\rho}]$

The Ehrenfest Approximation

Two fundamental parts:

1. Factor the total density operator into electronic and nuclear parts

$$\hat{\rho} = \hat{\rho}_{\rm ion} \otimes \hat{\rho}_{\rm e}$$

Uncorrelated ions and electrons

2. Assume the nuclei are sufficiently massive that their positions and momenta can be regarded as simultaneously well defined, and that the density operator is sharply peaked about the average values of both quantities:

$$\hat{\mathbf{R}}_I \to \overline{\mathbf{R}}_I = \langle \hat{\mathbf{R}}_I \rangle$$
$$\hat{\mathbf{P}}_I \to \overline{\mathbf{P}}_I = \langle \hat{\mathbf{P}}_I \rangle$$

'Classical' nuclei

So the parts of the Hamiltonian relevant to the electrons become

$$\hat{H}_{\rm e,eff}(\overline{\mathbf{R}}) = \hat{T}_e + \hat{V}_{\rm e-e} + \hat{V}_{\rm e-ion} \approx \sum_i \frac{\hat{p}_i^2}{2m_i} + \frac{e^2}{4\pi\epsilon_0} \sum_{i>j} \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} + \frac{-e^2}{4\pi\epsilon_0} \sum_{i,J} \frac{Z_J}{|\hat{\mathbf{r}}_i - \overline{\mathbf{R}}_J|}$$

Equations of motion in the Ehrenfest approximation

Within this approximation the Ehrenfest equations for nuclear motion become

$$\partial_t \overline{\mathbf{R}}_I = \frac{\overline{\mathbf{P}}_I}{M_I}$$

$$\partial_t \overline{\mathbf{P}}_I = -(\langle \nabla_{\overline{\mathbf{R}}_I} \hat{V}_{\mathrm{e-ion}}(\hat{\mathbf{r}}, \overline{\mathbf{R}})\rangle_{\mathrm{e}} + \nabla_{\overline{\mathbf{R}}_I} V_{\mathrm{ion}}(\overline{\mathbf{R}})) \equiv \langle \hat{\mathbf{F}}_{I,e}\rangle_{\mathrm{e}} + \frac{e^2}{4\pi\epsilon_0}\sum_J \frac{Z_I Z_J(\overline{\mathbf{R}}_I - \overline{\mathbf{R}}_J)}{|\overline{\mathbf{R}}_I - \overline{\mathbf{R}}_J|^3}$$

where

$$\hat{\mathbf{F}}_{I,e} \equiv -\nabla_{\overline{\mathbf{R}}_I} \hat{V}_{\mathrm{e-ion}}(\hat{\mathbf{r}}, \overline{\mathbf{R}}) \qquad \langle \ldots \rangle_{\mathrm{e}} = \mathrm{Tr}[\hat{\rho}_{\mathrm{e}} \ldots]$$

Note this is the same operator as appears in the Hellman-Feynman force, though we did not use the H-F theorem in our derivation

Electronic state determined by the electronic Hamiltonian along the average path:

$$\partial_t \hat{\rho}_{\mathrm{e}} = \frac{1}{\mathrm{i}\hbar}[\hat{H}_{\mathrm{e,eff}}(\overline{\mathbf{R}}), \hat{\rho}_{\mathrm{e}}]$$

When will the approximation fail?

- Either (or both) of the two fundamental assumptions could be wrong:
  - The nuclei might not *behave classically*
    - most important in situations involving low temperatures or tunnelling
  - The *factorization* into electrons and ions might fail
    - most important in situations involving excited electronic states, particularly when states are nearby in energy
    - has important consequences for the computation of energy transfer between ions and electrons

The Born-Oppenheimer approximation

Contrast Ehrenfest approximation with the *Born-Oppenheimer approximation*: initially *neglect* the nuclear kinetic energy term, so all remaining parts of the Hamiltonian are diagonal in **R**

Solve electronic problem to find electronic states and energies depending parametrically on **R**

$$\hat{H}_{\mathrm{e,eff}}(\mathbf{R})|\psi_n(\mathbf{R})\rangle = E_n(R)|\psi_n(\mathbf{R})\rangle$$

Then solve the nuclear problem on the electronic energy surface:

$$[\hat{H}_{\mathrm{ion}} + E_n(R)]|\chi_{n,m}\rangle = E_{n,m}|\chi_{n,m}\rangle$$

Born-Oppenheimer molecular dynamics

Treat the nuclear problem as classical and look at dynamics on an individual potential surface (most commonly the ground state):

$$\partial_t \overline{\mathbf{R}}_I = \frac{\overline{\mathbf{P}}_I}{M_I}$$

$$\partial_t \overline{\mathbf{P}}_I = \langle \psi_n(\mathbf{R}) | \hat{\mathbf{F}}_{I,e} | \psi_n(\mathbf{R}) \rangle + \mathbf{F}_{\mathrm{nuc},I} \equiv \mathbf{F}_{n,I}$$

All computed using an electronic state obtained from the *time-independent* Schrödinger equation:

$$\hat{H}_{\mathrm{e,eff}}(\mathbf{R}) | \psi_n(\mathbf{R}) \rangle = E_n(R) | \psi_n(\mathbf{R}) \rangle$$

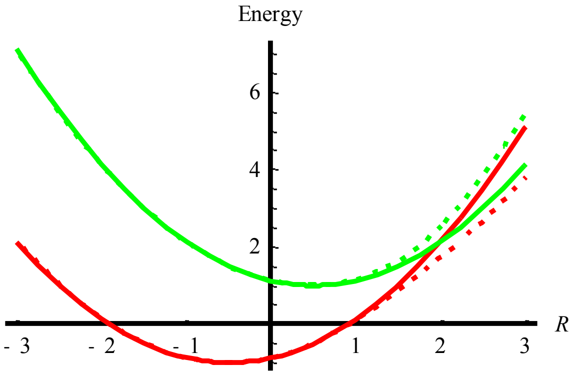
Can also use these as a basis to expand the Ehrenfest state:

$$\hat{\rho}_{\mathrm{e}} = \sum_{n,m} \rho_{nm}(t) | \psi_n(\mathbf{R}) \rangle \langle \psi_m(\mathbf{R}) | \mathrm{e}^{-\mathrm{i}(E_n(\mathbf{R}) - E_m(\mathbf{R}))t/\hbar}$$

$$\Rightarrow \partial_t \rho_{nm} = -\dot{\mathbf{R}} \cdot \sum_k \left[\langle n | \nabla_{\mathbf{R}} k \rangle \rho_{km} + \rho_{nk} \langle \nabla_{\mathbf{R}} k | m \rangle \right]$$

Avoided crossings

The classic point of failure for Born-Oppenheimer dynamics is the *avoided crossing*.



Degeneracy of two states of the same symmetry is a special condition, since it requires equal eigenvalues of

$$H = \begin{pmatrix} E1 & \Delta \\ \Delta^* & E_2 \end{pmatrix}$$

$$E = \frac{(E_1 + E_2)}{2} \pm \frac{1}{2}\sqrt{(E_1 - E_2)^2 + 4|\Delta|^2}$$

Requires $E_1 = E_2 \quad \text{and} \quad |\Delta| = 0$

- Two real conditions (real Hamiltonians, with time-reversal symmetry)
- Three real conditions (complex Hamiltonians, no time-reversal symmetry)

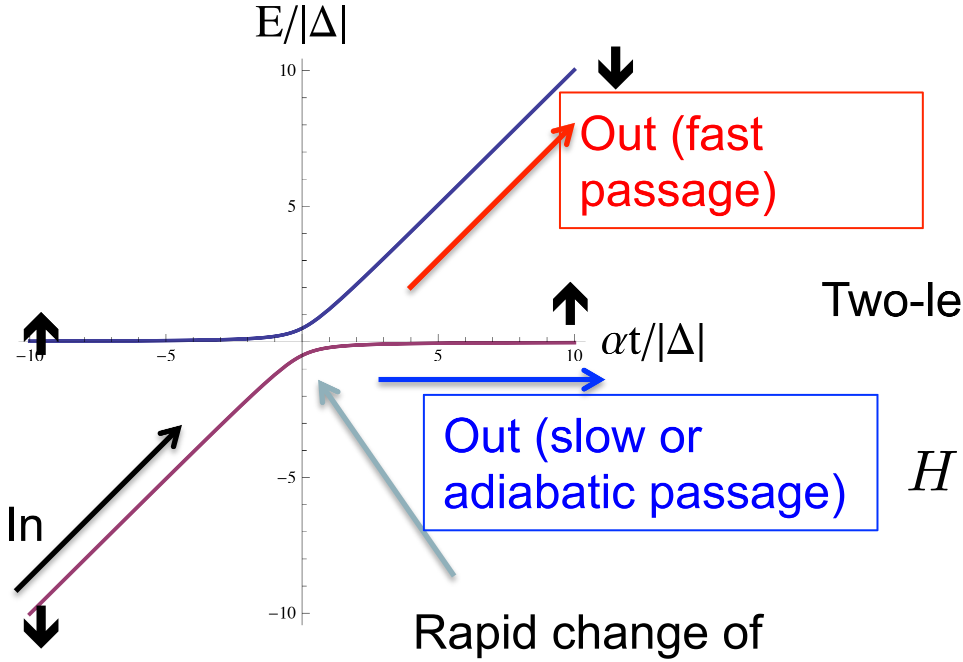
So degeneracies between adiabatic states are very unusual, occuring on surfaces of codimension two (or three) in nuclear coordinate space. In one dimension they are *avoided*.

The problem with degeneracies

Define a non-adiabatic coupling vector

$$\mathbf{d}_{mn}(\mathbf{R}) = \langle \psi_m(\mathbf{R}) | \nabla_{\mathbf{R}} \psi_n(\mathbf{R}) \rangle = \frac{\langle \psi_m | \nabla_{\mathbf{R}} \hat{H}_{\mathrm{e,eff}} | \psi_n \rangle}{E_m(\mathbf{R}) - E_n(\mathbf{R})}$$

Diverges near degeneracies



Out (fast passage)

Out (slow or adiabatic passage)

In

Rapid change of adiabatic (BO)state

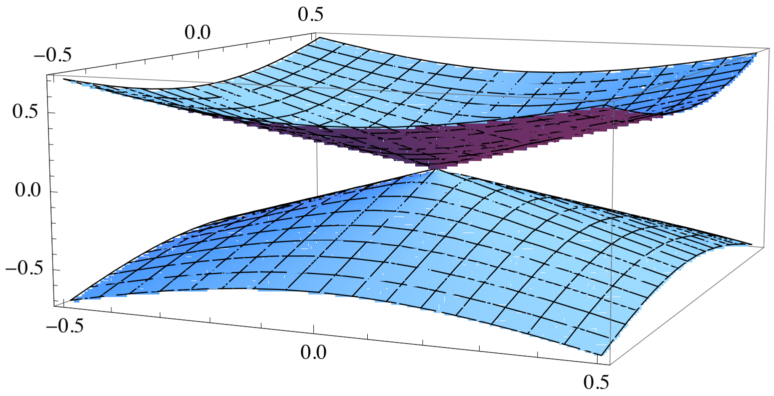
Two-level example:

$$H = \begin{array}{c} \\ \\ \end{array}\begin{array}{cc} \uparrow & \downarrow \end{array}$$

$$\begin{array}{cc} \uparrow & \downarrow \\ \end{array} \quad H = \begin{pmatrix} 0 & \Delta^*/2 \\ \Delta/2 & \alpha t \end{pmatrix}$$

Conical intersections

For a system with time reversal symmetry in two dimensions the intersection is at a single point in coordinate space



In higher dimensions the branching space is translated through a *seam* of dimension *n*-2

Many subtleties in adiabatic description; see Yarkony *Rev Mod Phys* **68** 985 (1996)

After traversing the seam, at least two adiabatic states contribute to total state, which becomes

$$|\Psi\rangle \approx \sum_n c_n(t)|\psi_n(\overline{\mathbf{R}}_n)\rangle \otimes |\chi(\overline{\mathbf{R}}_n)\rangle \neq \left(\sum_n c_n(t)|\psi_n(\overline{\mathbf{R}}_n)\rangle\right) \otimes |\chi(\overline{\mathbf{R}})\rangle$$

Different forces from different states, so different semi-classical paths dominate

Entangled state, not separable into electron and nuclear parts

The message

Conical intersections (or avoided crossings) break Ehrenfest, just as they break Born-Oppenheimer dynamics

Forces and energy transfer

Exact heating rate for ions is

$$\partial_t \langle \hat{T}_{\mathrm{ion}} \rangle = \sum_I \langle \frac{\hat{\mathbf{P}}_I}{M_I} \cdot \hat{\mathbf{F}}_I \rangle$$

but in Ehrenfest approximation it becomes

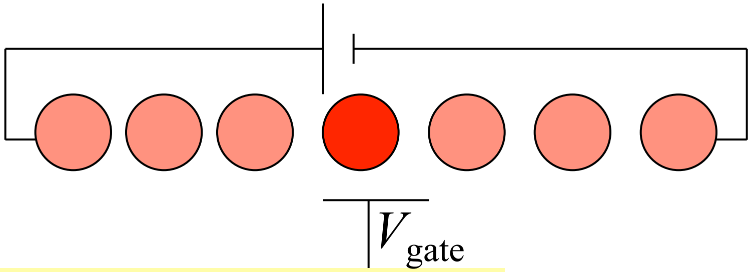
$$\sum_I \frac{\overline{\mathbf{P}}_I}{M_I} \cdot \langle \hat{\mathbf{F}}_I \rangle_{\mathrm{e}}$$

Average force on ions from electronic system, all fluctuations averaged away

Hence lack of spontaneous emission from electronic states in Ehrenfest approximation (Foulkes talk)

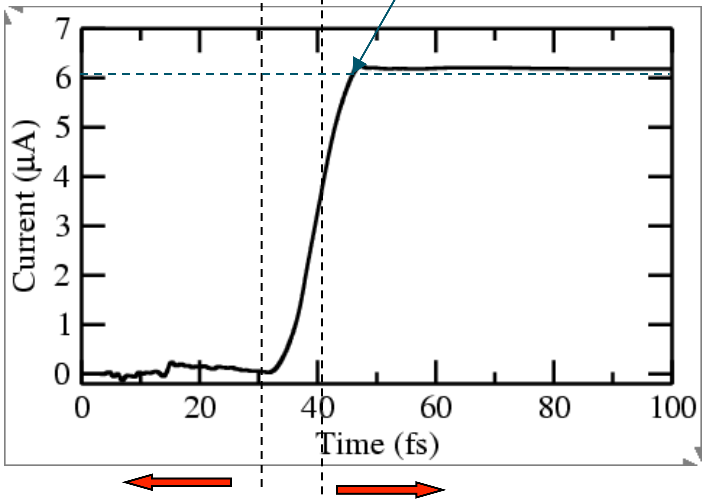
Example: dynamics of current-induced heating

Tight-binding model of a conducting chain:



Static atoms:

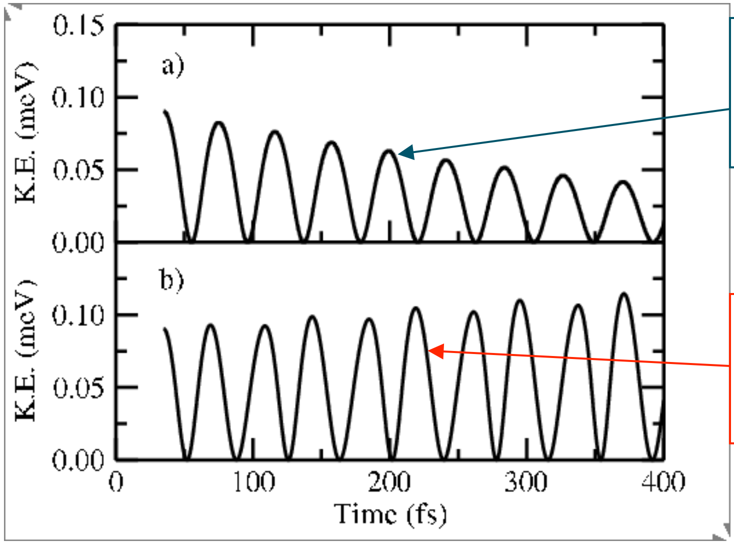
Landauer value



V_{bias}=0

V_{bias}=1.0V

Dynamic atoms ($T_{initial}$=300K)



V_{bias}=0.1V (cooling)

V_{bias}=1.0V (heating)

Horsfield *et al. J. Phys. Cond. Matt.* **16** 3609 (2004)

Beyond Ehrenfest? Several classes of method

- Some methods based on Born-Oppenheimer surfaces and transitions between them
- Others directly approximate the full evolution equations
- Some can be viewed as both
- I will discuss
  - Surface hopping
  - Mixed quantum-classical dynamics
  - ‘Frozen gaussians’ and ‘ab initio quantum molecular dynamics’

Explicit inclusion of fluctuating forces from electronic degrees of freedom: next talk

Surface hopping

Consider adiabatic electronic states (depending parametrically on nuclear coordinates) $|\psi_n(\mathbf{R})\rangle$

Use non-adiabatic coupling vector

$$\mathbf{d}_{mn}(\mathbf{R}) = \langle \psi_m(\mathbf{R}) | \nabla_{\mathbf{R}} \psi_n(\mathbf{R}) \rangle$$

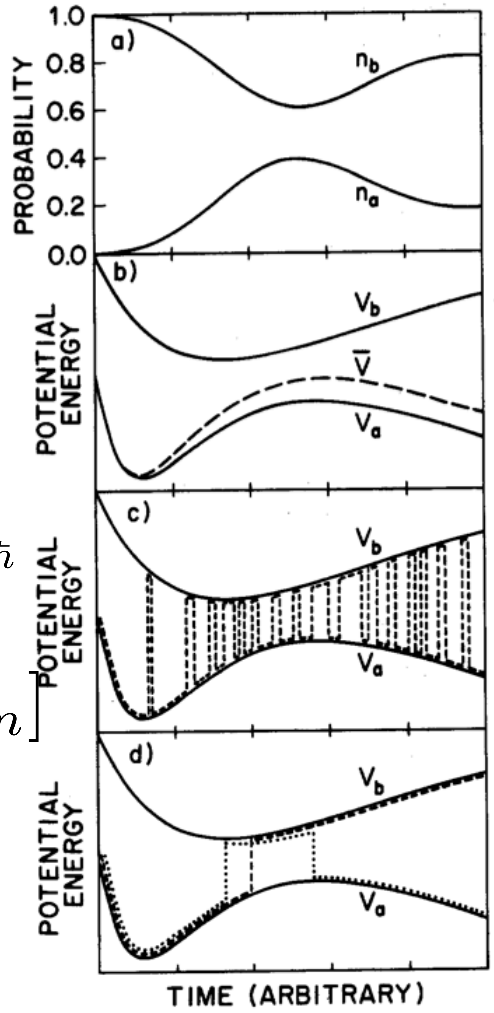
to evolve electronic density operator at a given nuclear position

$$\hat{\rho}_\mathrm{e} = \sum_{n,m} \rho_{nm}(t) |\psi_n(\mathbf{R})\rangle\langle\psi_m(\mathbf{R})| \mathrm{e}^{-\mathrm{i}(E_n - E_m)t/\hbar}$$

$$\Rightarrow \partial_t \rho_{nn} = -2 \sum_m \Re[\rho^*_{nm} \dot{\mathbf{R}} \cdot \mathbf{d}_{nm}]$$

Population of adiabatic state *n*

Transition rate *b*$_{nm}$ from *n* to *m*



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

Surface hopping (2)

Seek the hopping rate that gives the fewest possible transitions between adiabatic states consistent with this expression: hop with probability

$$g_{nm} = \frac{b_{nm}}{\rho_{nn}}$$

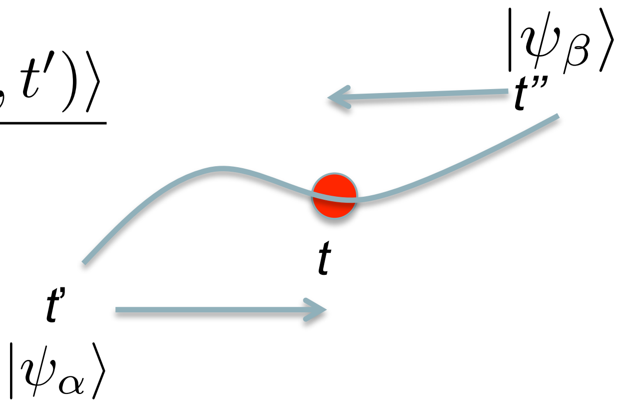
Minimal switching criterion

If the hop *n*➔*m* happens, velocities are altered in order to conserve total (nuclear + electronic) energy by adding a correction in the direction of $\mathbf{d}_{nm}(\mathbf{R})$

This correction can be derived from a path-integral approach to the dynamics due to Pechukas:

$$M_I \ddot{\mathbf{R}}_I(t) = -\Re \frac{\langle \tilde{\psi}_\beta(t,t'')) | \nabla_{\mathbf{R}_I} \hat{H}_{\mathrm{e,eff}} | \tilde{\psi}_\alpha(t,t') \rangle}{\langle \tilde{\psi}_\beta(t,t'') | \tilde{\psi}_\alpha(t,t') \rangle}$$

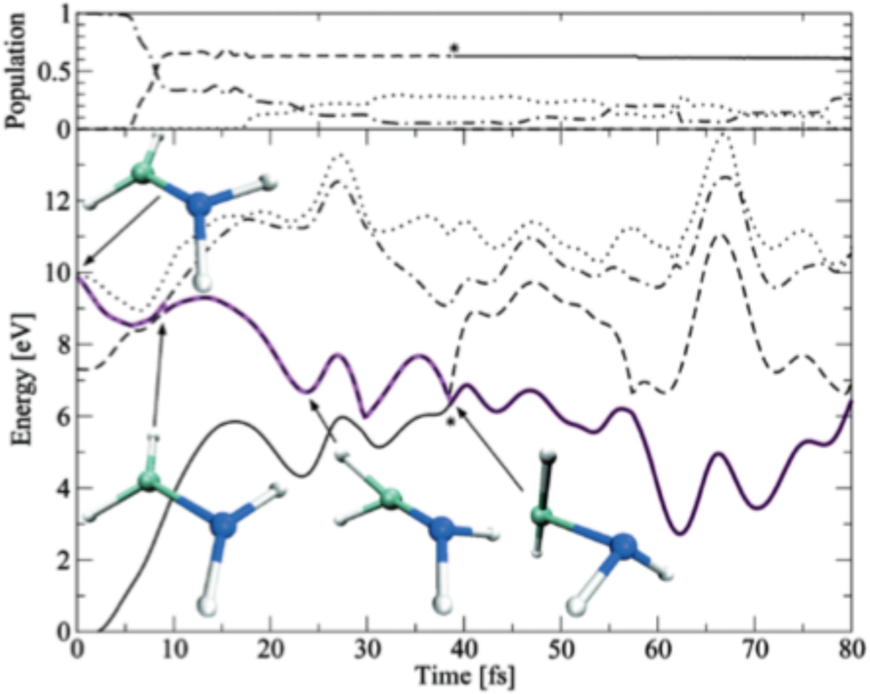
(non-local in time, so difficult to implement in full)

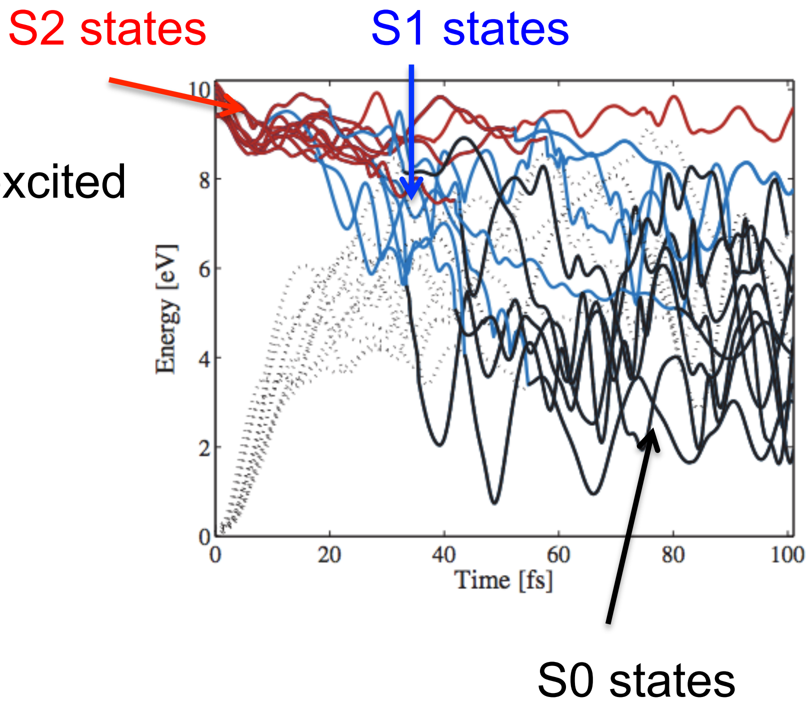


Coker and Xiao *J. Chem. Phys.* **102** 496 (1995)
Pechukas *Phys Rev* **181** 176 and 184 (1969)

Example

Response to photoexcitation of the second excited state (S2) of $CH_2NH_2^+$





S2 states

S1 states

S0 states

Tapavicza *et al. Phys. Rev. Lett.* **98** 023001 (2007)

Advantages and disadvantages

- Advantages
  - Efficient to implement
  - Retains some correlation between nuclear and electronic motions
  - Can be coupled with a range of electronic structure techniques

- Disadvantages
  - Assumes total loss of phase information after each surface-hopping event
  - Some procedures are *ad hoc*
  - Difficuly to improve systematically

Summary and conclusions

- Ehrenfest is a well-defined approximation with a wide range of applicability
- But it breaks down in important situations:
  - When considering energy transfer from hot electrons to cold ions
  - When working near conical intersections or avoided crossings
- Importance of adiabatic coupling vector to control approximations
- A range of approaches to the coupled electron-nuclear problem exist, each with its own advantages and disadvantages