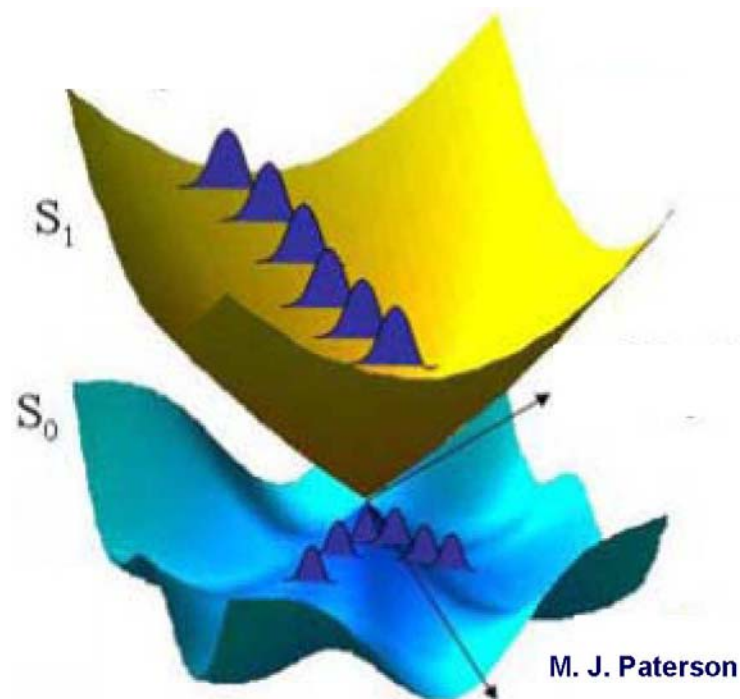


Mixed Quantum-Classical Dynamics: I. Fundamentals

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



1. Adiabatic Dynamics

- a. The Born-Oppenheimer Approximation
- b. Quantum Mechanical Nuclear Motion
- c. Semiclassical Nuclear Motion
- d. Classical Nuclear Motion

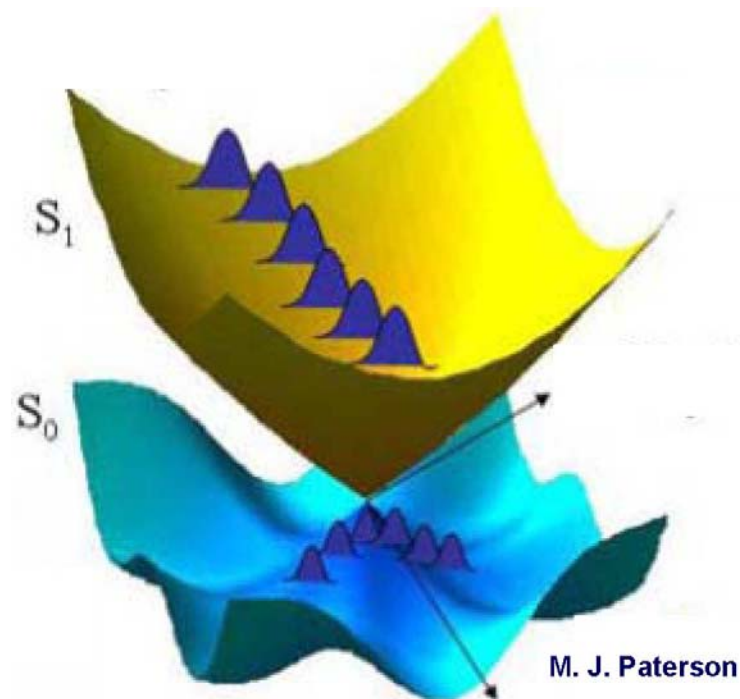
2. Beyond Born-Oppenheimer

- a. Nonadiabatic Interactions
- b. Avoided Crossings and Conical Intersections
- c. The Massey Criterion and the
Landau-Zener Approximation

Mixed Quantum-Classical Dynamics: II. Methods

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



3. Ehrenfest Dynamics

- The Self-Consistent Field Approximation
- Ehrenfest Mixed Quantum-Classical Dynamics
- Appraisal of the Ehrenfest Method

4. Surface Hopping Dynamics

- de Broglie-Bohm Derivation
- Fewest Switches Algorithm
- Appraisal of the Surface Hopping Method

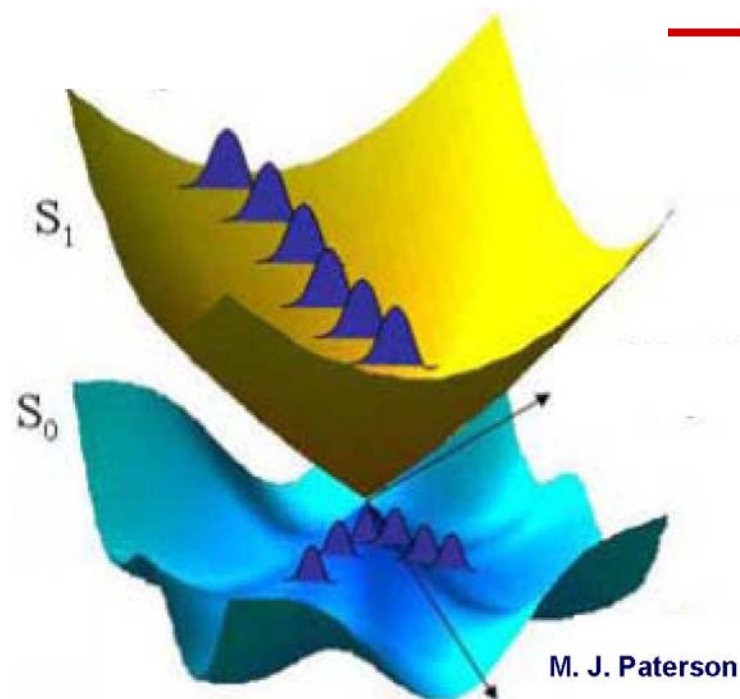
5. Mixed Quantum-Classical Nuclear Dynamics

- Time Scale Separation
- Proton Transfer in Solution
- Prognosis

Mixed Quantum-Classical Dynamics: I. Fundamentals

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



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1a. The Born-Oppenheimer Approximation

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



Objective: $i \hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) = \mathcal{H}(\mathbf{r}, \mathbf{R}) \Psi(\mathbf{r}, \mathbf{R}, t)$

\mathbf{r} = electrons \mathbf{R} = nuclei

$$\mathcal{H} = - \sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \nabla_{R_{\alpha}}^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_r^2 + V(\mathbf{r}, \mathbf{R})$$

1a. The Born-Oppenheimer Approximation

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



Objective: $i \hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) = \mathcal{H}(\mathbf{r}, \mathbf{R}) \Psi(\mathbf{r}, \mathbf{R}, t)$

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→ $\mathcal{H} = - \sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \nabla_{R_{\alpha}}^2 + \mathcal{H}_{el}(\mathbf{r}, \mathbf{R})$

1a. The Born-Oppenheimer Approximation

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



Define Adiabatic (Born-Oppenheimer) Potential Energy Surfaces $\mathcal{E}_j(\mathbf{R})$
and Electronic Wave Functions $\Phi_j(\mathbf{r};\mathbf{R})$

Fixed nuclear positions \mathbf{R} :

$$\mathcal{H}_{el}(\mathbf{r}, \mathbf{R}) \Phi_j(\mathbf{r}; \mathbf{R}) = \mathcal{E}_j(\mathbf{R}) \Phi_j(\mathbf{r}; \mathbf{R})$$

1a. The Born-Oppenheimer Approximation

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and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008

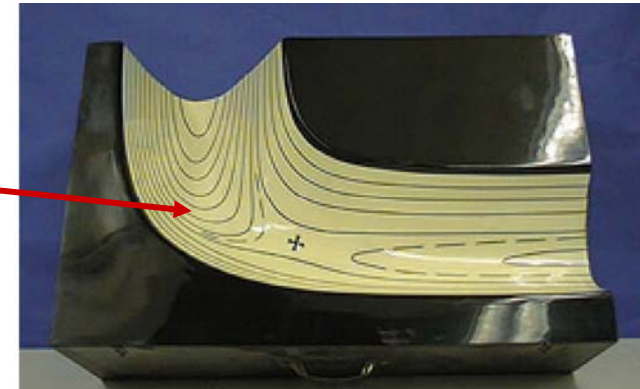


Define Adiabatic (Born-Oppenheimer) Potential Energy Surfaces $\mathcal{E}_j(\mathbf{R})$
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Fixed nuclear positions \mathbf{R} :

$$\mathcal{H}_{el}(\mathbf{r}, \mathbf{R}) \Phi_j(\mathbf{r}; \mathbf{R}) = \underbrace{\mathcal{E}_j(\mathbf{R})}_{\text{Adiabatic (Born-Oppenheimer) Potential Energy Surfaces}} \Phi_j(\mathbf{r}; \mathbf{R})$$

Adiabatic (Born-Oppenheimer)
Potential Energy Surfaces



1a. The Born-Oppenheimer Approximation

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



Define Adiabatic (Born-Oppenheimer) Potential Energy Surfaces $\mathcal{E}_j(\mathbf{R})$
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Fixed nuclear positions \mathbf{R} :

$$\mathcal{H}_{el}(\mathbf{r}, \mathbf{R}) \underbrace{\Phi_j(\mathbf{r}; \mathbf{R})}_{\text{Adiabatic (Born-Oppenheimer) electronic wave functions}} = \mathcal{E}_j(\mathbf{R}) \underbrace{\Phi_j(\mathbf{r}; \mathbf{R})}_{\text{Adiabatic (Born-Oppenheimer) electronic wave functions}}$$

Adiabatic (Born-Oppenheimer)
electronic wave functions

1a. The Born-Oppenheimer Approximation

Mixed Quantum-Classical Dynamics: Foundations and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



Exact Treatment:

Expand total wave function in terms of complete set of adiabatic wave functions:

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

Born-Oppenheimer Approximation = Adiabatic Approximation:

Approximate total wave function by a single product:

(Single adiabatic electronic state)

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \Phi_j(\mathbf{r}; \mathbf{R}) \Omega_j(\mathbf{R}, t)$$

1a. The Born-Oppenheimer Approximation

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008

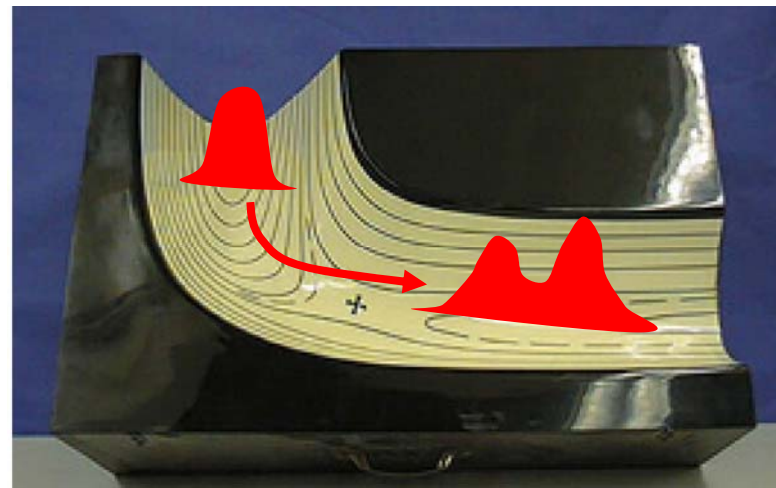


Born-Oppenheimer Approximation:

$$\Psi(\mathbf{r}, \mathbf{R}, t) \cong \Phi_j(\mathbf{r}; \mathbf{R}) \Omega_j(\mathbf{R}, t)$$

Substitute into TDSE, multiply from left by $\Phi_j^*(\mathbf{r}; \mathbf{R})$, integrate over \mathbf{r} :

$$i\hbar \frac{\partial}{\partial t} \Omega_j(\mathbf{R}, t) \cong \left[- \sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \nabla_{R_{\alpha}}^2 + \mathcal{E}_j(\mathbf{R}) \right] \Omega_j(\mathbf{R}, t)$$

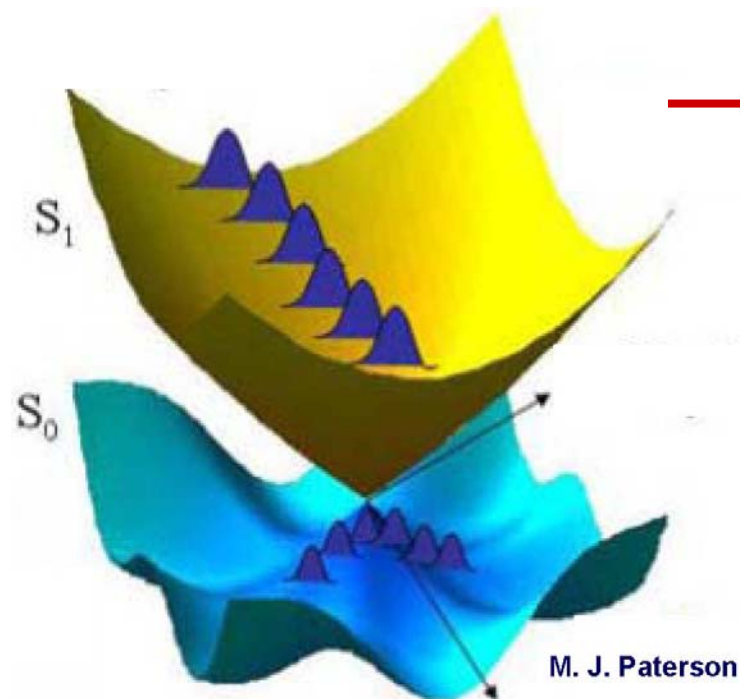


Adiabatic Potential
Energy Surface

Mixed Quantum-Classical Dynamics: I. Fundamentals

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



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1b. Quantum Mechanical Nuclear Motion

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

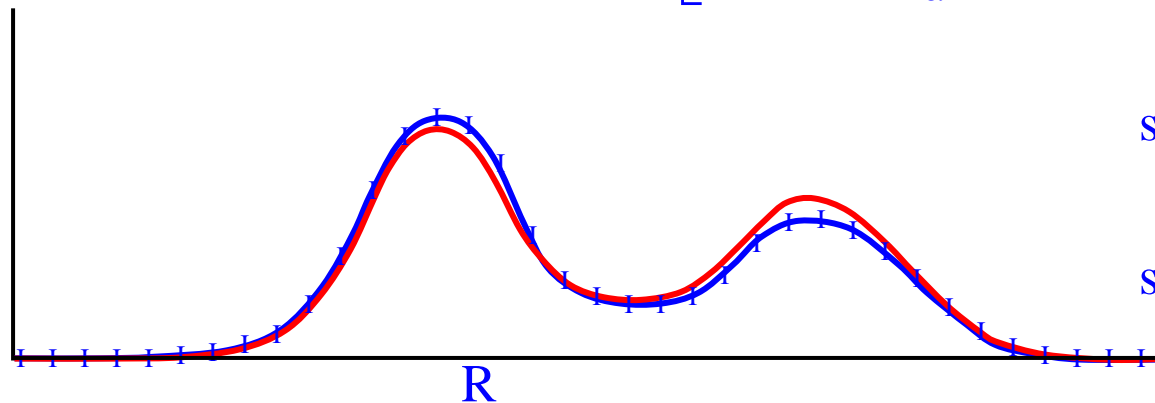
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$$i\hbar \frac{\partial}{\partial t} \Omega(\mathbf{R}, t) \cong \left[- \sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \nabla_{R_{\alpha}}^2 + \mathcal{E}(\mathbf{R}) \right] \Omega(\mathbf{R}, t)$$

Propagate wave function:

$$\begin{aligned} \Omega(\mathbf{R}, t + \delta t) &\approx \Omega(\mathbf{R}, t) + \delta t \frac{\partial}{\partial t} \Omega(\mathbf{R}, t) + \frac{(\delta t)^2}{2} \frac{\partial^2}{\partial t^2} \Omega(\mathbf{R}, t) + \dots \\ &\approx \Omega(\mathbf{R}, t) - \frac{i\delta t}{\hbar} \left[- \sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \nabla_{R_{\alpha}}^2 + \mathcal{E}(\mathbf{R}) \right] \Omega(\mathbf{R}, t) \end{aligned}$$



see: Feit and Fleck, split
operator method

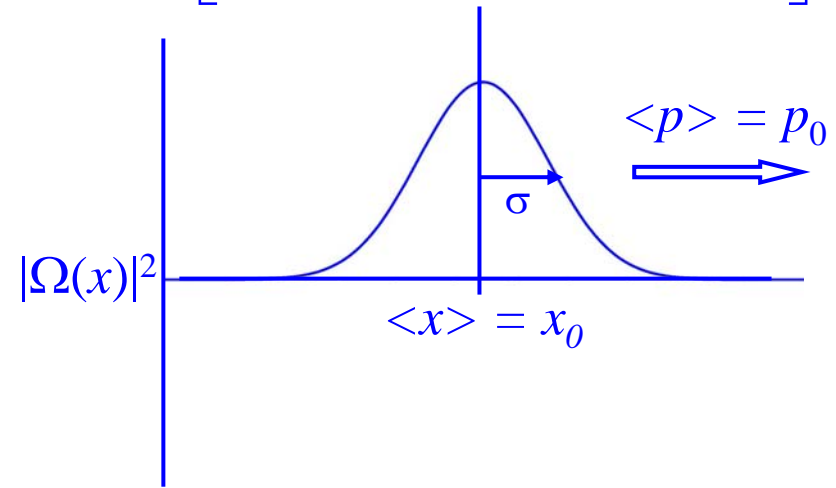
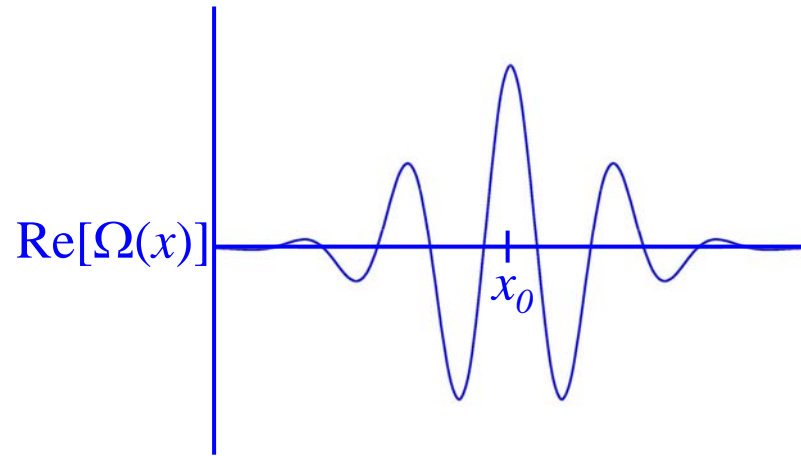
see: Kosloff, fourier
transform method

1b. Quantum Mechanical Nuclear Motion

Mixed Quantum-Classical Dynamics: Foundations and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



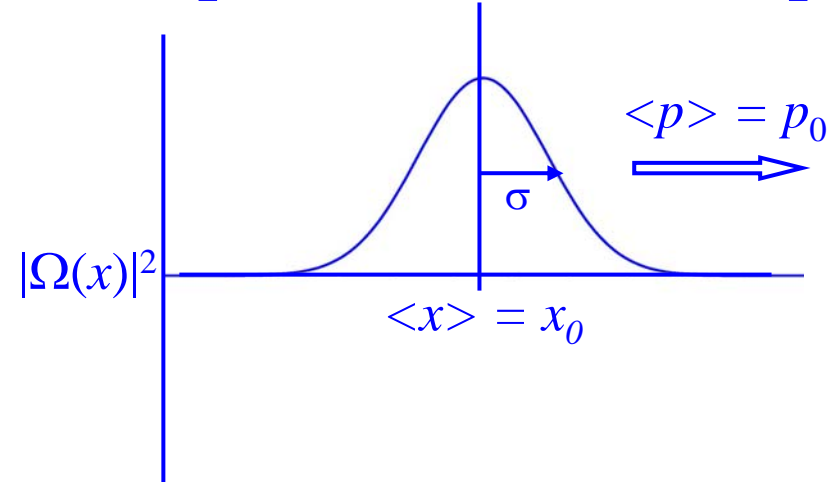
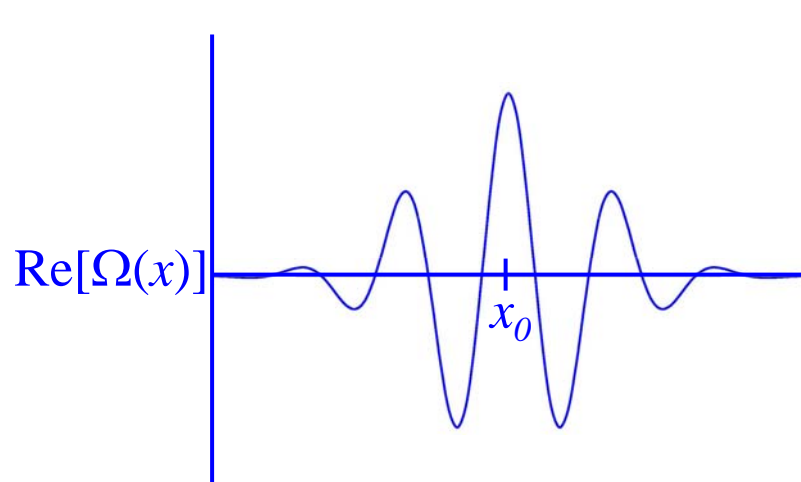
Gaussian wave packet:
$$\Omega(x) = (\sigma^2 \pi)^{-1/4} \exp \left[-\frac{(x-x_0)^2}{2\sigma^2} + ip_0(x-x_0)/\hbar \right]$$



1b. Quantum Mechanical Nuclear Motion



Gaussian wave packet:
$$\Omega(x) = (\sigma^2 \pi)^{-1/4} \exp \left[-\frac{(x-x_0)^2}{2\sigma^2} + ip_0(x-x_0)/\hbar \right]$$



$$\Delta x = \left[\langle x^2 \rangle - \langle x \rangle^2 \right]^{1/2} = \left[\int_{-\infty}^{\infty} \Omega^*(x) x^2 \Omega(x) dx - x_0^2 \right]^{1/2} = \sigma / \sqrt{2}$$

$$\Delta p = \left[\langle p^2 \rangle - \langle p \rangle^2 \right]^{1/2} = \left[\int_{-\infty}^{\infty} \Omega^*(x) \left[-\hbar^2 \frac{d^2}{dx^2} \right] \Omega(x) dx - p_0^2 \right]^{1/2} = \hbar / \sigma \sqrt{2}$$

→ $\Delta x \Delta p = \hbar / 2$ uncertainty principle

1b. Quantum Mechanical Nuclear Motion

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008

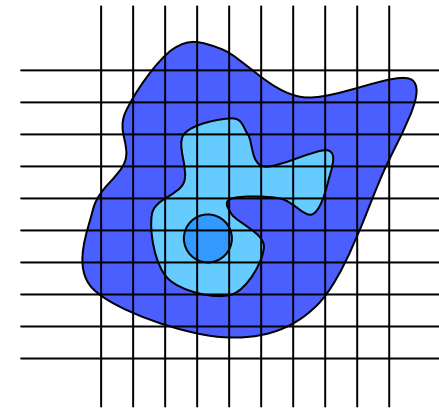


Ultimate Solution:

Treat all electrons and nuclei by quantum mechanics

However:

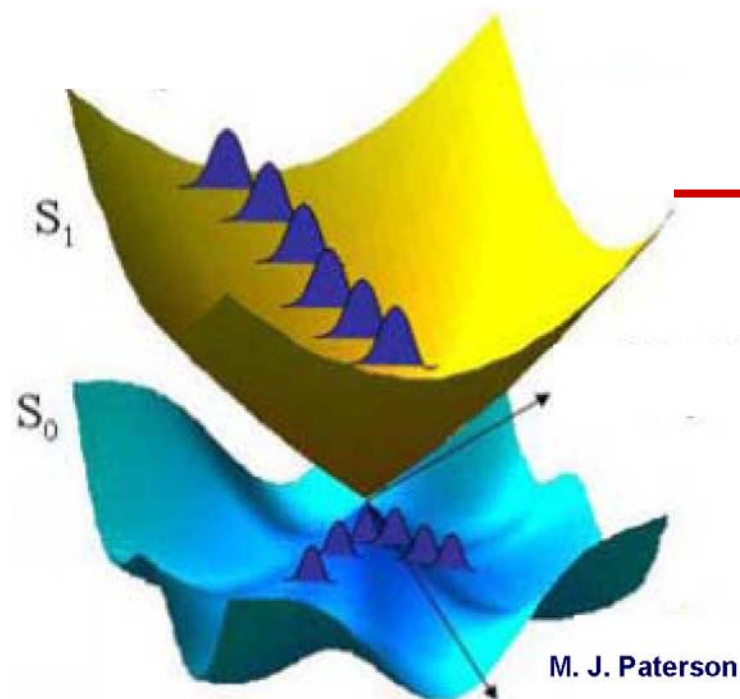
Quantum wavepacket propagation on a grid
scales prohibitively with dimensionality



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Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



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1c. Semiclassical Nuclear Motion



Gaussian wave packet:
$$\Omega(x) = (\sigma^2 \pi)^{-1/4} \exp \left[-\frac{(x-x_0)^2}{2\sigma^2} + ip_0(x-x_0)/\hbar \right]$$

$$\begin{aligned} \frac{d}{dt} \langle p \rangle &= \left\langle \frac{d\Omega^*}{dt} \left| -i\hbar \frac{d}{dx} \right| \Omega \right\rangle + \left\langle \Omega^* \left| -i\hbar \frac{d}{dx} \right| \frac{d\Omega}{dt} \right\rangle \\ &= \left\langle \frac{i}{\hbar} \mathcal{H} \Omega^* \left| -i\hbar \frac{d}{dx} \right| \Omega \right\rangle - \left\langle \Omega^* \left| -i\hbar \frac{d}{dx} \right| \frac{i}{\hbar} \mathcal{H} \Omega \right\rangle \\ &= \left\langle \mathcal{H} \Omega^* \left| \frac{d\Omega}{dx} \right\rangle - \left\langle \Omega^* \left| \frac{d\mathcal{H}}{dx} \right| \Omega \right\rangle - \left\langle \Omega^* \left| \mathcal{H} \right| \frac{d\Omega}{dx} \right\rangle \\ &= - \left\langle \Omega^* \left| \frac{d\mathcal{H}}{dx} \right| \Omega \right\rangle = - \left\langle \Omega^* \left| \frac{dV(x)}{dx} \right| \Omega \right\rangle = - \left\langle \frac{dV(x)}{dx} \right\rangle \end{aligned}$$

similarly,
$$\frac{d}{dt} \langle x \rangle = \langle p \rangle / m$$

1c. Semiclassical Nuclear Motion



Gaussian wave packet:
$$\Omega(x) = (\sigma^2 \pi)^{-1/4} \exp \left[-\frac{(x-x_0)^2}{2\sigma^2} + ip_0(x-x_0)/\hbar \right]$$

Quantum (Ehrenfest Theorem)

$$\frac{d}{dt} \langle x \rangle = \langle p \rangle / m$$

$$\frac{d}{dt} \langle p \rangle = - \left\langle \frac{dV(x)}{dx} \right\rangle$$

let $V(x) = Ax^n$

$$\frac{dV(x)}{dx} = nAx^{n-1}$$

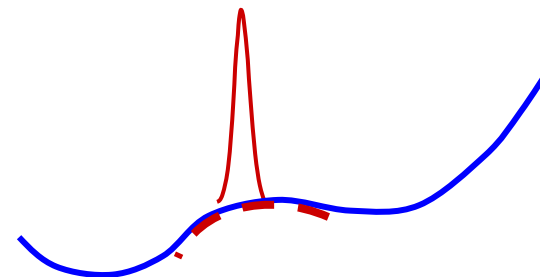
$$\langle x^{n-1} \rangle \neq \langle x \rangle^{n-1} \quad \text{for } n > 2$$

Classical (Hamilton's Equations)

$$\frac{d}{dt} x_0 = p_0 / m$$

$$\frac{d}{dt} p_0 = - \frac{dV(x_0)}{dx_0}$$

Semiclassical “Frozen Gaussian
Method” E. J. Heller



1c. Semiclassical Nuclear Motion

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008

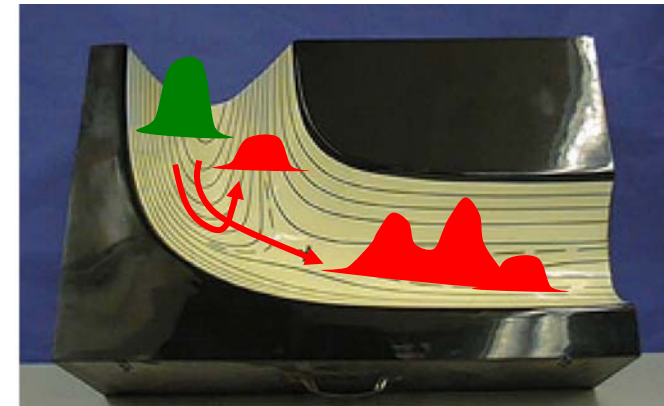


Limitation to frozen Gaussian approximation:

Gaussian wavepacket deforms and
splits into many parts



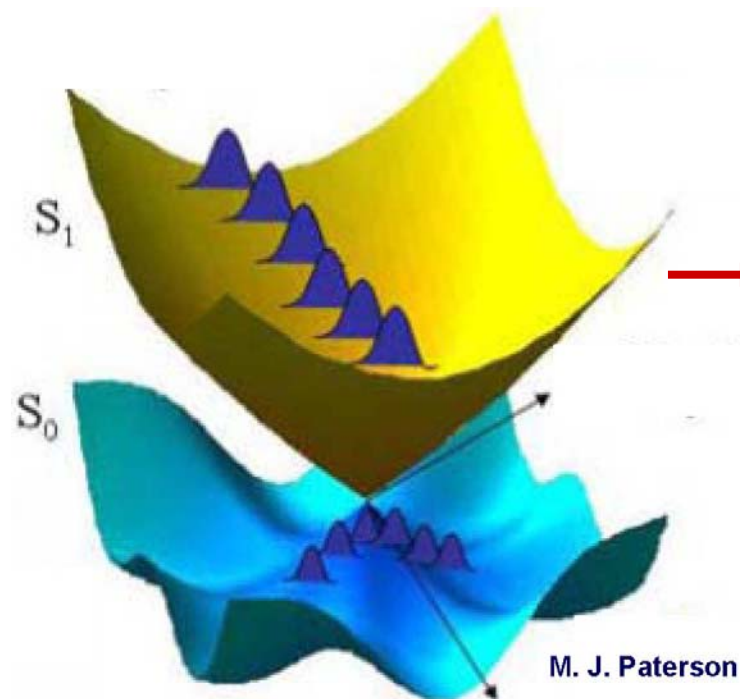
inaccurate for anharmonic
potential energy surfaces
(except for very short times)



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Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



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1d. Classical Nuclear Motion

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



Classical (Hamilton's Equations)

$$\frac{d}{dt} x_0 = p_0 / m$$

$$\frac{d}{dt} p_0 = -\frac{dV(x_0)}{dx_0}$$

Classical Molecular Dynamics

$$\frac{d}{dt} \mathbf{R} = \mathbf{p} / m$$

$$\frac{d}{dt} \mathbf{p} = -\frac{dE(\mathbf{R})}{d\mathbf{R}}$$

1. Empirical “classical” force fields
2. Semiempirical potential energy surfaces
3. Direct “on-the-fly” Dynamics
4. Car-Parrinello dynamics

1d. Classical Nuclear Motion

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



Direct Dynamics: Adiabatic “on-the-fly” Dynamics

The Hellman – Feynman Theorem for calculating forces:

$$\frac{d}{dR} \mathcal{E}_j(R) = \frac{d}{dR} \left\langle \Phi_j(r; R) \left| \mathcal{H}_{el}(r, R) \right| \Phi_j(r, R) \right\rangle_r$$

$$\text{subject to } \left\langle \Phi_j(r; R) \left| \Phi_j(r; R) \right\rangle_r = 1$$

1d. Classical Nuclear Motion

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



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$$\text{subject to } \left\langle \Phi_j(r; R) \left| \Phi_j(r; R) \right\rangle_r = 1$$

$$\text{let } \mathcal{H}_{el}(r, R) \left| \Phi_j(r; R) \right\rangle = \mathcal{E}_j(R) \left| \Phi_j(r; R) \right\rangle$$

1d. Classical Nuclear Motion



Direct Dynamics: Adiabatic “on-the-fly” Dynamics

The Hellman – Feynman Theorem for calculating forces:

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$$\text{subject to } \left\langle \Phi_j(r; R) \left| \Phi_j(r; R) \right\rangle_r = 1$$

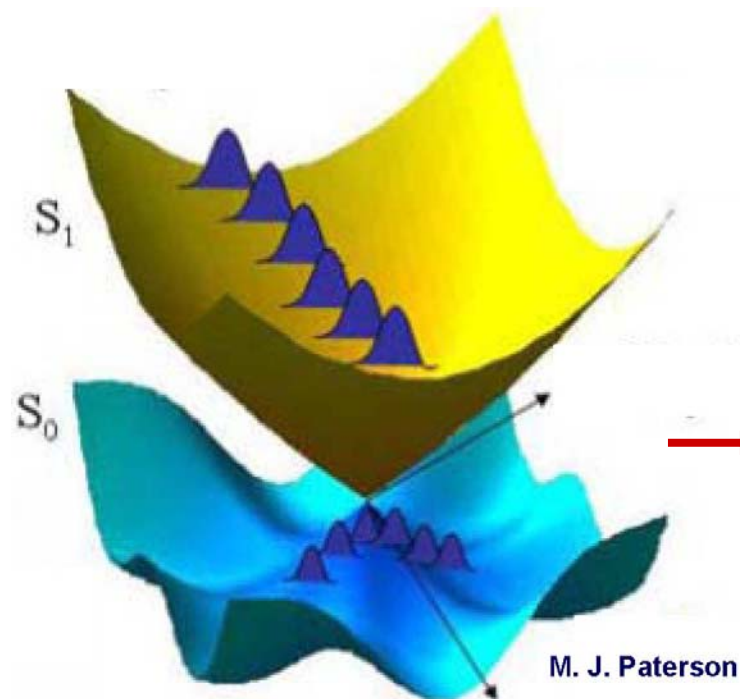
$$\text{let } \mathcal{H}_{el}(r, R) \left| \Phi_j(r; R) \right\rangle = \mathcal{E}_j(R) \left| \Phi_j(r; R) \right\rangle$$

$$\begin{aligned} \rightarrow \frac{d}{dR} \mathcal{E}_j(R) &= \left\langle \Phi_j(r; R) \left| \frac{d\mathcal{H}_{el}(r, R)}{dR} \right| \Phi_j(r; R) \right\rangle_r \\ &+ \left\langle \frac{d}{dR} \Phi_j(r; R) \left| \mathcal{H}_{el}(r, R) \right| \Phi_j(r; R) \right\rangle_r + \left\langle \Phi_j(r; R) \left| \mathcal{H}_{el}(r, R) \right| \frac{d}{dR} \Phi_j(r; R) \right\rangle_r \end{aligned}$$

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Summer School, Vienna, 7 – 12 July, 2008



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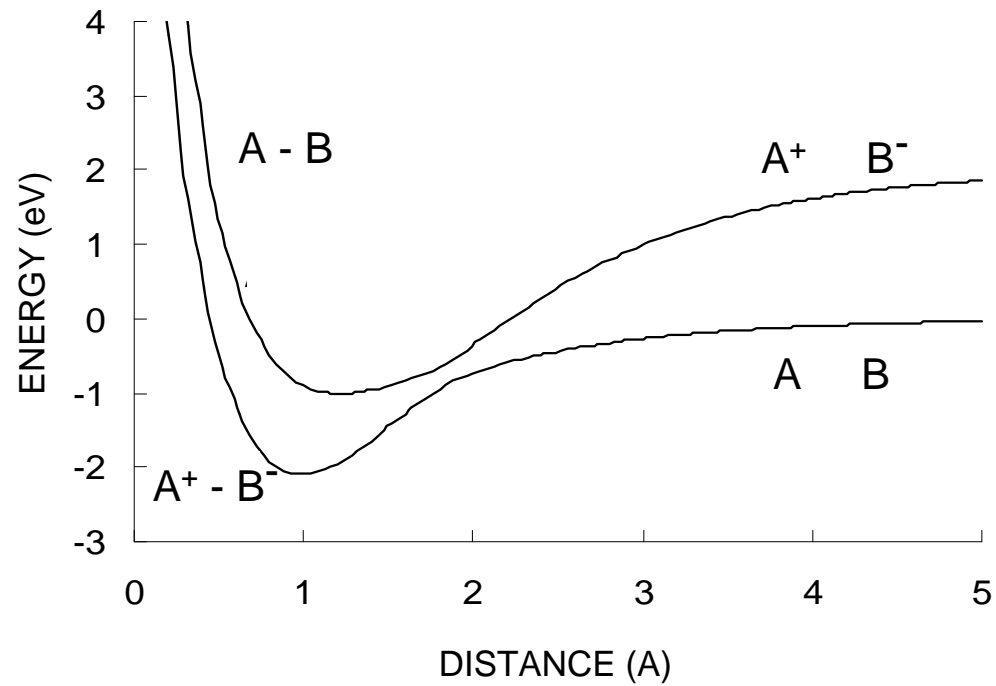
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- Avoided Crossings and Conical Intersections
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2a. Nonadiabatic Interactions

Mixed Quantum-Classical Dynamics: Foundations and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



Ionic Molecule
(alkali halide)

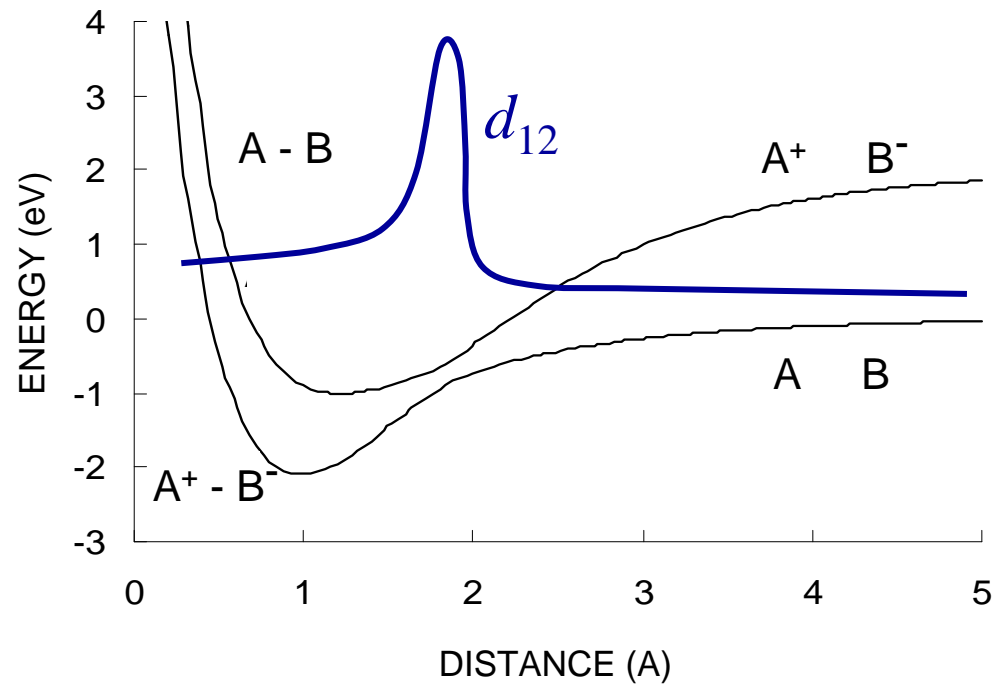


2a. Nonadiabatic Interactions

Mixed Quantum-Classical Dynamics: Foundations and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



Ionic Molecule
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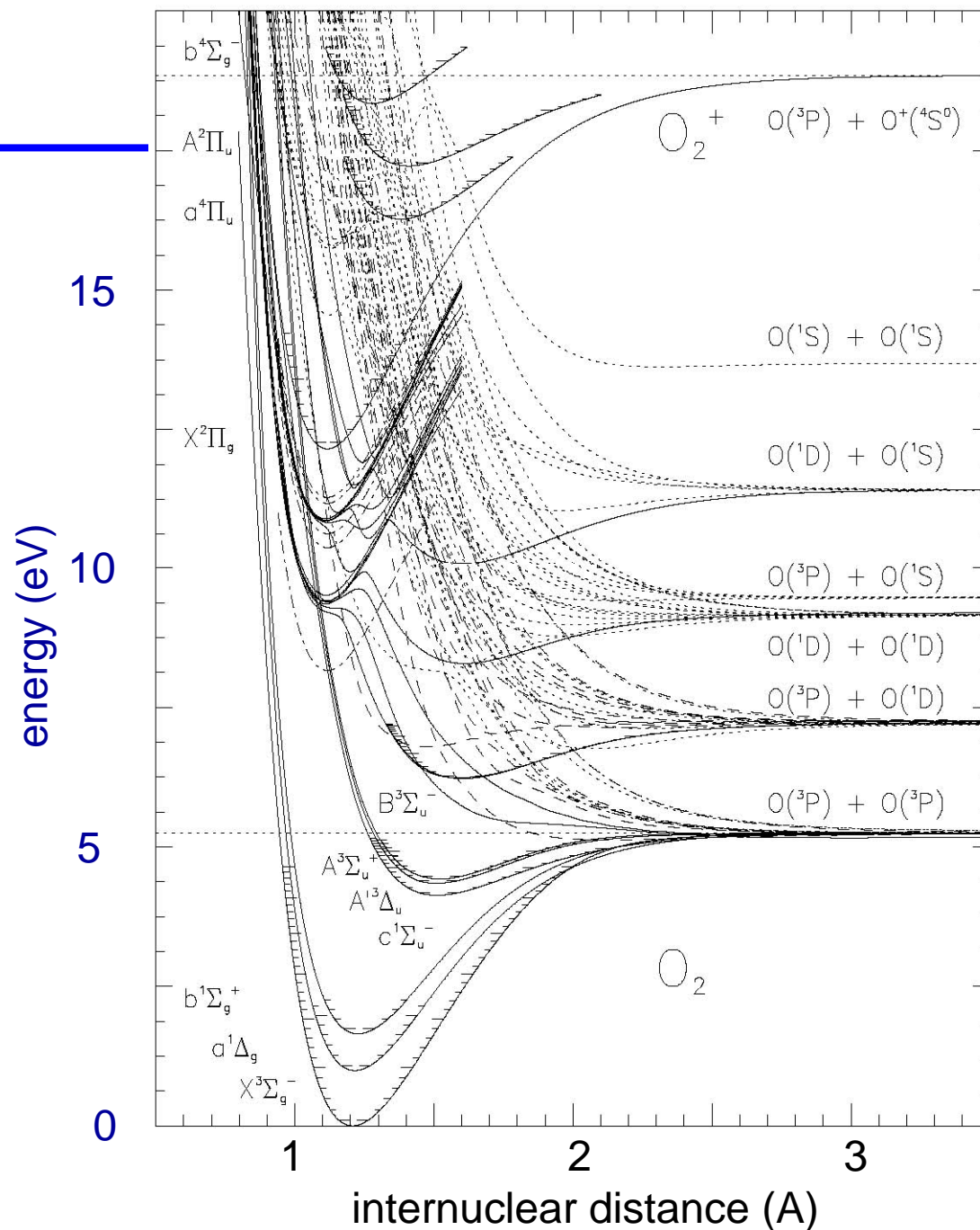


Nonadiabatic Coupling:
$$d_{12} = \langle \varphi_1 | \partial \varphi_2 / \partial x \rangle$$

2a. Nonadiabatic Interactions

Potential Energy Curves for the Oxygen Molecule

- electron transfer
- photochemistry
- laser-induced chemistry
- reactions of open shells
- energetic impacts
- radiationless transitions
- spin-orbit transitions
- reactions at metal surfaces
-
-
-



2a. Nonadiabatic Interactions

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



$$\Psi(\mathbf{r}, \mathbf{R}) \approx \cancel{\Phi_j(\mathbf{r}; \mathbf{R}) \Omega_j(\mathbf{R})} \rightarrow \Psi(\mathbf{r}, \mathbf{R}) = \sum_i \Phi_i(\mathbf{r}; \mathbf{R}) \Omega_i(\mathbf{R})$$

2a. Nonadiabatic Interactions



$$\Psi(\mathbf{r}, \mathbf{R}) \approx \Phi_j(\mathbf{r}; \mathbf{R}) \Omega_j(\mathbf{R}) \rightarrow \Psi(\mathbf{r}, \mathbf{R}) = \sum_i \Phi_i(\mathbf{r}; \mathbf{R}) \Omega_i(\mathbf{R})$$

Substitute into TISE, multiply from left by $\Phi_j^*(\mathbf{r}; \mathbf{R})$ integrate over \mathbf{r} :

$$\begin{aligned} -\frac{\hbar^2}{2} \sum_{\alpha} M_{\alpha}^{-1} \nabla_{R_{\alpha}}^2 \Omega_j(\mathbf{R}) + \mathcal{E}_j(\mathbf{R}) \Omega_j(\mathbf{R}) - E \Omega_j(\mathbf{R}) = \\ -\frac{\hbar^2}{2} \sum_i D_{ji}(\mathbf{R}) \Omega_i(\mathbf{R}) + \hbar^2 \sum_{i \neq j} \mathbf{d}_{ji}(\mathbf{R}) \cdot \nabla_{R_{\alpha}} \Omega_i(\mathbf{R}) \end{aligned}$$

2a. Nonadiabatic Interactions



$$\Psi(\mathbf{r}, \mathbf{R}) \approx \Phi_j(\mathbf{r}; \mathbf{R}) \Omega_j(\mathbf{R}) \rightarrow \Psi(\mathbf{r}, \mathbf{R}) = \sum_i \Phi_i(\mathbf{r}; \mathbf{R}) \Omega_i(\mathbf{R})$$

Substitute into TISE, multiply from left by $\Phi_j^*(\mathbf{r}; \mathbf{R})$ integrate over \mathbf{r} :

$$\begin{aligned} -\frac{\hbar^2}{2} \sum_{\alpha} M_{\alpha}^{-1} \nabla_{R_{\alpha}}^2 \Omega_j(\mathbf{R}) + \mathcal{E}_j(\mathbf{R}) \Omega_j(\mathbf{R}) - E \Omega_j(\mathbf{R}) = \\ -\frac{\hbar^2}{2} \sum_i D_{ji}(\mathbf{R}) \Omega_i(\mathbf{R}) + \hbar^2 \sum_{i \neq j} \mathbf{d}_{ji}(\mathbf{R}) \cdot \nabla_{R_{\alpha}} \Omega_i(\mathbf{R}) \end{aligned}$$

where nonadiabatic (derivative) couplings are defined by:

$$\mathbf{d}_{ij}(\mathbf{R}) = -\sum_{\alpha} M_{\alpha}^{-1} \int \left\{ \Phi_i^*(\mathbf{r}, \mathbf{R}) \left[\nabla_{R_{\alpha}} \Phi_j(\mathbf{r}, \mathbf{R}) \right] \right\} d\mathbf{r}$$

$$D_{ij}(\mathbf{R}) = -\sum_{\alpha} M_{\alpha}^{-1} \int \left\{ \Phi_i^*(\mathbf{r}, \mathbf{R}) \left[\nabla_{R_{\alpha}}^2 \Phi_j(\mathbf{r}, \mathbf{R}) \right] \right\} d\mathbf{r}$$

1a. The Born-Oppenheimer Approximation

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



Born-Oppenheimer Approximation:

$$\Psi(\mathbf{r}, \mathbf{R}, t) \cong \Phi_j(\mathbf{r}; \mathbf{R}) \Omega_j(\mathbf{R}, t)$$

Substitute into TDSE, multiply from left by $\Phi_j^*(\mathbf{r}; \mathbf{R})$, integrate over \mathbf{r} :

$$i\hbar \frac{\partial}{\partial t} \Omega_j(\mathbf{R}, t) \cong \left[- \sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \nabla_{R_{\alpha}}^2 + \underbrace{\mathcal{E}_j(\mathbf{R}) + D_{jj}(\mathbf{R})}_{\text{Adiabatic Potential Energy Surface}} \right] \Omega_j(\mathbf{R}, t)$$

Adiabatic Potential
Energy Surface

where

$$D_{jj}(\mathbf{R}) = - \sum_{\alpha} M_{\alpha}^{-1} \int \left\{ \Phi_j^*(\mathbf{r}, \mathbf{R}) \left[\nabla_{R_{\alpha}}^2 \Phi_j(\mathbf{r}, \mathbf{R}) \right] \right\} d\mathbf{r}$$

2a. Nonadiabatic Interactions



$$\Psi(\mathbf{r}, \mathbf{R}) \approx \Phi_j(\mathbf{r}; \mathbf{R}) \Omega_j(\mathbf{R}) \rightarrow \Psi(\mathbf{r}, \mathbf{R}) = \sum_i \Phi_i(\mathbf{r}; \mathbf{R}) \Omega_i(\mathbf{R})$$

Substitute into TISE, multiply from left by $\Phi_j^*(\mathbf{r}; \mathbf{R})$ integrate over \mathbf{r} :

$$\begin{aligned} -\frac{\hbar^2}{2} \sum_{\alpha} M_{\alpha}^{-1} \nabla_{R_{\alpha}}^2 \Omega_j(\mathbf{R}) + \mathcal{E}_j(\mathbf{R}) \Omega_j(\mathbf{R}) - E \Omega_j(\mathbf{R}) = \\ -\frac{\hbar^2}{2} \sum_i D_{ji}(\mathbf{R}) \Omega_i(\mathbf{R}) + \hbar^2 \sum_{i \neq j} \mathbf{d}_{ji}(\mathbf{R}) \cdot \nabla_{R_{\alpha}} \Omega_i(\mathbf{R}) \end{aligned}$$

where nonadiabatic (derivative) couplings are defined by:

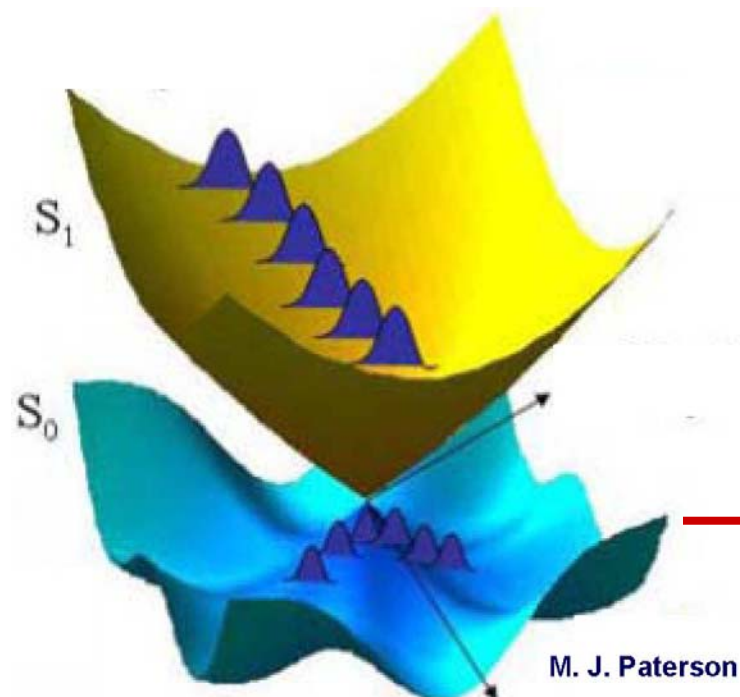
$$\mathbf{d}_{ij}(\mathbf{R}) = -\sum_{\alpha} M_{\alpha}^{-1} \int \left\{ \Phi_i^*(\mathbf{r}, \mathbf{R}) \left[\nabla_{R_{\alpha}} \Phi_j(\mathbf{r}, \mathbf{R}) \right] \right\} d\mathbf{r} \quad \leftarrow$$

$$D_{ij}(\mathbf{R}) = -\sum_{\alpha} M_{\alpha}^{-1} \int \left\{ \Phi_i^*(\mathbf{r}, \mathbf{R}) \left[\nabla_{R_{\alpha}}^2 \Phi_j(\mathbf{r}, \mathbf{R}) \right] \right\} d\mathbf{r}$$

Mixed Quantum-Classical Dynamics: I. Fundamentals

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



1. Adiabatic Dynamics

- a. The Born-Oppenheimer Approximation
- b. Quantum Mechanical Nuclear Motion
- c. Semiclassical Nuclear Motion
- d. Classical Nuclear Motion

2. Beyond Born-Oppenheimer

- a. Nonadiabatic Interactions
- b. Avoided Crossings and Conical Intersections
- c. The Massey Criterion and the Landau-Zener Approximation

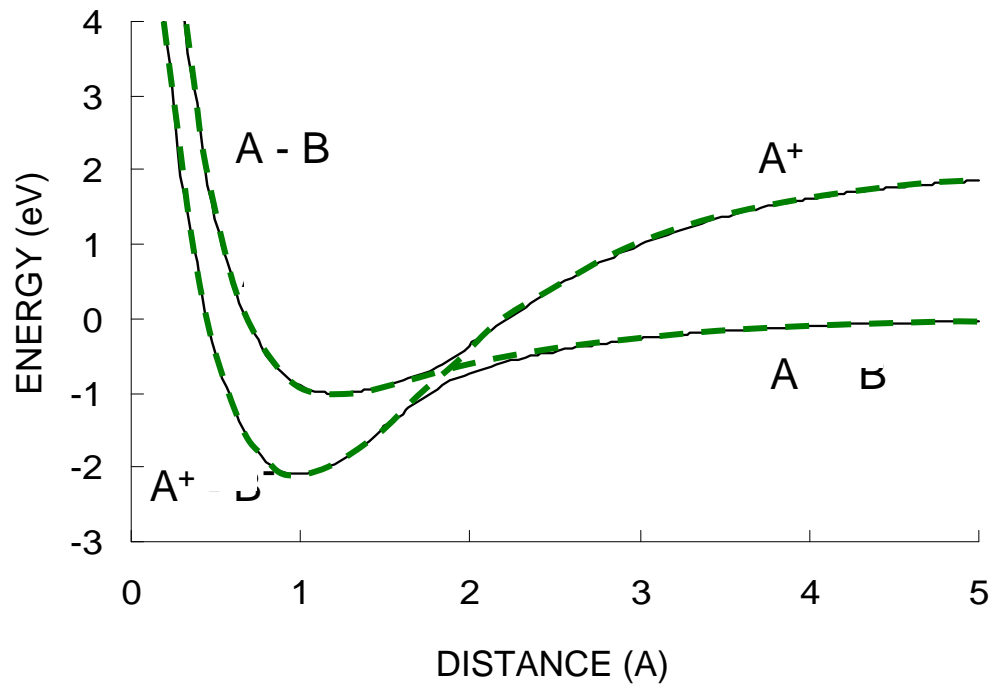
2b. Avoided Crossings and Conical Intersections

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Ionic Molecule
(alkali halide)

Avoided Crossing

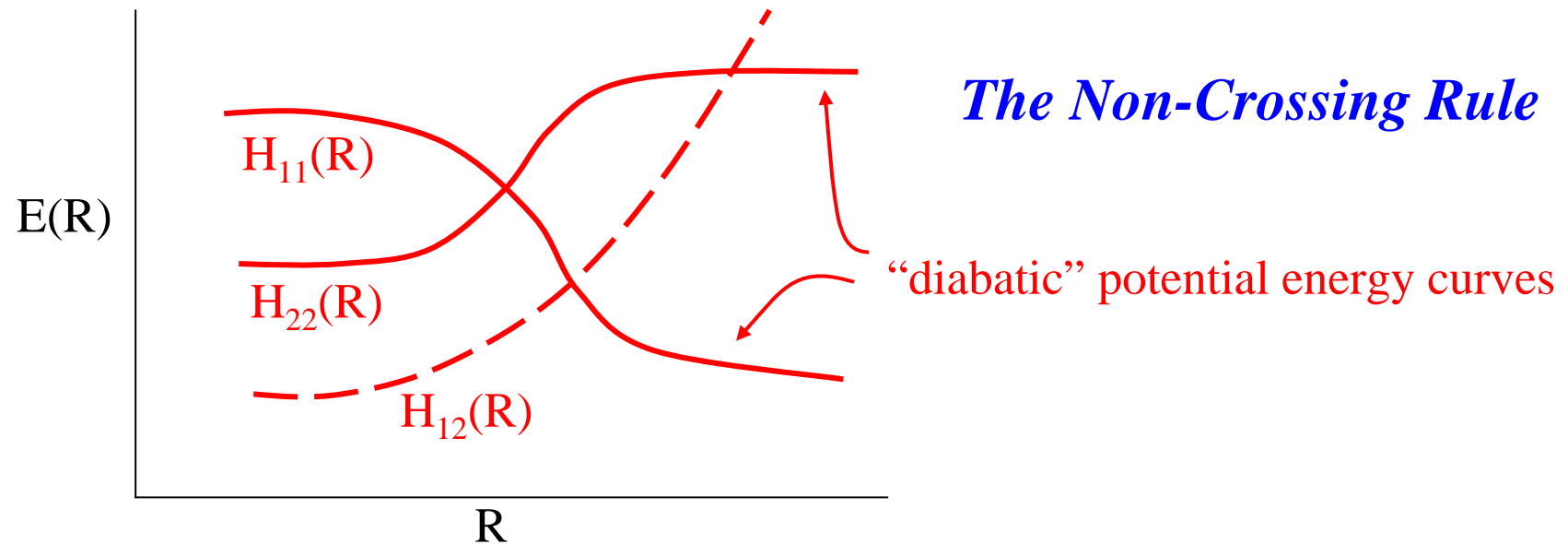


“diabatic” potential energy curves

2b. Avoided Crossings and Conical Intersections



$$\mathcal{H}(R) = \begin{bmatrix} H_{11}(R) & H_{12}(R) \\ H_{12}(R) & H_{22}(R) \end{bmatrix}$$



$$\mathcal{E}_{\pm}(R) = \frac{H_{11}(R) + H_{22}(R)}{2} \pm \frac{1}{2} \sqrt{[H_{11}(R) - H_{22}(R)]^2 + 4[H_{12}(R)]^2}$$

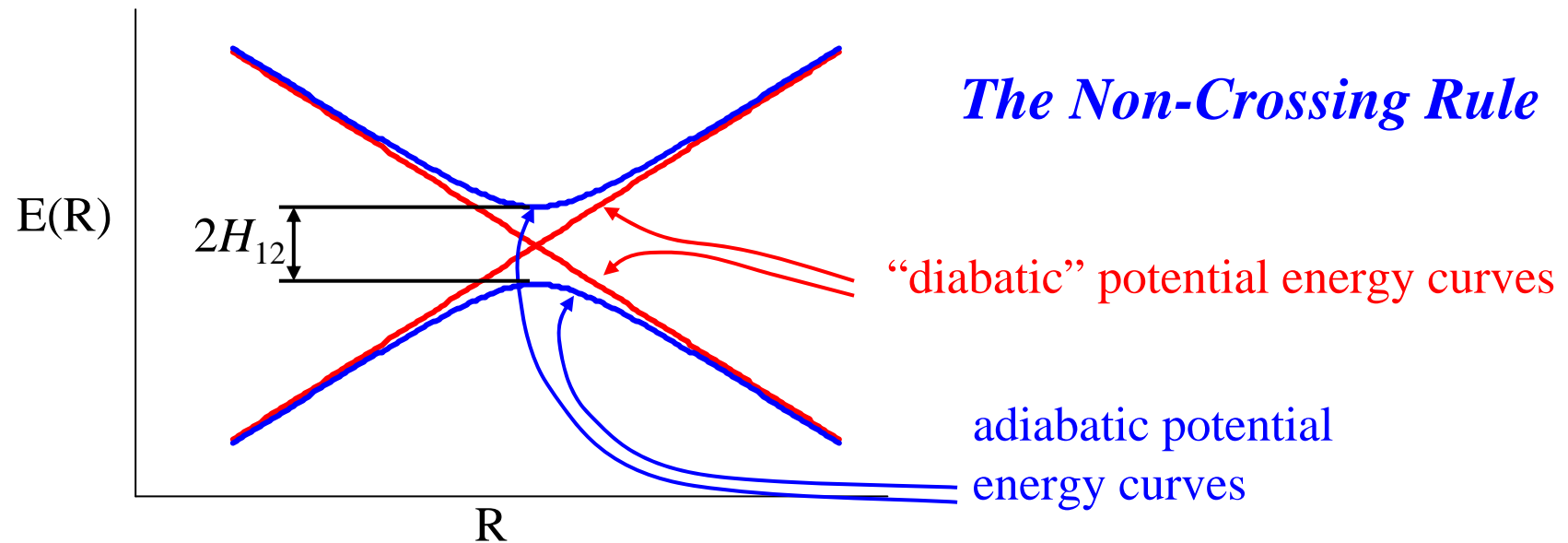
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and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



$$\mathcal{H}(R) = \begin{bmatrix} H_{11}(R) & H_{12}(R) \\ H_{12}(R) & H_{22}(R) \end{bmatrix}$$

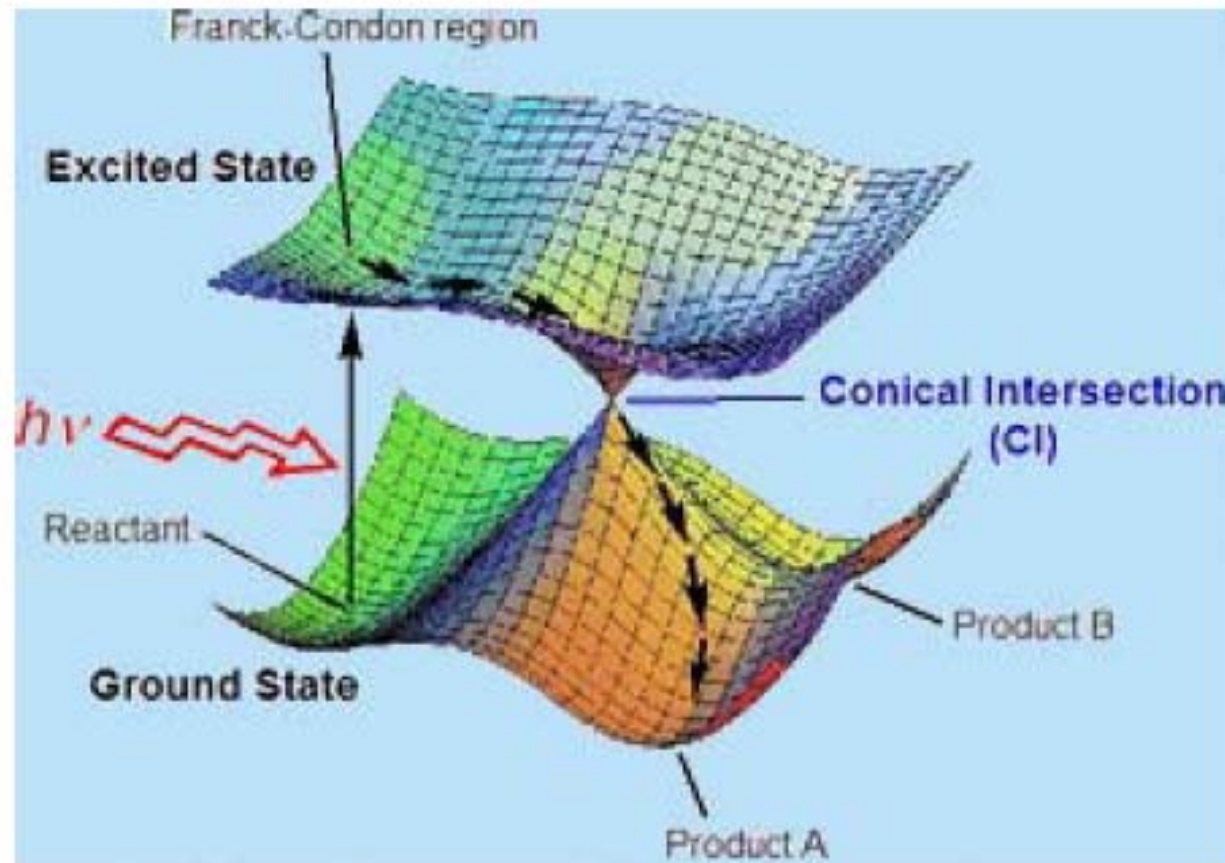


$$E_{\pm}(R) = \frac{H_{11}(R) + H_{22}(R)}{2} \pm \frac{1}{2} \sqrt{[H_{11}(R) - H_{22}(R)]^2 + 4[H_{12}(R)]^2}$$

2b. Avoided Crossings and Conical Intersections

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and Applications to Photo-Biological Questions

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The non-crossing rule
for more than 1 degree
of freedom:

“Conical Intersection”

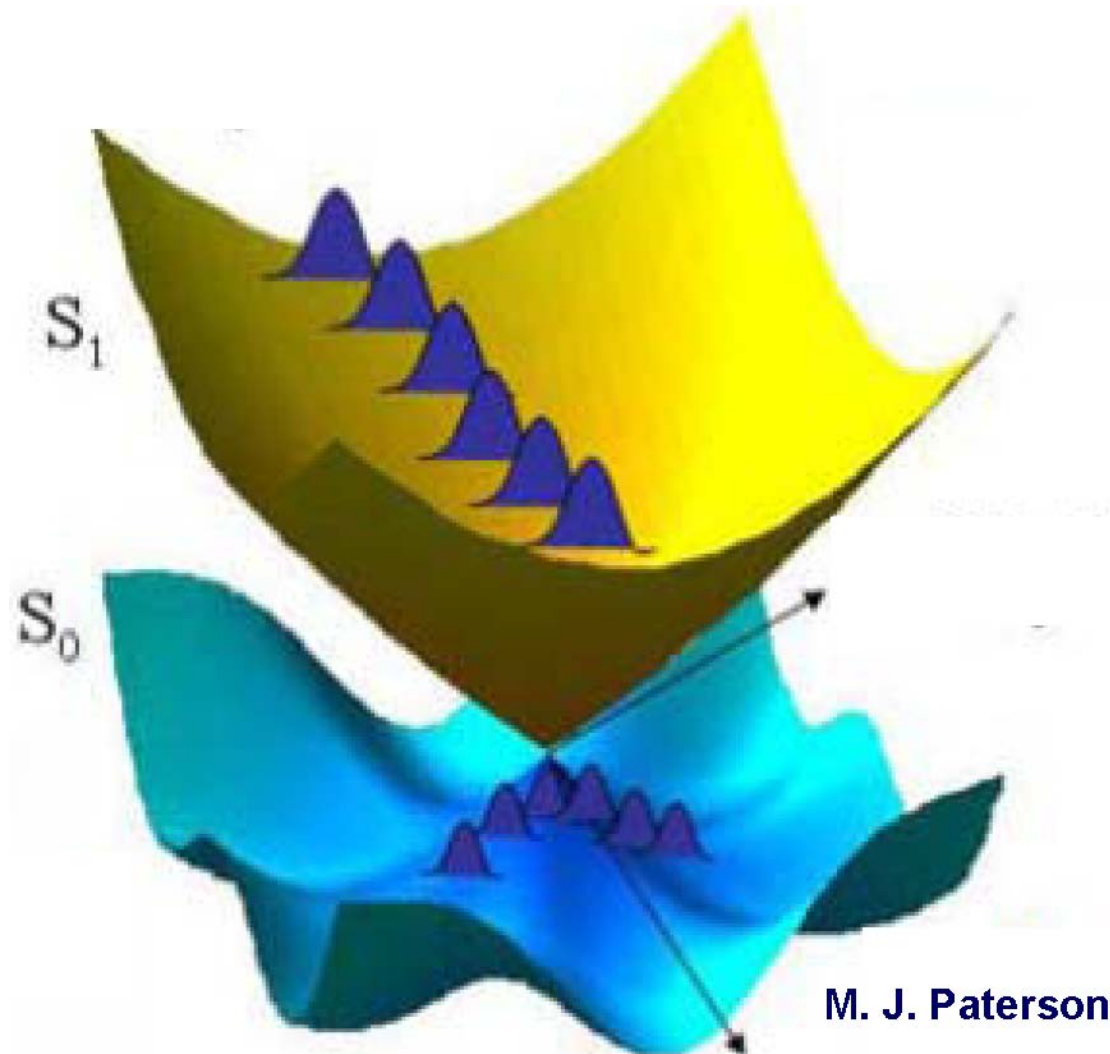
N degrees of freedom:

$N-2$ dimensional “seam”

$$\mathcal{E}_{\pm}(R_1, R_2) = \frac{H_{11}(R_1, R_2) + H_{22}(R_1, R_2)}{2} \pm \frac{1}{2} \sqrt{[H_{11}(R_1, R_2) - H_{22}(R_1, R_2)]^2 + 4[H_{12}(R_1, R_2)]^2}$$

2b. Avoided Crossings and Conical Intersections

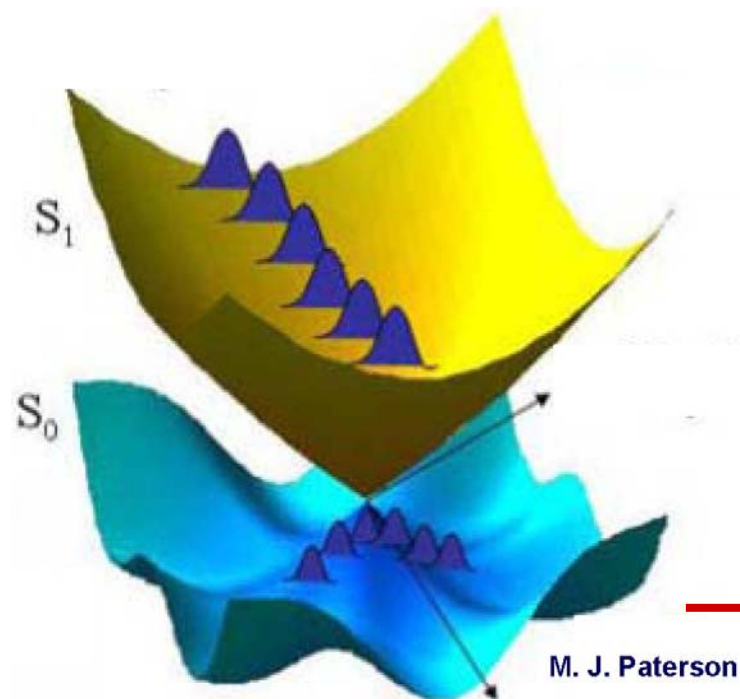
Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



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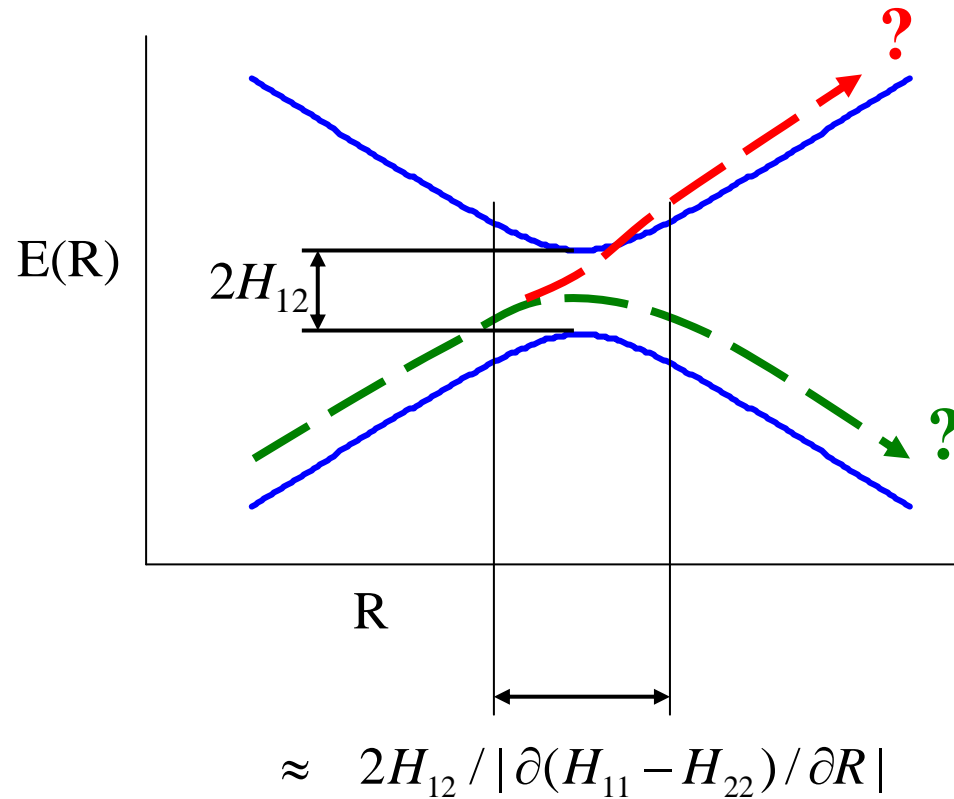
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- The Massey Criterion and the Landau-Zener Approximation

2c. The Massey Criterion & the Landau-Zener Approx

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The Massey Criterion:

$$\Delta E \Delta t \ll \hbar$$

$$\Delta E \approx 2 H_{12}$$

$$\Delta t \approx \text{distance/velocity}$$

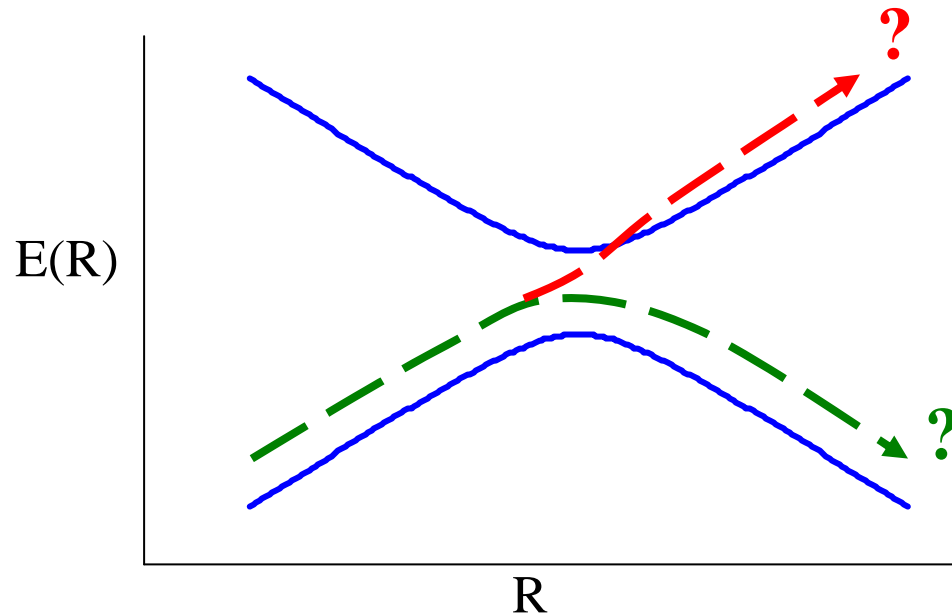
$$\approx 2H_{12} / |\partial(H_{11} - H_{22}) / \partial R| / \dot{R}$$

$$\longrightarrow \frac{\hbar \dot{R} |\partial(H_{11} - H_{22}) / \partial R|}{4H_{12}^2} \ll 1 \longrightarrow \text{adiabatic}$$

2c. The Massey Criterion & the Landau-Zener Approx

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Landau-Zener Approximation

Assumptions:

1. H_{11} and H_{22} linear
2. H_{12} constant
3. Velocity constant

$$P_{nonad} \approx \exp \left[\frac{-2\pi H_{12}^2}{\hbar \dot{R} \left| \partial(H_{11} - H_{22}) / \partial R \right|} \right]$$

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and Applications to Photo-Biological Questions

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→ 3. Ehrenfest Dynamics

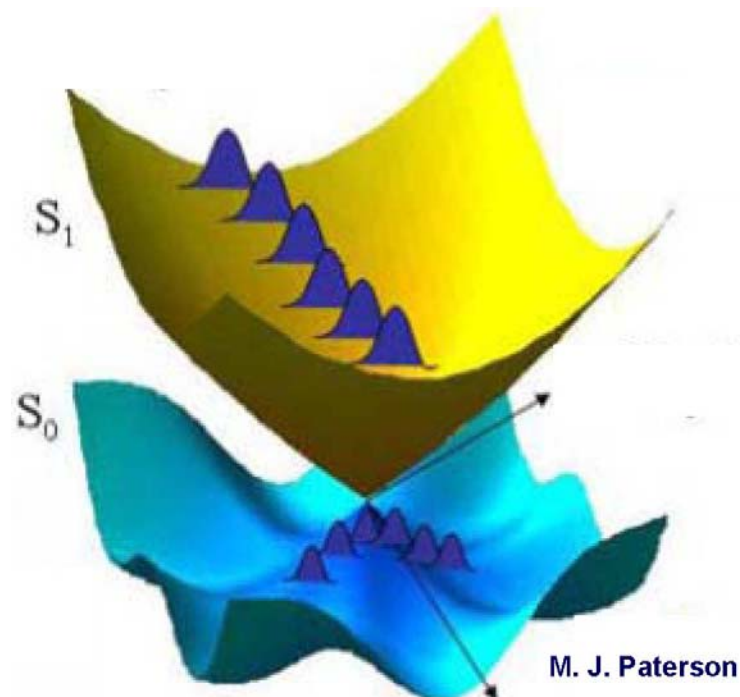
- a. The Self-Consistent Field Approximation
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- c. Appraisal of the Ehrenfest Method

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- a. de Broglie-Bohm Derivation
- b. Fewest Switches Algorithm
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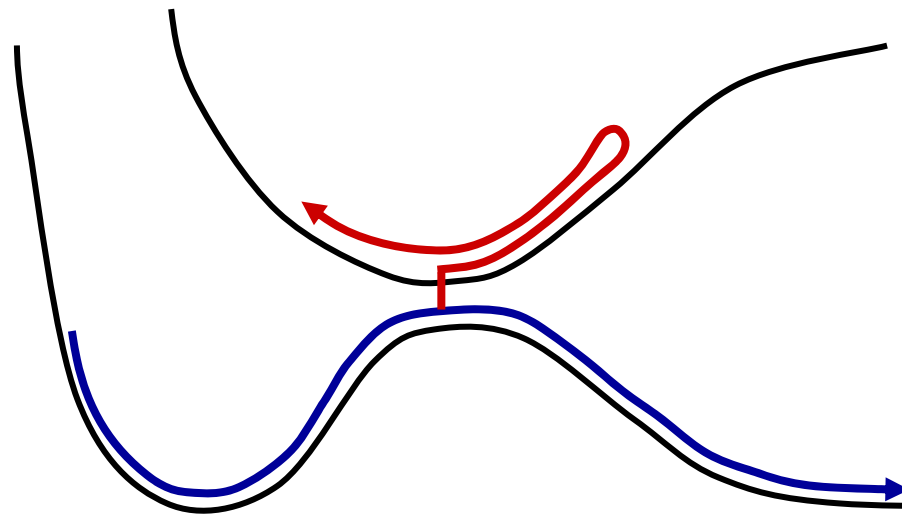
5. Mixed Quantum-Classical Nuclear Dynamics

- a. Time Scale Separation
- b. Proton Transfer in Solution
- c. Prognosis



Mixed Quantum-Classical Dynamics: II. Methods

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



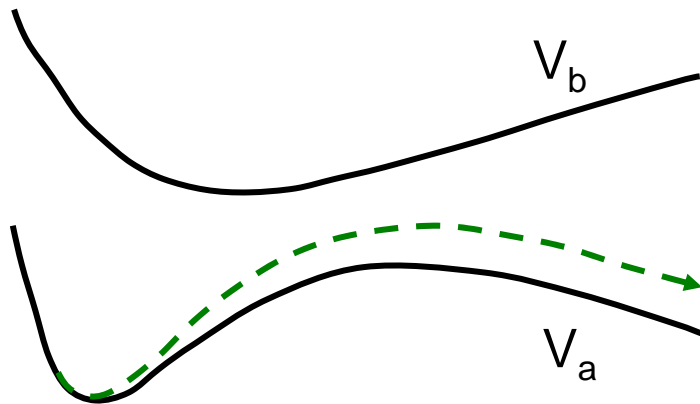
- Classical motion induces electronic transitions
 - Quantum state determines classical forces
- Quantum – Classical Feedback: Self-Consistency

Mixed Quantum-Classical Dynamics: II. Methods

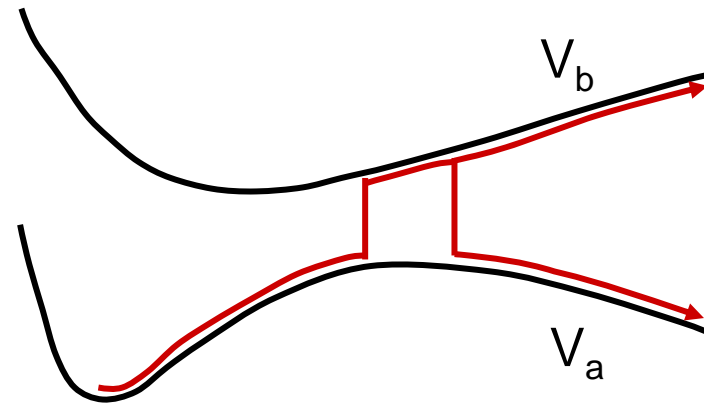
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TWO GENERAL MIXED QUANTUM-CLASSICAL APPROACHES FOR INCLUDING FEEDBACK



Ehrenfest (SCF)



Surface-Hopping

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and Applications to Photo-Biological Questions
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$$i\hbar \frac{\partial \Psi(r,t)}{\partial t} = \mathcal{H}_{el} \Psi(r,t)$$

$$\Psi(r,t) = \sum_i c_i(t) \Phi_i(r;R) \quad (\text{adiabatic states})$$

$$dc_j/dt = -\frac{i}{\hbar} V_{jj} c_j - \dot{R} \cdot \sum_i \langle \Phi_j(r;R) | \nabla_R \Phi_i(r;R) \rangle c_i$$

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and Applications to Photo-Biological Questions
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$$i\hbar \frac{\partial \Psi(r,t)}{\partial t} = \mathcal{H}_{el} \Psi(r,t)$$

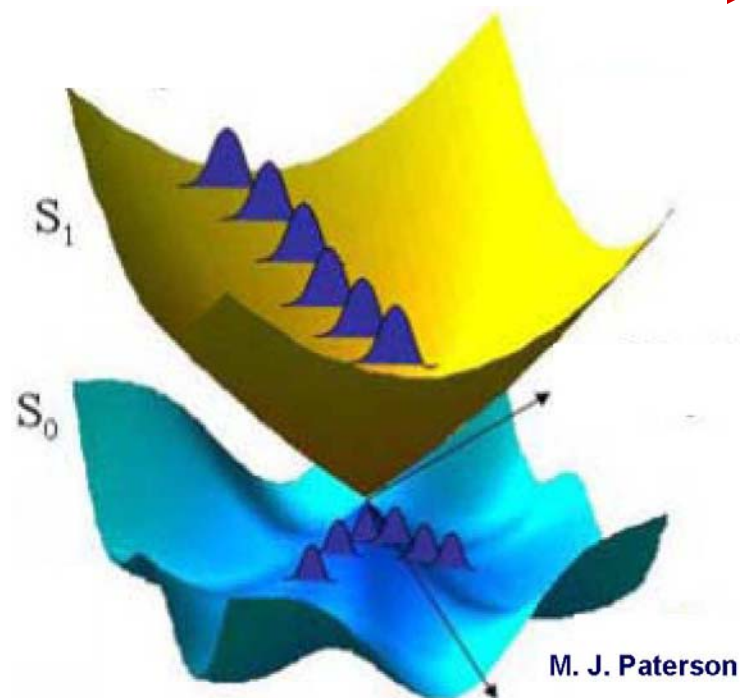
Classical path must respond **self-consistently** to
quantum transitions: “quantum back-reaction”

Ehrenfest and Surface Hopping differ
only in how classical path is defined

Mixed Quantum-Classical Dynamics: II. Methods

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



3. Ehrenfest Dynamics

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3a. The Self-Consistent Field Approximation



$$i \hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) = \mathcal{H}(\mathbf{r}, \mathbf{R}) \Psi(\mathbf{r}, \mathbf{R}, t) \quad (1)$$

Self-consistent Field Approximation (fully quantum):

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \Xi(\mathbf{r}, t) \Omega(\mathbf{R}, t) \exp \left[\frac{i}{\hbar} \int^t E_r(t') dt' \right] \quad (2)$$

Substituting (2) into (1), multiplying on the left by $\Omega(\mathbf{R}, t)$ and integrating over \mathbf{R} gives the SCF equation for the electronic wave function $\Xi(\mathbf{r}, t)$:

$$i \hbar \frac{\partial \Xi(\mathbf{r}, t)}{\partial t} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 \Xi(\mathbf{r}, t) + \tilde{V}_{rR}(\mathbf{r}, \mathbf{R}) \Xi(\mathbf{r}, t) \quad (3)$$

$$\text{where } \tilde{V}_{rR}(\mathbf{r}, \mathbf{R}) = \int \Omega^*(\mathbf{R}, t) V_{rR}(\mathbf{r}, \mathbf{R}) \Omega(\mathbf{R}, t) d\mathbf{R} \quad (4)$$

3a. The Self-Consistent Field Approximation



Substituting (2) into (1), multiplying on the left by $\Xi(\mathbf{r}, t)$ and integrating over \mathbf{r} gives the equivalent SCF equation for the nuclear wave function $\Omega(\mathbf{R}, t)$:

$$i\hbar \frac{\partial \Omega(\mathbf{R}, t)}{\partial t} = -\frac{\hbar^2}{2} \sum_{\alpha} M_{\alpha}^{-1} \nabla_{R_{\alpha}}^2 \Omega(\mathbf{R}, t) + \int \Xi^*(\mathbf{r}, t) \mathcal{H}_{el}(\mathbf{r}, \mathbf{R}) \Xi(\mathbf{r}, t) d\mathbf{r} \Omega(\mathbf{R}, t) \quad (5)$$

The classical (Ehrenfest) limit requires 2 steps:

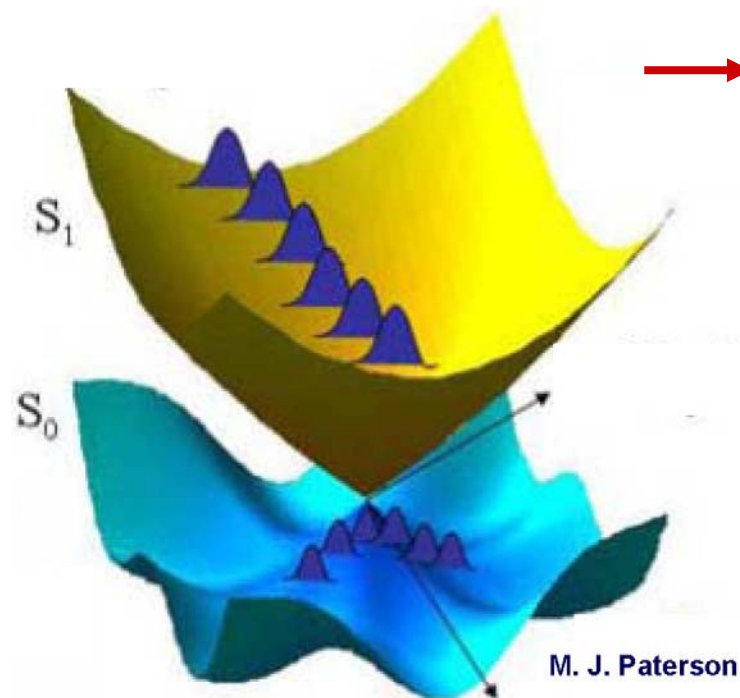
1. Replace $\Omega(\mathbf{R}, t)$ with a delta function in Eq. (4)
2. Take the classical limit of Eq. (5) (eg. using the Bohm formulation as above).

Thus, the potential energy function governing the nuclei becomes

$$\int \Xi^*(\mathbf{r}, t) \mathcal{H}_{el}(\mathbf{r}, \mathbf{R}) \Xi(\mathbf{r}, t) d\mathbf{r} \quad \text{instead of the adiabatic energy } \mathcal{E}_j(\mathbf{R}).$$

Mixed Quantum-Classical Dynamics: II. Methods

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



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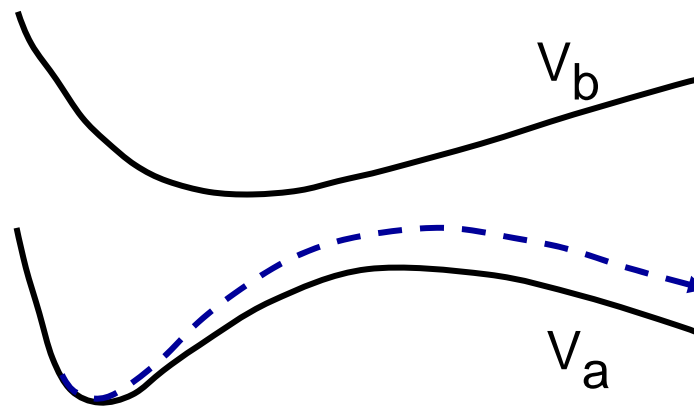
3b. Ehrenfest Dynamics: Classical Limit

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and Applications to Photo-Biological Questions
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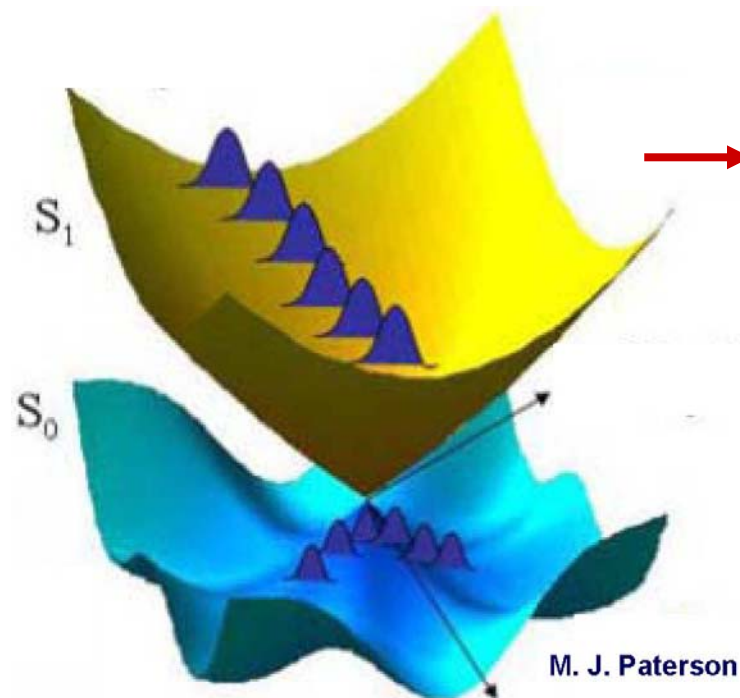
$$i\hbar \frac{\partial \Psi(r,t)}{\partial t} = \mathcal{H}_{el} \Psi(r,t)$$

$$M \ddot{R}(t) = -\nabla_R \langle \Psi(t) | \mathcal{H}_{el} | \Psi(t) \rangle$$



Mixed Quantum-Classical Dynamics: II. Methods

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



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3c. Appraisal of Ehrenfest

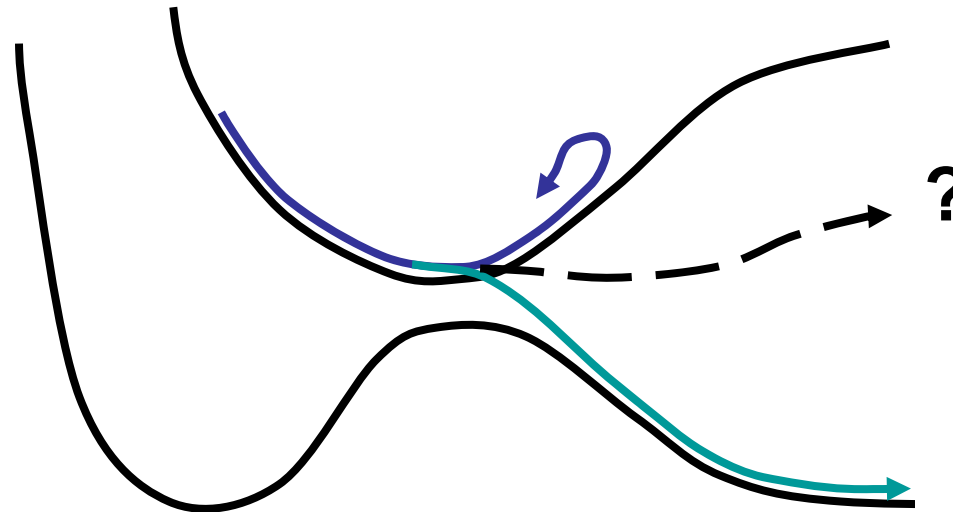
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and Applications to Photo-Biological Questions



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$$M \ddot{R}(t) = -\nabla_R \langle \Psi(t) | \mathcal{H}_{el} | \Psi(t) \rangle$$

Problem:
single configuration
→ average path



3c. Appraisal of Ehrenfest

Mixed QM-Classical Dynamics

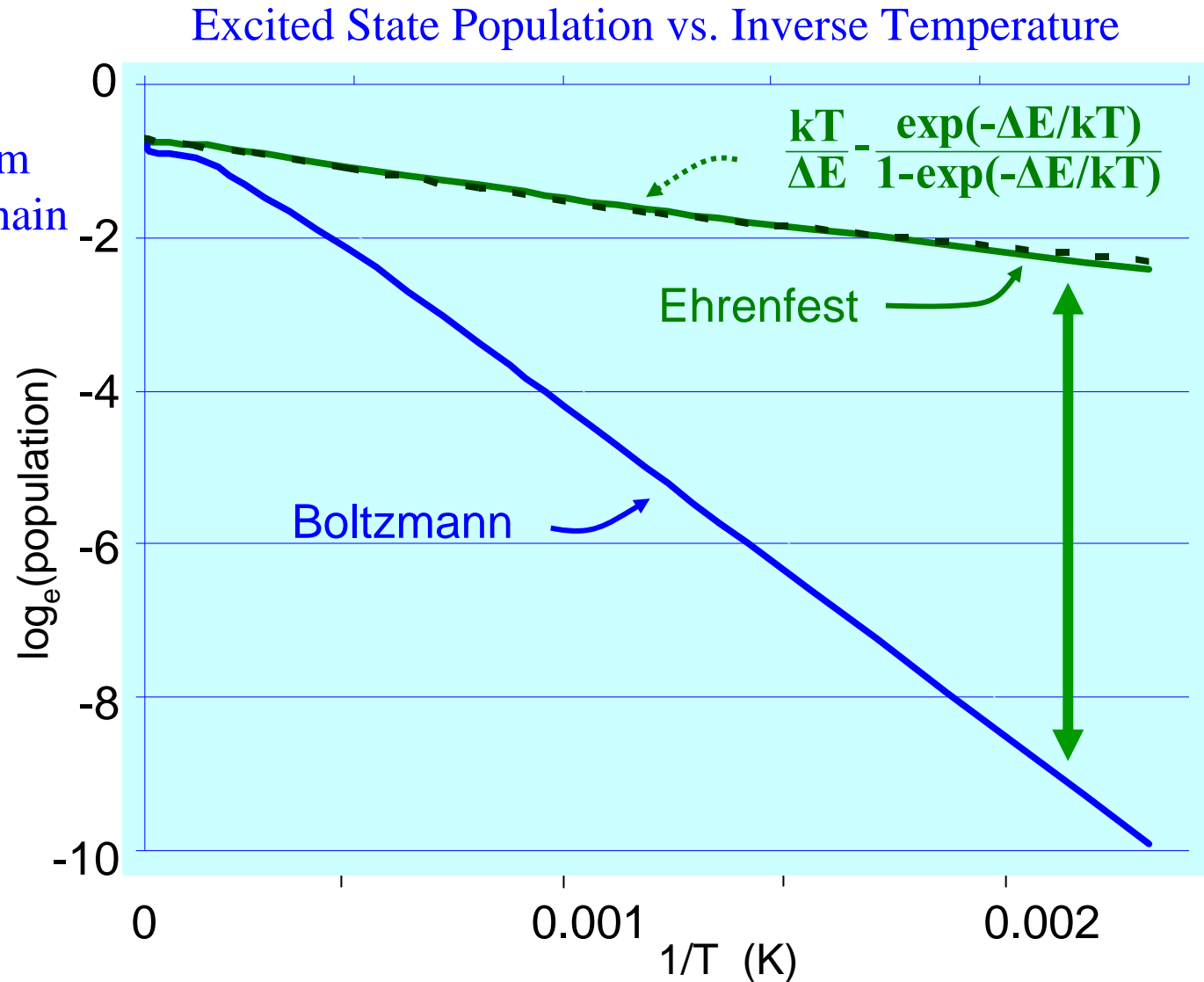
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Detailed Balance

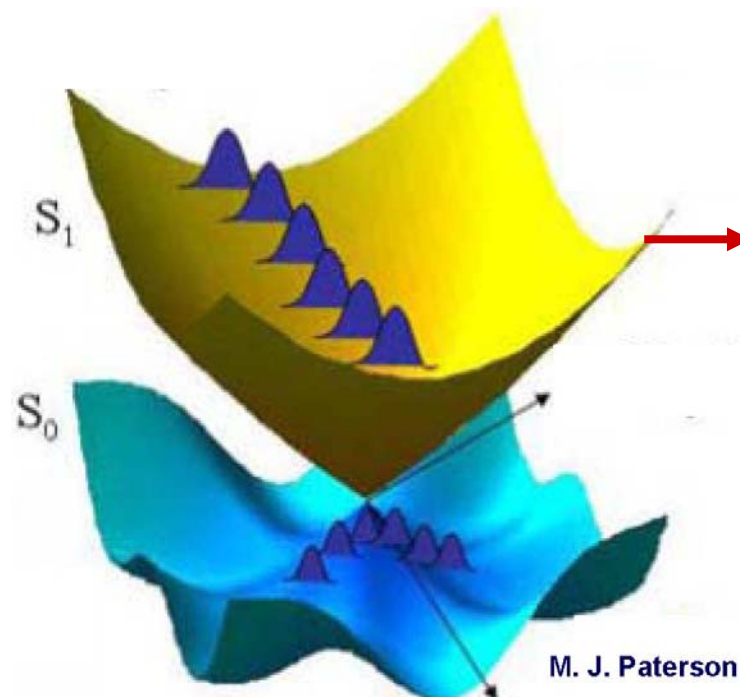
2-state quantum system
coupled to classical chain
 $\Delta E = 34.6$ kJ/mole



Mixed Quantum-Classical Dynamics: II. Methods

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and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



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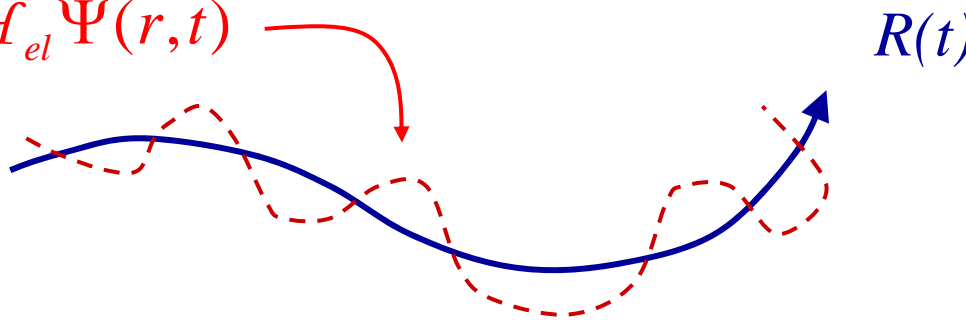
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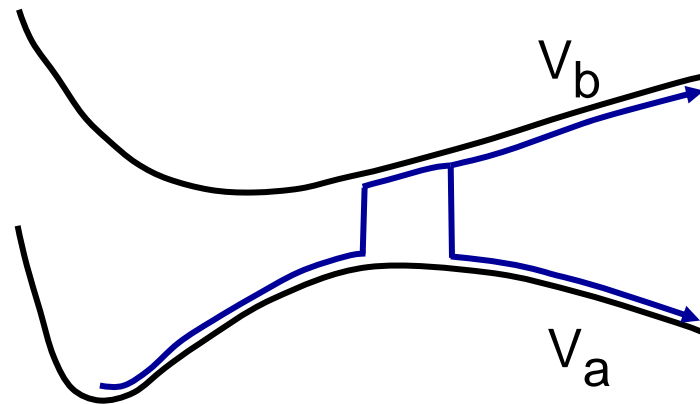
5. Mixed Quantum-Classical Nuclear Dynamics

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4. Surface Hopping



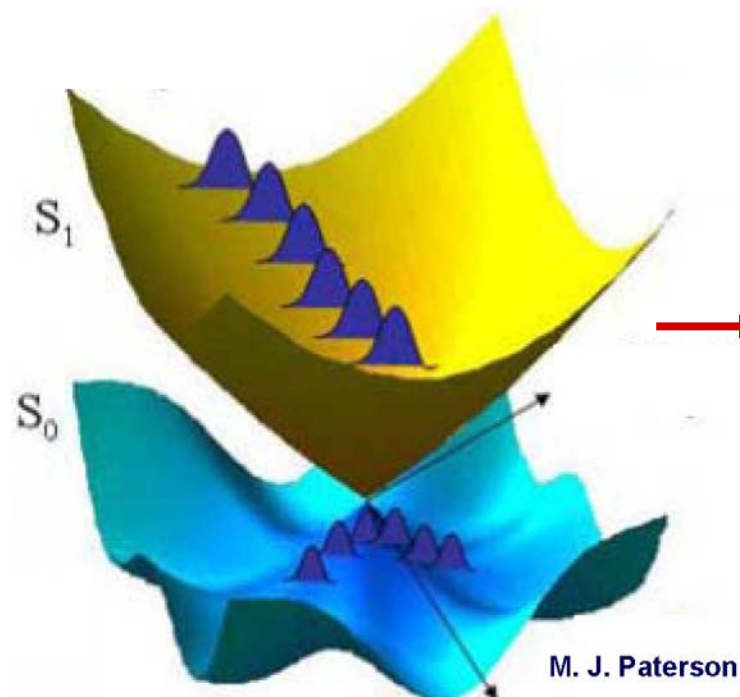
$$i\hbar \frac{\partial \Psi(r,t)}{\partial t} = \mathcal{H}_{el} \Psi(r,t)$$




Mixed Quantum-Classical Dynamics: II. Methods

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



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4a. DeBroglie-Bohm Derivation

Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008



Multi-Configuration Wave Function:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_j \Phi_j(\mathbf{r}, \mathbf{R}) \Omega_j(\mathbf{R}, t)$$

Substitute into Schrodinger Eq and take classical limit:

→ Surface Hopping

However, a rigorous classical limit has not been achieved !

4a. DeBroglie-Bohm Derivation



One Approach: Multi-Configuration Bohm Equations:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_j \Phi_j(\mathbf{r}, \mathbf{R}) \Omega_j(\mathbf{R}, t)$$

$$\Omega_j(\mathbf{R}, t) = A_j(\mathbf{R}, t) \exp\left[\frac{i}{\hbar} S_j(\mathbf{R}, t)\right]$$

$$\dot{S}_j = -\frac{1}{2M} (\nabla_R S_j)^2 - E_j(\mathbf{R}) - \frac{\hbar^2}{2M} \frac{\nabla_R^2 A_j}{A_j}$$

small $\hbar \rightarrow$

$$\dot{S}_j = -\frac{1}{2M} (\nabla_R S_j)^2 - E_j(\mathbf{R})$$

\rightarrow motion on potential energy surface j

4a. DeBroglie-Bohm Derivation

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and Applications to Photo-Biological Questions

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$$\dot{A}_n = \nabla_R A_n \cdot \dot{\mathbf{R}} - \frac{1}{2M} A_n \nabla_R^2 S_n - \sum_m A_m \langle \Phi_n | \nabla_R \Phi_m \rangle \cdot \dot{\mathbf{R}} \exp\left[\frac{i}{\hbar} (S_m - S_n)\right]$$

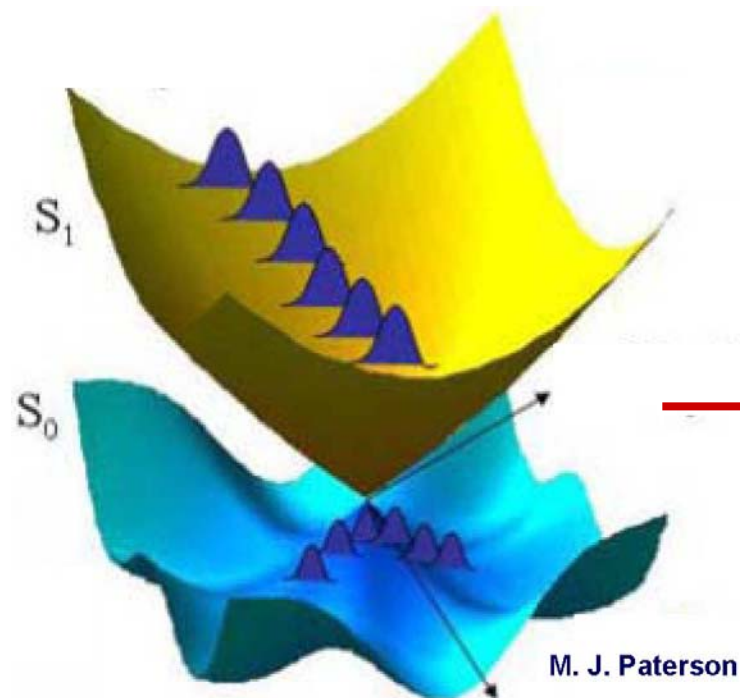
Surface Hopping:

Evaluate all quantities along a single path

Sum over many stochastic paths

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Mixed Quantum-Classical Dynamics: Foundations
and Applications to Photo-Biological Questions
Summer School, Vienna, 7 – 12 July, 2008



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4b. Fewest Switches Surface Hopping Algorithm

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Multi-Configuration Theory: *Surface Hopping*

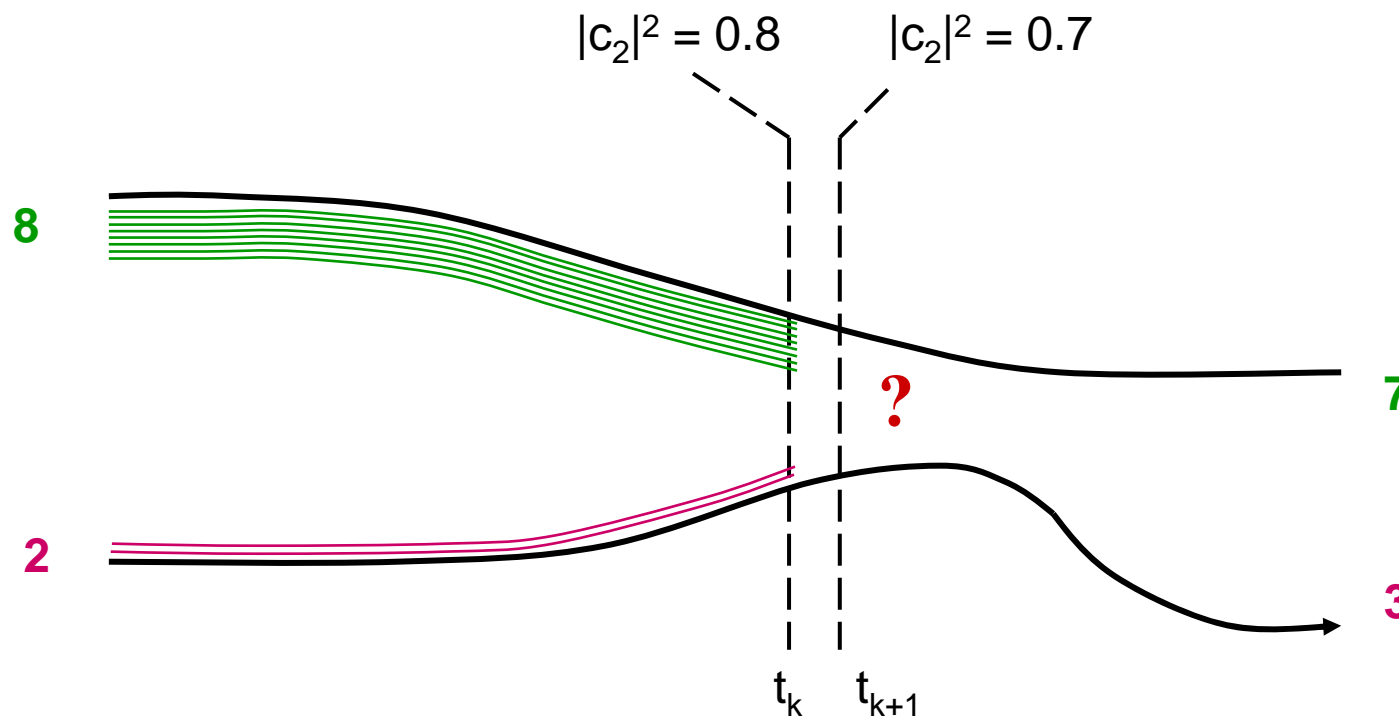
$$i\hbar \frac{\partial \Psi(t)}{\partial t} = \mathcal{H}_{el} \Psi(t)$$

- 1] $M \ddot{R}(t) = -\nabla_R \mathcal{E}_k$, i.e., motion on single p.e.s.
- 2] Stochastic “hops” between states so that probability = $|c_k|^2$
- 3] Apply instantaneous “Pechukas Force” to conserve energy
- 4] “Fewest Switches”: achieve [2] with fewest possible hops:

4b. Fewest Switches Surface Hopping Algorithm

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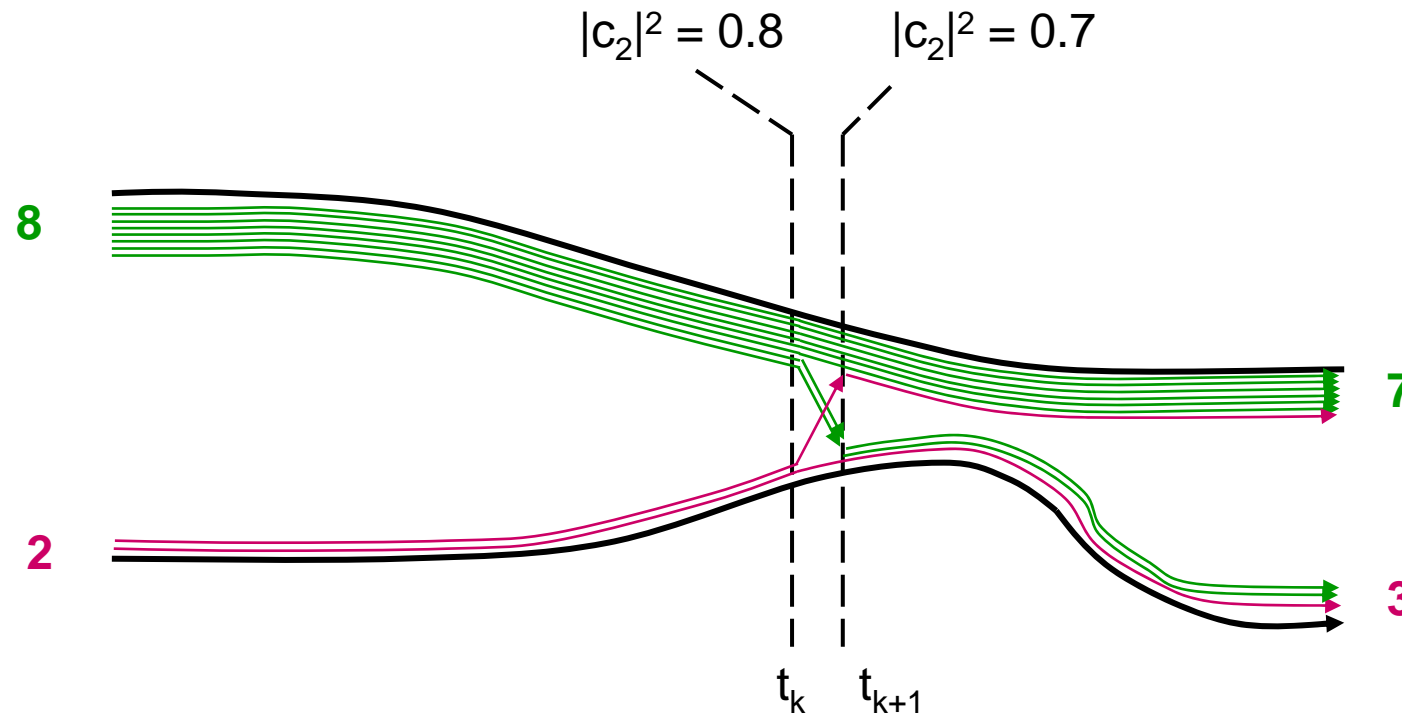
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Stochastic *Fewest Switches* algorithm (2-state):

4b. Fewest Switches Surface Hopping Algorithm

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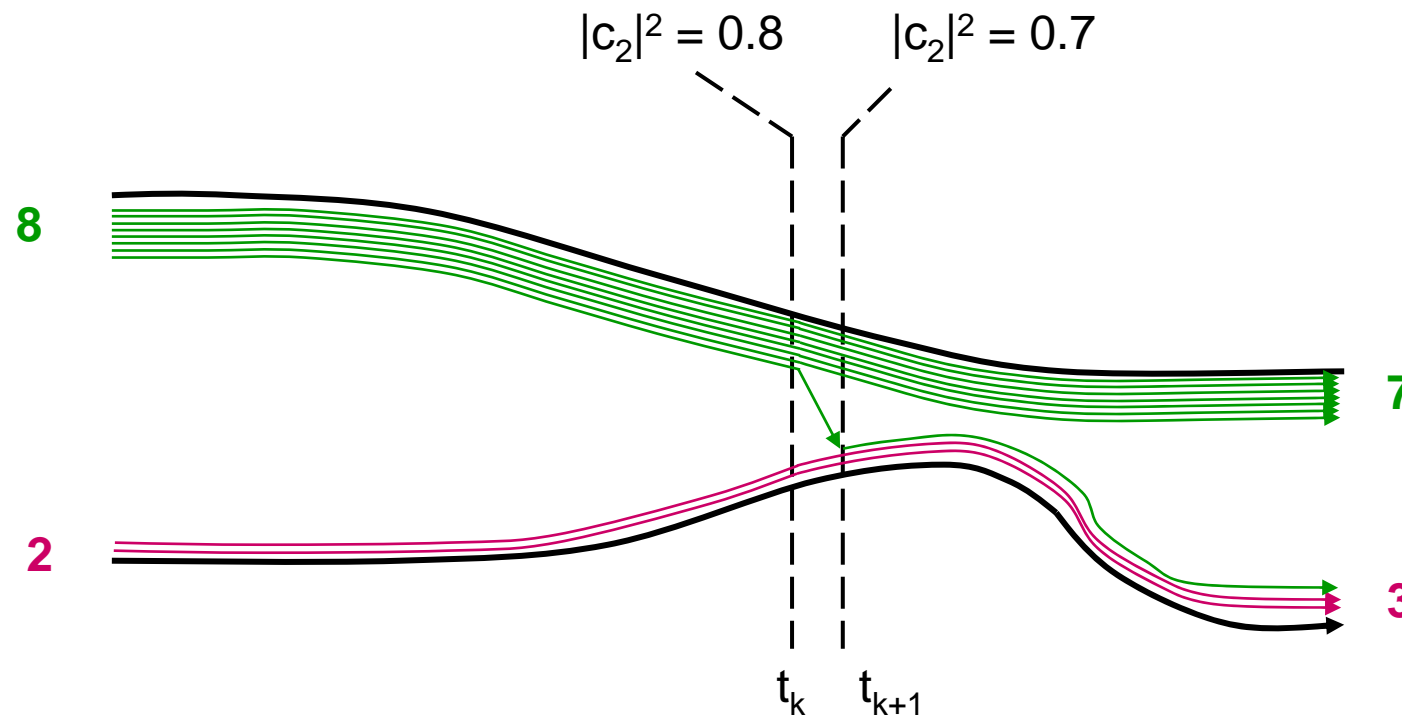


Stochastic *Fewest Switches* algorithm (2-state):

4b. Fewest Switches Surface Hopping Algorithm

Mixed Quantum-Classical Dynamics: Foundations and Applications to Photo-Biological Questions

Summer School, Vienna, 7 – 12 July, 2008

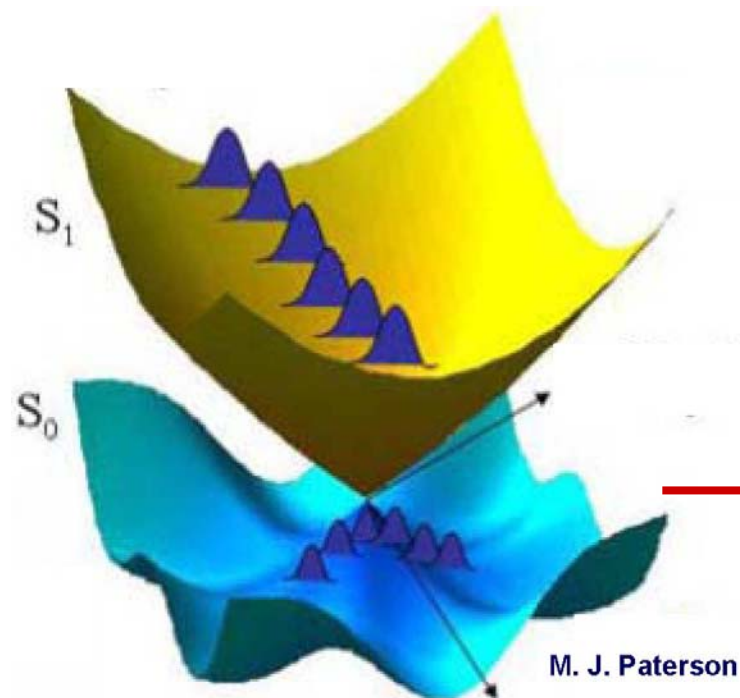


Stochastic *Fewest Switches* algorithm (2-state):

$$P_{2 \rightarrow 1} = \begin{cases} \frac{|c_2(k)|^2 - |c_2(k+1)|^2}{|c_2(k)|^2}, & |c_2(k)|^2 > |c_2(k+1)|^2 \\ 0, & |c_2(k)|^2 \leq |c_2(k+1)|^2 \end{cases}$$

Mixed Quantum-Classical Dynamics: II. Methods

Mixed Quantum-Classical Dynamics: Foundations
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3. Ehrenfest Dynamics

- The Self-Consistent Field Approximation
- Ehrenfest Mixed Quantum-Classical Dynamics
- Appraisal of the Ehrenfest Method

4. Surface Hopping Dynamics

- de Broglie-Bohm Derivation
- Fewest Switches Algorithm
- Appraisal of the Surface Hopping Method

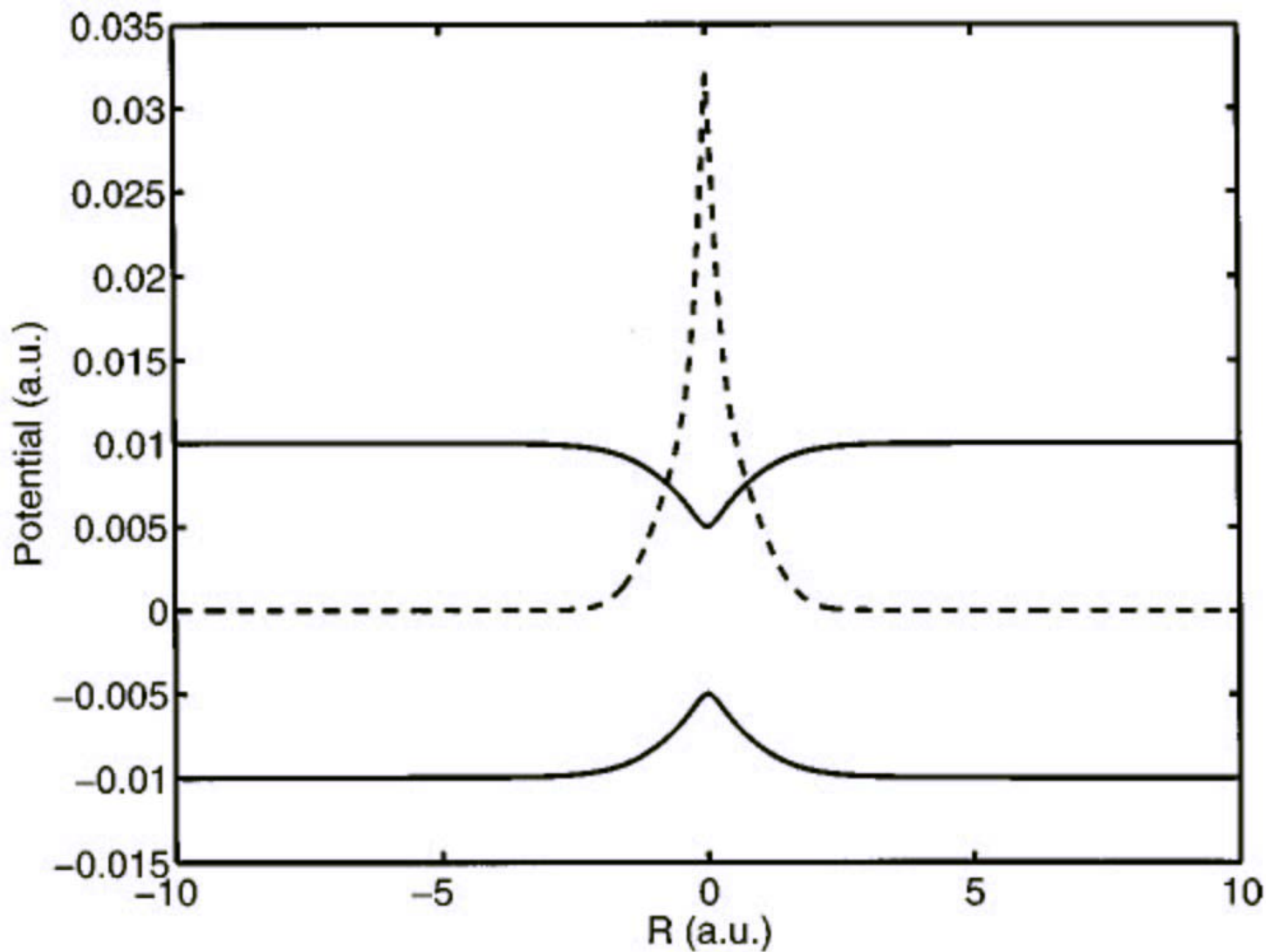
5. Mixed Quantum-Classical Nuclear Dynamics

- Time Scale Separation
- Proton Transfer in Solution
- Prognosis

4c. Appraisal of Surface Hopping

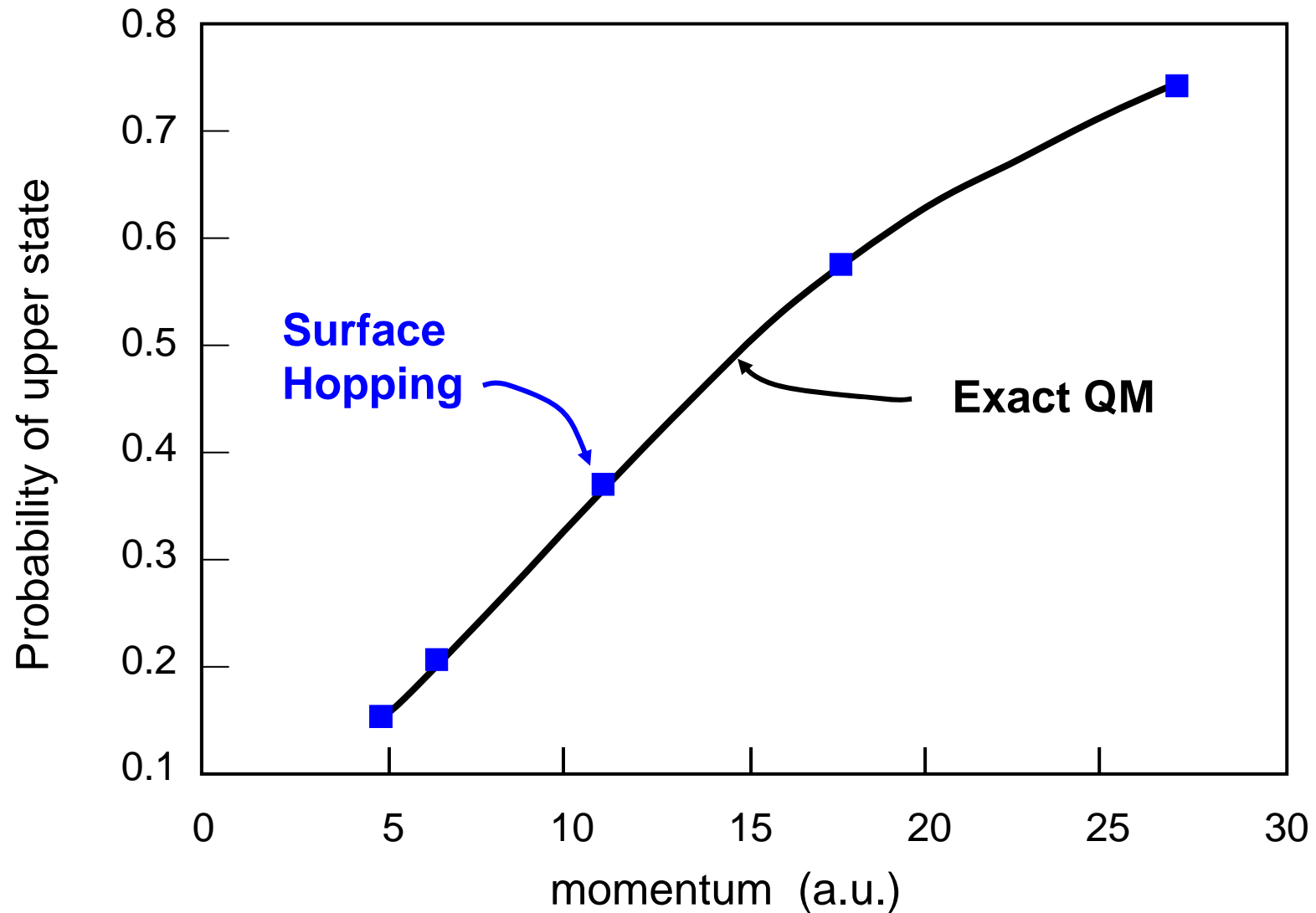
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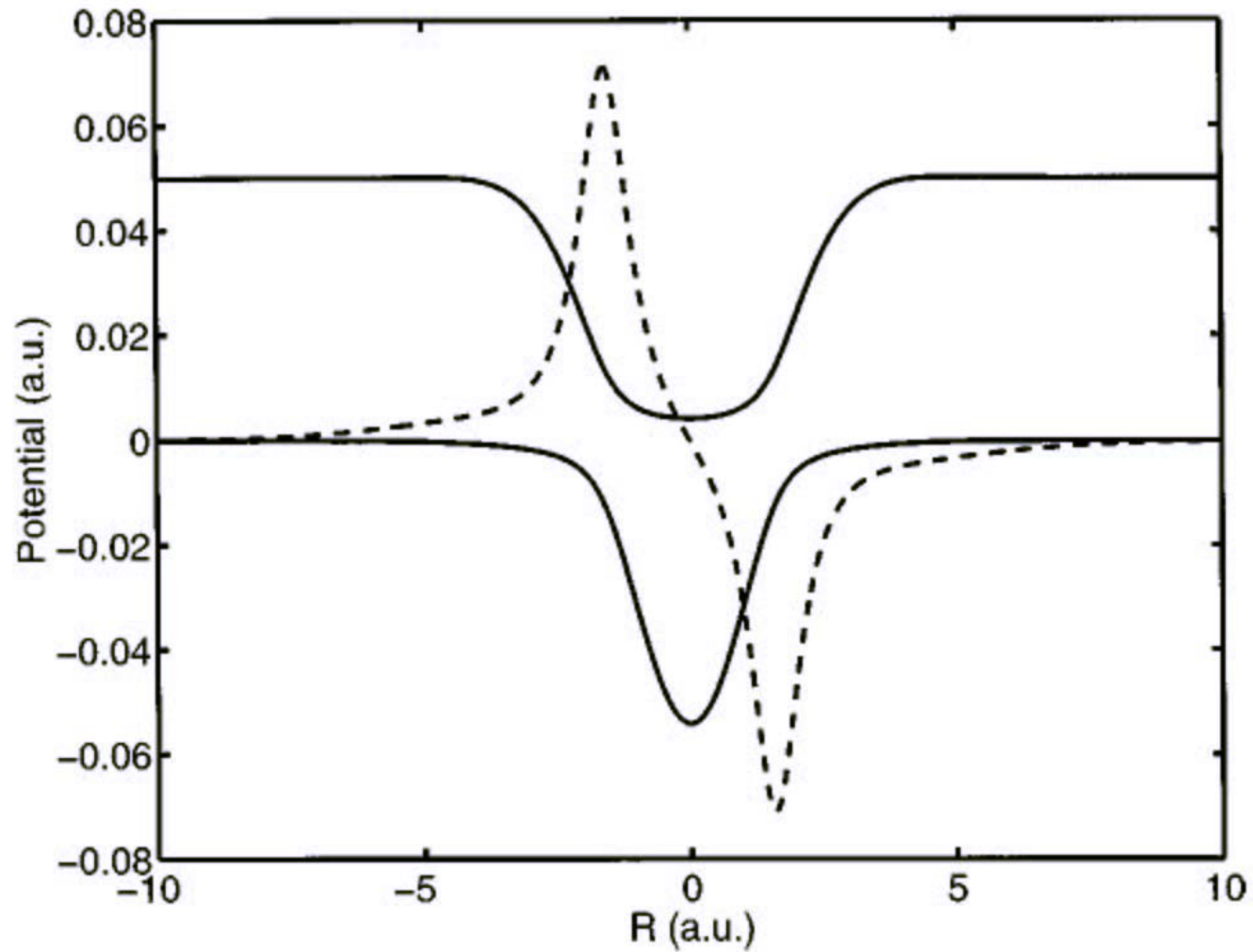
4c. Appraisal of Surface Hopping

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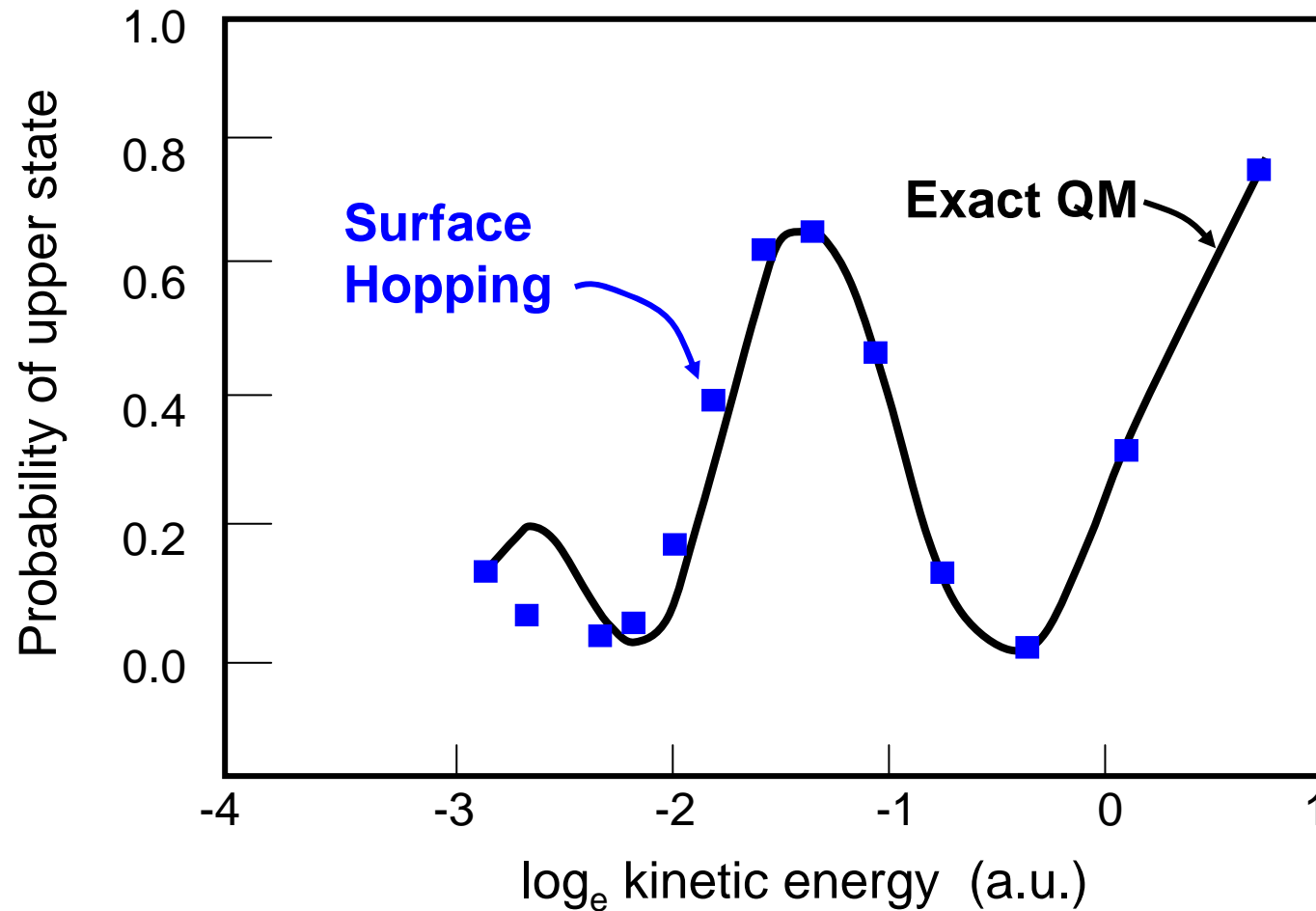
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4c. Appraisal of Surface Hopping

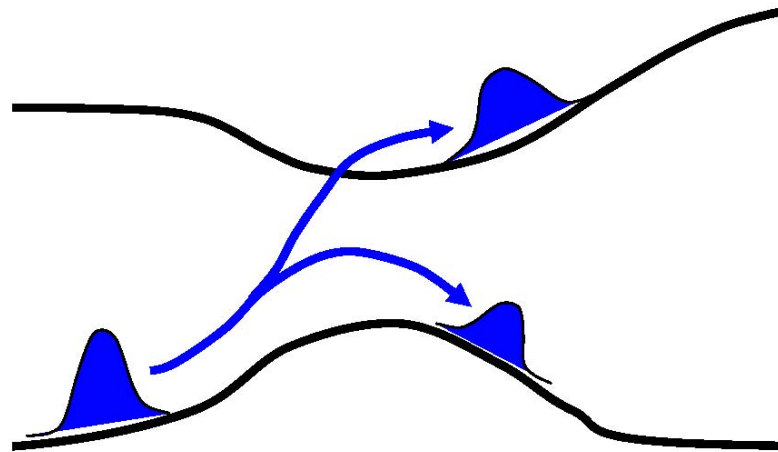
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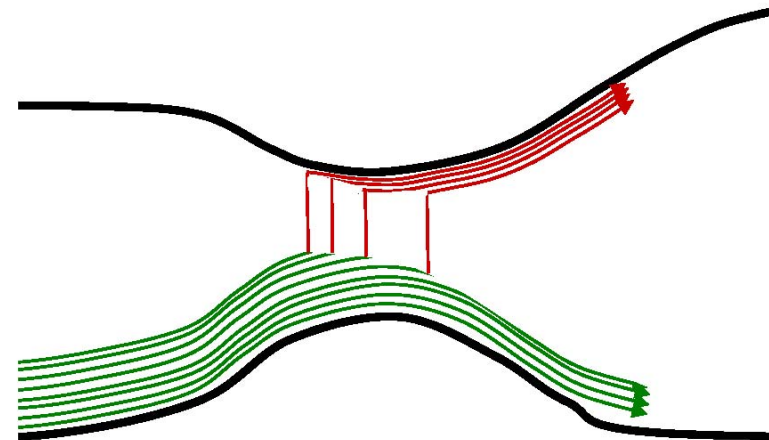
SHORTCOMINGS OF SURFACE HOPPING

1] Trajectories are independent

Trajectories should talk to each other



quantum wave packet



surface hopping

Fundamental approximation, but required to make practical

4c. Appraisal of Surface Hopping

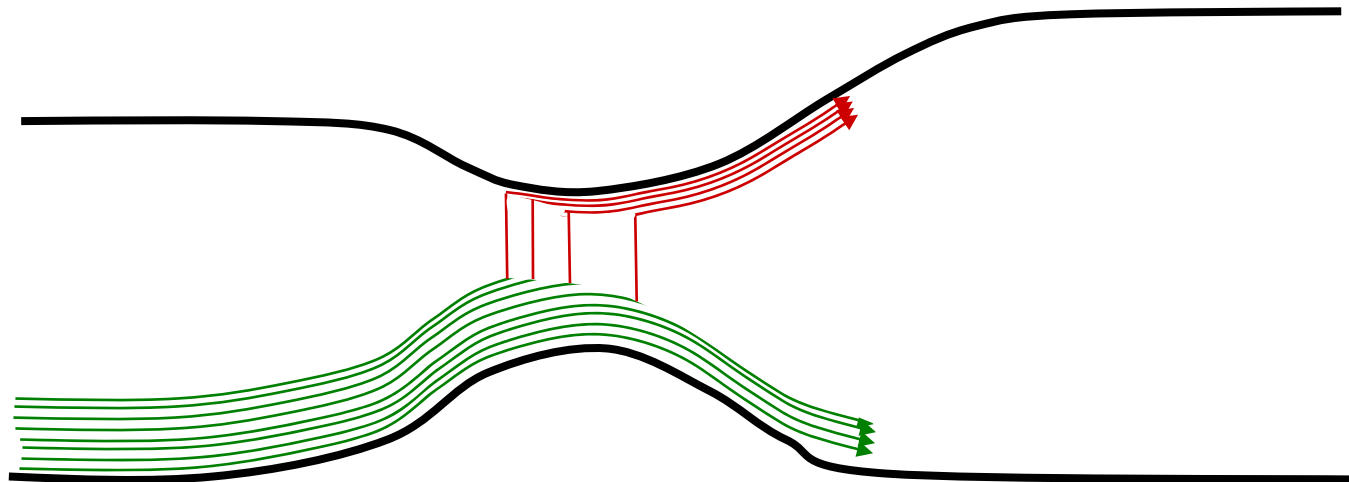
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SHORTCOMINGS OF SURFACE HOPPING

2] Too drastic: hops require sudden change of velocity

Consider swarm of trajectories –
trajectories hop stochastically at different times



→ gradual evolution of flux

4c. Appraisal of Surface Hopping

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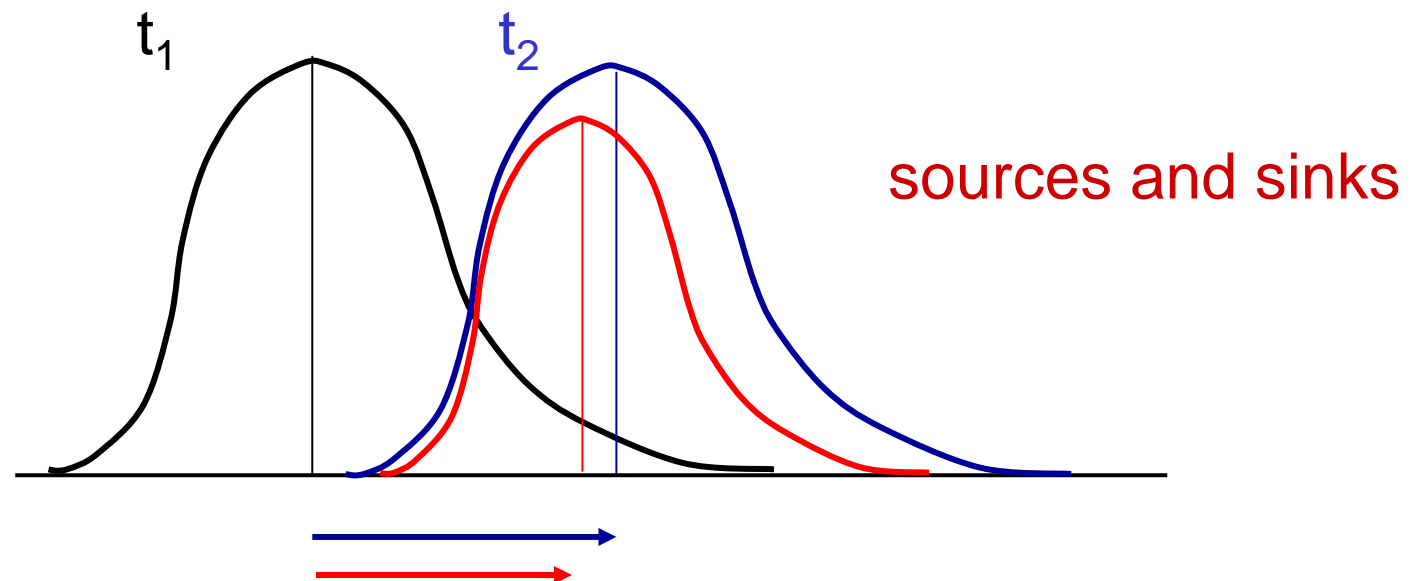


SHORTCOMINGS OF SURFACE HOPPING

- 3] Trajectories should evolve on some effective potential, not on a single adiabatic potential energy surface

Consider swarm of trajectories –

trajectories hop stochastically at different times:



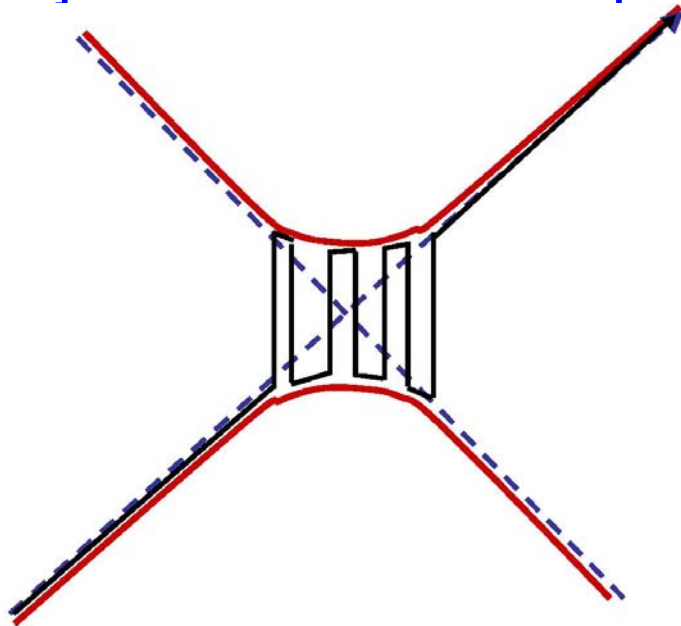
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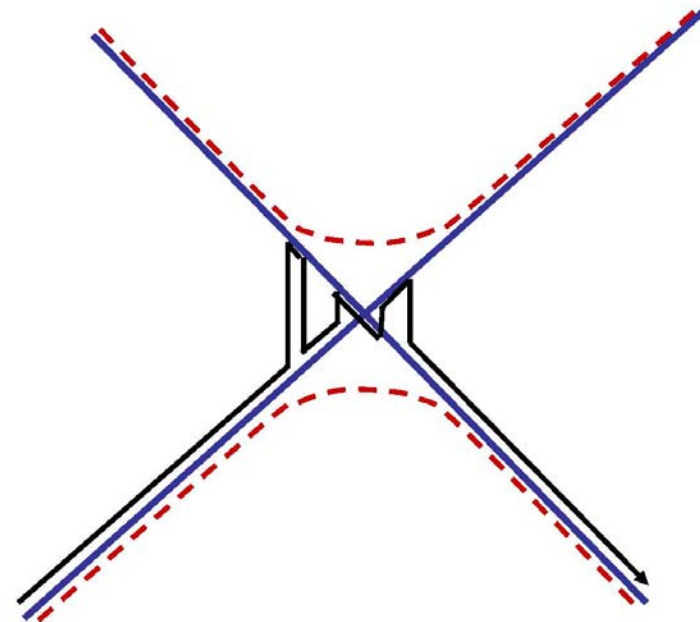


SHORTCOMINGS OF SURFACE HOPPING

4] Not invariant to representation



adiabatic representation



diabatic representation

The natural representation for surface hopping is *adiabatic*

4c. Appraisal of Surface Hopping



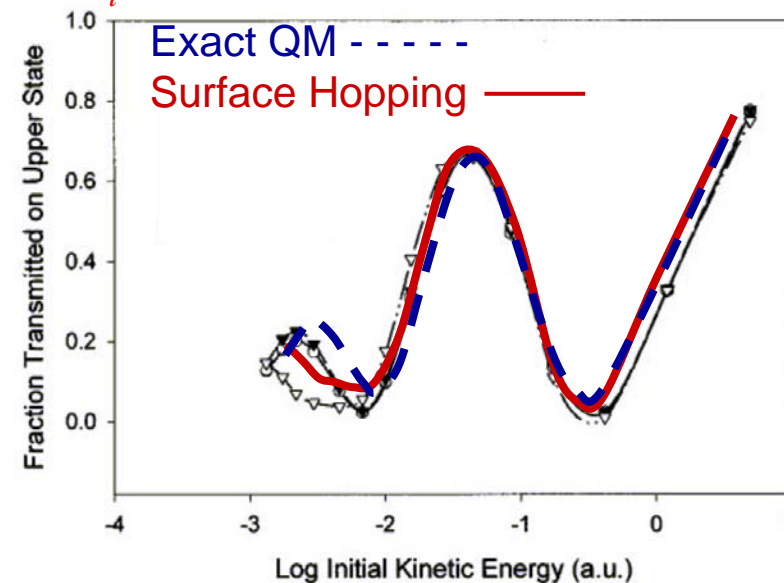
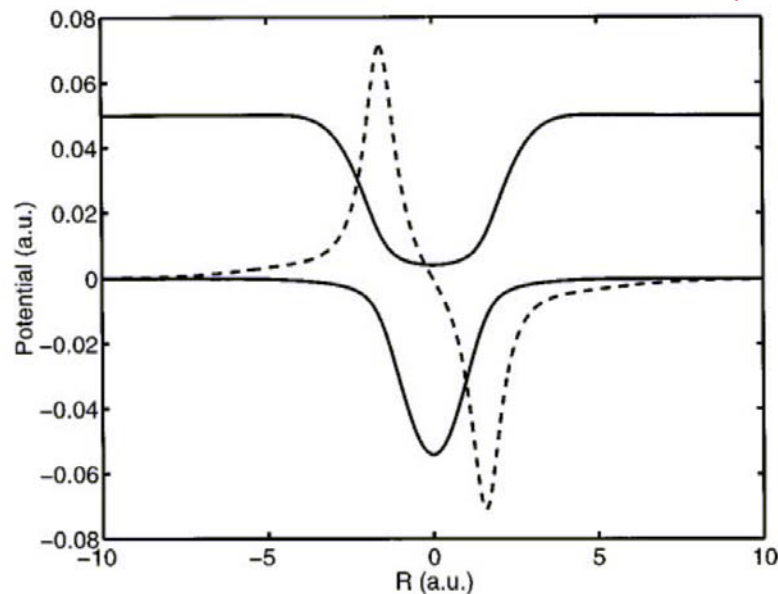
SHORTCOMINGS OF SURFACE HOPPING

5] Quantum Mechanical Coherence Neglected –

~~uses probabilities, not amplitudes~~ FALSE

$$\Psi(t) = \sum_i c_i(t) \varphi_i(R)$$

$$dc_j/dt = -\frac{i}{\hbar} V_{jj} c_j - \dot{R} \cdot \sum_i \langle \varphi_j | \nabla_R \varphi_i \rangle c_i$$



4c. Appraisal of Surface Hopping

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SHORTCOMINGS OF SURFACE HOPPING

6] Decoherence Neglected ?

see talks by:

Maurizio Persico

Irene Burghardt

Mario Barbatti

4c. Appraisal of Surface Hopping

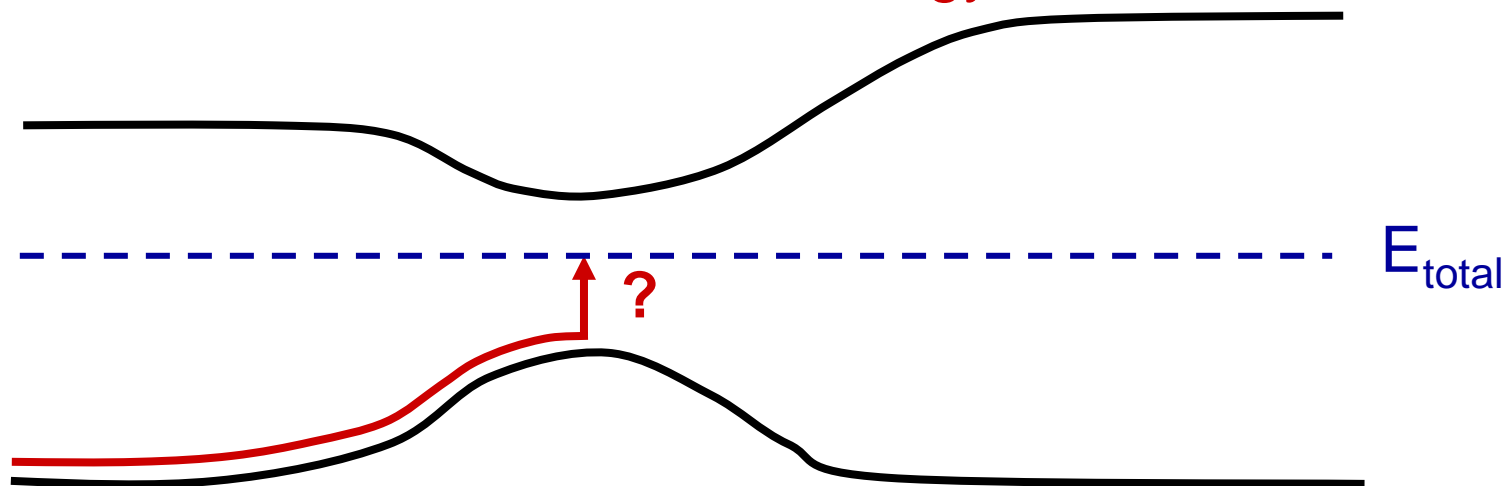
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SHORTCOMINGS OF SURFACE HOPPING

7] Forbidden Hops (or *frustrated hops*)

Hopping algorithm calls for a hop but
there is insufficient kinetic energy



→ probability on state $k \neq |c_k|^2$

4c. Appraisal of Surface Hopping

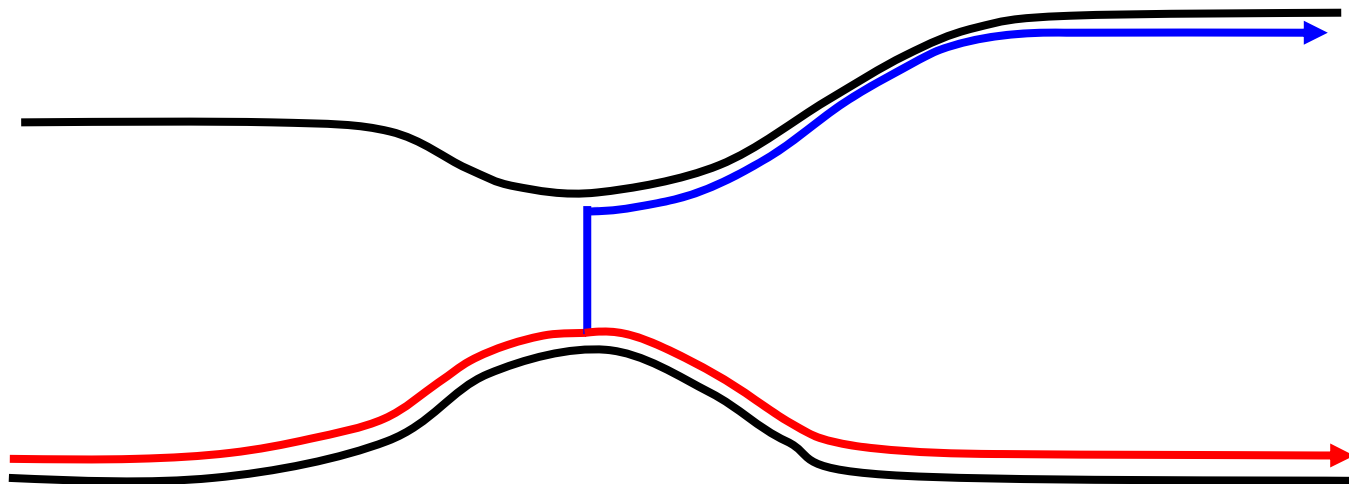
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SHORTCOMINGS OF SURFACE HOPPING

7] Detailed Balance?

What are the populations of the quantum states at equilibrium?



4c. Appraisal of Surface Hopping

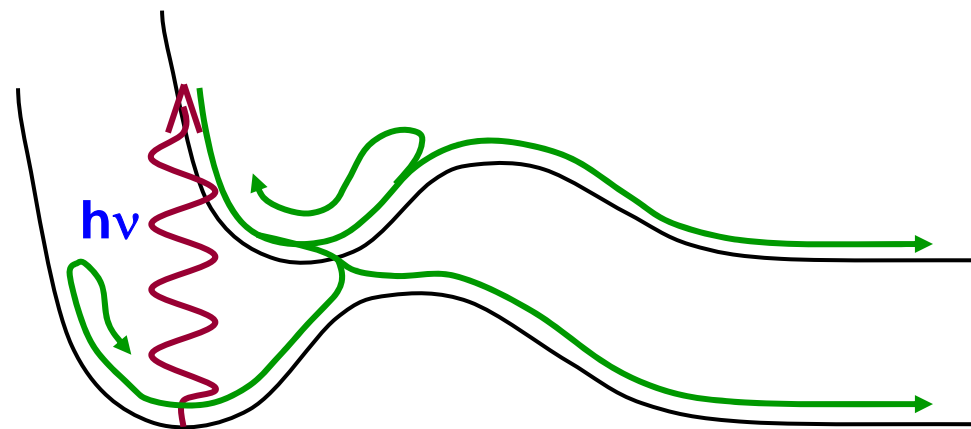
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Detailed Balance: $\mathcal{N}_1 P_{1 \rightarrow 2} = \mathcal{N}_2 P_{2 \rightarrow 1} \rightarrow \text{Equilibrium}$

- Long Timescales
- Multiple Transitions
- Relaxation Processes
- Infrequent events



e.g., nonradiative transition
vs. reaction on excited state

4c. Appraisal of Surface Hopping

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“In theories in which the reservoir is treated classically and its effects on the system described in terms of random functions instead of noncommuting operators, it follows that $W_{mn} = W_{nm}$. This is a serious shortcoming of all semiclassical theories of relaxation.” K. Blum, Density Matrix Theory and Applications, 2nd Ed., (Plenum, NY, 1996).

However

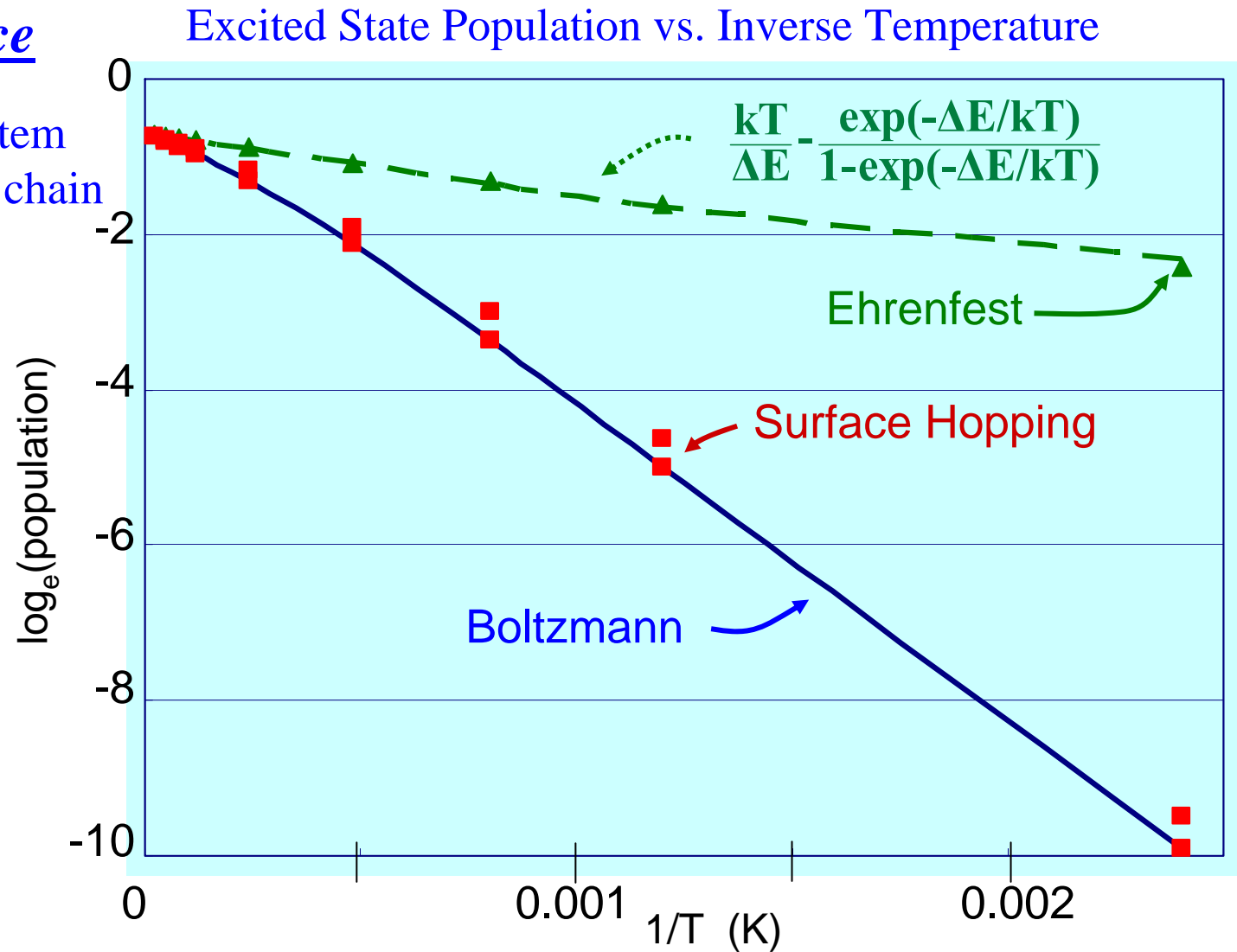
This is **not** true for either Ehrenfest or Surface Hopping

4c. Appraisal of Surface Hopping



Detailed Balance

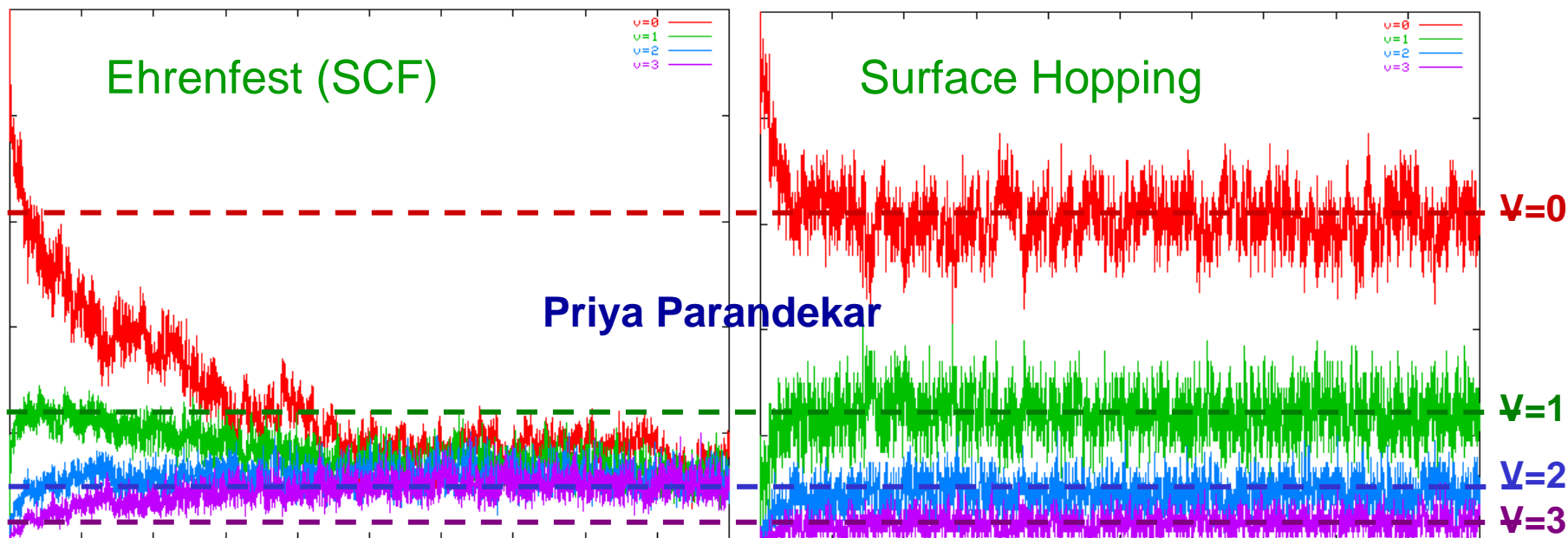
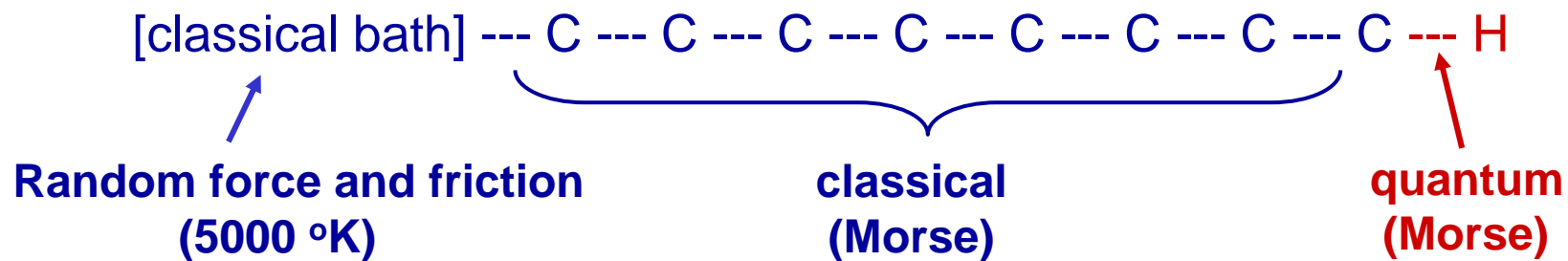
2-state quantum system
coupled to classical chain
 $\Delta E = 34.6$ kJ/mole



4c. Appraisal of Surface Hopping



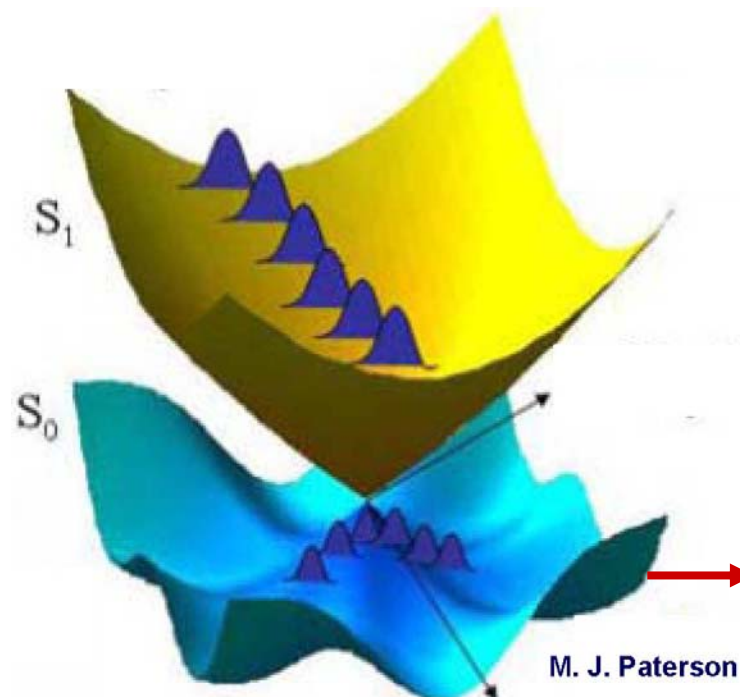
Many Quantum States



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5. Mixed Quantum-Classical Nuclear Motion

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Tenets of Conventional Molecular Dynamics

1. The Born-Oppenheimer
Approximation

Multiple Electronic
States, Metals, ...

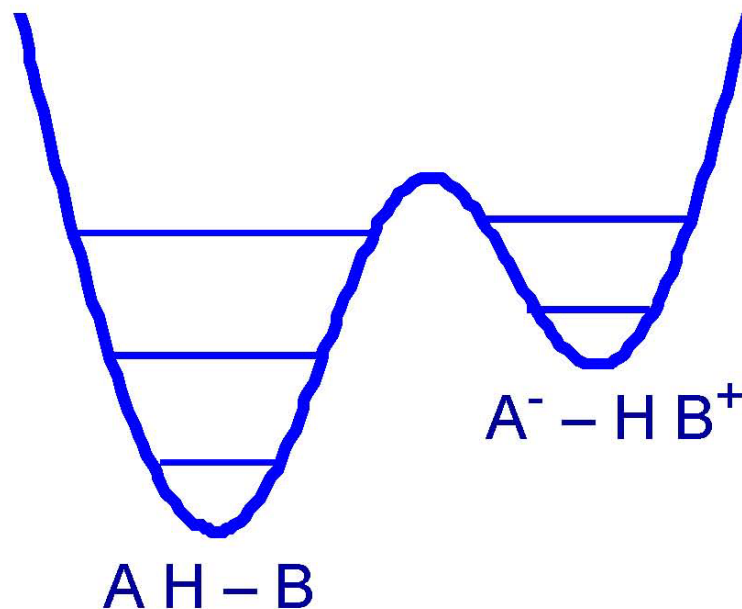
2. Classical Mechanical
Nuclear Motion

Zero Point Motion,
Quantized Energy
Levels, Tunneling

5. Mixed Quantum-Classical Nuclear Motion

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Quantum Effects:

Zero-Point Energy

Quantized Energy Levels

Tunneling