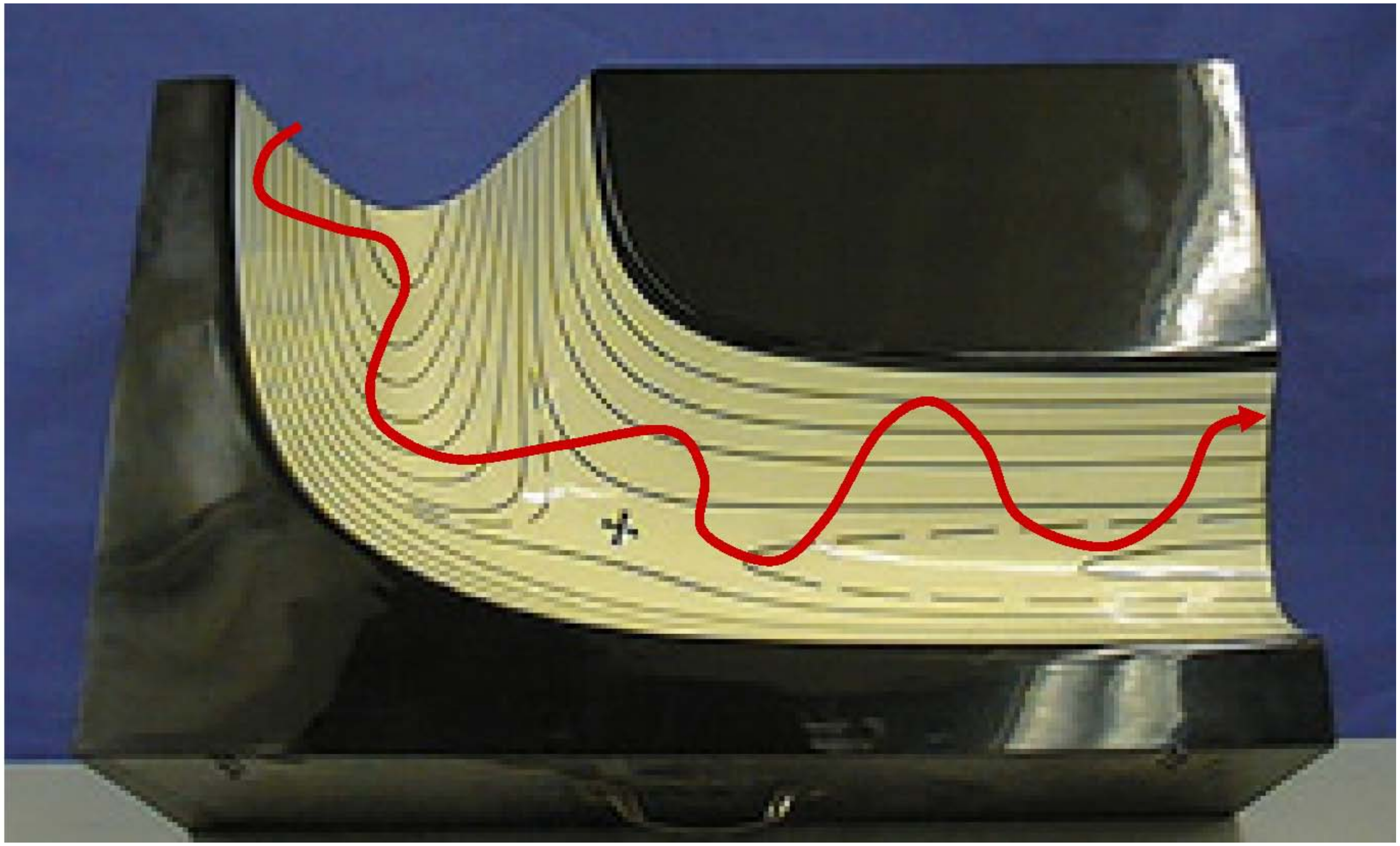
Molecular Dynamics



1 John Lance Natasa Vinod Xiaosong

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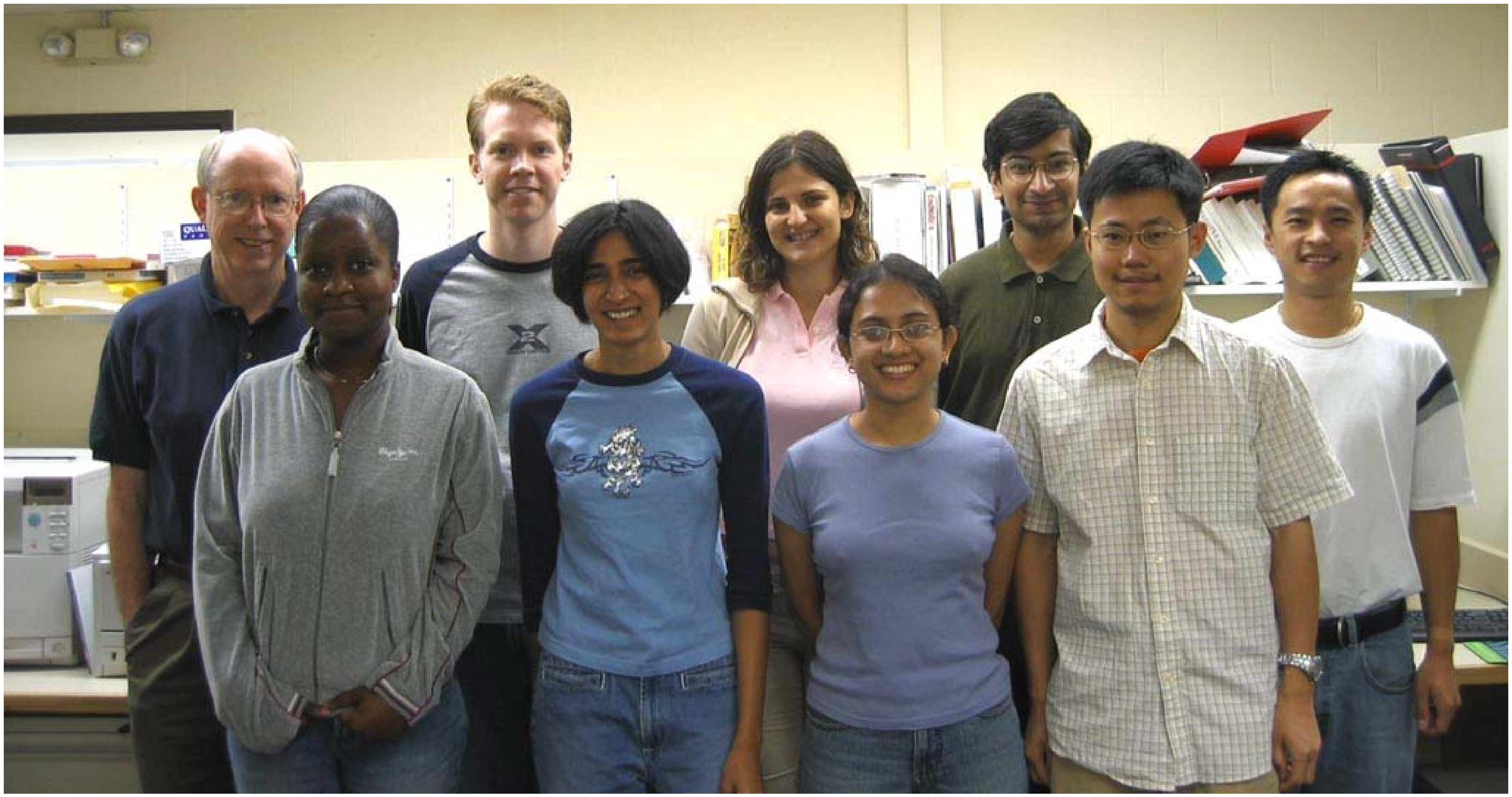
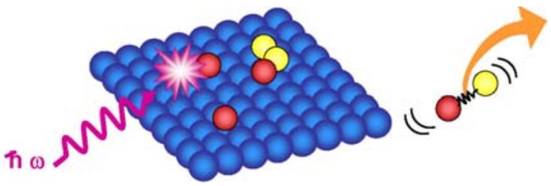


Tully Group: August, 2004



Prelude: Classical Mechanics

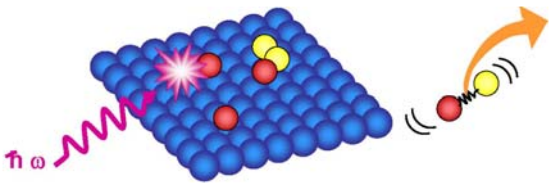
Newton's equations:

$$F \quad = \quad ma \quad = \quad m\ddot{q} \quad = \quad \dot{p}$$

Force is the gradient of the potential:

$$F \quad = \quad -\partial V(q)/\partial q$$

$\longrightarrow$ $$m\ddot{q} \quad = \quad \dot{p} \quad = \quad -\partial V(q)/\partial q$$ Newton's Equations



Prelude: Classical Mechanics

Hamilton’s equations:

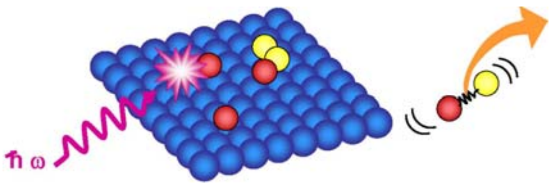
Define total energy = *Hamiltonian*, $\mathcal{H}$:

$$\begin{aligned} \dot{q} &= \partial\mathcal{H}(p,q)/\partial p \\ \dot{p} &= -\partial\mathcal{H}(q,p)/\partial q \end{aligned}$$

Hamilton’s Equations

if $\quad \mathcal{H}(p,q) = \mathcal{T}(p) + V(q) = p^2/2m + V(q)$

$$\longrightarrow \quad \begin{aligned} \dot{q} &= p/m \\ \dot{p} &= -\partial V(q)/\partial q \end{aligned}$$



Prelude: Classical Mechanics

Lagrangian Mechanics:

Define *Lagrangian* L:

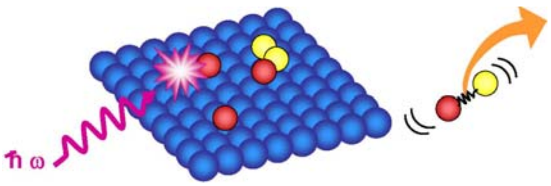
$$\mathcal{L}(q,\dot{q}) \quad = \quad \mathcal{T}(\dot{q}) - V(q)$$

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}}\right) \quad = \quad \frac{\partial \mathcal{L}}{\partial q}$$

Euler-Lagrange Equations

if $\quad \mathcal{L}(q,\dot{q}) \quad = \quad \mathcal{T}(\dot{q}) - V(q) \quad = \quad \frac{1}{2} m\dot{q}^2 - V(q)$

$$\longrightarrow \quad m\ddot{q} \quad = \quad \dot{p} \quad = \quad -\partial V(q)/\partial q$$



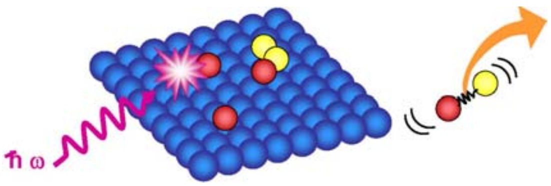
Hamilton-Jacobi Equation:

Define *Hamilton's Principle Function* S:

$$S \;=\; \int p\, dq \qquad = \text{“classical action” integral}$$

$$\frac{\partial S}{\partial t} \;=\; -\mathcal{H}\left(q, \frac{\partial S}{\partial q}\right) \qquad \text{Hamilton-Jacobi Equations}$$

$$\longrightarrow \quad \frac{\partial}{\partial q}\left[\frac{\partial S}{\partial t} + \mathcal{H}\left(q, \frac{\partial S}{\partial q}\right)\right] \;=\; \dot{p} + \frac{\partial V(q)}{\partial q} \;=\; 0$$



Molecular Dynamics

I. The Potential Energy Surface

II. The Classical Limit via the Bohm Equations

III. Adiabatic “on-the-fly” Dynamics

IV. Car-Parrinello Dynamics

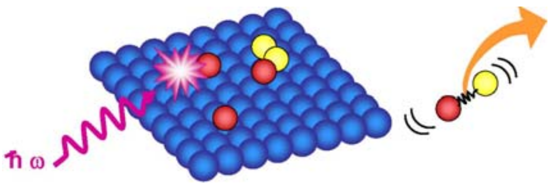
V. Beyond Born Oppenheimer

VI. Ehrenfest Dynamics

VII. Surface Hopping

VIII. Equilibrium in Mixed Quantum-Classical Dynamics

IX. Mixed Quantum-Classical Nuclear Motion



I. The Potential Energy Surface

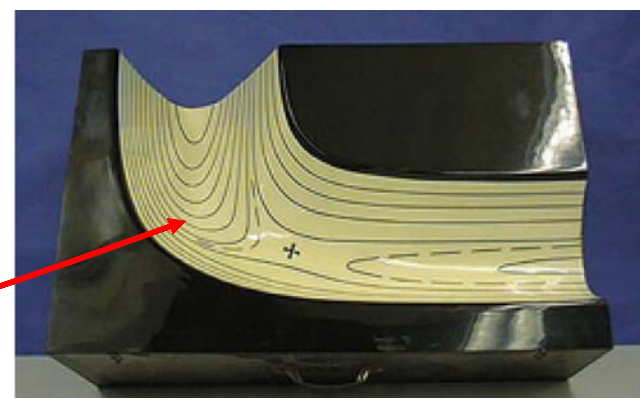
Objective: $$i\hbar \frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t) = \mathcal{H}(\mathbf{r},\mathbf{R})\Psi(\mathbf{r},\mathbf{R},t)$$

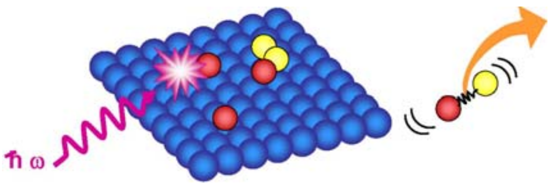
$\mathbf{r}$ = electrons $\qquad$ $\mathbf{R}$ = nuclei

$$\mathcal{H} = -\sum_{\alpha}\frac{\hbar^2}{2M_\alpha}\nabla^2_{R_\alpha} \underbrace{-\sum_i \frac{\hbar^2}{2m_e}\nabla^2_r + V(\mathbf{r},\mathbf{R})} = -\sum_{\alpha}\frac{\hbar^2}{2M_\alpha}\nabla^2_{R_\alpha} + \mathcal{H}_{el}(\mathbf{r};\mathbf{R})$$

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

Adiabatic (Born-Oppenheimer)
Potential Energy Surface





I. The Potential Energy Surface

Born-Oppenheimer Approximation:

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

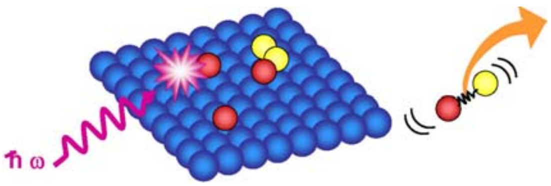
Substitute into TDSE, multiply from left by $\Phi_j^*\left(\mathbf{r};\mathbf{R}\right)$, integrate over **r**:

$$i\hbar\frac{\partial}{\partial t}\Omega_j\left(\mathbf{R},t\right) \;=\; <\Phi_j(\mathbf{r},\mathbf{R})\,|\,\mathcal{H}_{el}\,|\,\Phi_j(\mathbf{r},\mathbf{R})>\Omega_j\left(\mathbf{R},t\right)$$

$$\left[-\sum_\alpha\frac{\hbar^2}{2M_\alpha}<\Phi_j(\mathbf{r},\mathbf{R})\,|\,\nabla^2_{R_\alpha}\Phi_j(\mathbf{r},\mathbf{R})\Omega_j(\mathbf{R})>\right]$$

$$= \quad \mathcal{E}_j(\mathbf{R})\,\Omega_j\left(\mathbf{R},t\right)-\sum_\alpha\frac{\hbar^2}{2M_\alpha}\Big[\;<\Phi_j(\mathbf{r},\mathbf{R})\,|\,\Phi_j(\mathbf{r},\mathbf{R})>\nabla^2_{R_\alpha}$$

$$+\,2<\Phi_j(\mathbf{r},\mathbf{R})\,|\,\nabla_{R_\alpha}\Phi_j(\mathbf{r},\mathbf{R})>\nabla_{R_\alpha}+<\Phi_j(\mathbf{r},\mathbf{R})\,|\,\nabla^2_{R_\alpha}\Phi_j(\mathbf{r},\mathbf{R})>\;\Big]\,\Omega_j(\mathbf{R},t)$$



I. The Potential Energy Surface

Born-Oppenheimer Approximation:

$$i\hbar\frac{\partial}{\partial t}\Omega_j(\mathbf{R},t) \;=\; \mathcal{E}_j(\mathbf{R})\,\Omega_j(\mathbf{R},t) - \sum_\alpha \frac{\hbar^2}{2M_\alpha}\Big[<\Phi_j(\mathbf{r},\mathbf{R})\,|\,\Phi_j(\mathbf{r},\mathbf{R})> \nabla^2_{R_\alpha}$$

$$+\,2<\Phi_j(\mathbf{r},\mathbf{R})\,|\,\nabla_{R_\alpha}\Phi_j(\mathbf{r},\mathbf{R})>\nabla_{R_\alpha} + <\Phi_j(\mathbf{r},\mathbf{R})\,|\,\nabla^2_{R_\alpha}\Phi_j(\mathbf{r},\mathbf{R})> \Big]\,\Omega_j(\mathbf{R},t)$$

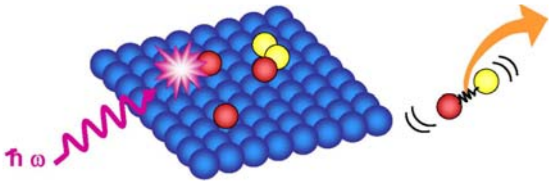
$$\nabla_{R_\alpha} <\Phi_j(\mathbf{r},\mathbf{R})\,|\,\Phi_j(\mathbf{r},\mathbf{R})> \;=\; \nabla_{R_\alpha}(1) \;=\; 0$$

$$=\; <\Phi_j(\mathbf{r},\mathbf{R})\nabla_{R_\alpha}\Phi_j(\mathbf{r},\mathbf{R})> + <\nabla_{R_\alpha}\Phi_j(\mathbf{r},\mathbf{R})\,|\,\Phi_j(\mathbf{r},\mathbf{R})>$$

$$i\hbar\frac{\partial}{\partial t}\Omega_j(\mathbf{R},t) \;=\; \mathcal{E}_j(\mathbf{R})\,\Omega_j(\mathbf{R},t) - \sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla^2_{R_\alpha}\Omega_j(\mathbf{R})$$

$$\cancel{+ <\Phi_j(\mathbf{r},\mathbf{R})\nabla^2_{R_\alpha}\Phi_j(\mathbf{r},\mathbf{R})>\Omega_j(\mathbf{R},t)}$$

???

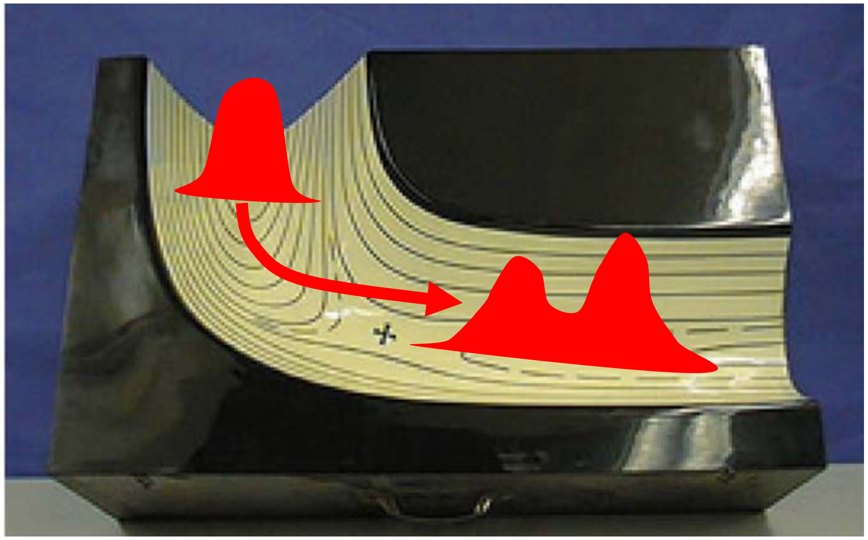


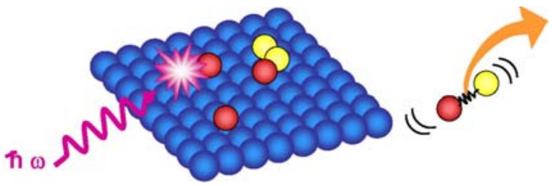
I. The Potential Energy Surface

Born-Oppenheimer Approximation:

$$i\hbar \frac{\partial}{\partial t}\Omega_j(\mathbf{R},t) \quad = \quad -\sum_{\alpha} \frac{\hbar^2}{2M_\alpha}\nabla^2_{R_\alpha}\Omega_j(\mathbf{R}) + \mathcal{E}_j(\mathbf{R})\,\Omega_j(\mathbf{R},t)$$

where $$\mathcal{E}_j(\mathbf{R}) \quad = \quad \langle \Phi_j(\mathbf{r},\mathbf{R}) \,|\, \mathcal{H}_{el} \,|\, \Phi_j(\mathbf{r},\mathbf{R}) \rangle$$





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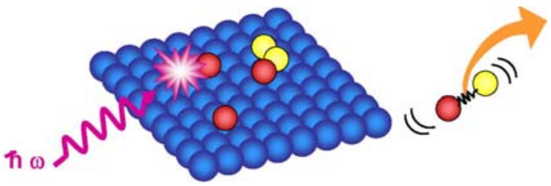


II. Classical Limit via Bohm Eqs.

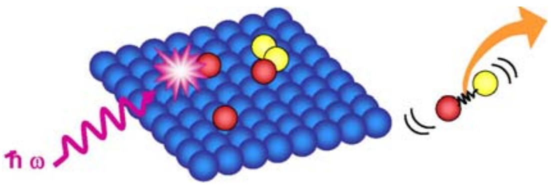
$$i\hbar \frac{\partial}{\partial t}\Omega_j(\mathbf{R},t) = \left[-\sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla^2_{R_\alpha} + \mathcal{E}_j(\mathbf{R}) \right]\Omega_j(\mathbf{R},t) \qquad (1)$$

$$\Omega_j(\mathbf{R},t) = A_j(\mathbf{R},t)\exp[\frac{i}{\hbar}S_j(\mathbf{R},t)] \qquad (2)$$

Substitute (2) into (1) and separate real and imaginary parts:

$$\rightarrow \quad \dot{S}_j = -\sum_\alpha \frac{1}{2M_\alpha}[\nabla_{R_\alpha}S_j]^2 - \mathcal{E}_j(\mathbf{R}) - \sum_\alpha \frac{\hbar^2}{2M_\alpha}\frac{\nabla^2_{R_\alpha}A_j}{A_j} \qquad (3)$$

$$\rightarrow \quad \dot{A}_j = \sum_\alpha \frac{1}{2M_\alpha}\left\{2[\nabla_{R_\alpha}A_j]\bullet[\nabla_{R_\alpha}S_j] - A_j\nabla^2_{R_\alpha}S_j\right\} \qquad (4)$$



II. Classical Limit via Bohm Eqs.

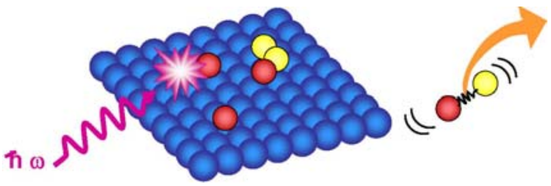
Compare Eq. (3) with Hamilton-Jacobi Equation:

$$\frac{\partial S}{\partial t} = -\mathcal{H}\left(q, \frac{\partial S}{\partial q}\right) \qquad \text{where} \qquad \frac{\partial S}{\partial q} = p$$

$$\dot{S}_j = -\sum_\alpha \frac{1}{2M_\alpha}[\nabla_{R_\alpha} S_j]^2 - \mathcal{E}_j(\mathbf{R}) - \sum_\alpha \frac{\hbar^2}{2M_\alpha} \frac{\nabla^2_{R_\alpha} A_j}{A_j} \qquad (3)$$

the "quantum potential"

$$\hbar \to 0: \qquad \dot{S}_j = -\sum_\alpha \frac{1}{2M_\alpha}[\nabla_{R_\alpha} S_j]^2 - \mathcal{E}_j(\mathbf{R})$$



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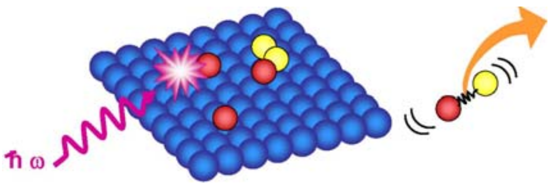


III. Adiabatic “on-the-fly” Dynamics

The Hellman – Feynman Theorem:

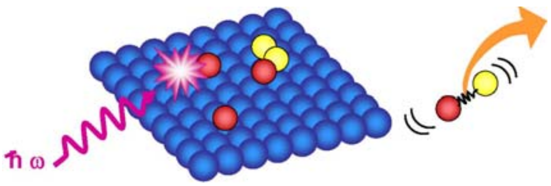
$$\frac{d}{dR}\mathcal{E}_j(R) = \frac{d}{dR}\langle \Phi_j(R) \,|\, \mathcal{H}_{el}(R) \,|\, \Phi_j(R) \rangle$$

subject to $$\langle \Phi_j(R) \,|\, \Phi_j(R) \rangle = 1$$

and $$\mathcal{H}_{el}(R) \,|\, \Phi_j(R) \rangle = \mathcal{E}_j(R) \,|\, \Phi_j(R) \rangle$$

$$\Rightarrow \quad \frac{d}{dR}\mathcal{E}_j(R) = \left\langle \Phi_j(R) \,\middle|\, \frac{d\mathcal{H}_{el}(R)}{dR} \,\middle|\, \Phi_j(R) \right\rangle$$

$$+ \left\langle \frac{d}{dR}\Phi_j(R) \,\middle|\, \mathcal{H}_{el}(R) \,\middle|\, \Phi_j(R) \right\rangle + \left\langle \Phi_j(R) \,\middle|\, \mathcal{H}_{el}(R) \,\middle|\, \frac{d}{dR}\Phi_j(R) \right\rangle$$



III. Adiabatic “on-the-fly” Dynamics

The Hellman – Feynman Theorem:

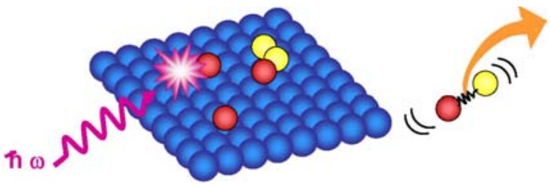
$$\frac{d}{dR}\mathcal{E}_j(R) \;=\; \left\langle \Phi_j(R) \,\middle|\, \frac{d\mathcal{H}_{el}(R)}{dR} \,\middle|\, \Phi_j(R) \right\rangle$$

$$+\left\langle \frac{d}{dR}\Phi_j(R) \,\middle|\, \mathcal{H}_{el}(R) \,\middle|\, \Phi_j(R) \right\rangle + \left\langle \Phi_j(R) \,\middle|\, \mathcal{H}_{el}(R) \,\middle|\, \frac{d}{dR}\Phi_j(R) \right\rangle$$

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

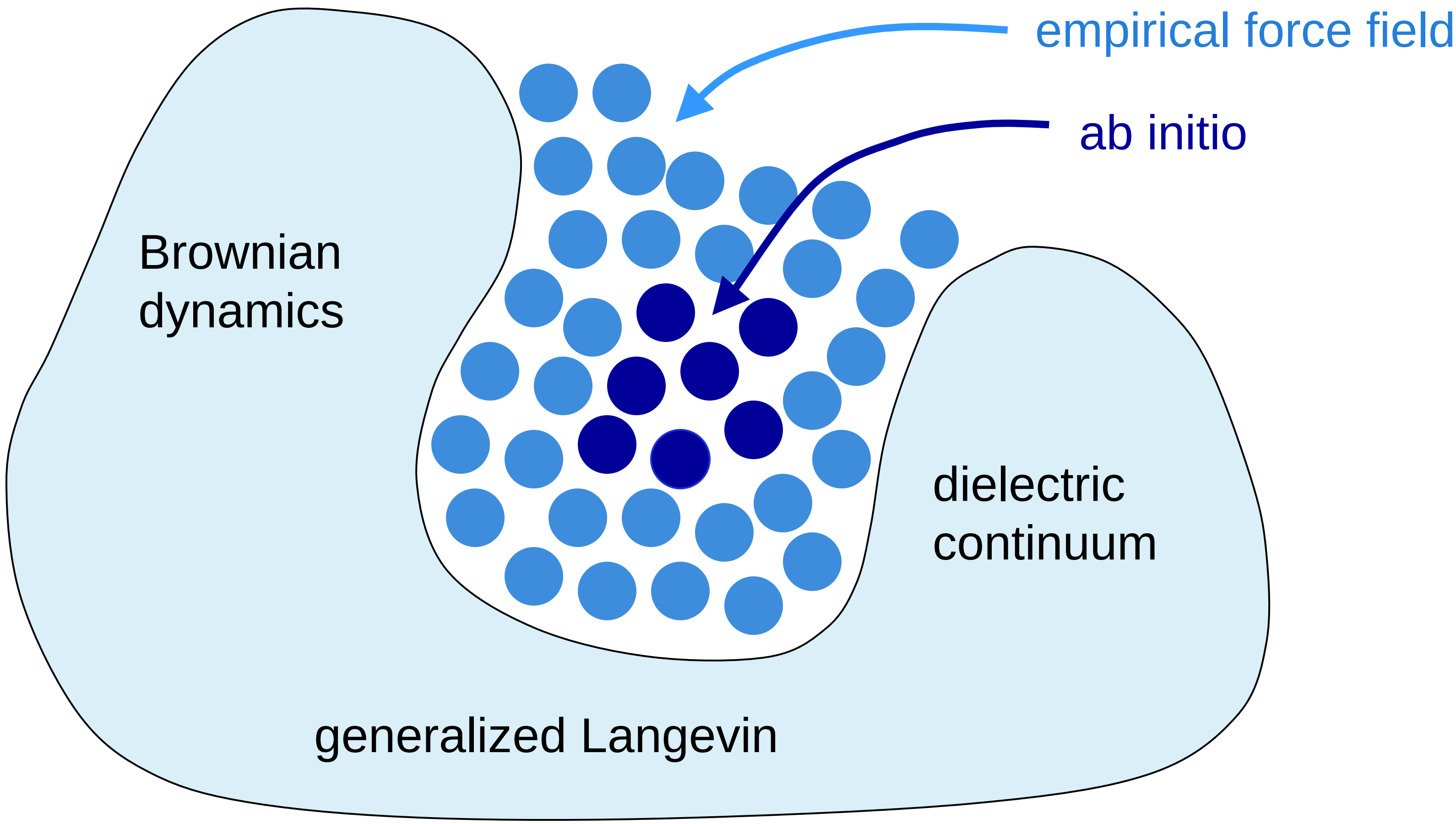
$$+\,\mathcal{E}_j(R)\left[\underbrace{\left\langle \frac{d}{dR}\Phi_j(R) \,\middle|\, \Phi_j(R) \right\rangle + \left\langle \Phi_j(R) \,\middle|\, \frac{d}{dR}\Phi_j(R) \right\rangle}_{}\right]$$

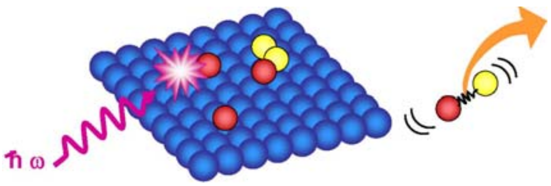
$$= \;\frac{d}{dR}\Big[\big\langle \Phi_j(R) \,\big|\, \Phi_j(R) \big\rangle\Big] \;=\; 0$$



III. Adiabatic "on-the-fly" Dynamics

QM/MM Approach:





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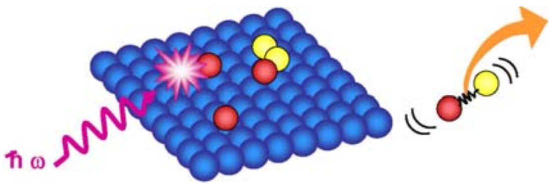


IV. Car-Parrinello Dynamics

Euler-Lagrange equations: $$\frac{d}{dt}\frac{d\mathcal{L}}{d\dot{q}} = \frac{\partial \mathcal{L}}{\partial q}$$

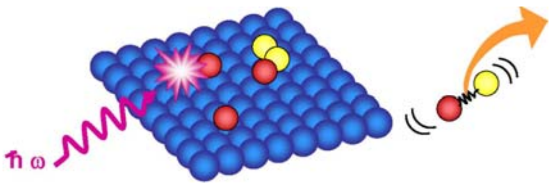
Classical Lagrangian: $$\mathcal{L} = T - V = \sum_{\alpha} \tfrac{1}{2} M_{\alpha} \dot{R}^2 - \mathcal{E}_j(\mathbf{R})$$

$$\longrightarrow \quad M_{\alpha} \ddot{R}_{\alpha} = -\partial \mathcal{E}_j(\mathbf{R}) / \partial R_{\alpha}$$

Car-Parrinello Lagrangian: $$\mathcal{L} = \sum_{\alpha} \tfrac{1}{2} M_{\alpha} \dot{R}^2 - < \Psi_j \,|\, \mathcal{H}_{el} \,|\, \Psi_j > + \sum_{n} \tfrac{1}{2} \mu_n < \dot{\varphi}_n \,|\, \dot{\varphi}_n > + \sum_{nm} \lambda_{nm} [< \varphi_n \,|\, \varphi_m > - \delta_{nm}]$$

$$\longrightarrow \quad M_{\alpha} \ddot{R}_{\alpha} = -\partial < \Psi_j \,|\, \mathcal{H}_{el} \,|\, \Psi_j > / \partial R_{\alpha}$$

$$\longrightarrow \quad \mu_n \ddot{\varphi}_n = -\delta < \Psi_j \,|\, \mathcal{H}_{el} \,|\, \Psi_j > / \delta \varphi_n^{*} + \sum_{m} \lambda_{nm} \varphi_m$$



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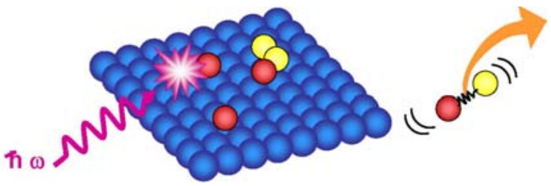

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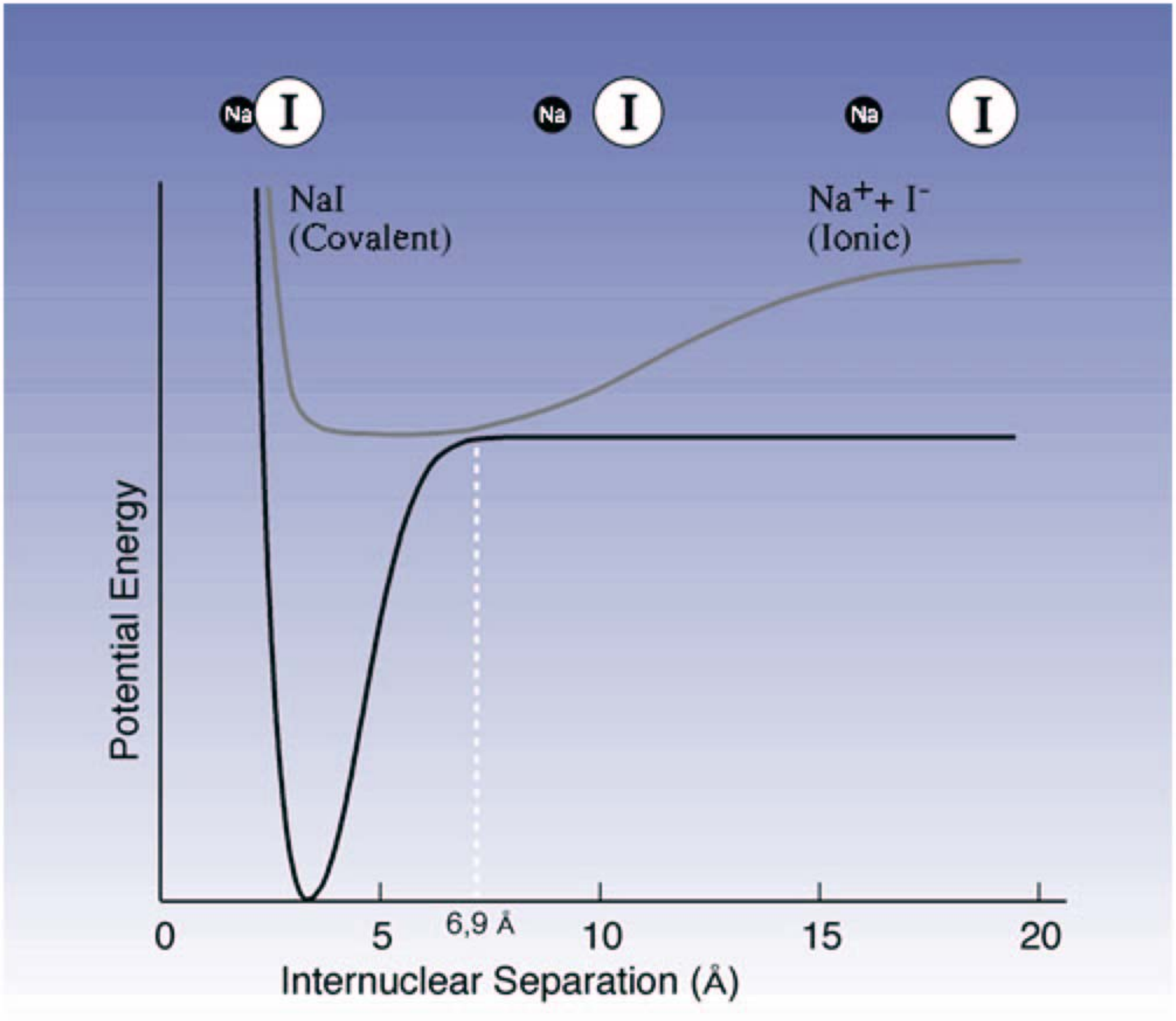
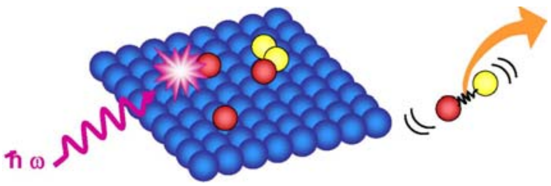




V. Beyond Born-Oppenheimer

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

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

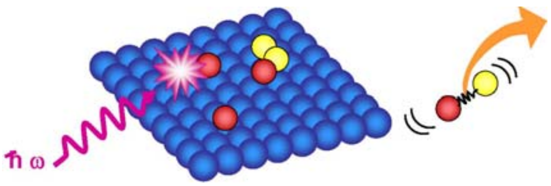
$$-\frac{\hbar^2}{2}\sum_\alpha M_\alpha^{-1}\nabla^2_{R_\alpha}\Omega_j(\mathbf{R}) + \mathcal{E}_j(\mathbf{R})\,\Omega_j(\mathbf{R}) - E\,\Omega_j(\mathbf{R}) =$$

$$-\frac{\hbar^2}{2}\sum_i D_{ji}(\mathbf{R})\,\Omega_i(\mathbf{R}) + \hbar^2\sum_{i\neq j}\mathbf{d}_{ji}(\mathbf{R})\cdot\nabla_{R_\alpha}\Omega_i(\mathbf{R})$$

where nonadiabatic (derivative) couplings are defined by:

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

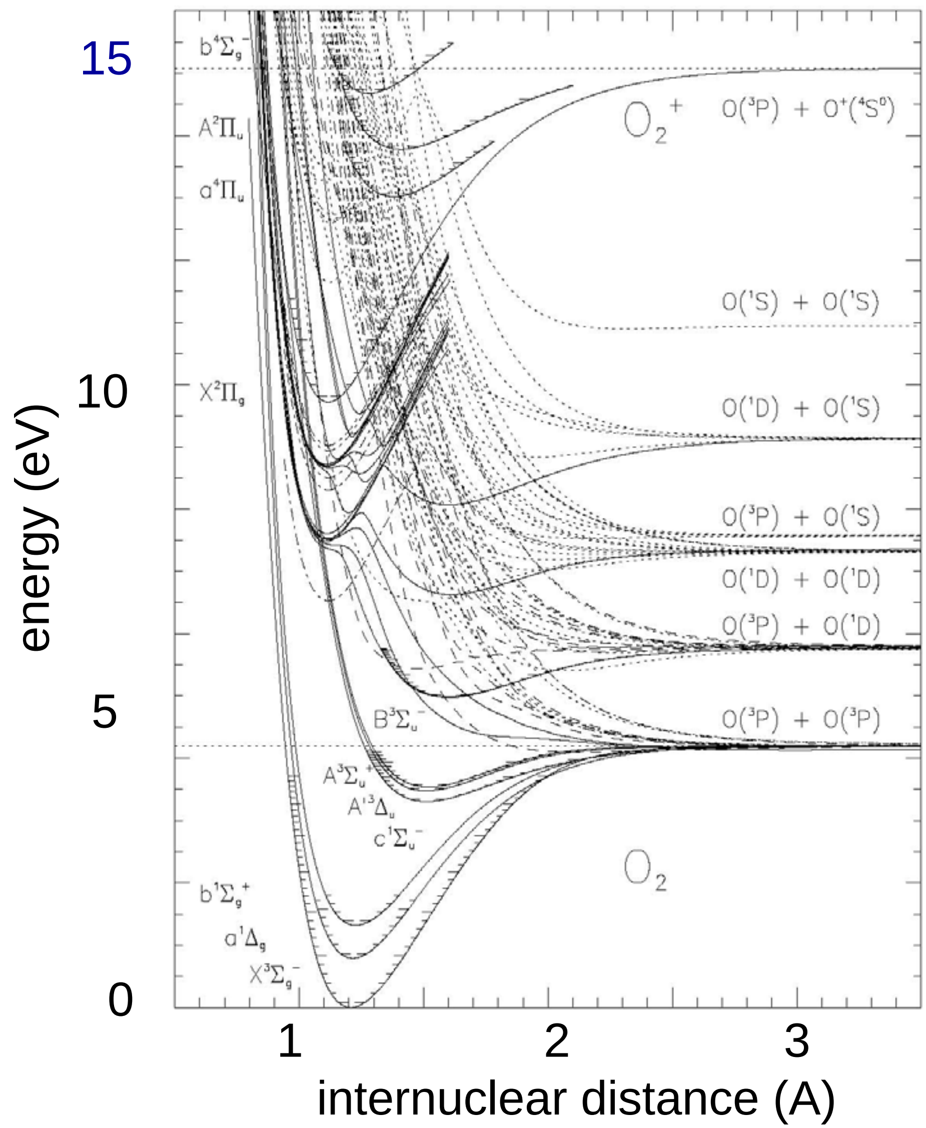
$$D_{ij}(\mathbf{R}) = -\sum_\alpha M_\alpha^{-1}\int\left\{\Phi_i^*(\mathbf{r},\mathbf{R})\left[\nabla^2_{R_\alpha}\Phi_j(\mathbf{r},\mathbf{R})\right]\right\}d\mathbf{r}$$

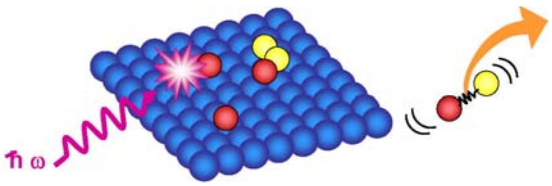


V. Beyond Born-Oppenheimer

Potential Energy Curves
for the
Oxygen Molecule

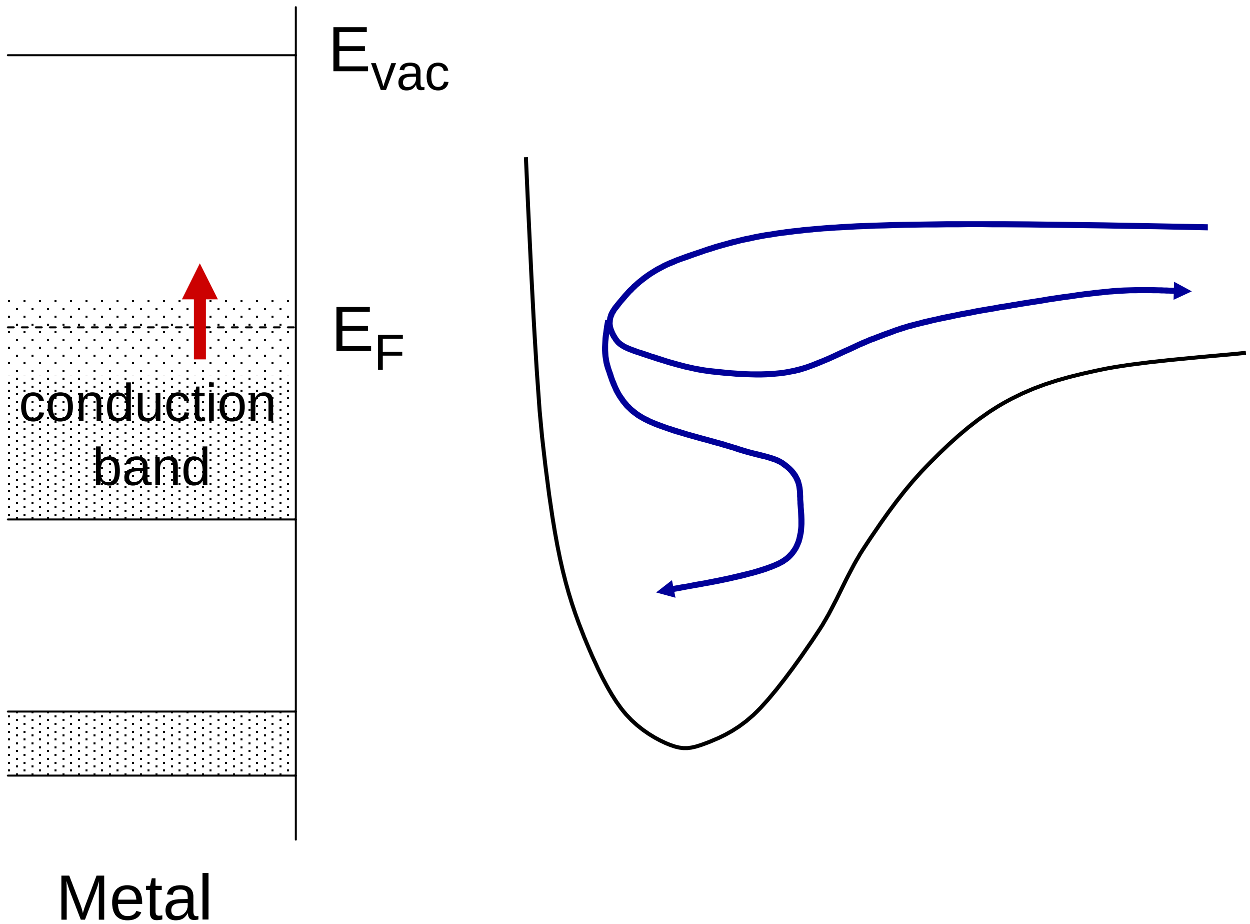
from
R. P. Saxon and B. Liu,
J. Chem. Phys. 1977

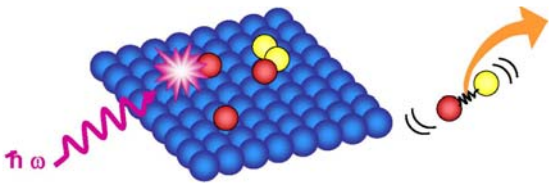




V. Beyond Born-Oppenheimer

Nonadiabatic Transitions at Metal Surfaces: Electron-Hole Pairs

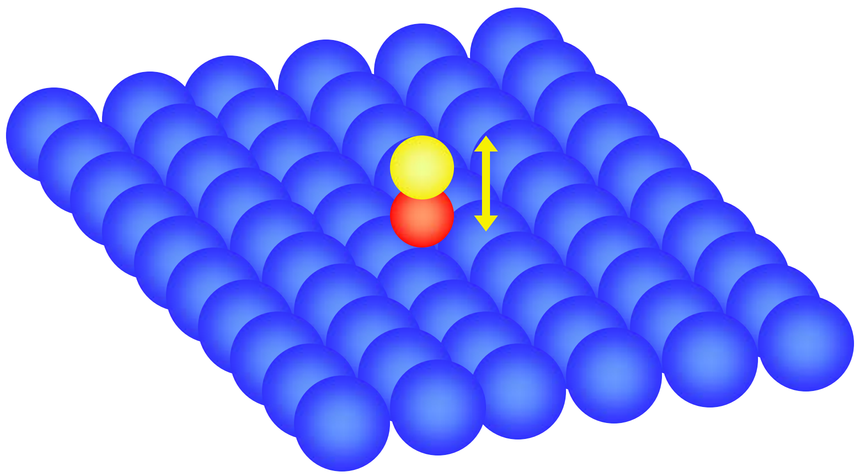




V. Beyond Born-Oppenheimer

Vibrational Lifetime of CO on Cu(100)

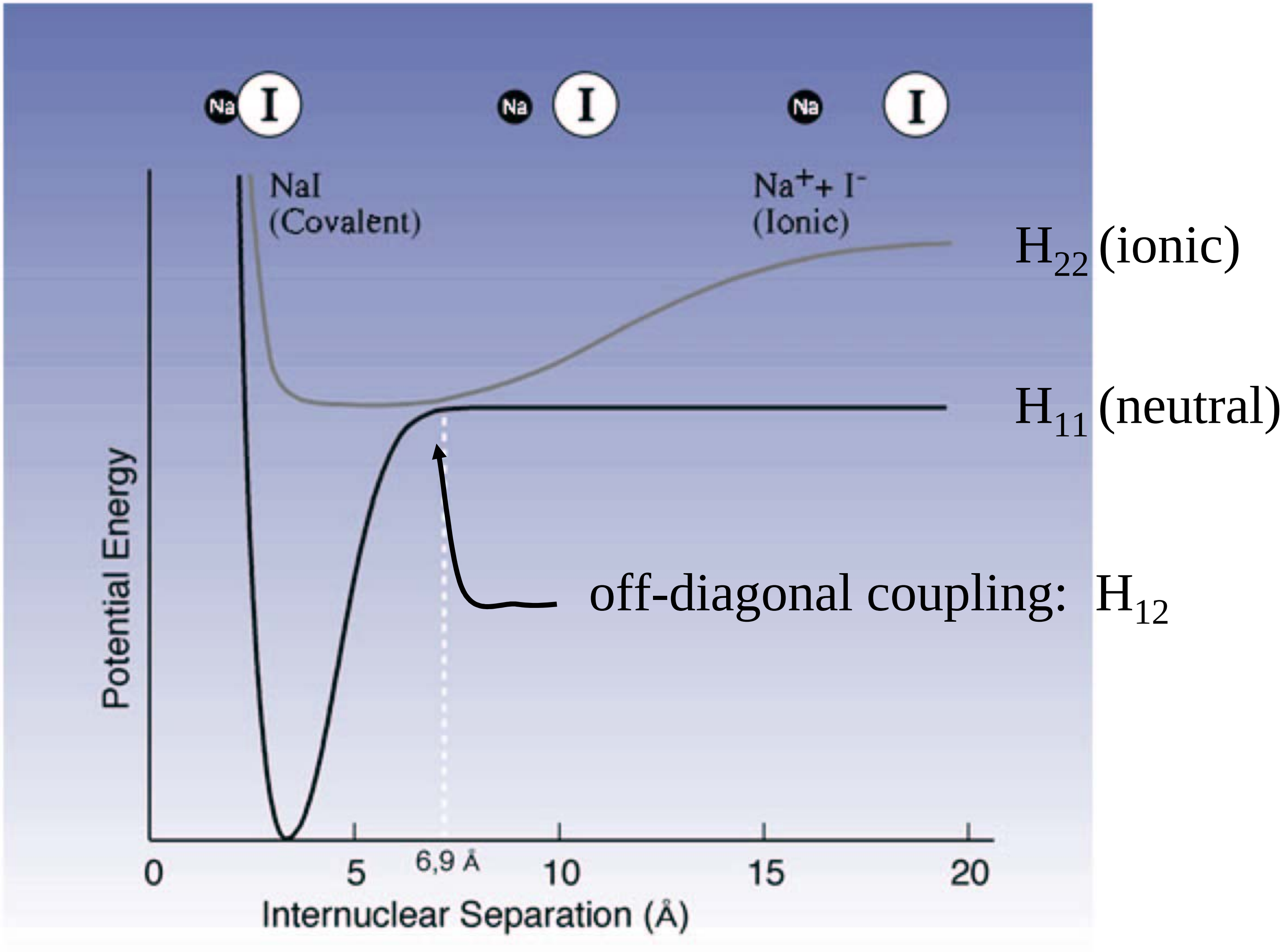
$$v = 1 \longrightarrow v = 0$$



Molecular Dynamics: $t \sim 10^{-3}$ s.

Experiment (A. Harris et al.): $t = 2.5$ ps.

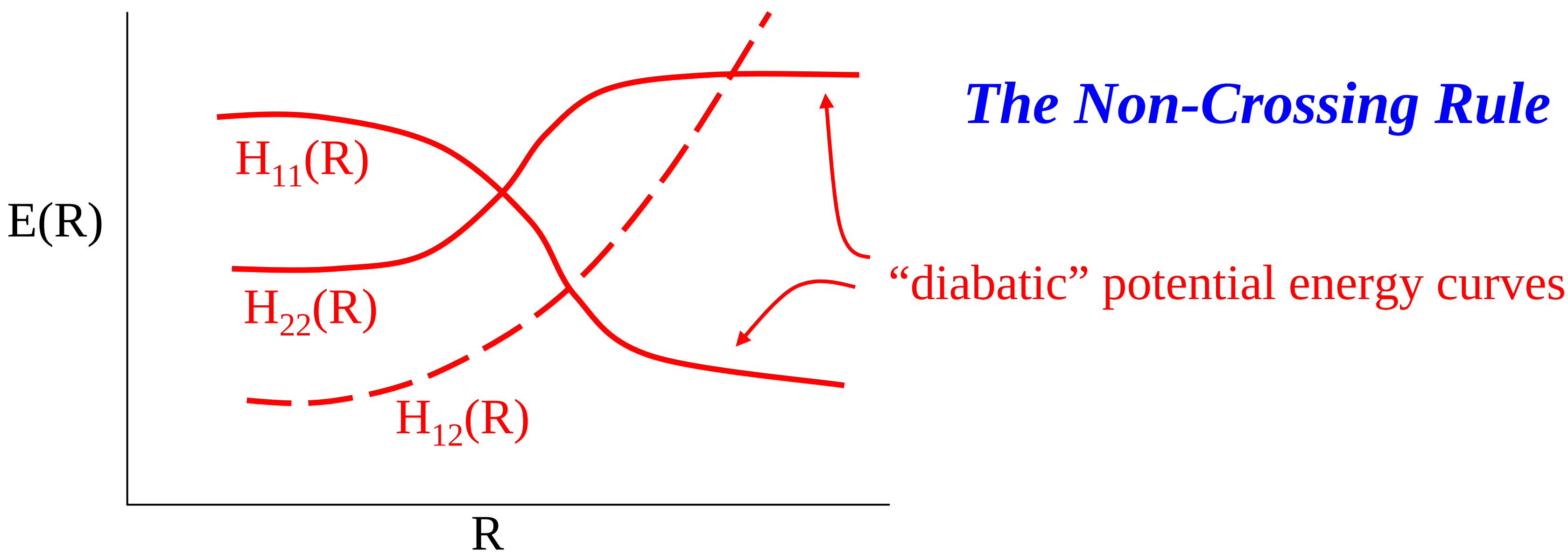
V. Beyond Born-Oppenheimer



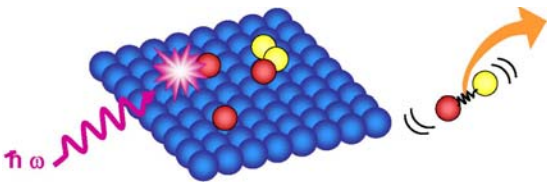
V. Beyond Born-Oppenheimer

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

The Non-Crossing Rule

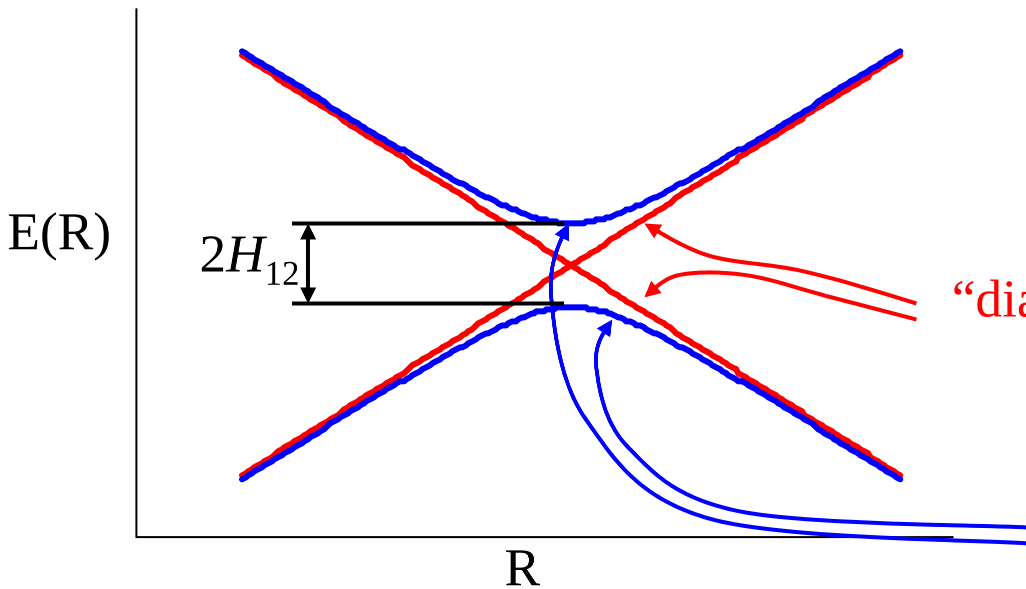


$$\mathcal{E}_{\pm}(R) = \frac{H_{11}(R) + H_{22}(R)}{2} \pm \frac{1}{2}\sqrt{[H_{11}(R) - H_{22}(R)]^2 + 4[H_{12}(R)]^2}$$



V. Beyond Born-Oppenheimer

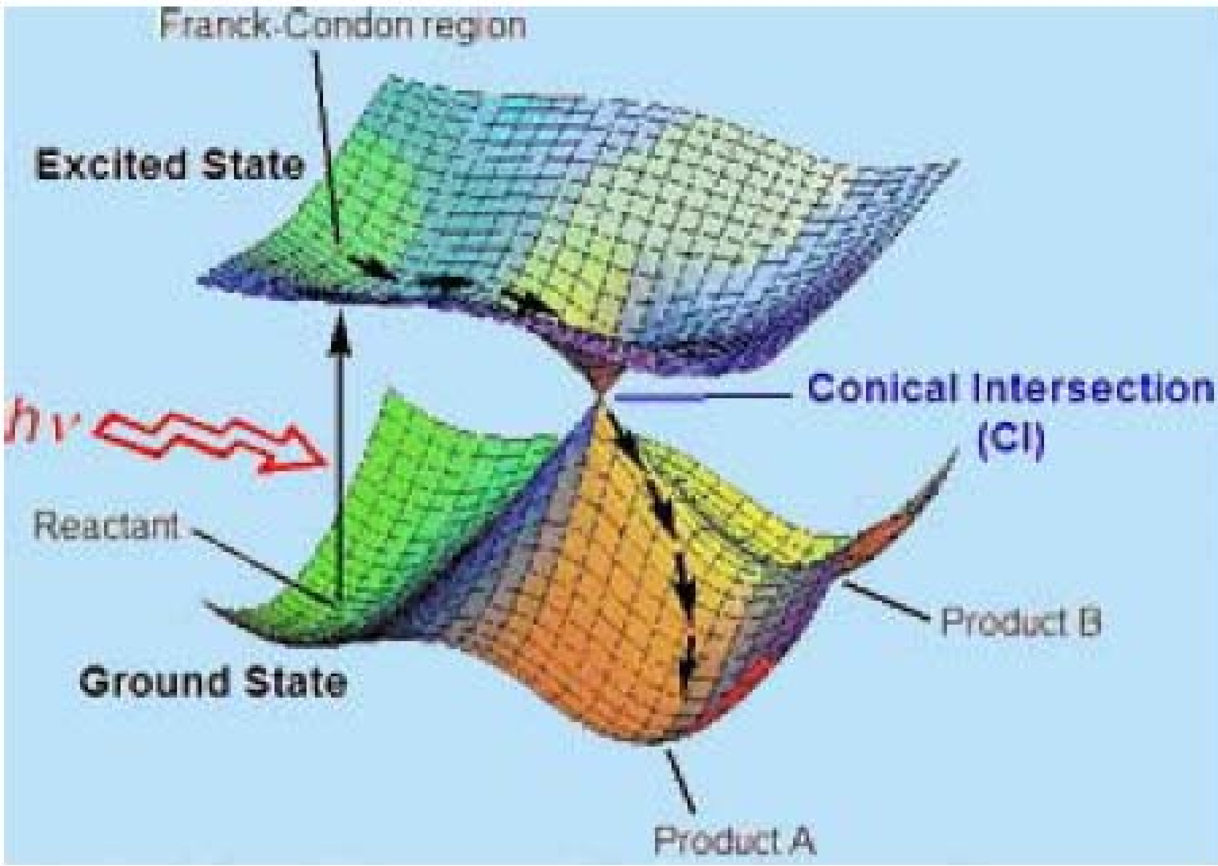
$$\mathcal{H}(R) = \begin{bmatrix} H_{11}(R) & H_{12}(R) \\ H_{12}(R) & H_{22}(R) \end{bmatrix}$$



The Non-Crossing Rule

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

V. Beyond Born-Oppenheimer



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

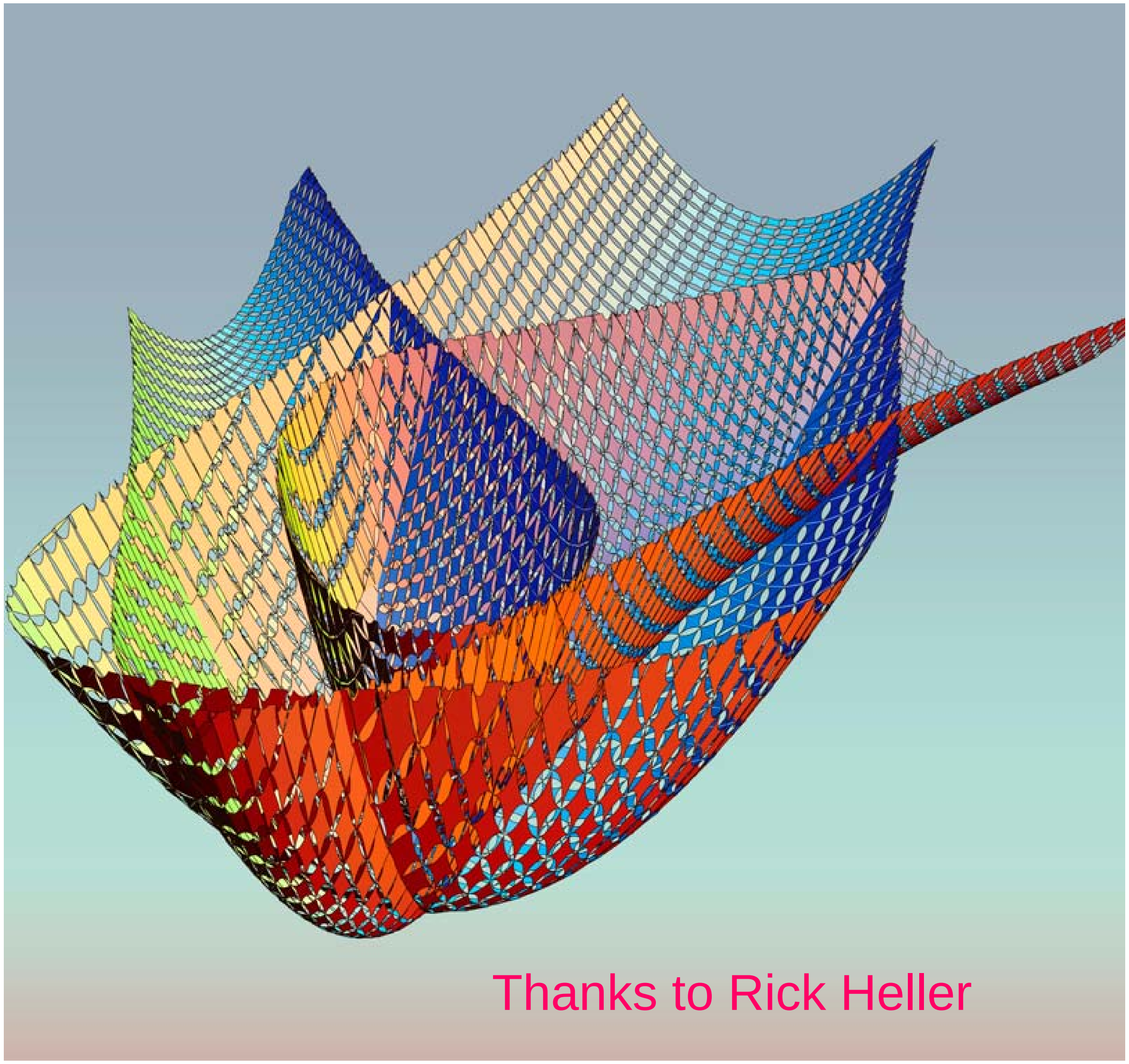
"Conical Intersection"

N degrees of freedom:

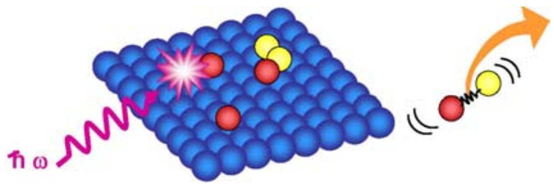
N-2 dimensional "seam"

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

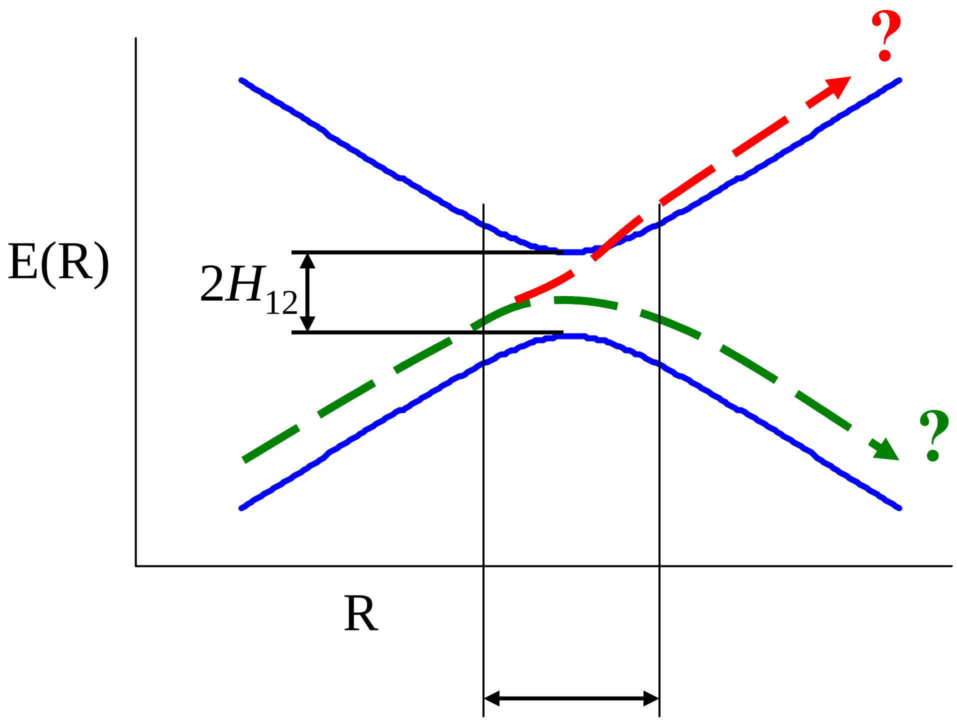
V. Beyond Born-Oppenheimer



Thanks to Rick Heller



V. Beyond Born-Oppenheimer



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

The Massey Criterion:

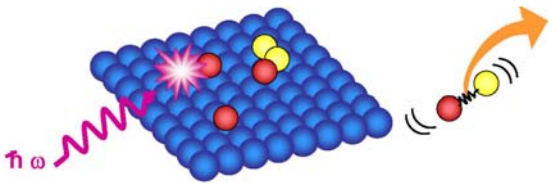
$$\Delta\mathcal{E}\,\Delta t \quad \gg \quad \hbar$$

$$\Delta\mathcal{E} \quad \approx \quad 2\,H_{12}$$

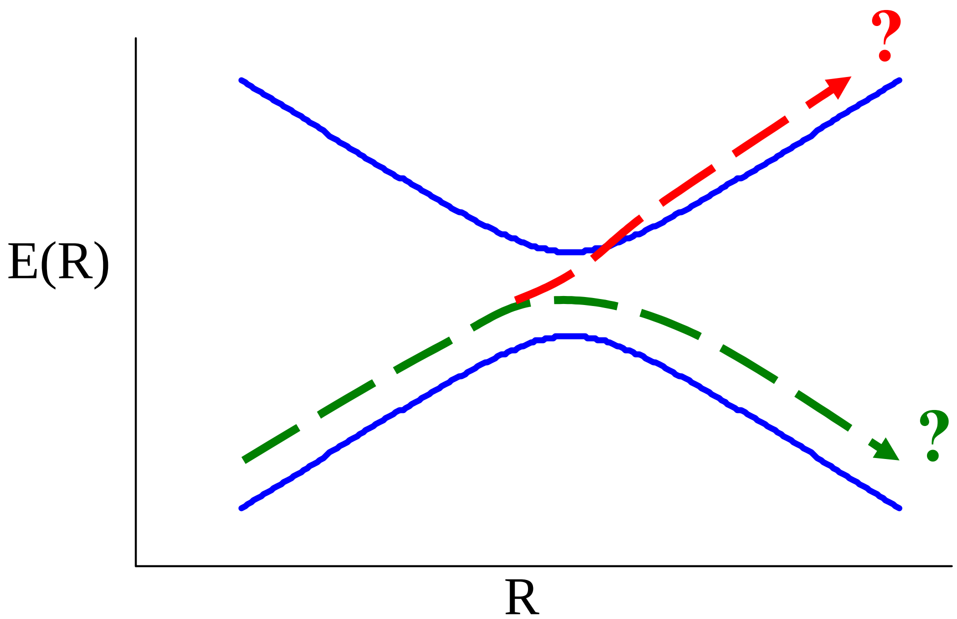
$$\Delta t \quad \approx \quad \text{distance/velocity}$$

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

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



V. Beyond Born-Oppenheimer

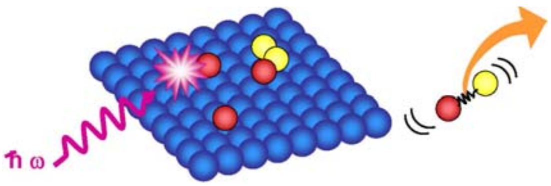


Landau-Zener Approximation

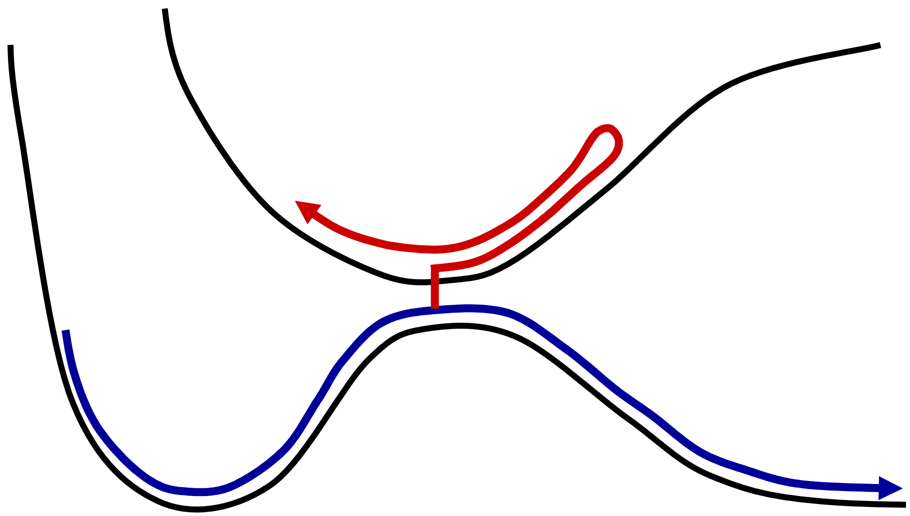
Assumptions:

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

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

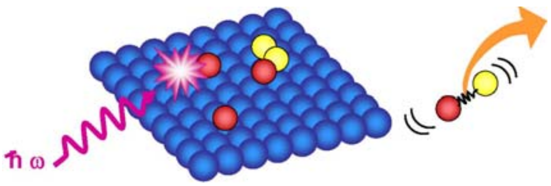


V. Beyond Born-Oppenheimer



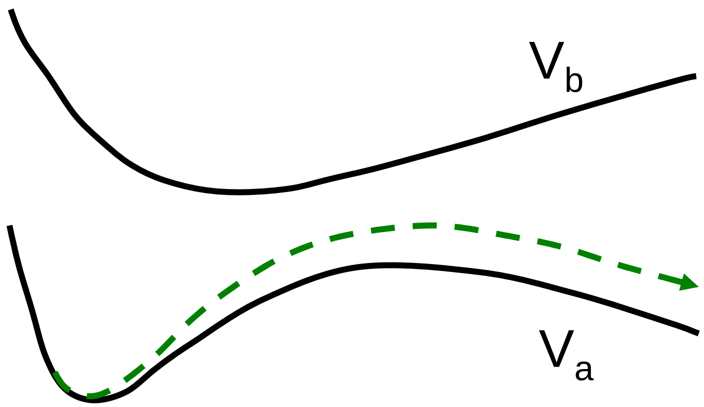
- Classical motion induces electronic transitions
- Quantum state determines classical forces

→ Quantum – Classical Feedback: Self-Consistency

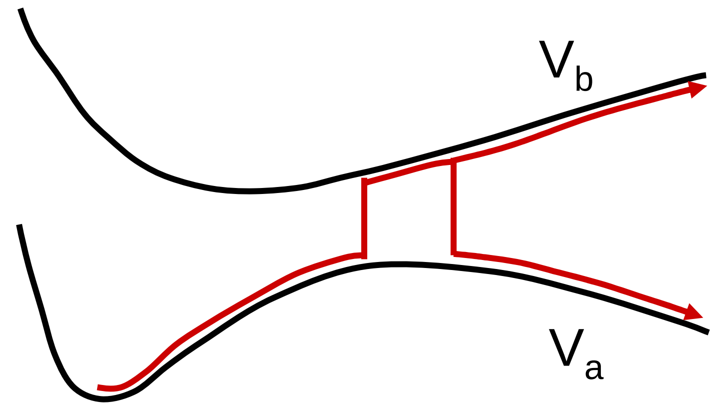


V. Beyond Born-Oppenheimer

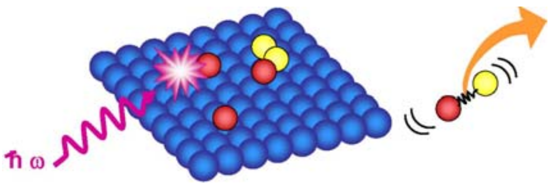
TWO GENERAL MIXED QUANTUM-CLASSICAL APPROACHES FOR INCLUDING FEEDBACK



Ehrenfest (SCF)

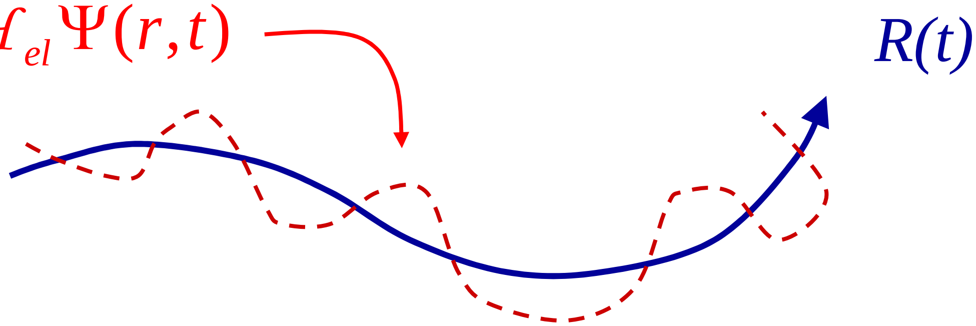


Surface-Hopping



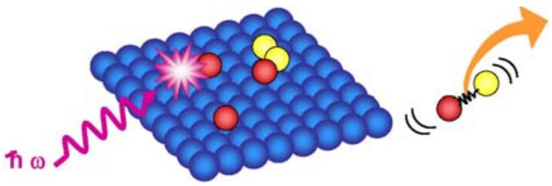
V. Beyond Born-Oppenheimer

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



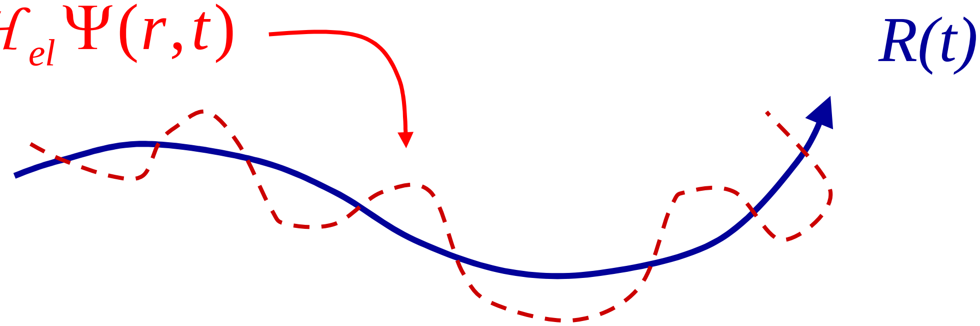
$$\Psi(r,t) = \sum_i c_i(t)\ \Phi_i(r;R)$$ (adiabatic states)

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



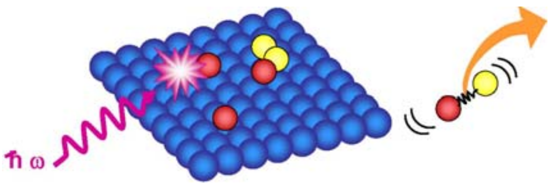
V. Beyond Born-Oppenheimer

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

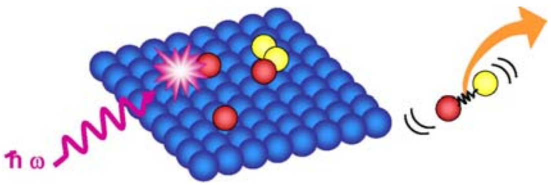


Classical path must respond **self-consistently** to quantum transitions: "quantum back-reaction"

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



Molecular Dynamics



VI. Ehrenfest Dynamics

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

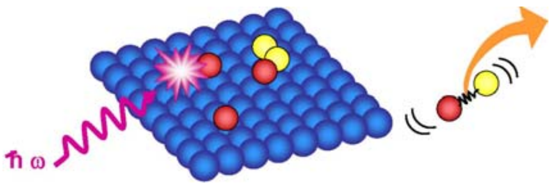
Self-consistent Field Approximation (fully quantum):

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

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 $\Xi(\mathbf{r},t)$:

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

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



VI. Ehrenfest Dynamics

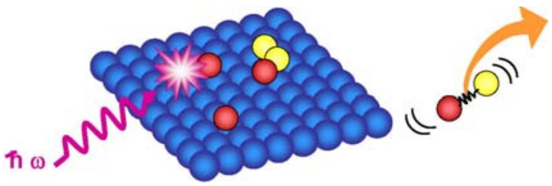
Substituting (2) into (1), multiplying on the left by $\Xi(\mathbf{r},t)$ and integrating over $\mathbf{r}$ gives the equivalent SCF equation for the nuclear wave function $\Omega(\mathbf{R},t)$:

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

The classical (Ehrenfest) limit requires 2 steps:

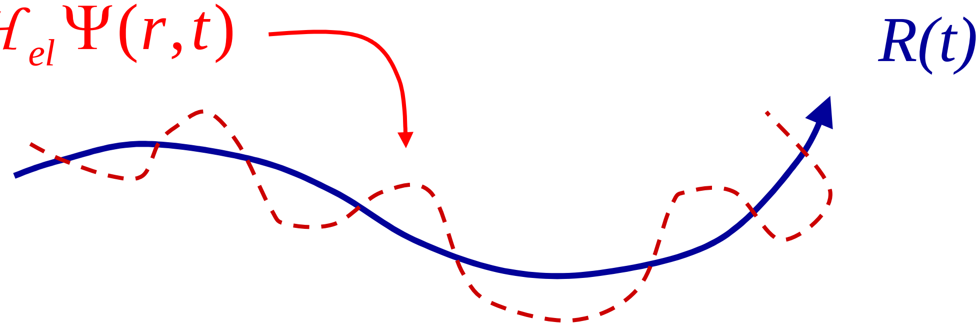
1. Replace $\Omega(\mathbf{R},t)$ with a delta function in Eq. (4)
2. Take the classical limit of Eq. (5) (eg. using the Bohm formulation as above).

Thus, the potential energy function governing the nuclei becomes
$\int \Xi^*(\mathbf{r},t)\mathcal{H}_{el}(\mathbf{r},\mathbf{R})\Xi(\mathbf{r},t)\,d\mathbf{r}$ instead of the adiabatic energy $\mathcal{E}_j(\mathbf{R})$.

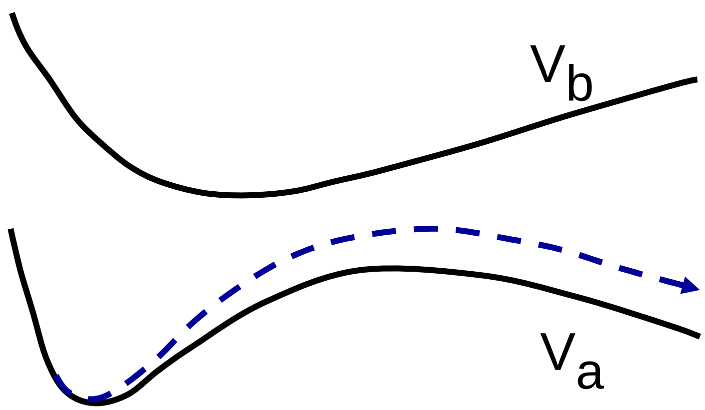


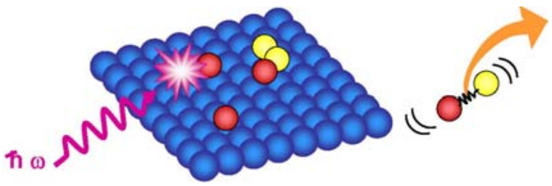
VI. Ehrenfest Dynamics

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



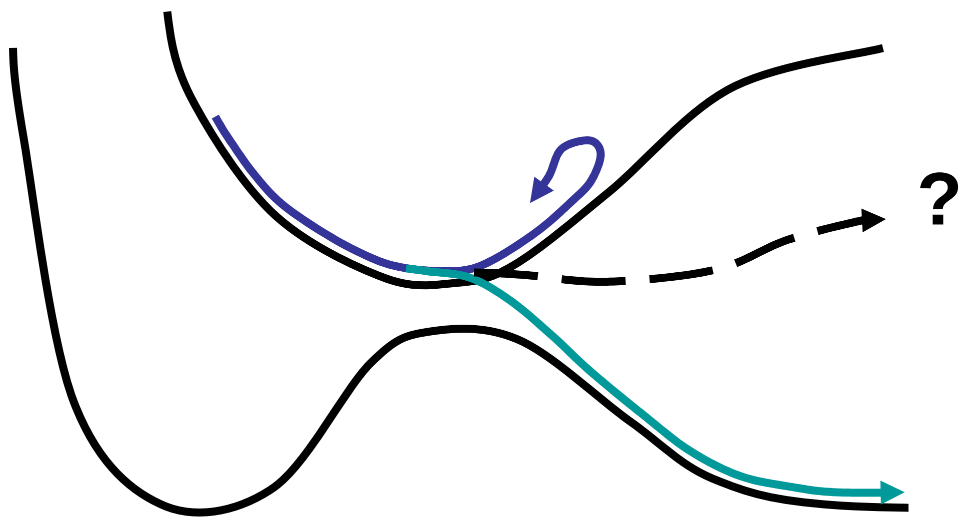
$$M\,\ddot{R}(t) = -\nabla_R \langle \Psi(t) | \mathcal{H}_{el} | \Psi(t) \rangle$$



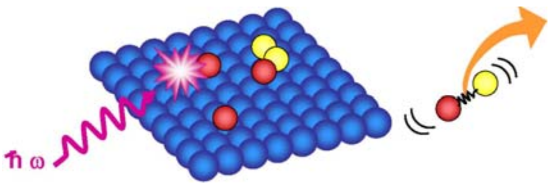


VI. Ehrenfest Dynamics

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



Problem:
single configuration
→ average path



I. The Potential Energy Surface

II. The Classical Limit via the Bohm Equations

III. Adiabatic “on-the-fly” Dynamics

IV. Car-Parrinello Dynamics

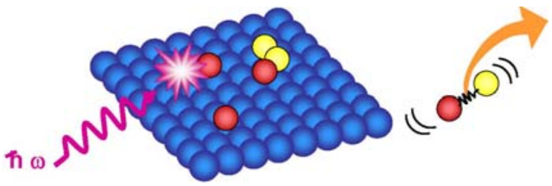
V. Beyond Born Oppenheimer

VI. Ehrenfest Dynamics

VII. Surface Hopping

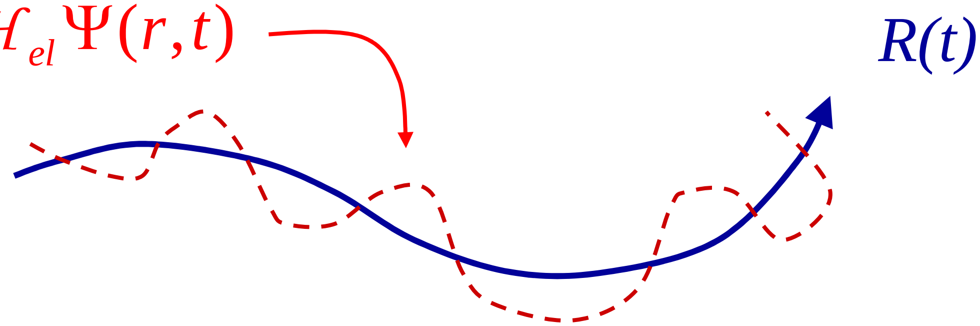
VIII. Equilibrium in Mixed Quantum-Classical Dynamics

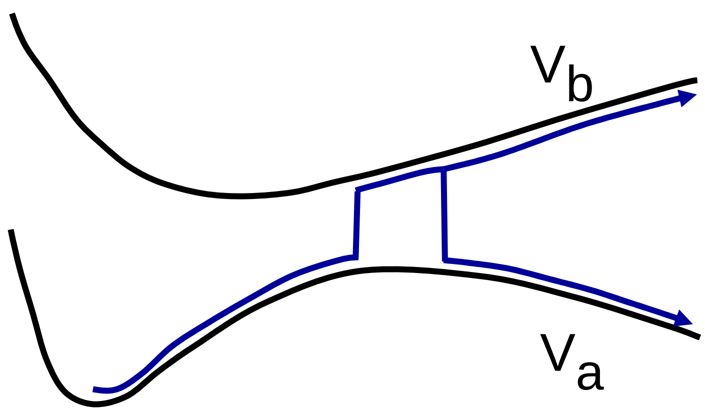
IX. Mixed Quantum-Classical Nuclear Motion

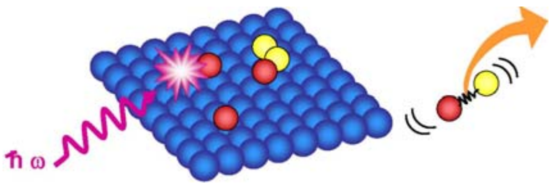


VII. Surface Hopping

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







VII. Surface Hopping

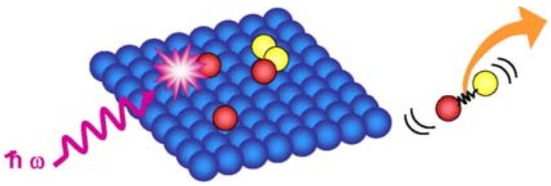
Multi-Configuration Wave Function:

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

Substitute into Schrodinger Eq and take classical limit:

→ Surface Hopping

<u>However, a rigorous classical limit has not been achieved</u> !



VII. Surface Hopping

One Approach: Multi-Configuration Bohm Equations:

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

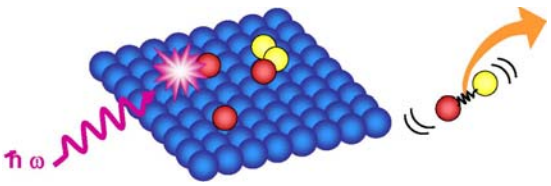
$$\Omega_j(\mathbf{R},t) = A_j(\mathbf{R},t)\exp\left[\tfrac{i}{\hbar}S_j(\mathbf{R},t)\right]$$

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

small $\hbar$ →

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

→ motion on potential energy surface *j*



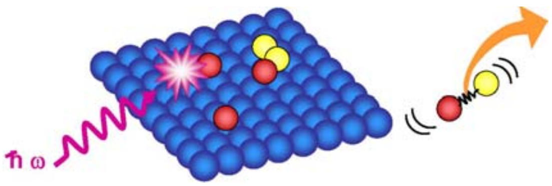
VII. Surface Hopping

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

Surface Hopping:

Evaluate all quantities along a single path

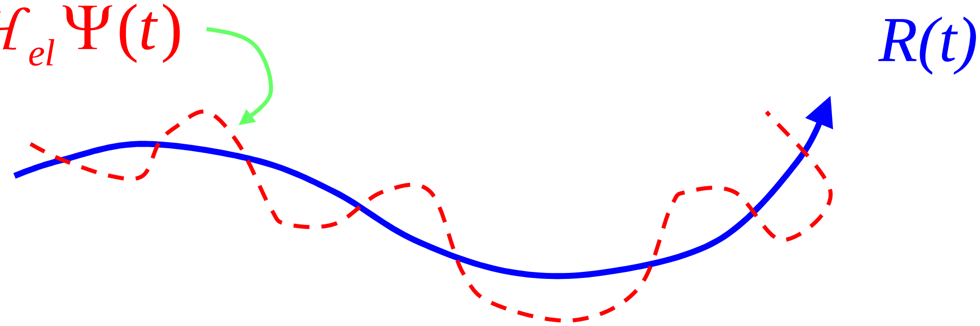
Sum over many stochastic paths



VII. Surface Hopping

Multi-Configuration Theory: *Surface Hopping*

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

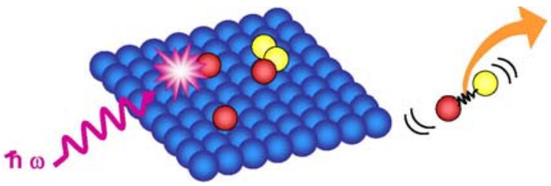


1] $M \ddot{R}(t) = -\nabla_R \mathcal{E}_k$, i.e., motion on single p.e.s.

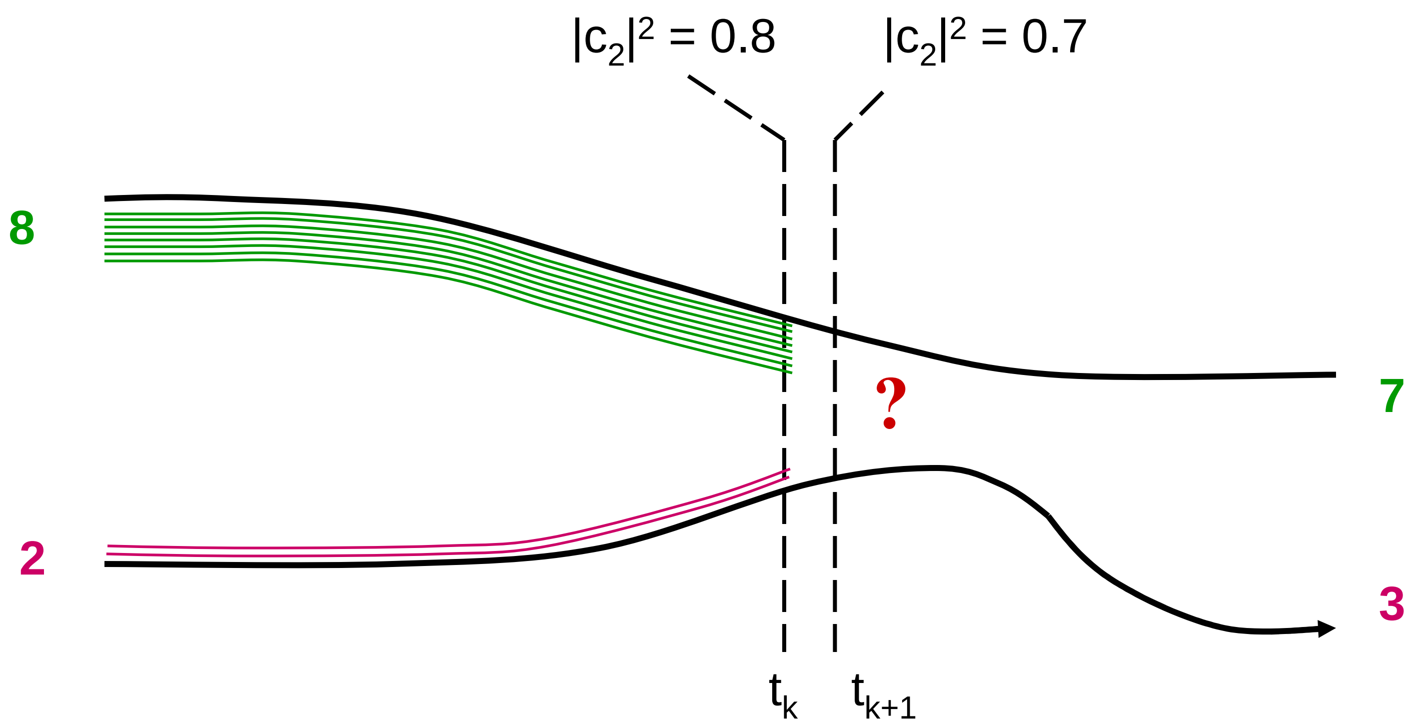
2] Stochastic “hops” between states so that probability = $|c_k|^2$

3] Apply instantaneous “Pechukas Force” to conserve energy

4] “Fewest Switches”: achieve [2] with fewest possible hops:

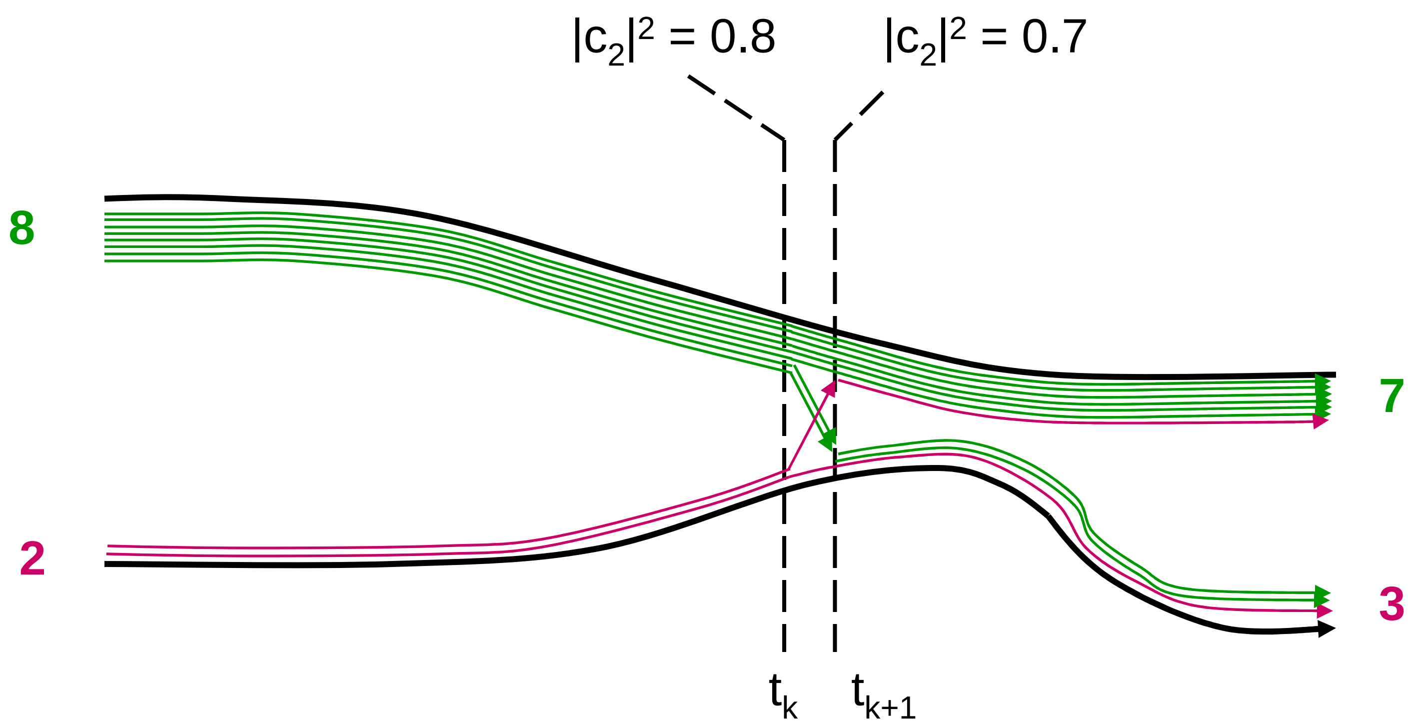


VII. Surface Hopping

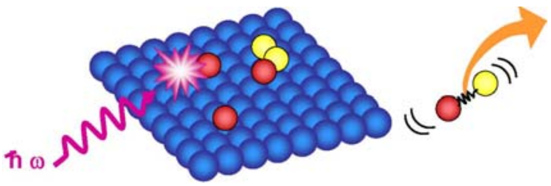


Stochastic *Fewest Switches* algorithm (2-state):

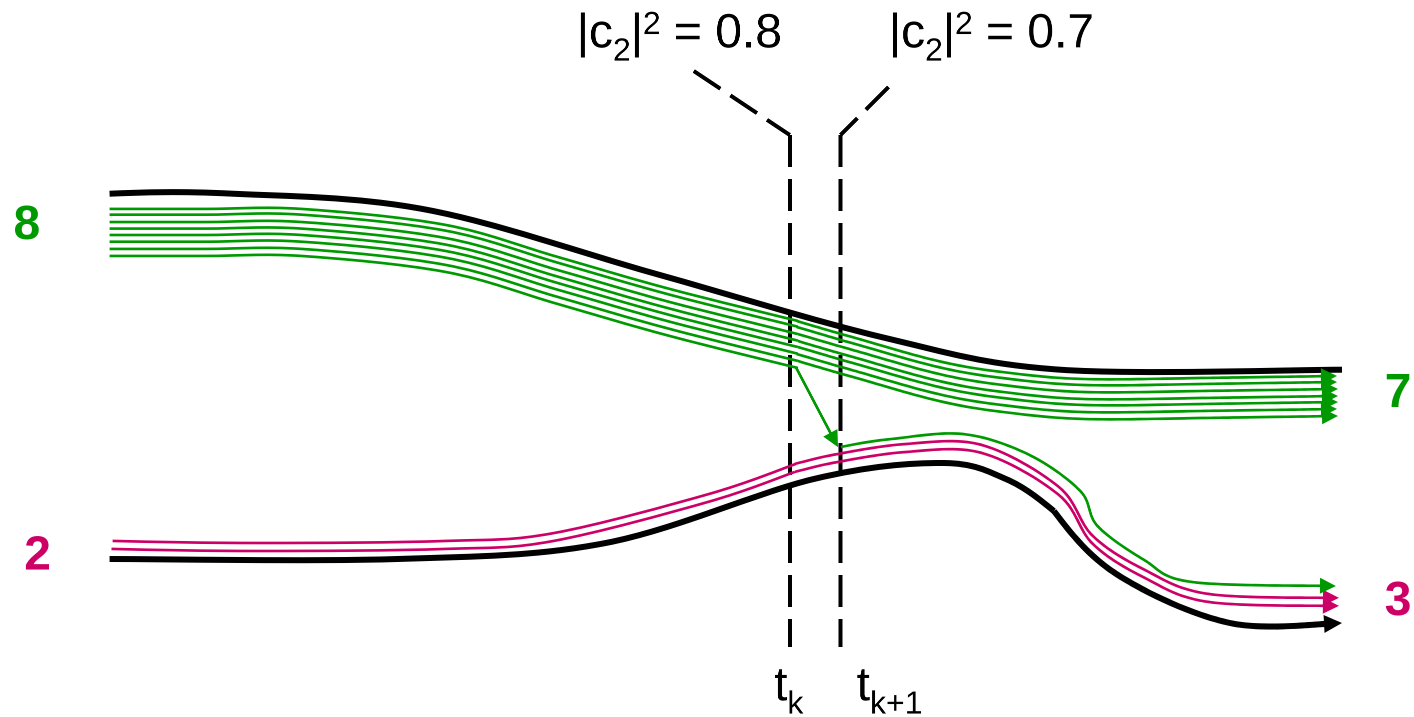
VII. Surface Hopping



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

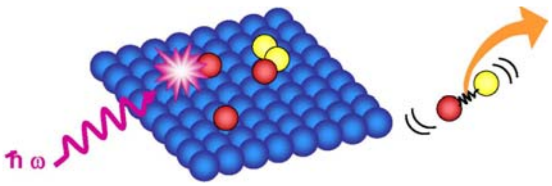


VII. Surface Hopping

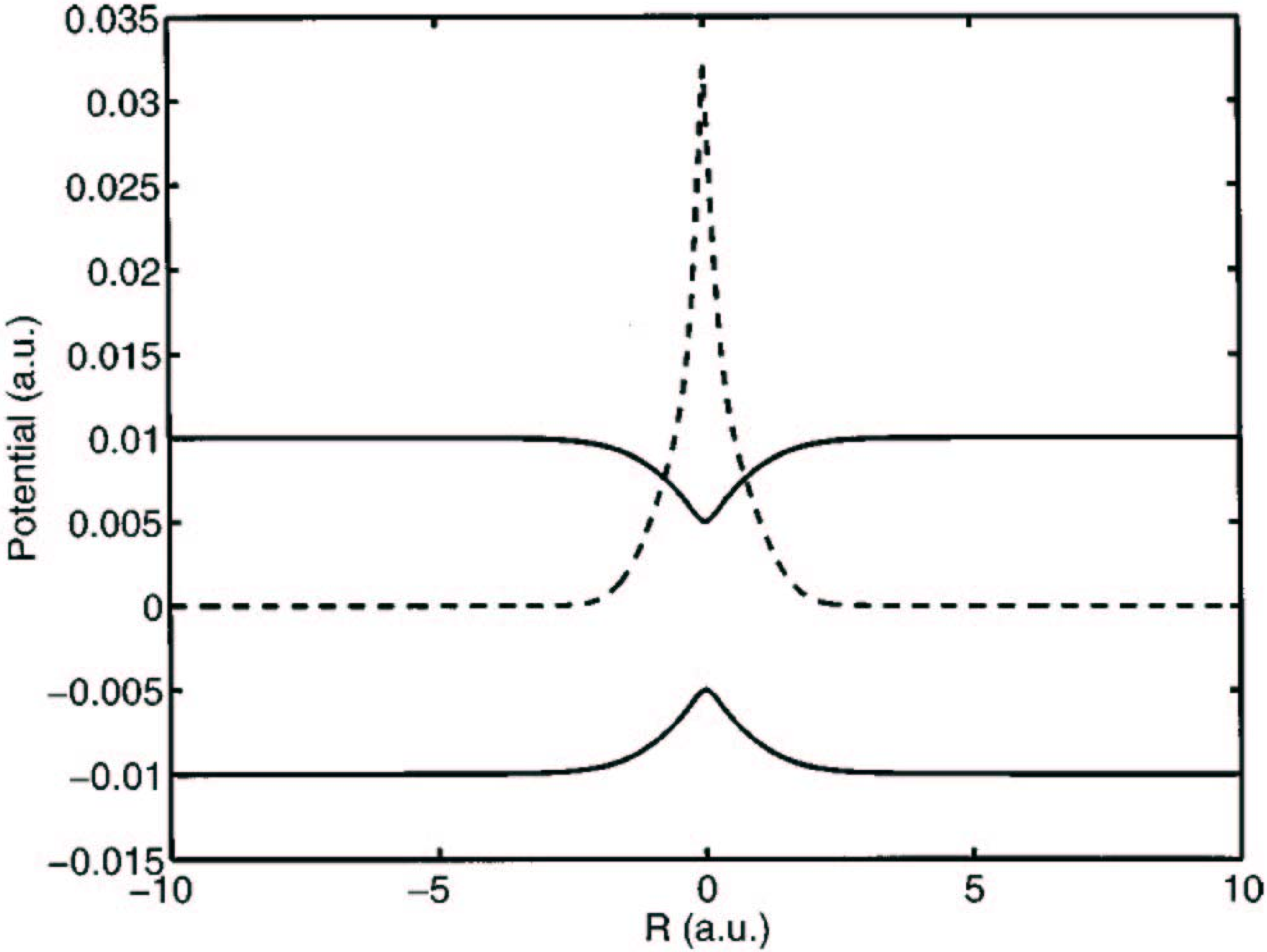


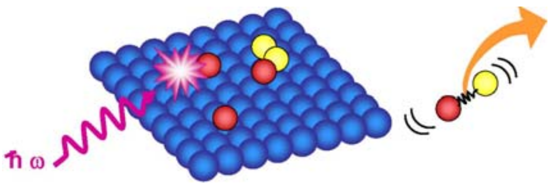
Stochastic *Fewest Switches* algorithm (2-state):

$$P_{2\to1} = \begin{cases} \dfrac{|c_2(k)|^2 - |c_2(k+1)|^2}{|c_2(k)|^2}, & |c_2(k)|^2 > |c_2(k+1)|^2 \\ 0\,, & |c_2(k)|^2 \le |c_2(k+1)|^2 \end{cases}$$

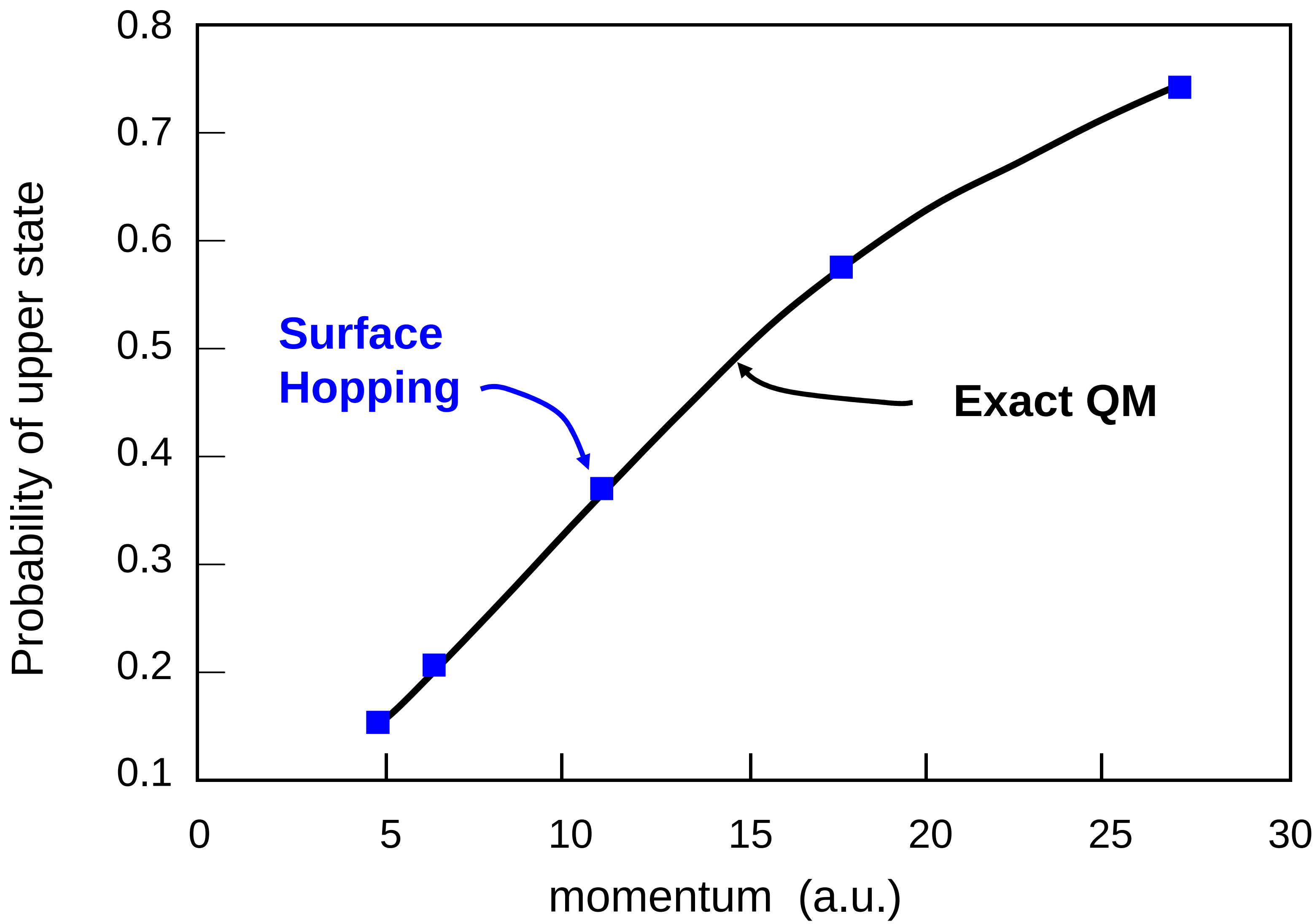


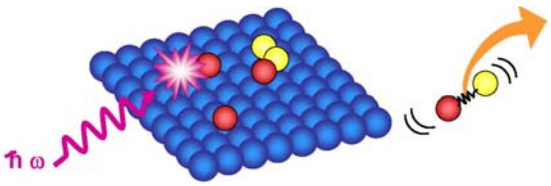
VII. Surface Hopping



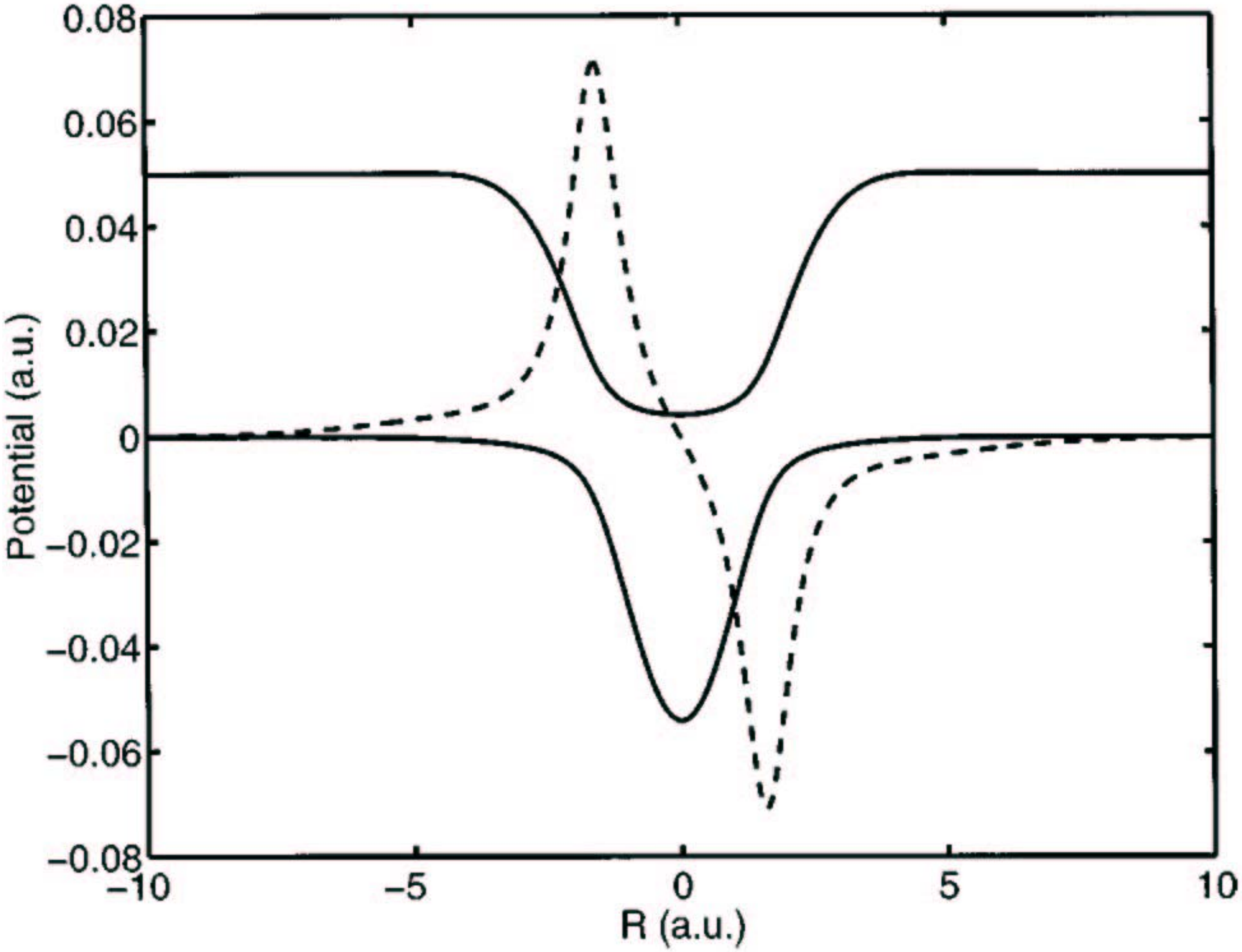


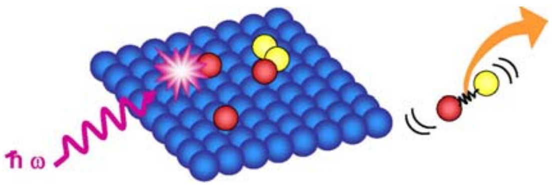
VII. Surface Hopping



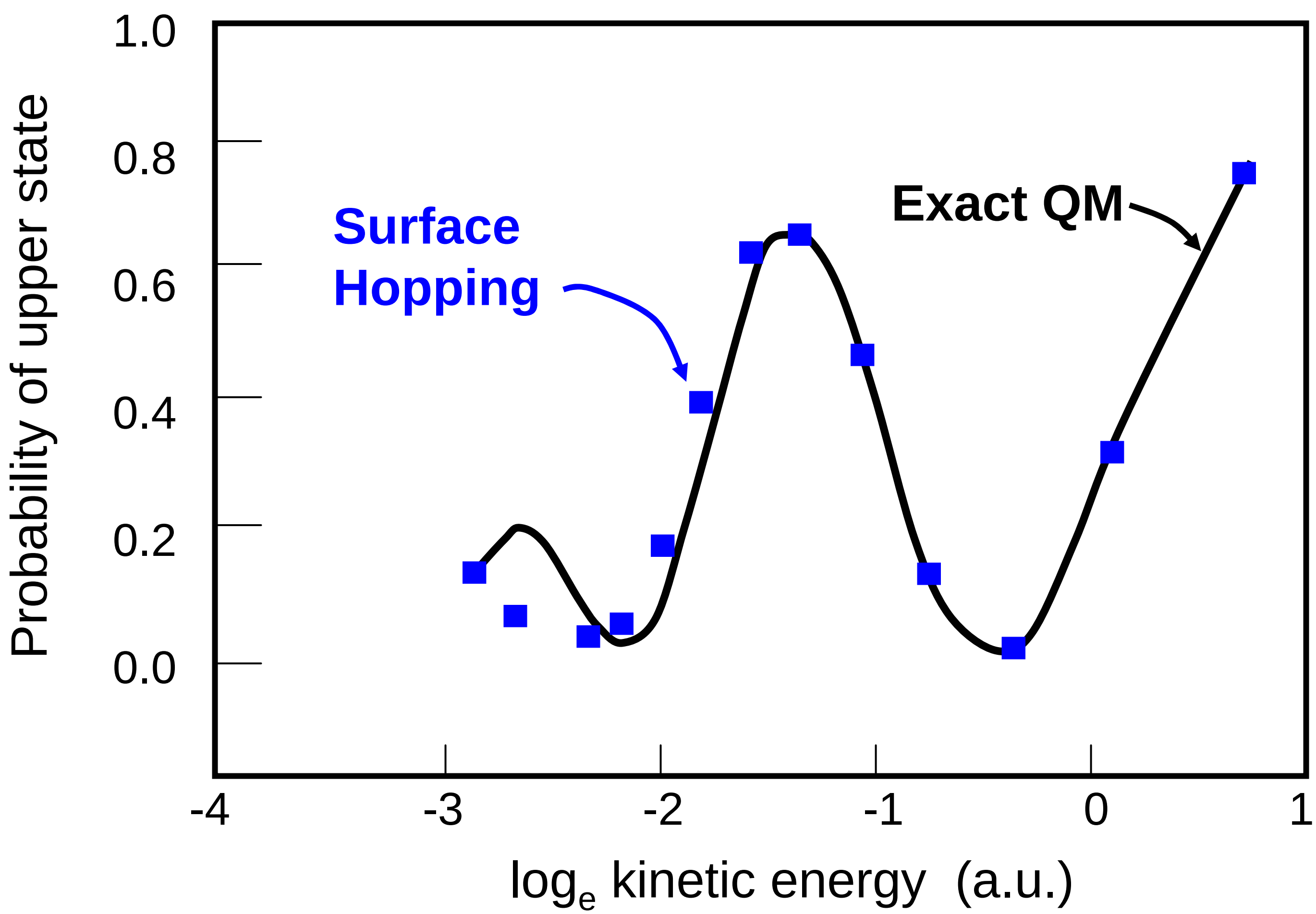


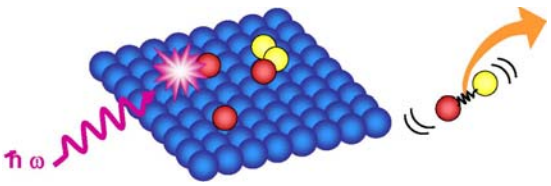
VII. Surface Hopping





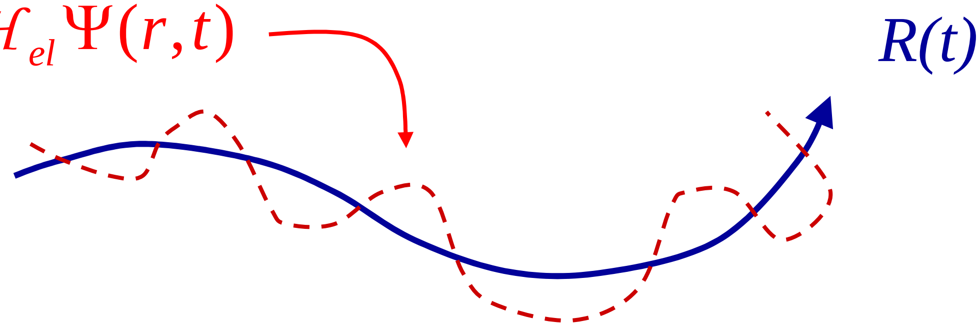
VII. Surface Hopping

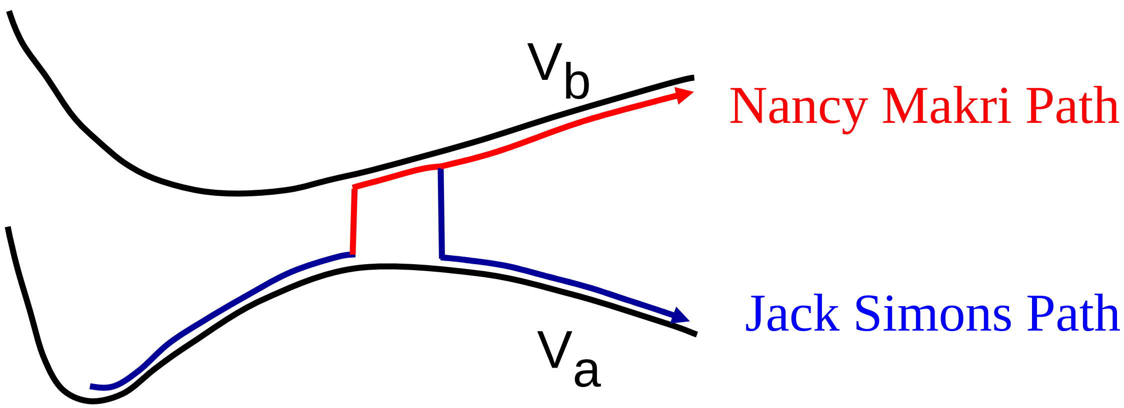


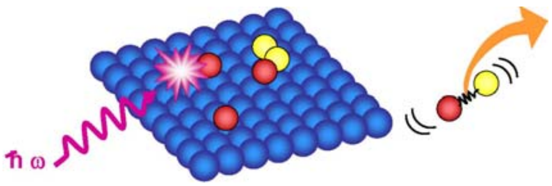


VII. Surface Hopping

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



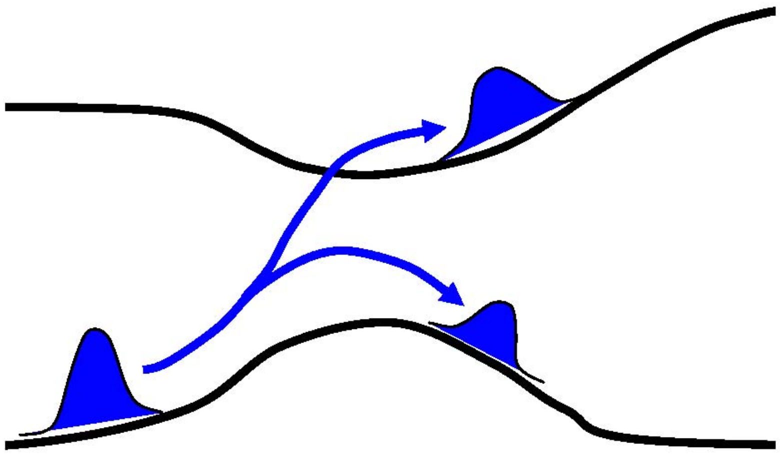




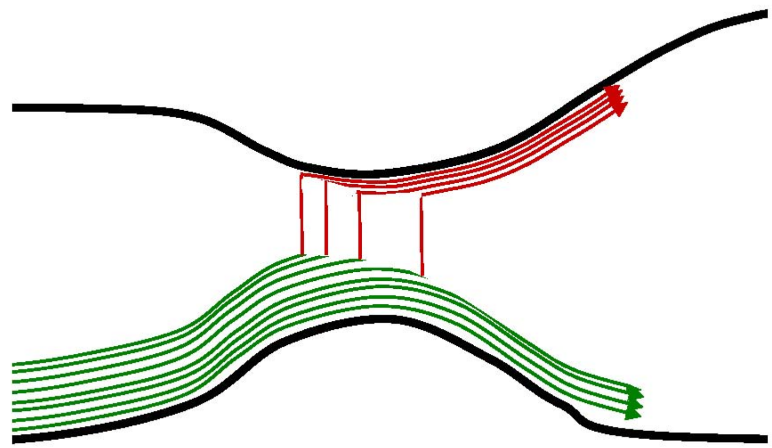
SHORTCOMINGS OF SURFACE HOPPING

1] Trajectories are independent

Trajectories should talk to each other

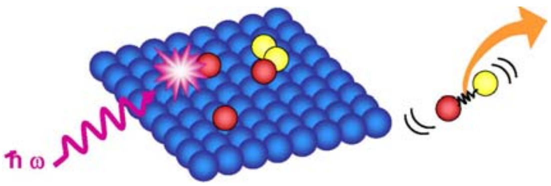


quantum wave packet



surface hopping

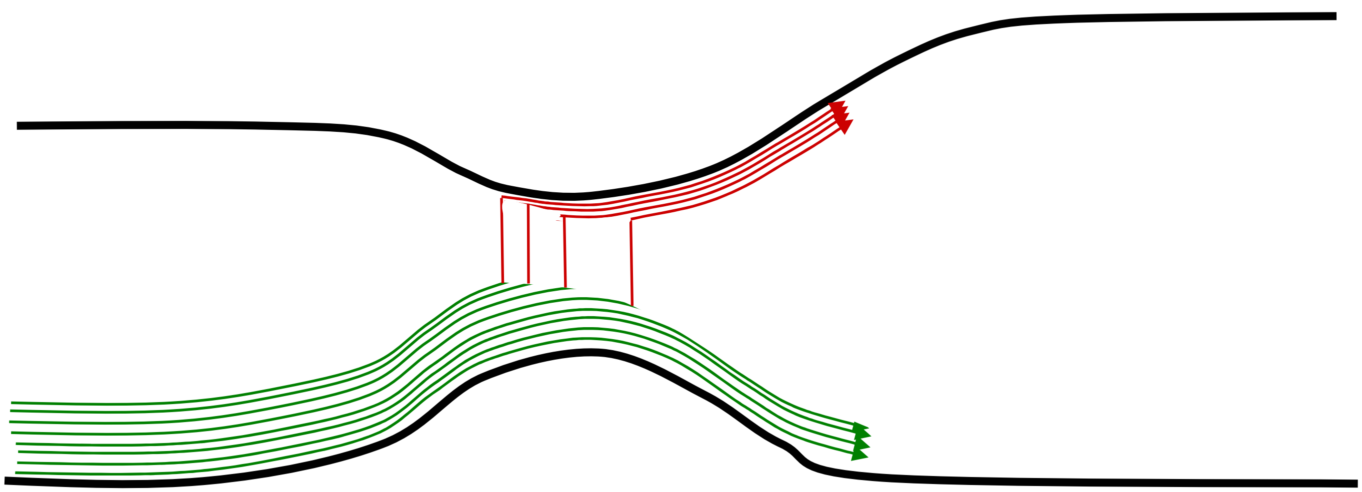
Fundamental approximation, but required to make practical



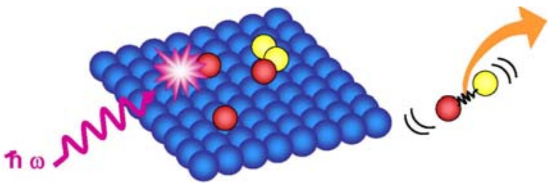
SHORTCOMINGS OF SURFACE HOPPING

2] Too drastic: hops require sudden change of velocity

Consider swarm of trajectories –
trajectories hop stochastically at different times



→ gradual evolution of flux



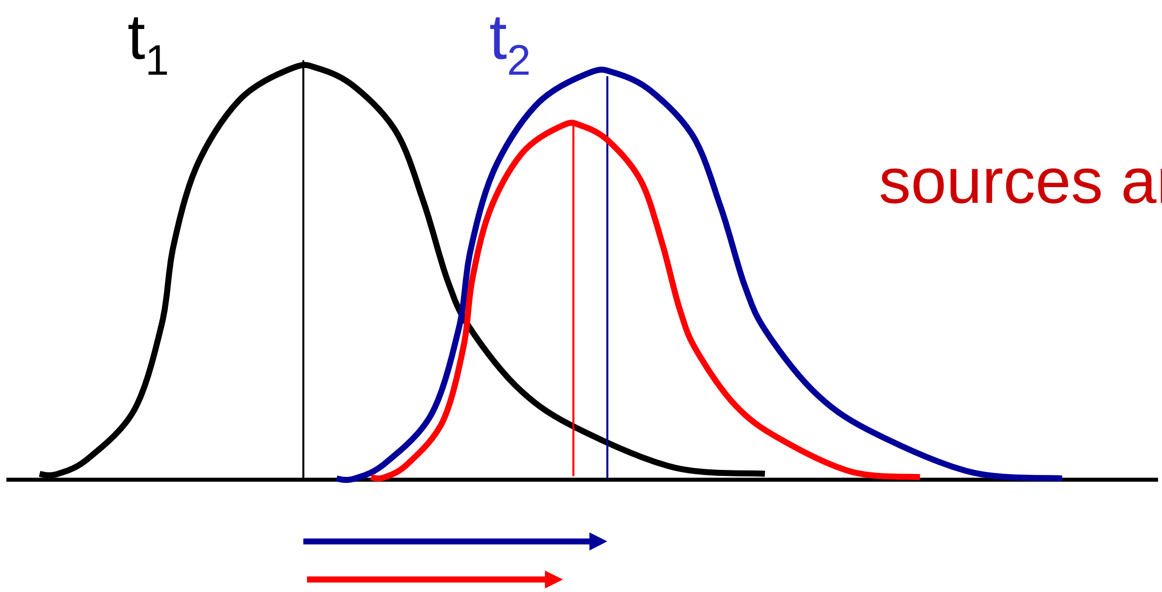
VII. Surface Hopping

SHORTCOMINGS OF SURFACE HOPPING

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

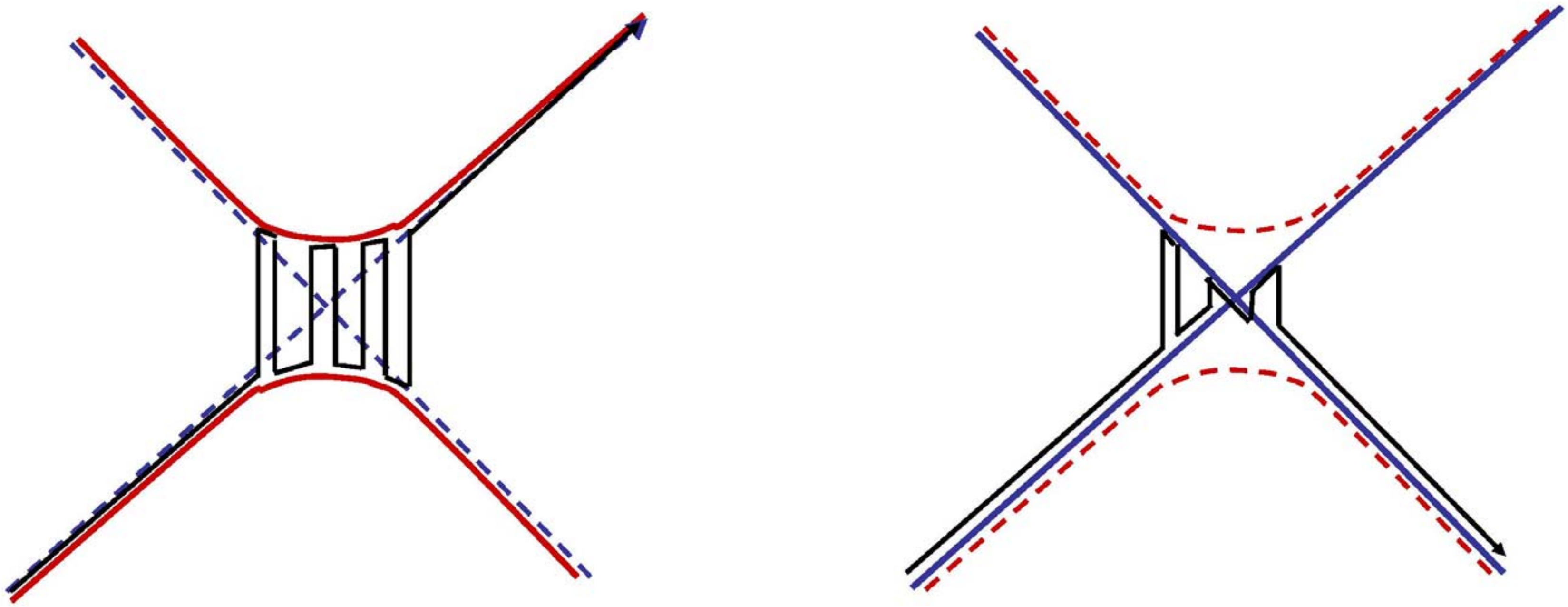
Consider swarm of trajectories –

trajectories hop stochastically at different times:



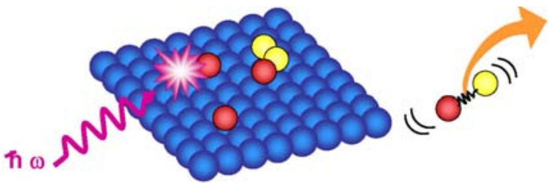
SHORTCOMINGS OF SURFACE HOPPING

4] Not invariant to representation



adiabatic representation   diabatic representation

The natural representation for surface hopping is *adiabatic*

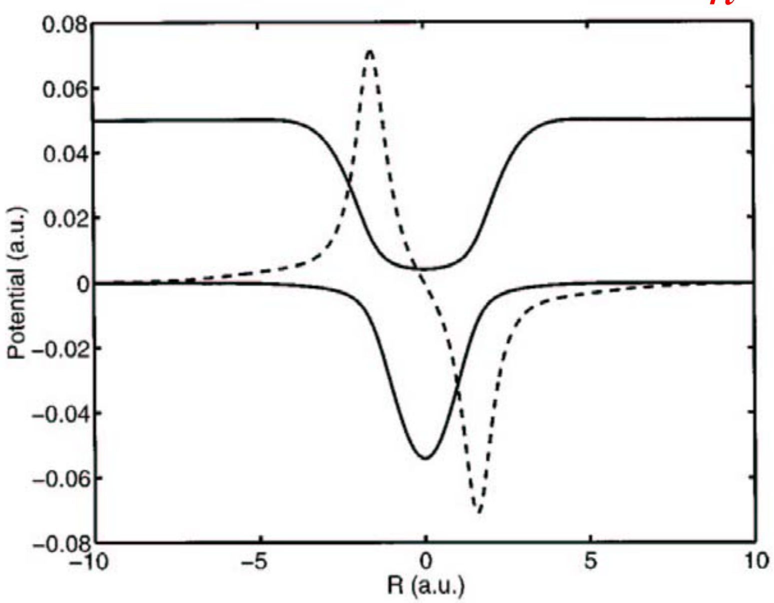


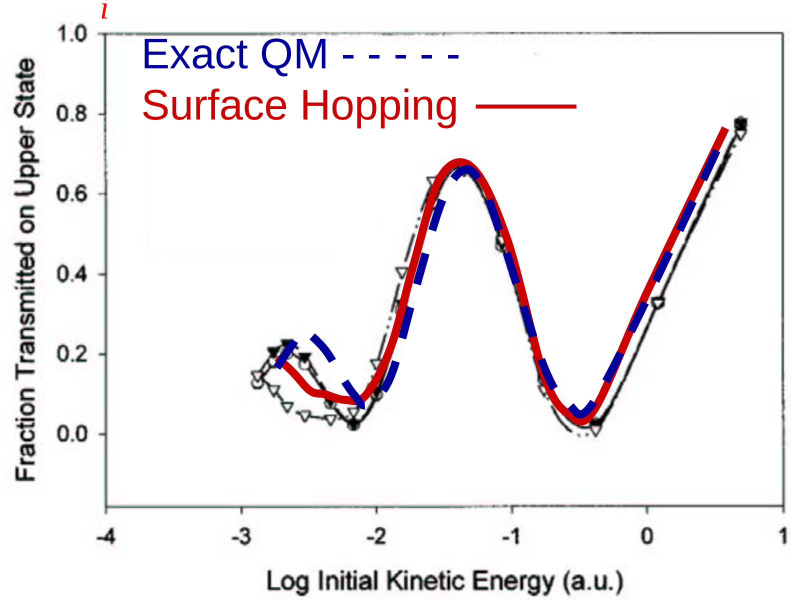
SHORTCOMINGS OF SURFACE HOPPING

5] Quantum Mechanical Coherence Neglected –
~~uses probabilities, not amplitudes~~ FALSE

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

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

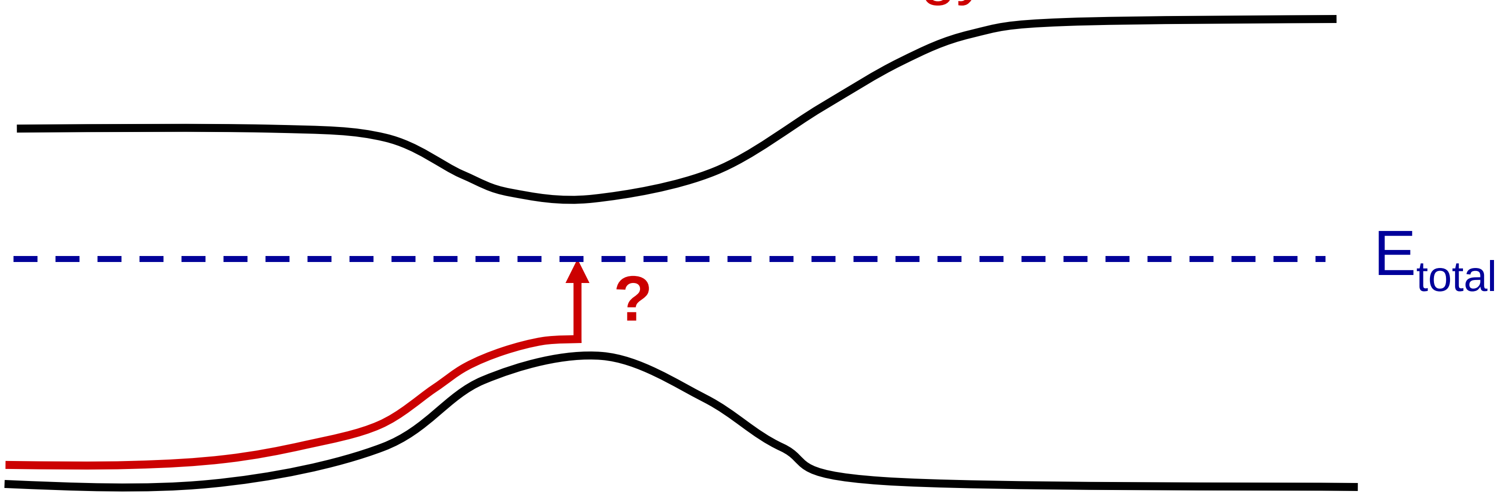




SHORTCOMINGS OF SURFACE HOPPING

6] Forbidden Hops (or *frustrated hops*)

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

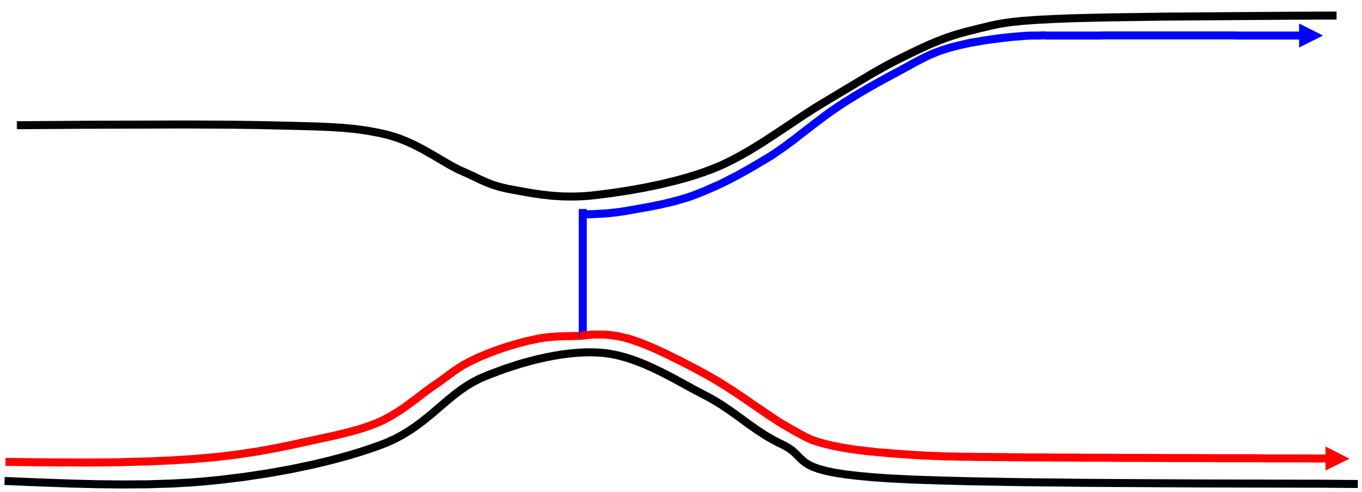


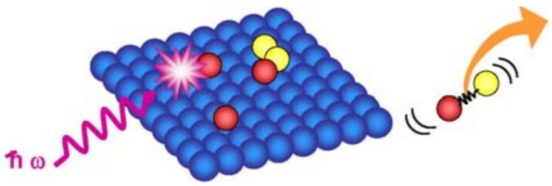
→ probability on state k $\neq$ $|c_k|^2$

SHORTCOMINGS OF SURFACE HOPPING

7] Detailed Balance?

What are the populations of the quantum states at equilibrium?





Molecular Dynamics

I. The Potential Energy Surface

II. The Classical Limit via the Bohm Equations

III. Adiabatic “on-the-fly” Dynamics

IV. Car-Parrinello Dynamics

V. Beyond Born Oppenheimer

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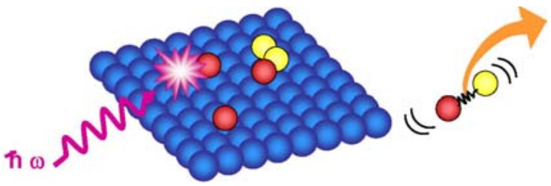
VIII. Equilibrium in Mixed Quantum-Classical Dynamics

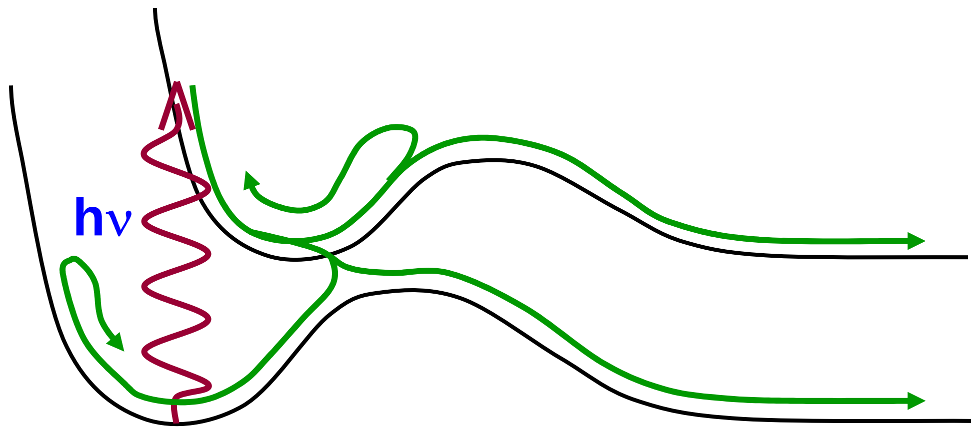
IX. Mixed Quantum-Classical Nuclear Motion



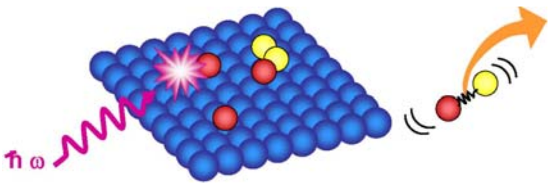
VIII. Equilibrium in Mixed Quantum-Classical Dynamics

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

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



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

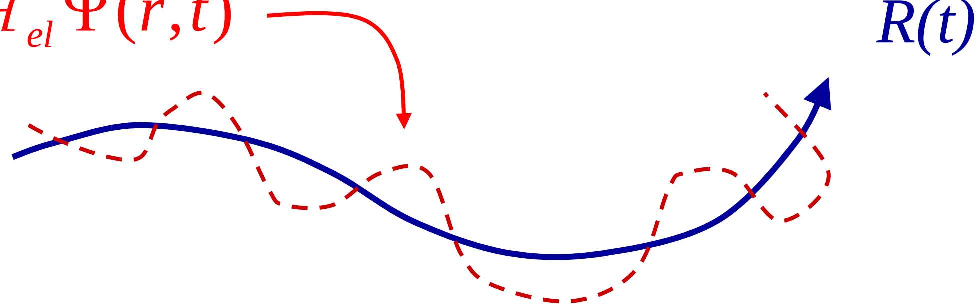


VIII. Equilibrium in Mixed Quantum-Classical Dynamics

Park City
June 2005
Tully

Detailed Balance: $\mathcal{N}_1 \, P_{1\to 2} = \mathcal{N}_2 \, P_{2\to 1}$

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

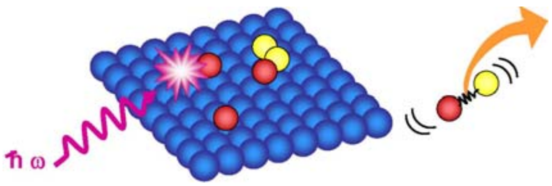


$$dc_j / dt = -\frac{i}{\hbar} V_{jj} c_j - \dot{R} \cdot \sum_i < \Phi_j(r;R) \,|\, \nabla_R \Phi_i(r;R) > c_i$$

time reversible

$$P_{1\to 2} = P_{2\to 1} \quad \to \quad |c_1|^2 = |c_2|^2$$

probabilities of each quantum state are equal: infinite temperature

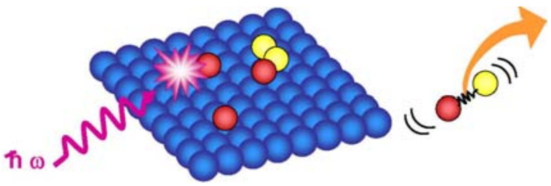


VIII. Equilibrium in Mixed Quantum-Classical Dynamics

"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



VIII. Equilibrium in Mixed Quantum-Classical Dynamics

Ehrenfest (SCF)

$$\rho(E_{QM}) \;\propto\; \int_0^{\infty} H(E_{TOT}-E_{QM})\,\exp(-\beta E_{TOT})\,dE_{TOT}$$

$$\langle E_{QM}\rangle \;=\; \int_0^{\Delta} E_{QM}\;\rho(E_{QM})\,dE_{QM} \Big/ \int_0^{\Delta}\rho(E_{QM})\,dE_{QM}$$

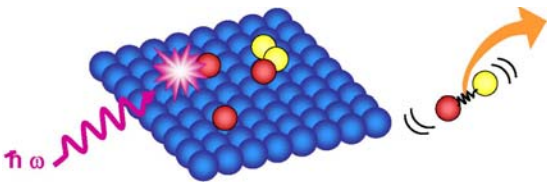
$$\rightarrow\;\langle E_{QM}\rangle \;=\; \frac{1}{\beta}-\frac{\Delta\exp(-\beta\Delta)}{1-\exp(-\beta\Delta)}$$

$$\langle |c_2|^2\rangle \;=\; \frac{1}{\beta\Delta}-\frac{\exp(-\beta\Delta)}{1-\exp(-\beta\Delta)}$$

Boltzmann:

$$\langle E_{QM}\rangle \;=\; \frac{\Delta\exp(-\beta\Delta)}{1+\exp(-\beta\Delta)}$$

$$\langle |c_2|^2\rangle \;=\; \frac{\exp(-\beta\Delta)}{1+\exp(-\beta\Delta)}$$



VIII. Equilibrium in Mixed Quantum-Classical Dynamics

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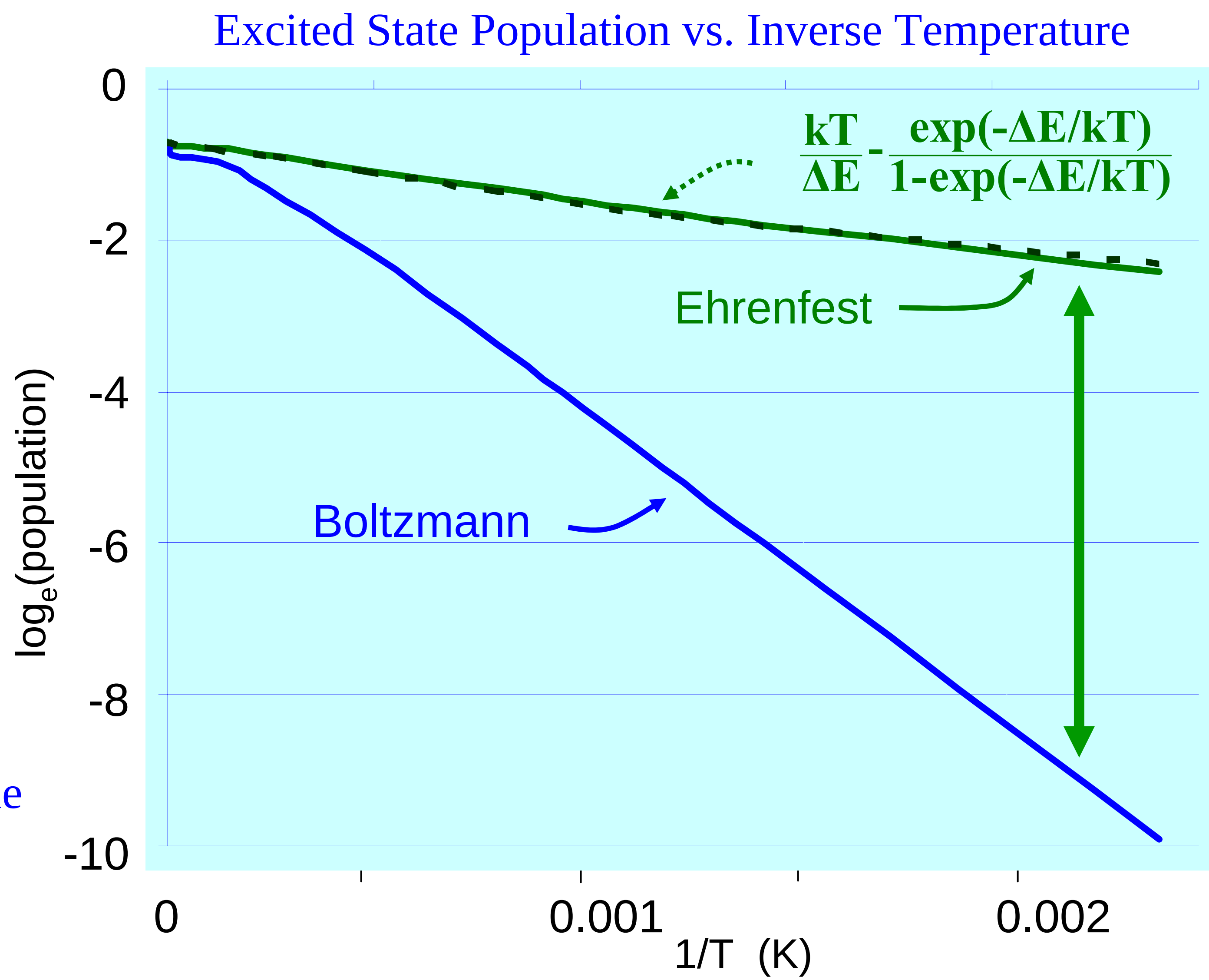
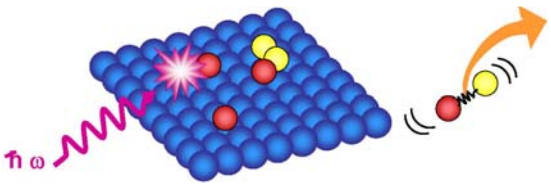


2-state system
$\Delta E = 34.6$ kJ/mole



VIII. Equilibrium in Mixed Quantum-Classical Dynamics

Park City
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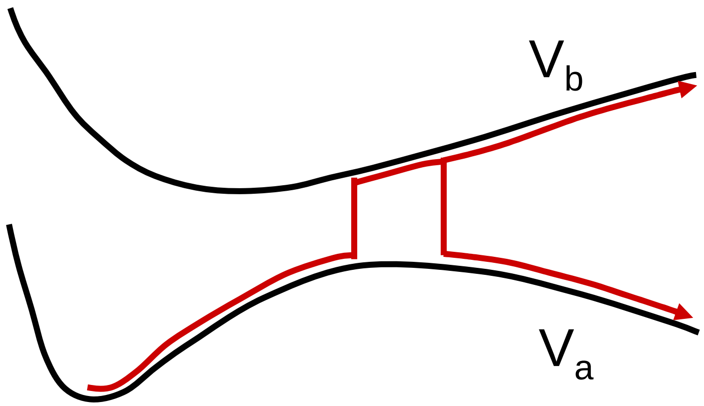
Tully

What about surface hopping ?



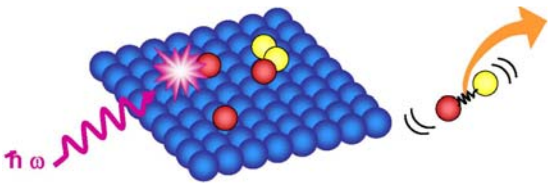
$$dc_j/dt \;=\; -\frac{i}{\hbar}V_{jj}c_j - \dot{R}\cdot\sum_i \langle \Phi_j(r;R)|\nabla_R\Phi_i(r;R)\rangle c_i$$

time reversible

$$P_{1\rightarrow 2} \;=\; P_{2\rightarrow 1} \qquad \rightarrow \qquad |c_1|^2 \;=\; |c_2|^2$$

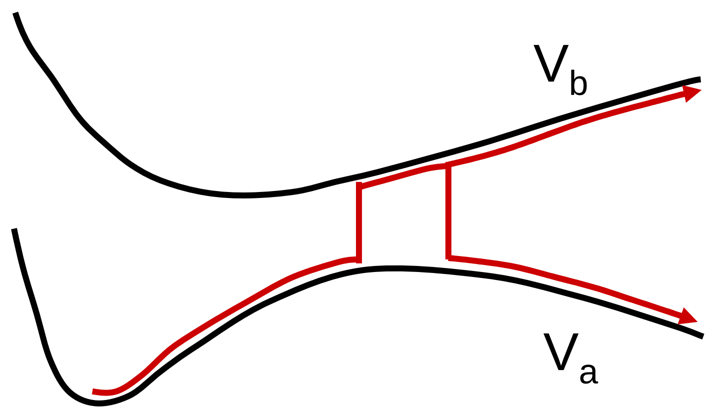
probabilities of each quantum state are equal: infinite temperature

looks bad



VIII. Equilibrium in Mixed Quantum-Classical Dynamics

What about surface hopping ?

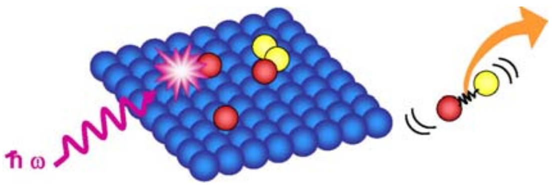


$$dc_j/dt = -\frac{i}{\hbar}V_{jj}c_j - \dot{R}\cdot\sum_i <\Phi_j(r;R)|\nabla_R\Phi_i(r;R)> c_i$$

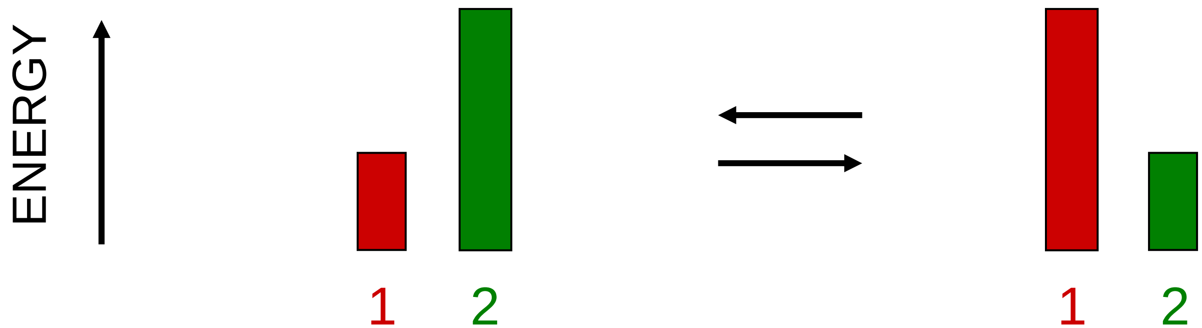
time reversible

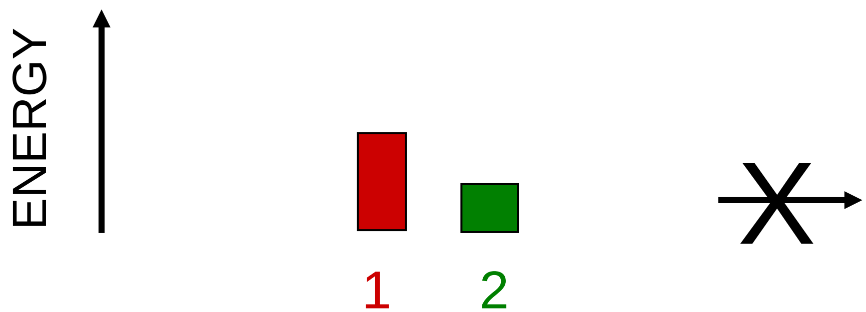
$$P_{1\to 2} = P_{2\to 1} \quad \to \quad |c_1|^2 = |c_2|^2$$

but surface hopping probabilities ≠ $|c_k|^2$ ***frustrated hops***



VIII. Equilibrium in Mixed Quantum-Classical Dynamics

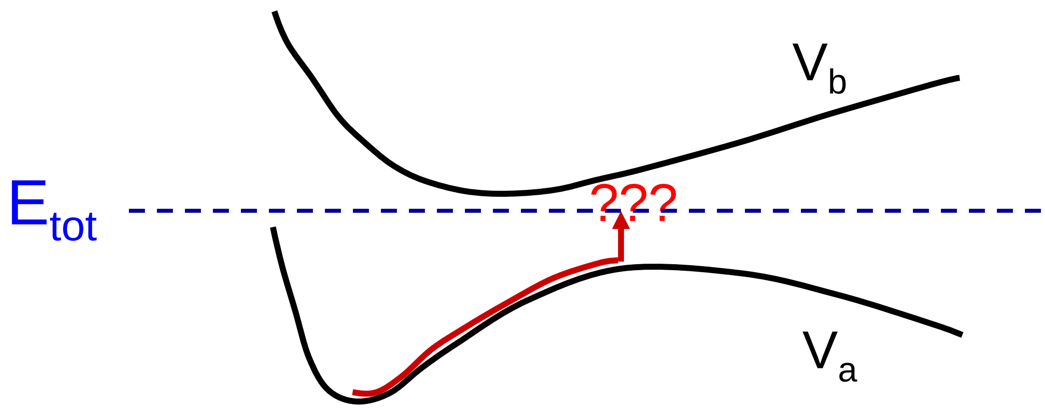




frustrated hop!

→ More configurations with low energy

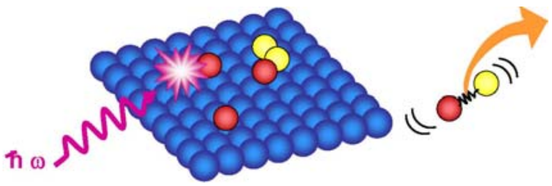
VIII. Equilibrium in Mixed Quantum-Classical Dynamics



"frustrated hop"

$$P_{1\to2} \quad = \quad \exp(\,-\,\Delta E\,/\,kT\,)\;P_{2\to1}$$

$$T_{quantum} \quad \to \quad \text{correct}$$



VIII. Equilibrium in Mixed Quantum-Classical Dynamics

P_{hop} = $-\Delta|c_k|^2$ / $|c_k|^2$ = fractional decrease of state *k* population

$$= \; -2\,\Delta\,\mathrm{Re}[c_k^*\,\dot{c}_k]\,/\,|\,c_k\,|^2$$

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

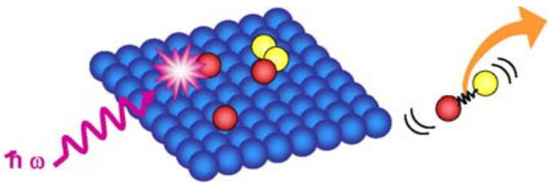
Adiabatic representation

$$\boxed{P_{hop} \quad \propto \quad v}$$

$$P_{1\to 2} \quad \propto \quad v_1\;\rho(v_1)\;dv_1 \quad \propto \quad v_1\;\exp(-\tfrac{1}{2}mv_1^2\,/\,kT)\;dv_1$$

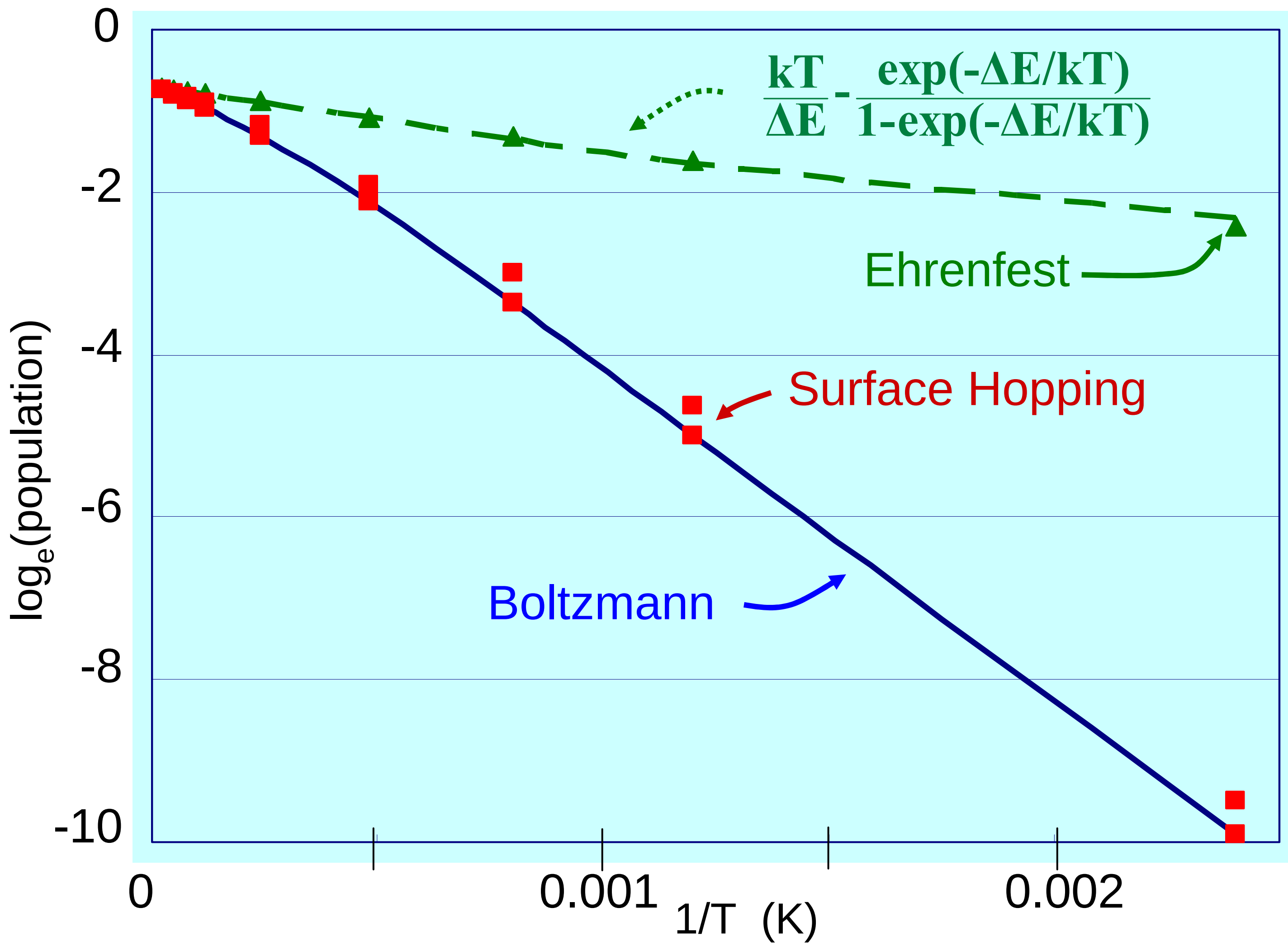
$$\propto \quad \exp(-E_1\,/\,kT)$$

$$\mathcal{N}_1\;P_{1\to 2} \;=\; \mathcal{N}_2\;P_{2\to 1} \qquad \to \qquad \frac{\mathcal{N}_2}{\mathcal{N}_1} \;=\; \exp[-(E_2 - E_1)\,/\,kT]$$



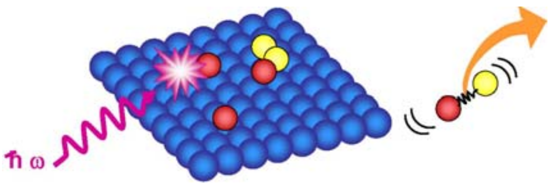
VIII. Equilibrium in Mixed Quantum-Classical Dynamics

Excited State Population vs. Inverse Temperature



2-State System

$\Delta E = 34.6$ kJ/mole



VIII. Equilibrium in Mixed Quantum-Classical Dynamics

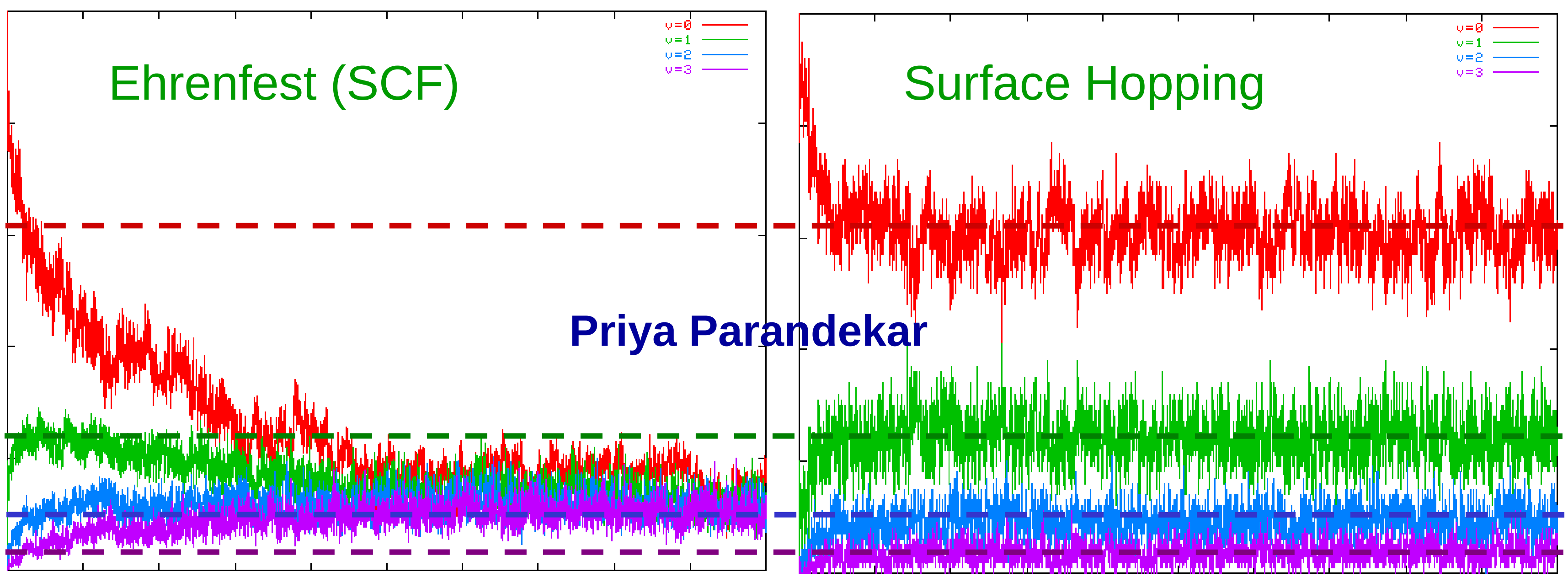
Many Quantum States

[classical bath] --- C --- C --- C --- C --- C --- C --- C --- C --- H

Random force and friction (5000 ºK)

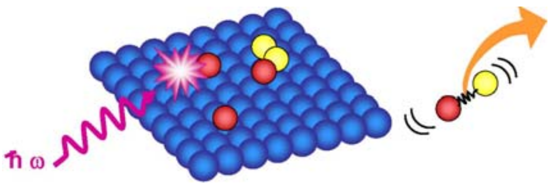
classical (Morse)

quantum (Morse)



Priya Parandekar

V=0
V=1
V=2
V=3



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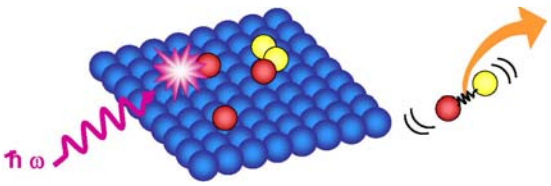
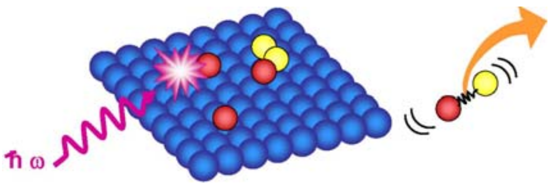


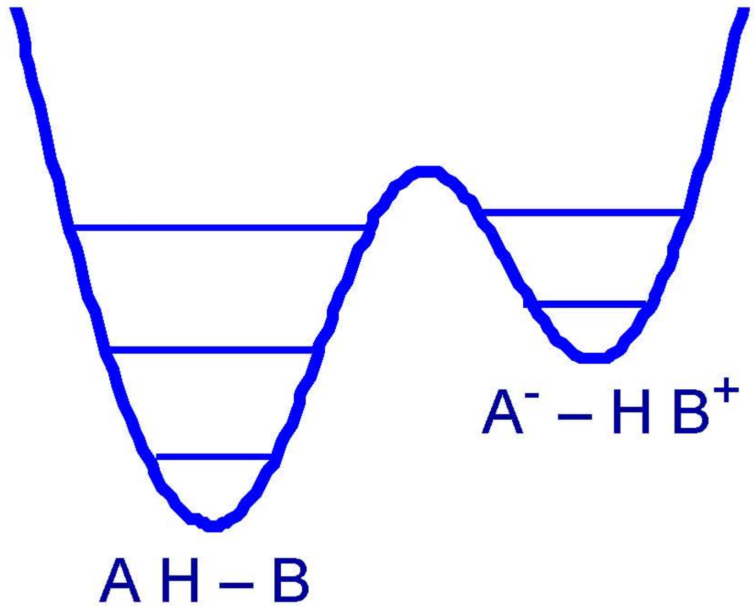
Tenets of Conventional Molecular Dynamics

1. The Born-Oppenheimer Approximation	Multiple Electronic States, Metals, …
2. Classical Mechanical Nuclear Motion	Zero Point Motion, Quantized Energy Levels, Tunneling



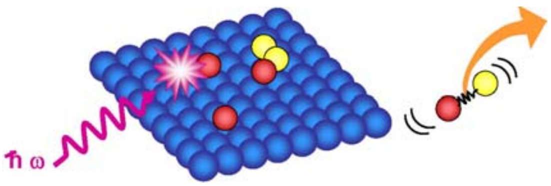
XI. Mixed Quantum-Classical Nuclear Motion

Proton Transfer Reaction: A H – B $\rightleftharpoons$ A$^-$ – H B$^+$



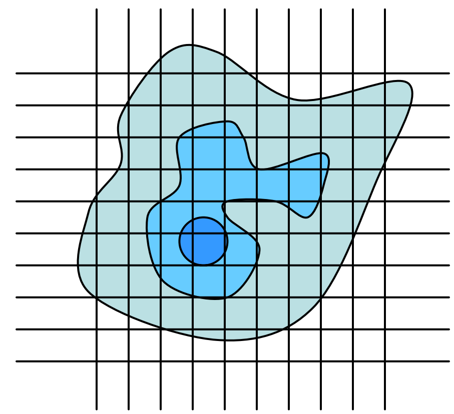
Quantum Effects:

- Zero-Point Energy
- Quantized Energy Levels
- Tunneling



Ultimate Solution:

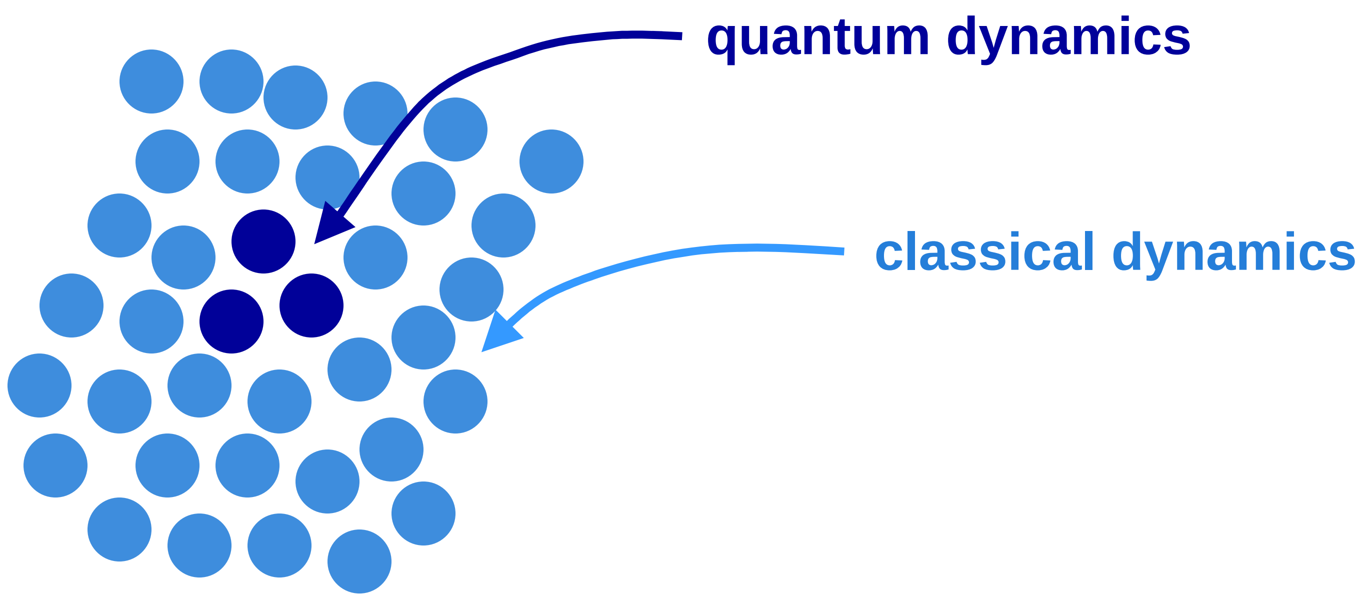
Treat All Electrons and Nuclei
by Quantum Mechanics

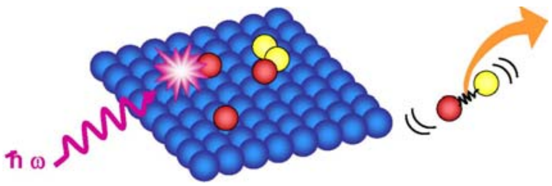


Problem:

Scaling with Size is Prohibitive

AN ALTERNATIVE STRATEGY:
MIXED QUANTUM–CLASSICAL DYNAMICS



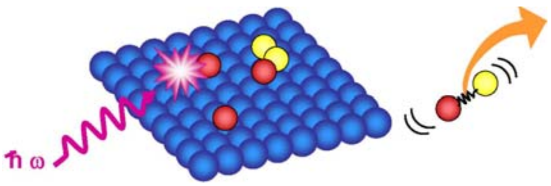


AN ALTERNATIVE STRATEGY:
MIXED QUANTUM–CLASSICAL DYNAMICS

Treat crucial electronic or nuclear degrees of freedom by quantum mechanics, and the remaining nuclei by classical mechanics.

self-consistency

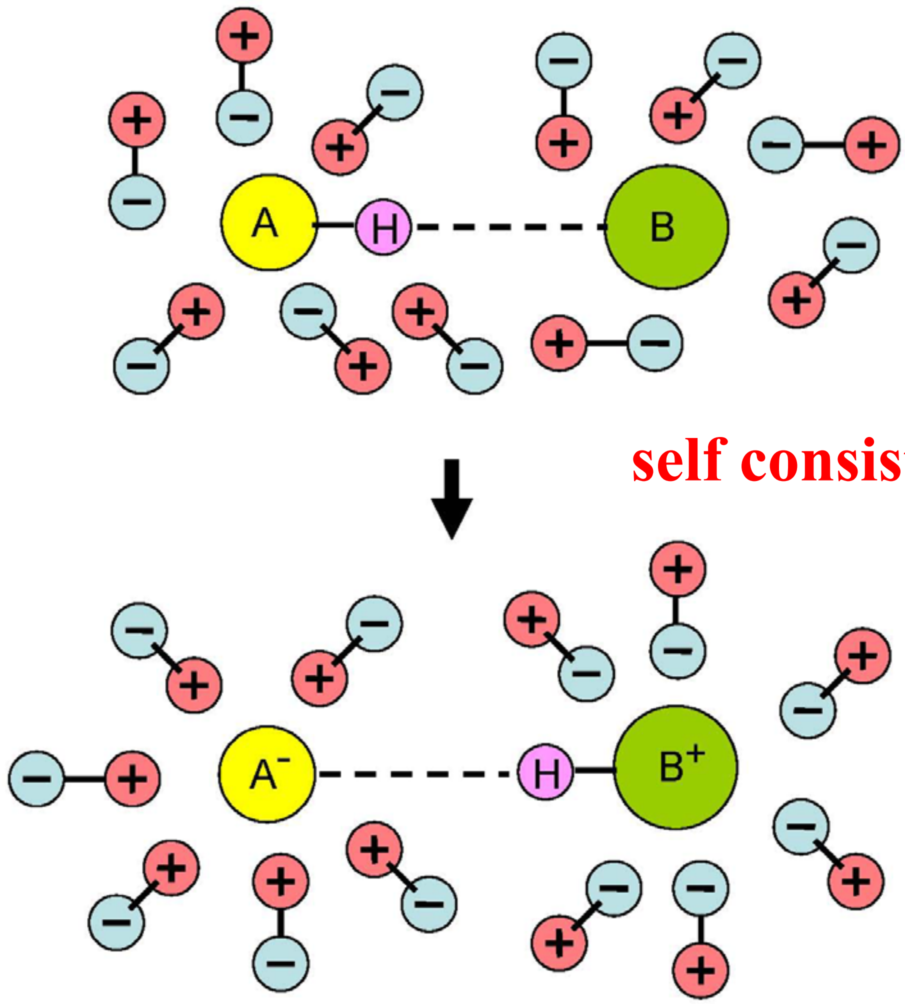
quantum “back-reaction” on classical particles



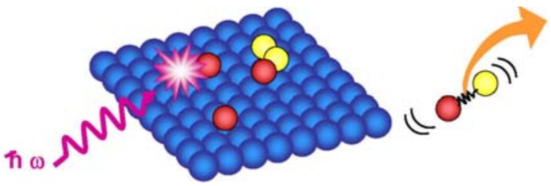
PROTON TRANSFER IN SOLUTION

covalent reactant:

ionic product:

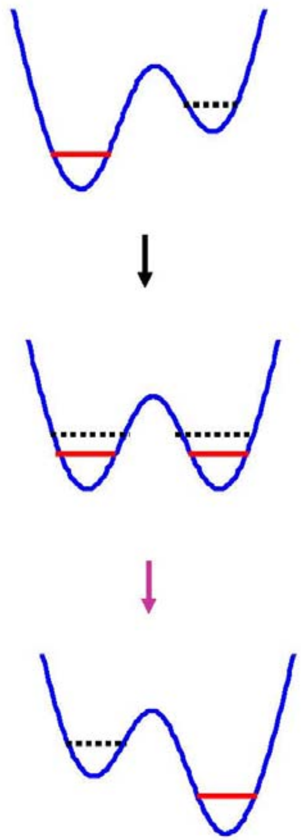


self consistency !

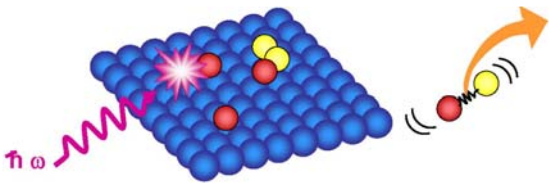


XI. Mixed Quantum-Classical Nuclear Motion

ADIABATIC vs. NON-ADIABATIC



ADIABATIC → REACTION



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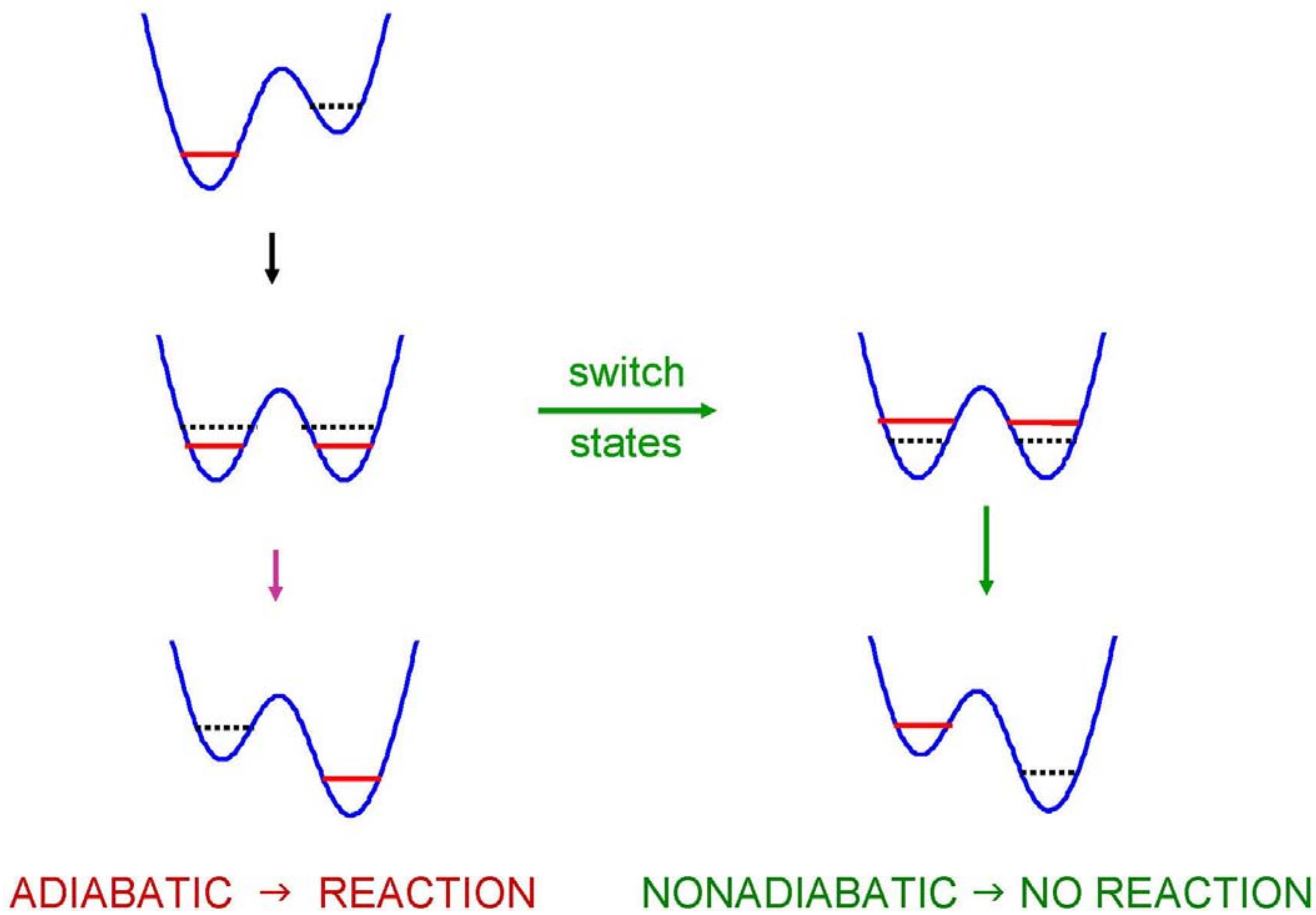
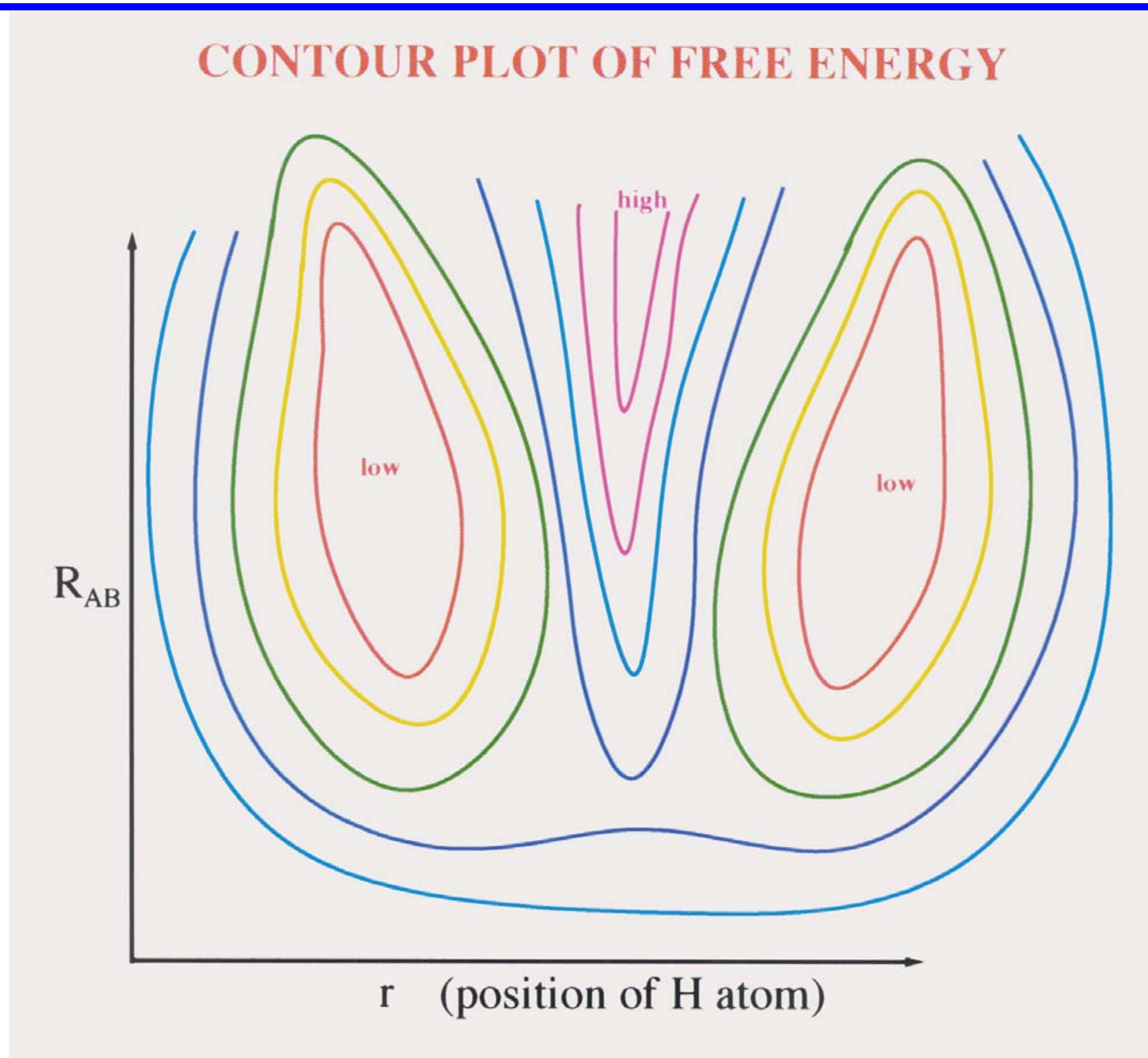


XI. Mixed Quantum-Classical Nuclear Motion

R_{AB}

A----H----B

r



XI. Mixed Quantum-Classical Nuclear Motion

Proton and Hydride Transfer in Enzymes:

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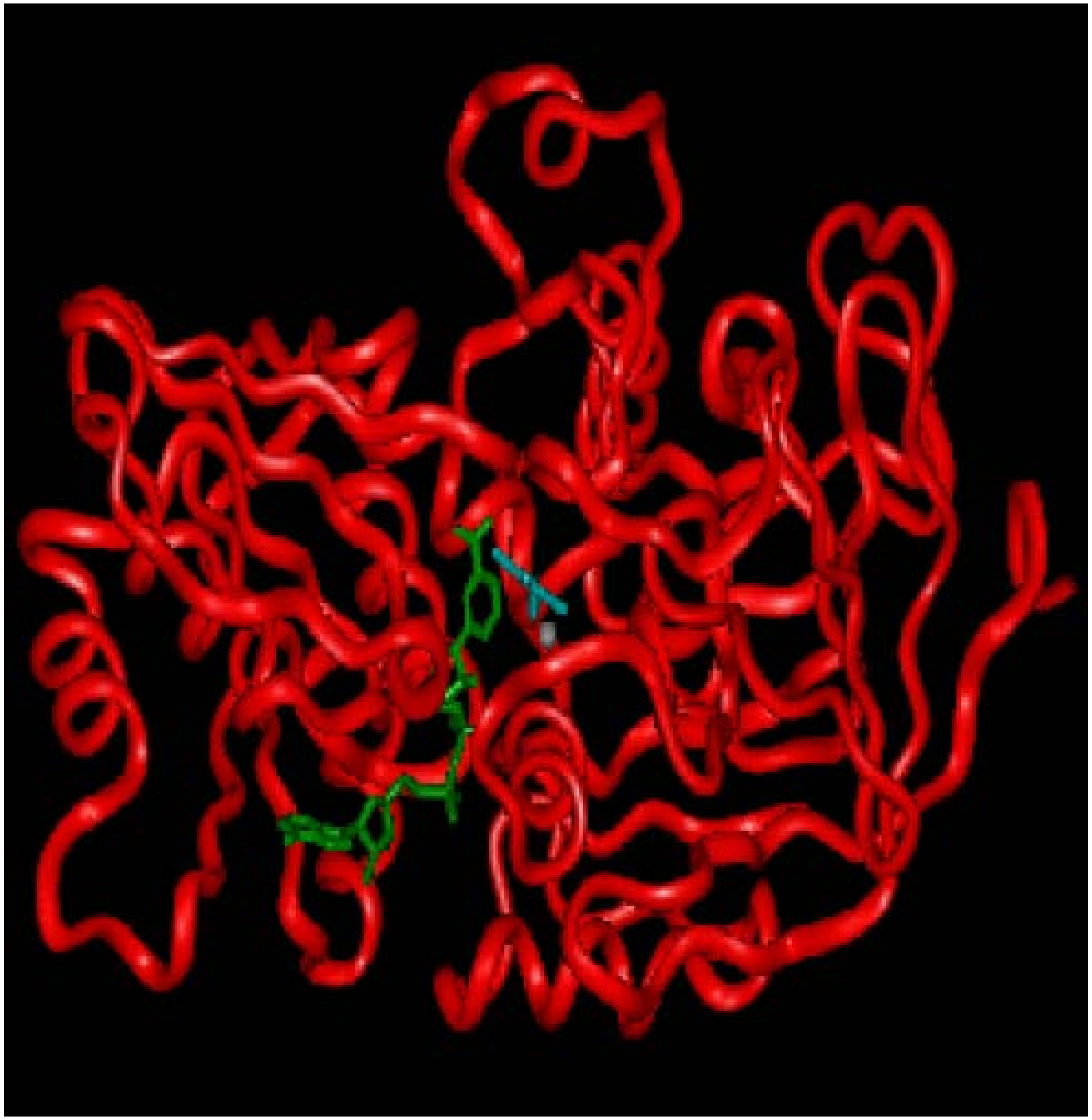

liver alcohol dehydrogenase (LADH)

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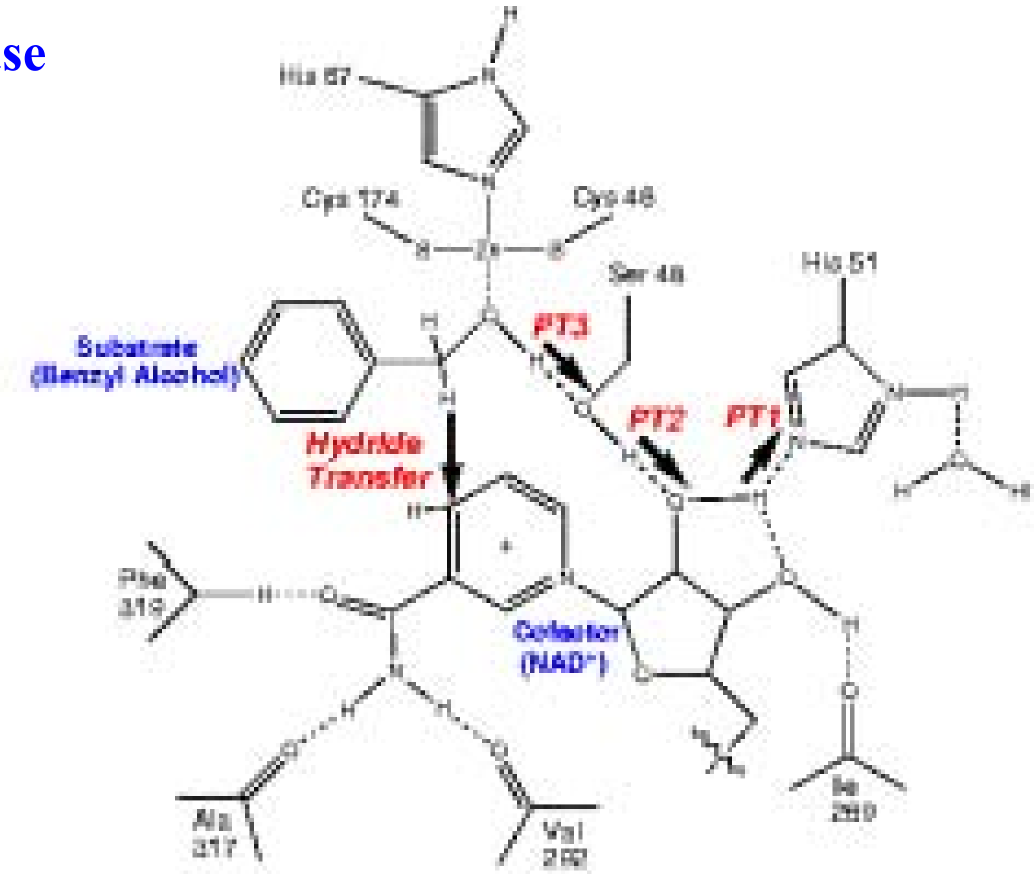
liver alcohol dehydrogenase



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