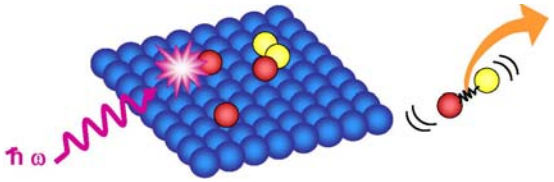

IV. Classical Molecular Dynamics

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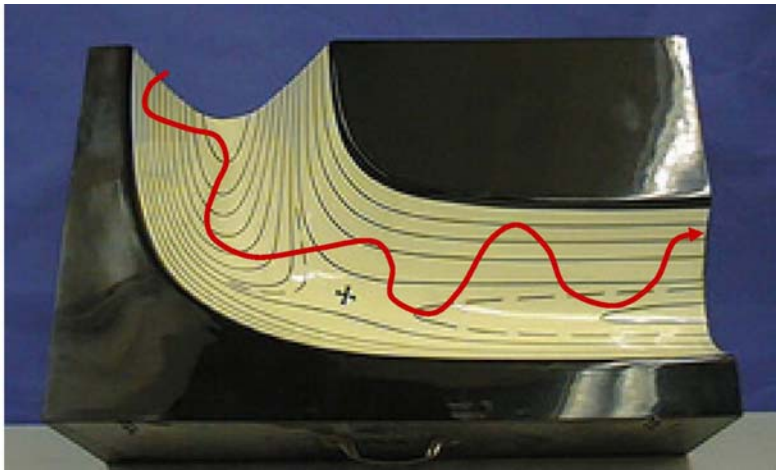
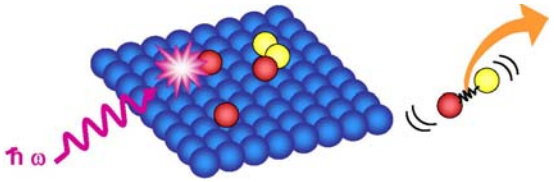


Basic Assumptions:

1. Born-Oppenheimer Approximation
2. Classical mechanical nuclear motion

Unavoidable Additional Approximations:

→ 1. Approximate potential energy surface
2. Incomplete sampling
3. (often) Extrapolate to longer timescales
4. Too few atoms
5. Continuum solvent and other shortcuts



V. Adiabatic "on-the-fly" Dynamics

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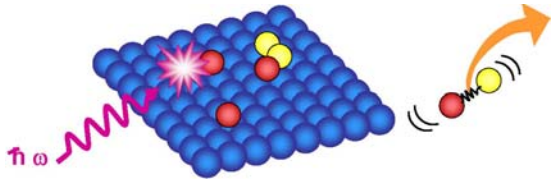
What about the potential energy surface? i.e., the forces?

empirical (sometimes called "classical" - bad terminology)

semi-empirical (Huckel, valence-bond, PPP-Rossky…)

analytic fit to ab initio (HF, DFT, MC-SCF, CCSD,…)

on-the-fly ab initio (HF, DFT,,…)



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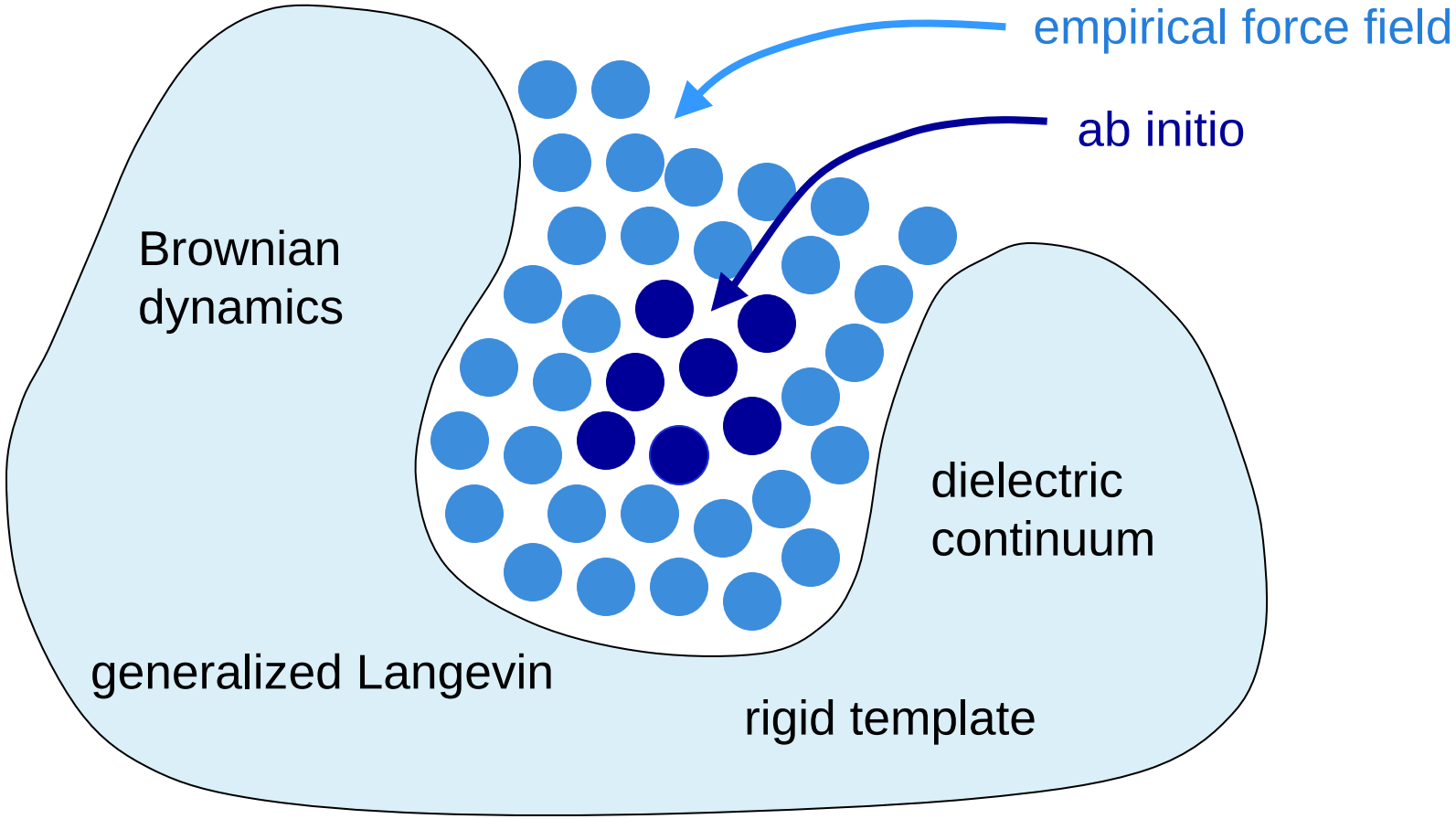
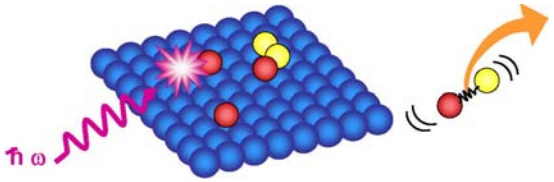
QM/MM Approach:





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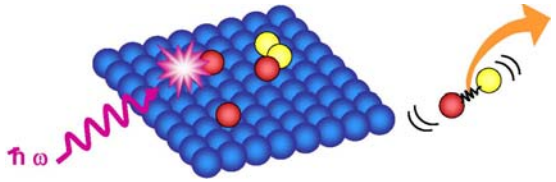

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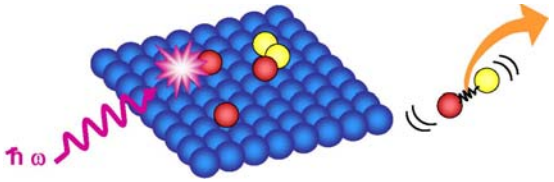

V. Adiabatic "on-the-fly" Dynamics

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The Hellman – Feynman Theorem:

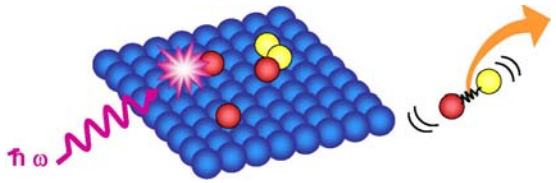
$$\frac{d}{dR}\mathcal{E}_j(R) \;=\; \frac{d}{dR}\left\langle \Phi_j(R)\,|\,\mathcal{H}_{el}(R)\,|\,\Phi_j(R)\right\rangle \;=\; \text{force}$$

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

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

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

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



V. Adiabatic "on-the-fly" Dynamics

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The Hellman – Feynman Theorem:

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

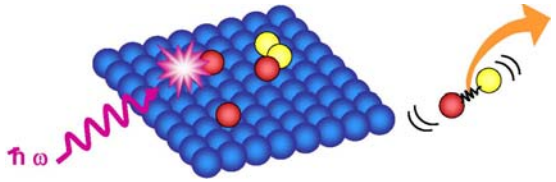
$$+\left\langle \frac{d}{dR}\Phi_j(R) \left| \mathcal{H}_{el}(R) \right| \Phi_j(R) \right\rangle + \left\langle \Phi_j(R) \left| \mathcal{H}_{el}(R) \right| \frac{d}{dR}\Phi_j(R) \right\rangle$$

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

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

$$= \frac{d}{dR}\left[\left\langle \Phi_j(R) \middle| \Phi_j(R) \right\rangle\right] = 0$$

Pulay corrections



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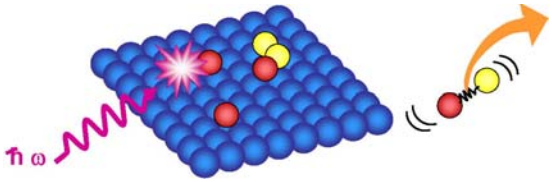

VI. Car-Parrinello Dynamics

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Euler-Lagrange equations:

$$\frac{d}{dt}\frac{d\mathcal{L}}{d\dot{q}} = \frac{\partial \mathcal{L}}{\partial q}$$

Classical Lagrangian:

$$\mathcal{L} = T - V = \sum_{\alpha} \tfrac{1}{2} M_{\alpha} \dot{R}^2 - E_j(\mathbf{R})$$

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

Car-Parrinello Lagrangian:

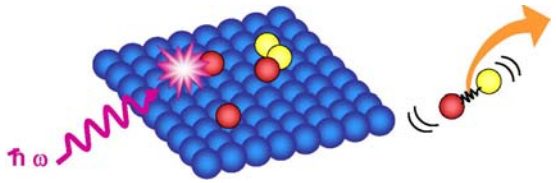
$$\mathcal{L} = \sum_{\alpha} \tfrac{1}{2} M_{\alpha} \dot{R}^2 - \langle \Psi_j | \mathcal{H}_{el} | \Psi_j \rangle$$

fictitious electronic dynamics

$$+ \sum_{n} \tfrac{1}{2} \mu_n \langle \dot{\varphi}_n | \dot{\varphi}_n \rangle + \sum_{nm} \lambda_{nm} [\langle \varphi_n | \varphi_m \rangle - \delta_{nm}]$$

Kohn-Sham orbital

Roberto Car, Michele Parrinello



VI. Car-Parrinello Dynamics

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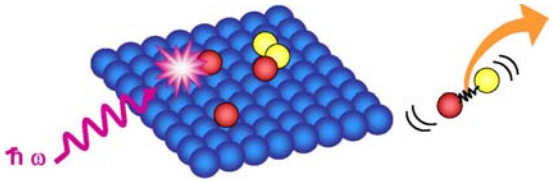
Student problem: Lagrange (undetermined) parameter problem

find the minimum of the function $f(x,y) = x^2 + y^2$

subject to $x + y = 2$, using the method of Lagrange parameters

define $h(x,y) = f(x,y) + \lambda(x + y - 2)$

and minimize wrt x, y and λ



VI. Car-Parrinello Dynamics

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

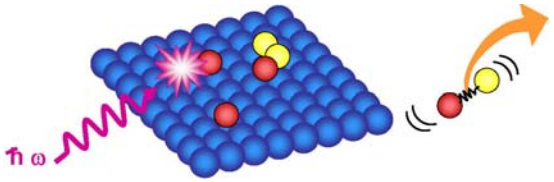
Car-Parrinello Lagrangian:

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

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

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

Roberto Car, Michele Parrinello



IV. Classical Molecular Dynamics

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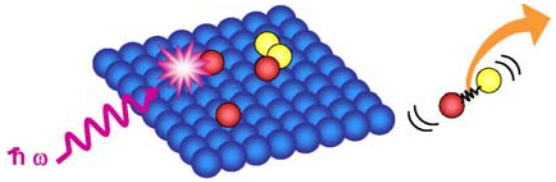
V. Adiabatic "on-the-fly" Dynamics
VI. Car-Parrinello Dynamics

} **CAUTION!**

"exact" PES	+	"exact" quantum dynamics	→	exact
"exact" PES	+	classical dynamics	→	inaccurate ???
empirical PES	+	classical dynamics	→	maybe accurate ???

is "first-principles" synonymous with "less accurate"?



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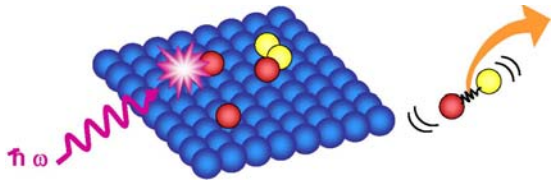

VII. Infrequent Events

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Molecular Dynamics Time Step: ~ 10^{-15} s

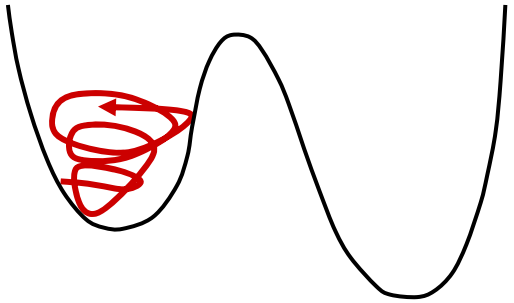
Feasible number of integration steps: ~ 10^{6} - 10^{9}

Maximum Time for Direct MD Integration: ~ 10^{-6} s

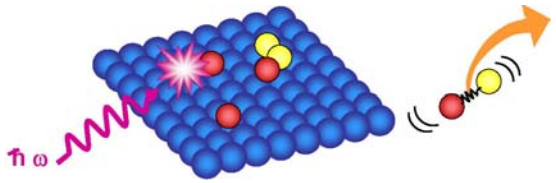
Moreover, need to sample multiple trajectories, different conditions, etc.

Examples:

- High activation energy processes
- Slow relaxation times (timescale mismatch, glasses, …)
- Concerted movement of many atoms (protein folding)



Infrequent Event



VII. Infrequent Events

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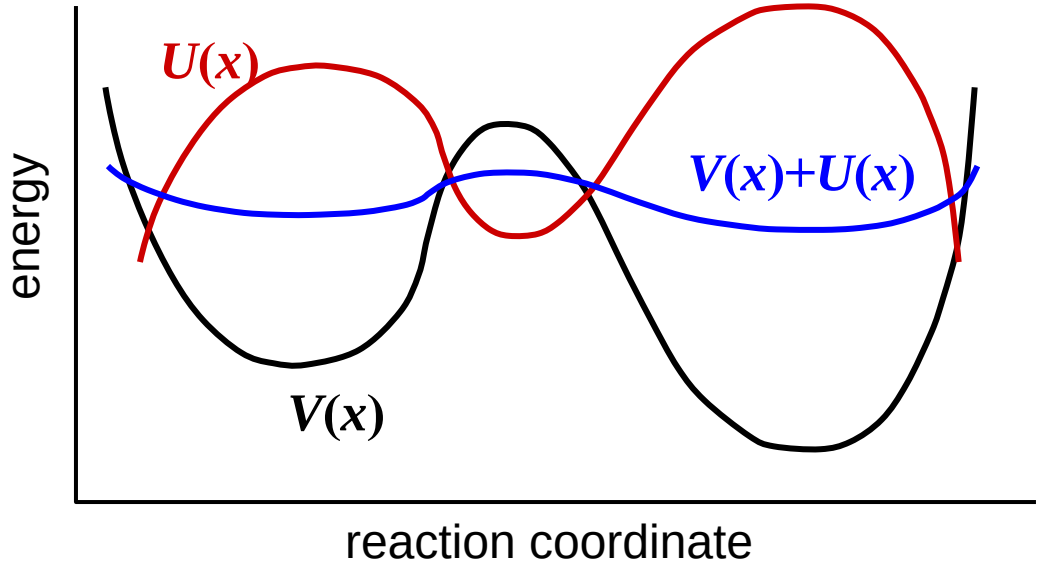
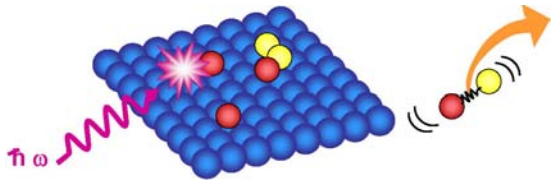
Many methods to enhance sampling for **equilibrium** simulations.

Non-Boltzmann sampling, e.g., **umbrella sampling**



Un-bias by weighting each point by $\exp[+U(x)/kT]$

But what about dynamics?



VII. Infrequent Events

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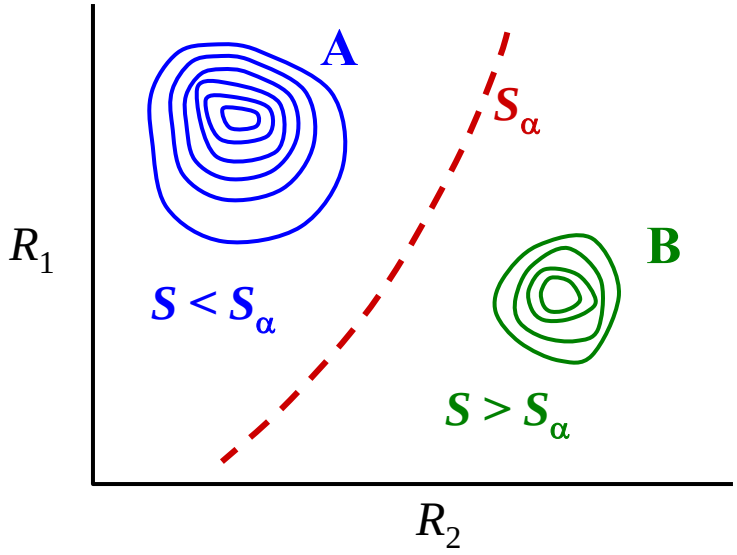
Reaction Rate Theory (Classical)

1. Define reactant and product regions and "equilibrium reaction rate"

2. Define reaction variable ***S*** and dividing surface S_α

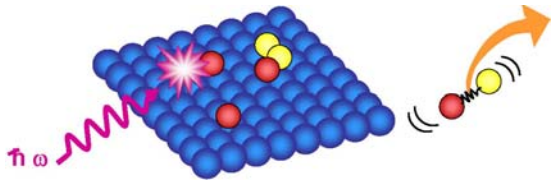


3. Compute one-way flux through dividing plane: $k_\alpha^\dagger = \int_0^\infty G_\alpha(p_s)\left(\frac{p_s}{m}\right) dp_s$

forward only

fraction of molecules at $S = S_\alpha$ with momentum p_s

velocity at S_α



VII. Infrequent Events

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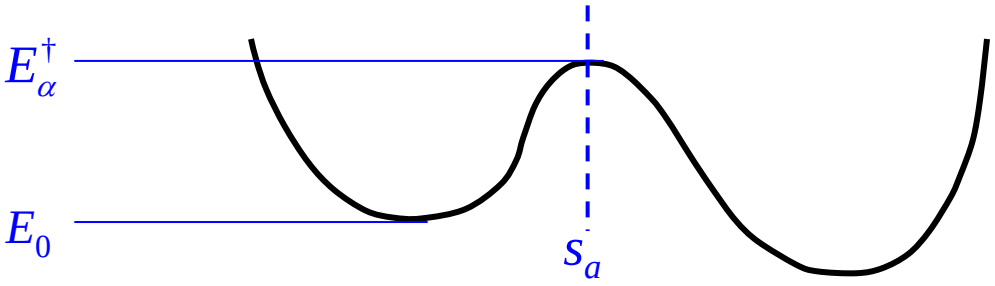
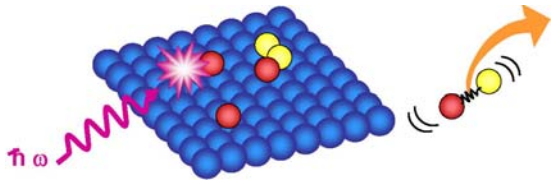
$$G_\alpha(p_s) = \frac{\int_{s_\alpha} \ldots \int \exp[-\mathcal{H}(s, p_s, \underset{\sim}{q}, \underset{\sim}{p}_q)/kT]\,\delta(s - s_\alpha)\,ds\,d\underset{\sim}{q}\,d\underset{\sim}{p}_q}{\int_{-\infty}^{s_\alpha} \ldots \int \exp[-\mathcal{H}(s, p_s, \underset{\sim}{q}, \underset{\sim}{p}_q)/kT]\,ds\,dp_s\,d\underset{\sim}{q}\,d\underset{\sim}{p}_q}$$

define: $Q_0 \exp(-E_0/kT) = h^{-M} \int_{-\infty}^{s_\alpha} \ldots \int \exp[-\mathcal{H}(s, p_s, \underset{\sim}{q}, \underset{\sim}{p}_q)/kT]\,ds\,dp_s\,d\underset{\sim}{q}\,d\underset{\sim}{p}_q$

Planck's constant: conventional quantum-classical correspondence





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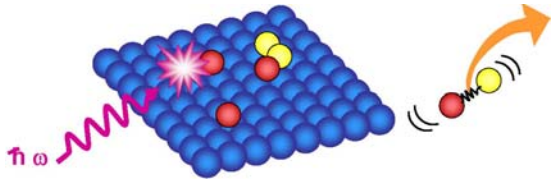
Planck's constant: conventional quantum-classical correspondence

student problem: simple harmonic oscillator: $V(x) = \frac{1}{2}K\,x^2 = \frac{1}{2}m\,\omega^2 x^2$

show that at high temperatures, the quantum and classical partition functions are equal if the classical partition function is defined by

$$Q_{classical} = \frac{1}{h}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left[-V(x)/kT\right]\exp\left[-p^2/2mkT\right]dx\,dp$$



VII. Infrequent Events

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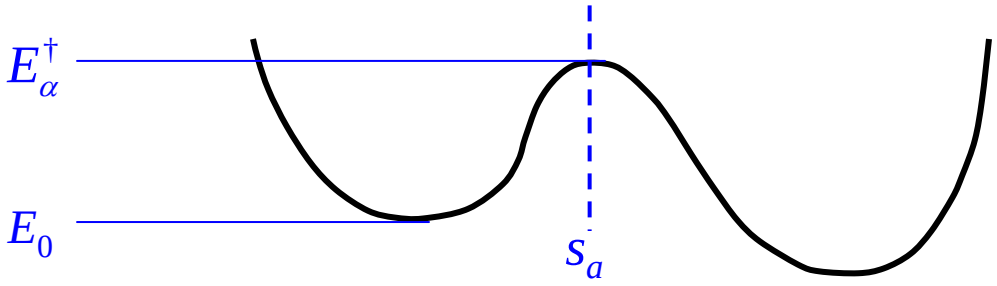
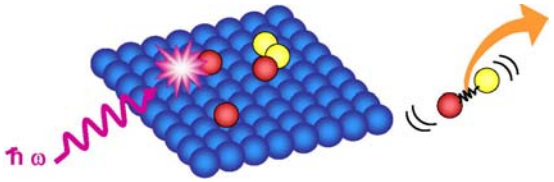
define: $$Q_0 \exp(-E_0/kT) = h^{-M}\int_{-\infty}^{s_\alpha}\!\!\int \exp[-\mathcal{H}(s, p_s, \underset{\sim}{q}, \underset{\sim}{p}_q)/kT]\,ds\,dp_s\,d\underset{\sim}{q}\,d\underset{\sim}{p}_q$$

and $$Q_\alpha^\dagger \exp(-E_\alpha^\dagger/kT) = h^{-(M-1)}\int\!\!\int \exp[-\mathcal{H}^\dagger(s_\alpha, \underset{\sim}{q}, \underset{\sim}{p}_q)/kT]\,d\underset{\sim}{q}\,d\underset{\sim}{p}_q$$

where $$\mathcal{H}^\dagger(s_\alpha, \underset{\sim}{q}, \underset{\sim}{p}_q) = \mathcal{H}(s_\alpha, p_s, \underset{\sim}{q}, \underset{\sim}{p}_q) - p_s^2/2m$$





VII. Infrequent Events

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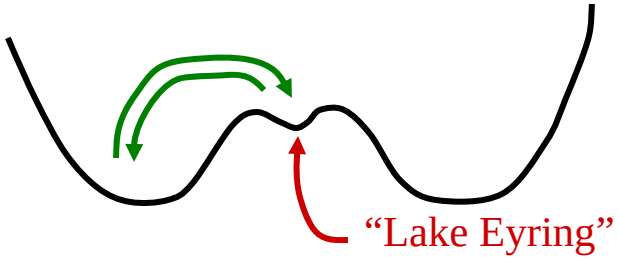
$$G_\alpha(p_s) = \exp\left(-\frac{p_s^2}{2mkT}\right)\frac{Q_\alpha^\dagger}{hQ_0}\exp[-(E_\alpha^\dagger - E_0)/kT]$$

$$k_\alpha^\dagger = \int_0^\infty \left(\frac{p_s}{m}\right)\exp\left(\frac{p_s^2}{2mkT}\right)\frac{Q_\alpha^\dagger}{hQ_0}\exp\left[-\frac{(E_\alpha^\dagger - E_0)}{kT}\right]dp_s$$

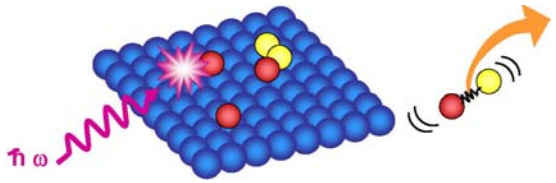
$$k_\alpha^\dagger = \frac{kT}{h}\frac{Q_\alpha^\dagger}{Q_0}\exp\left[-\frac{(E_\alpha^\dagger - E_0)}{kT}\right] \quad \text{transition state theory}$$

Activated Complex Theory

equilibration?



Henry Eyring



VII. Infrequent Events

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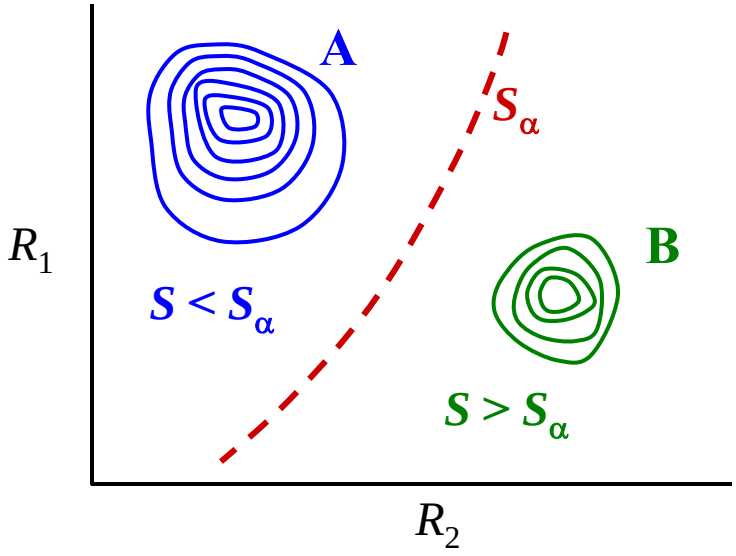
Transition State Theory is an upper limit to the true reaction rate

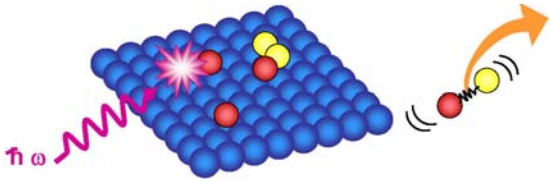
⟶ **Variational Transition State Theory**

VTST: Choose location of dividing surface to minimize transition state theory rate



But still not the true rate

⟶ **Recrossing correction**



VII. Infrequent Events

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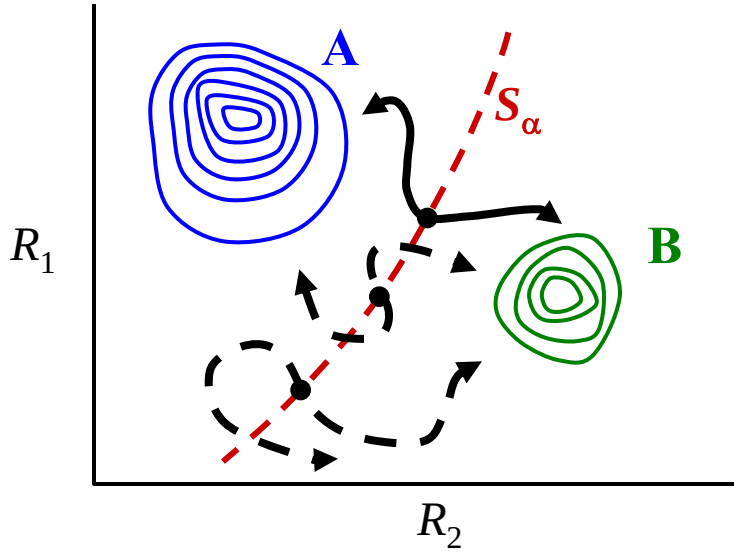
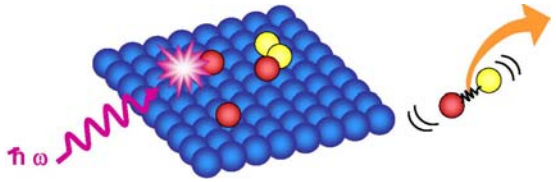
Recrossing correction:

rate $k = f_\alpha \, k_\alpha^\dagger$

1. f_α = fraction of reactive trajectories, $f_\alpha < 1$
2. TST rate depends on location of dividing surface S_α.
3. True rate does not depend on location of dividing surface S_α.
4. $k \leq k_\alpha^\dagger$





Chemical Dynamics

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I. Quantum Dynamics

II. Semiclassical Dynamics

aside: tutorial on classical mechanics

III. The Classical Limit via the Bohm Equations

IV. Classical Molecular Dynamics

V. Adiabatic "on-the-fly" Dynamics

VI. Car-Parrinello Dynamics

VII. Infrequent Events

aside: transition state theory and re-crossing

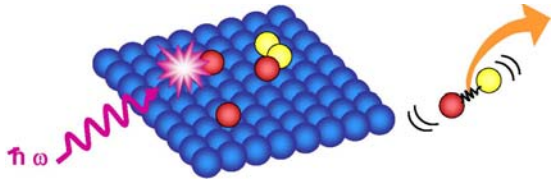
VIII. Beyond Born Oppenheimer

IX. Ehrenfest Dynamics

X. Surface Hopping

XI. Dynamics at Metal Surfaces

XII. Mixed Quantum-Classical Nuclear Dynamics



VIII. Beyond Born-Oppenheimer

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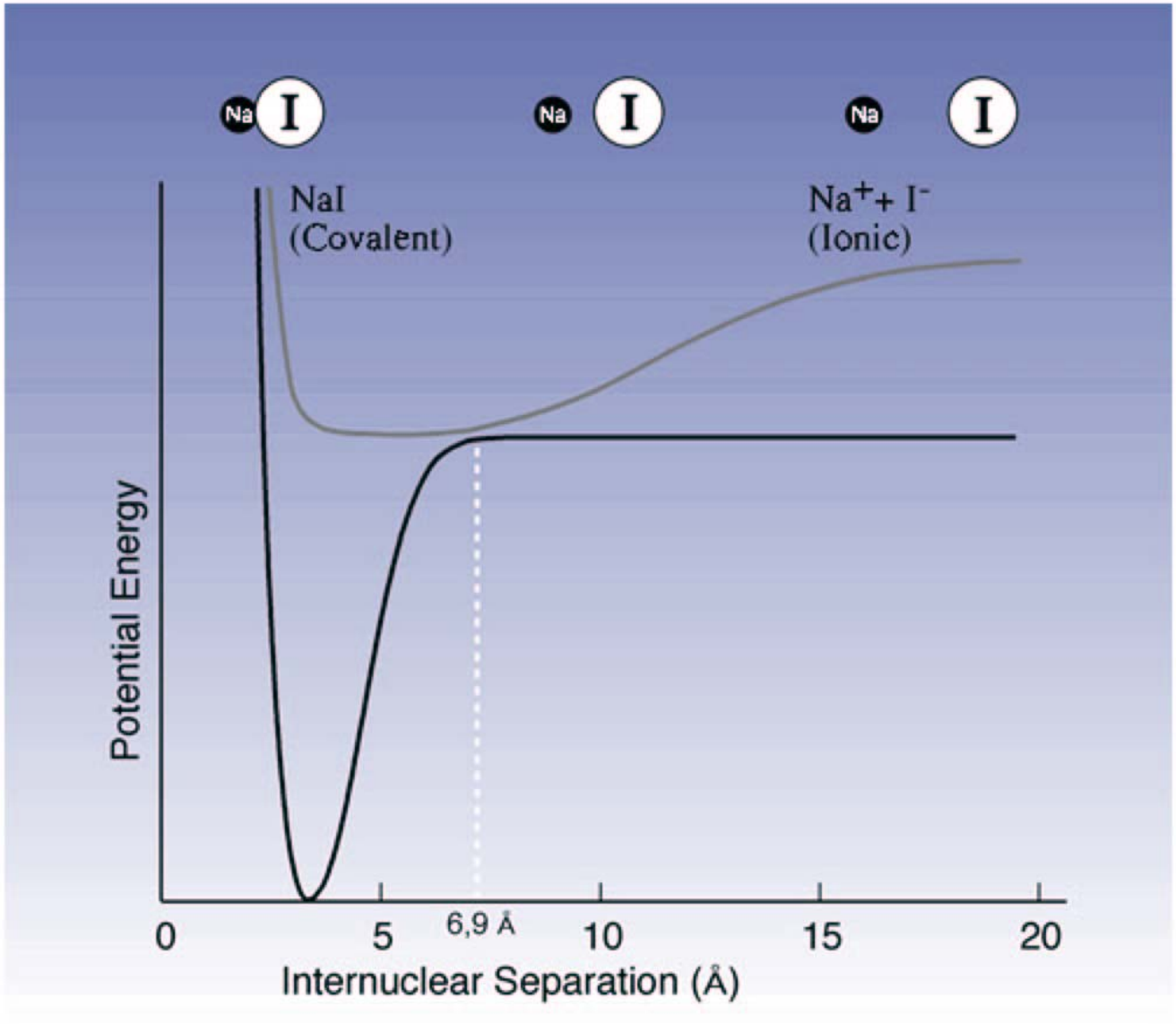
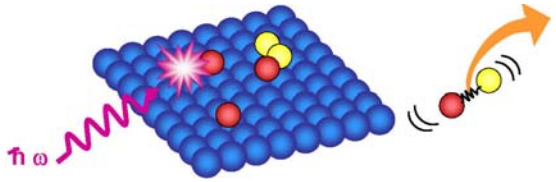


Ahmed Zewail



VIII. Beyond Born-Oppenheimer

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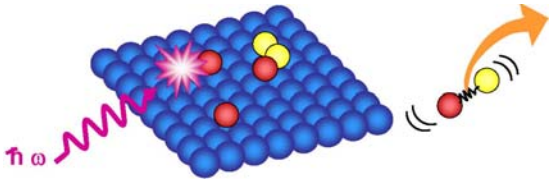
$$\Psi(\mathbf{r},\mathbf{R}) \;=\; \Phi_i(\mathbf{r};\mathbf{R})\,\Omega_i(\mathbf{R})$$

Born-Oppenheimer



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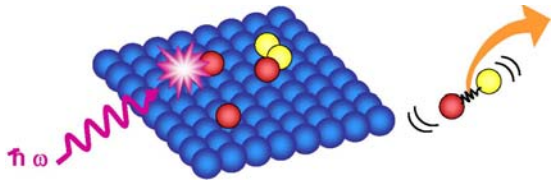
$$\Psi(\mathbf{r},\mathbf{R}) = \sum_i \Phi_i(\mathbf{r};\mathbf{R})\,\Omega_i(\mathbf{R})$$

Beyond Born-Oppenheimer



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

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

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

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

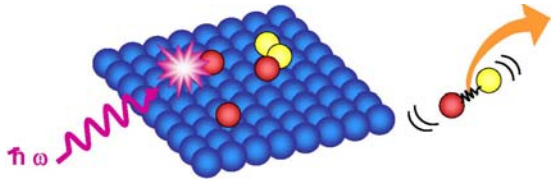
student problem:

show that $d_{ij}(\mathbf{R})$ is anti-Hermitian and its diagonal elements are zero

where nonadiabatic (derivative) couplings are defined by:

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

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



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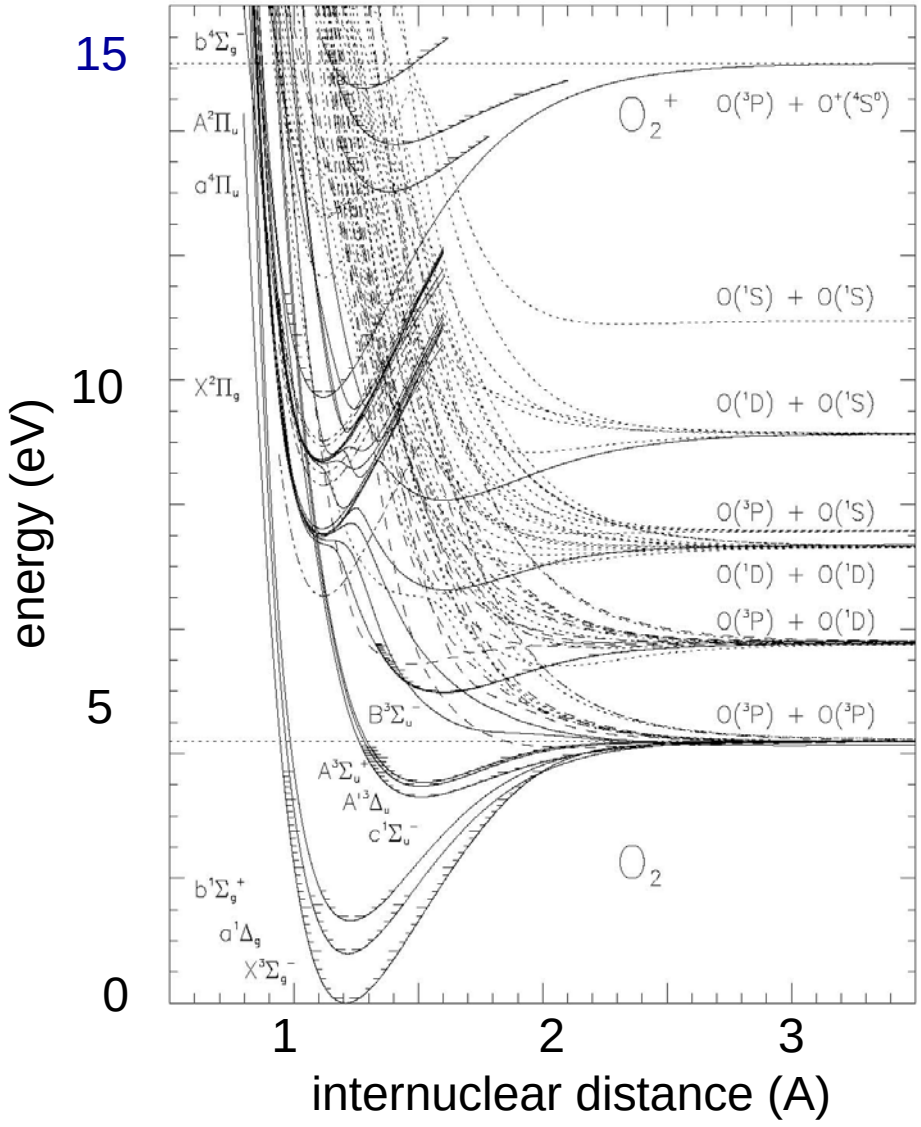
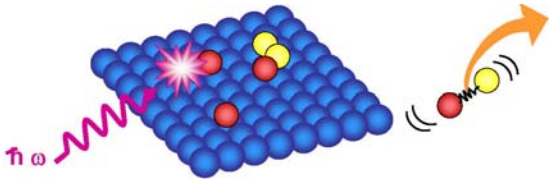
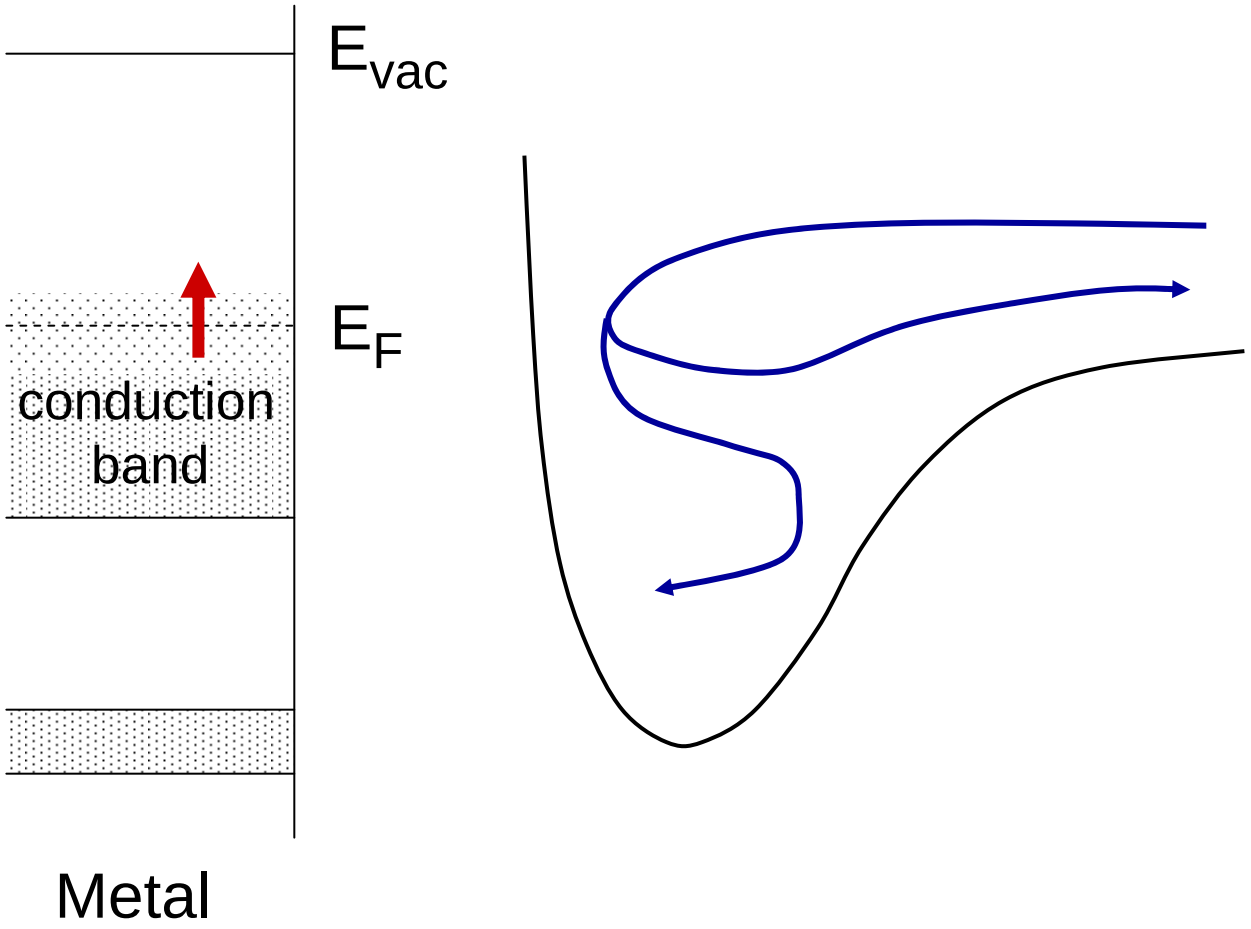
Potential Energy Curves for the Oxygen Molecule

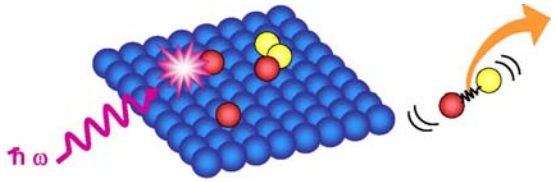
from
R. P. Saxon and B. Liu,
J. Chem. Phys. 1977





Nonadiabatic Transitions at Metal Surfaces: Electron-Hole Pairs





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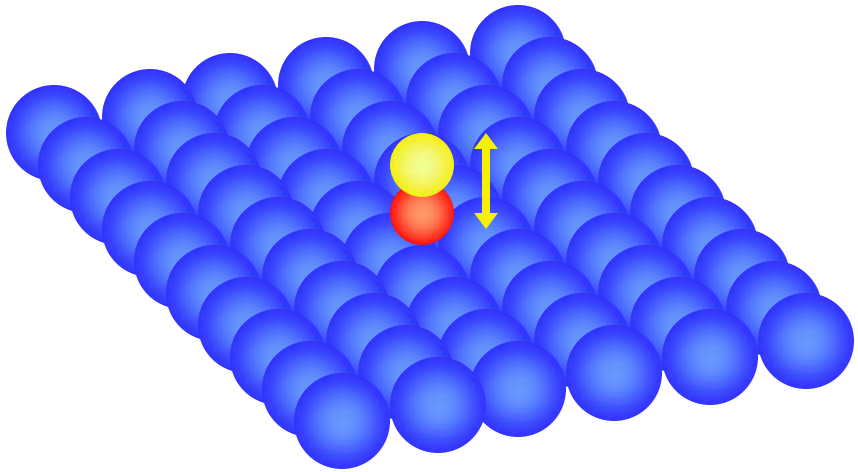
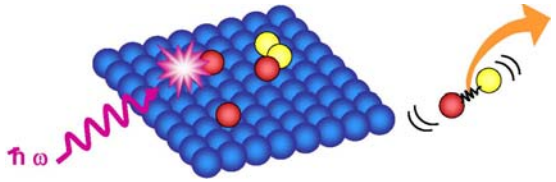
Vibrational Lifetime of CO on Cu(100)

$v = 1 \longrightarrow v = 0$



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

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



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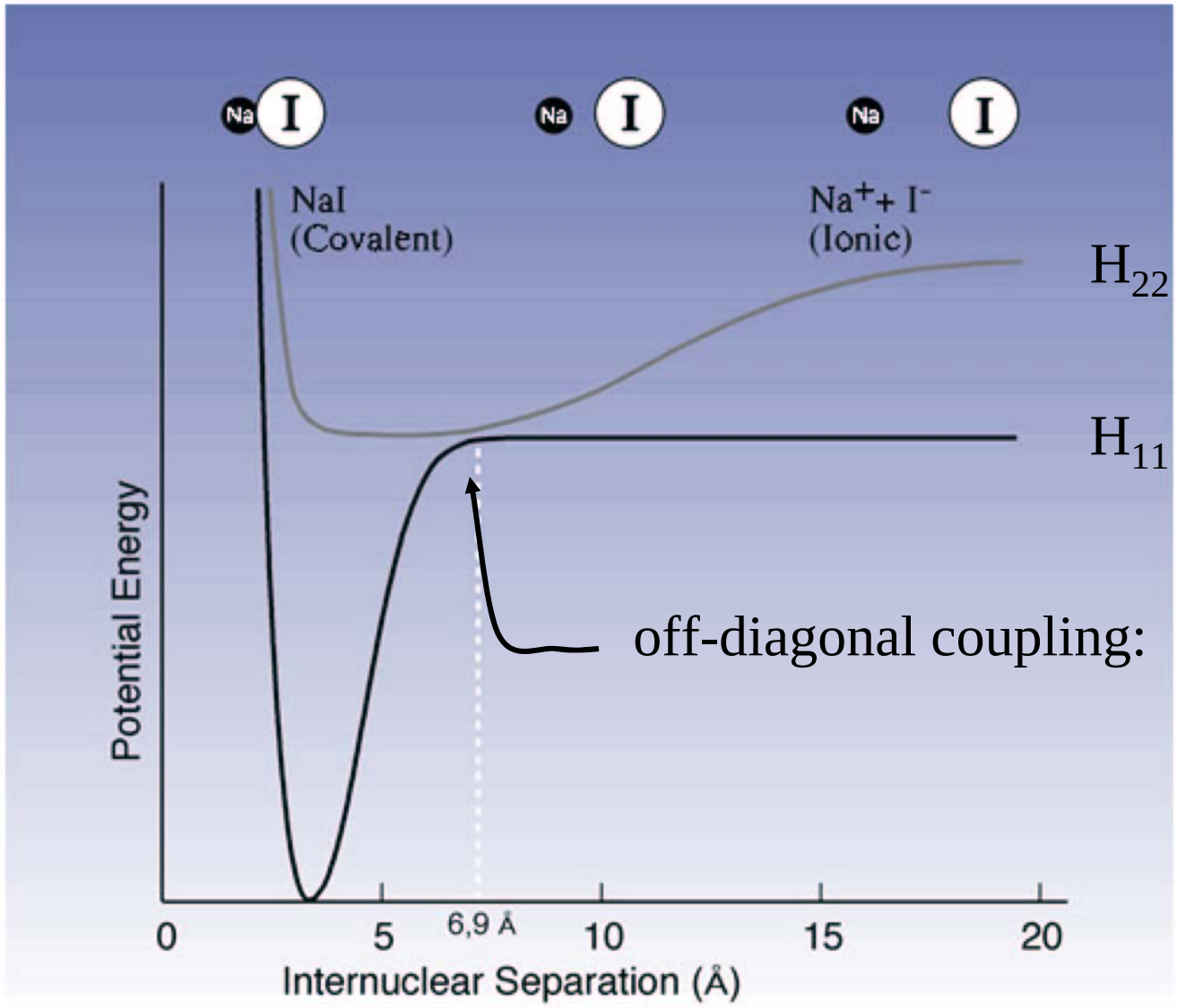
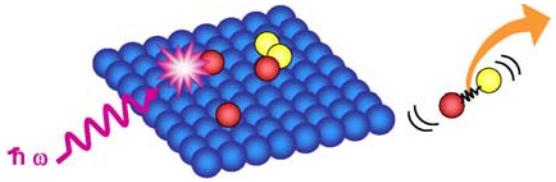


H_{22} (ionic)

H_{11} (neutral)

off-diagonal coupling: H_{12}



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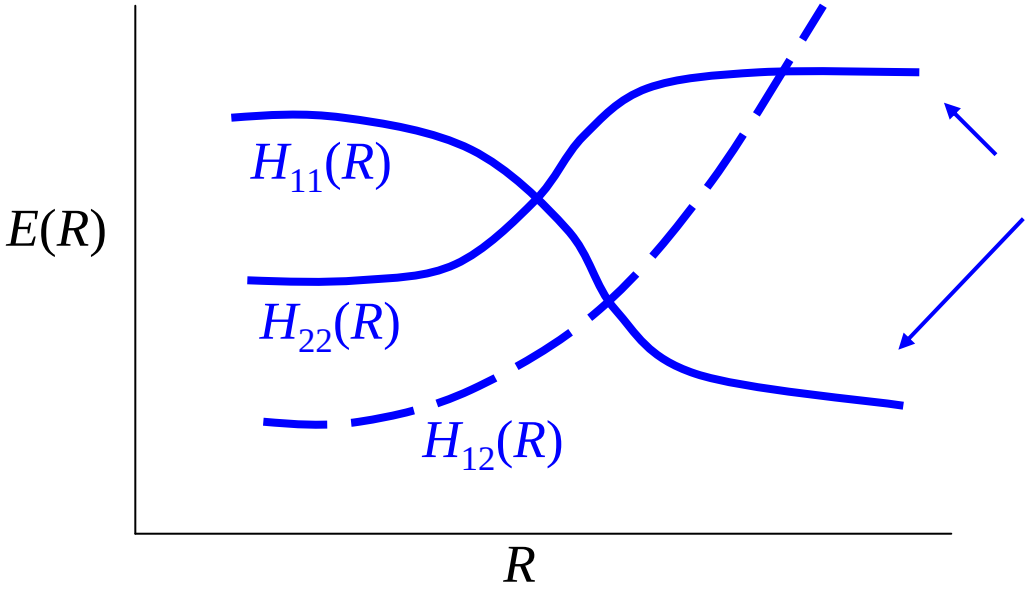
The Non-Crossing Rule

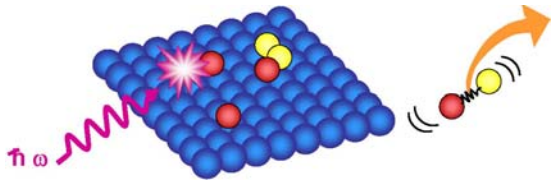
$$\mathcal{H}(R) = \begin{bmatrix} H_{11}(R) & H_{12}(R) \\ H_{12}(R) & H_{22}(R) \end{bmatrix}$$



"diabatic" potential energy curves

H. C. Longuet-Higgins

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



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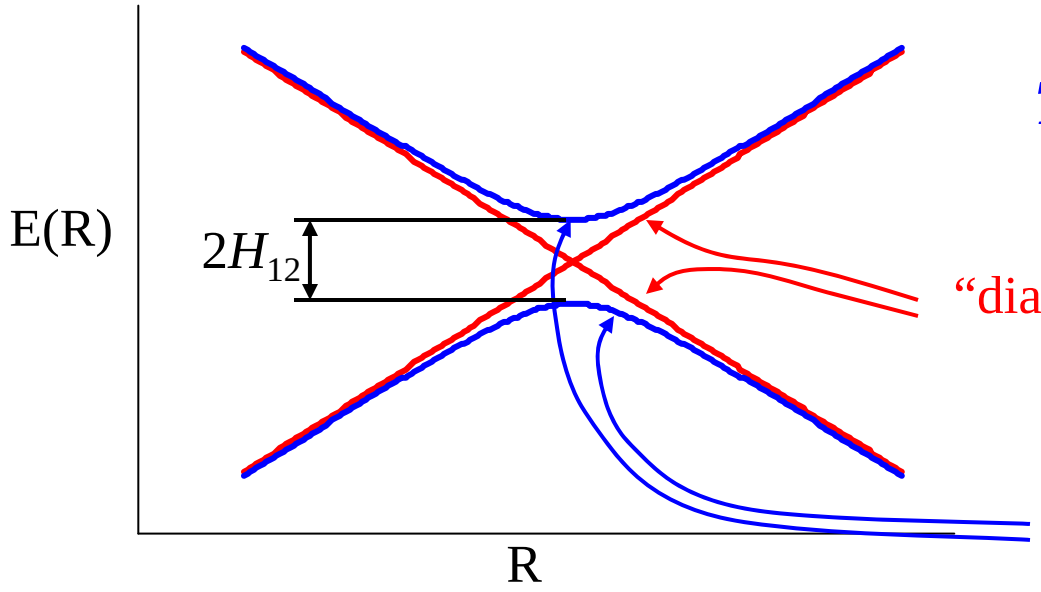
$$\mathcal{H}(R) = \begin{bmatrix} H_{11}(R) & H_{12}(R) \\ H_{12}(R) & H_{22}(R) \end{bmatrix}$$

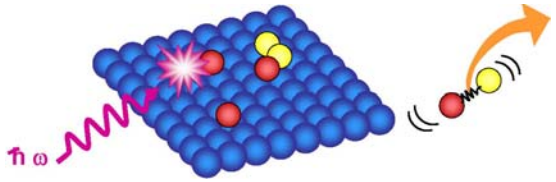


The Non-Crossing Rule

"diabatic" potential energy curves

adiabatic potential energy curves

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



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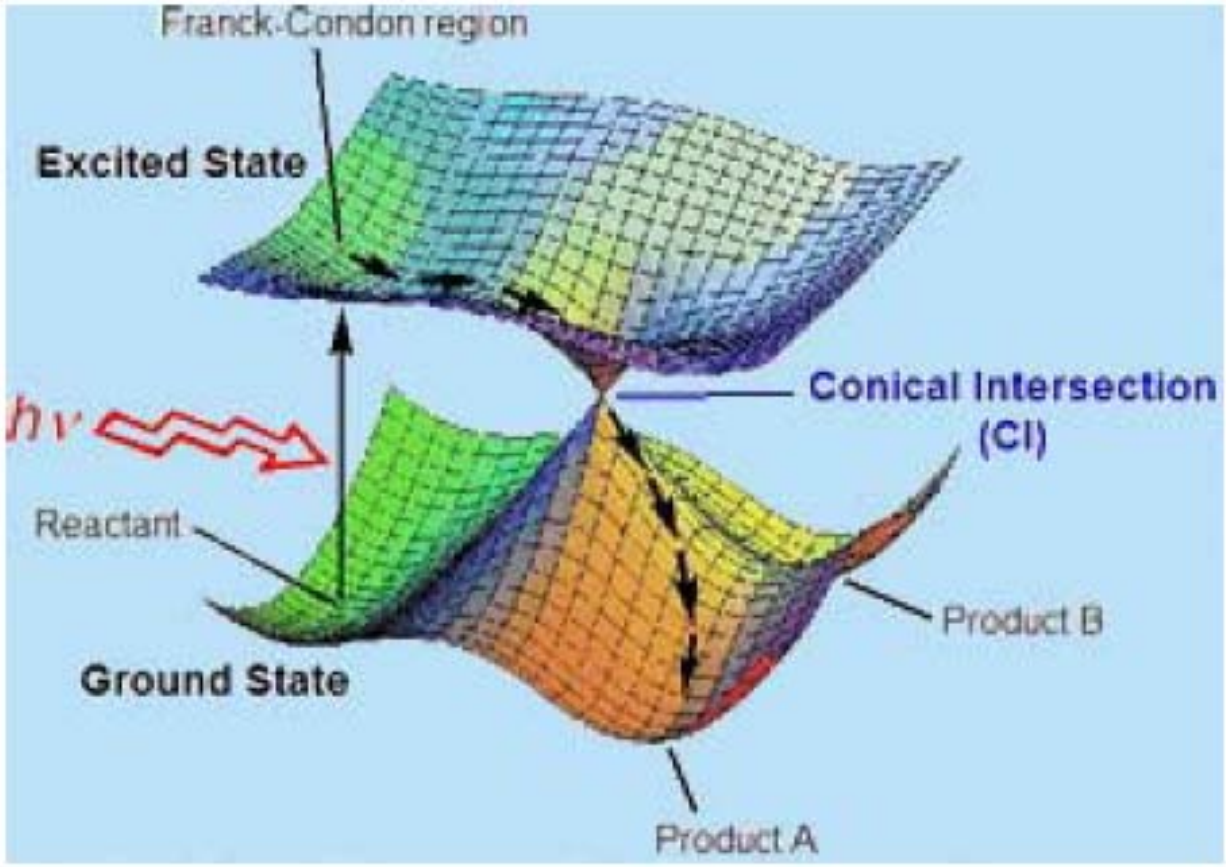


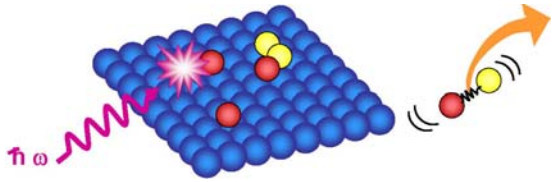
The non-crossing rule for more than 1 degree of freedom:

"Conical Intersection"

N degrees of freedom:

N-2 dimensional "seam"

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



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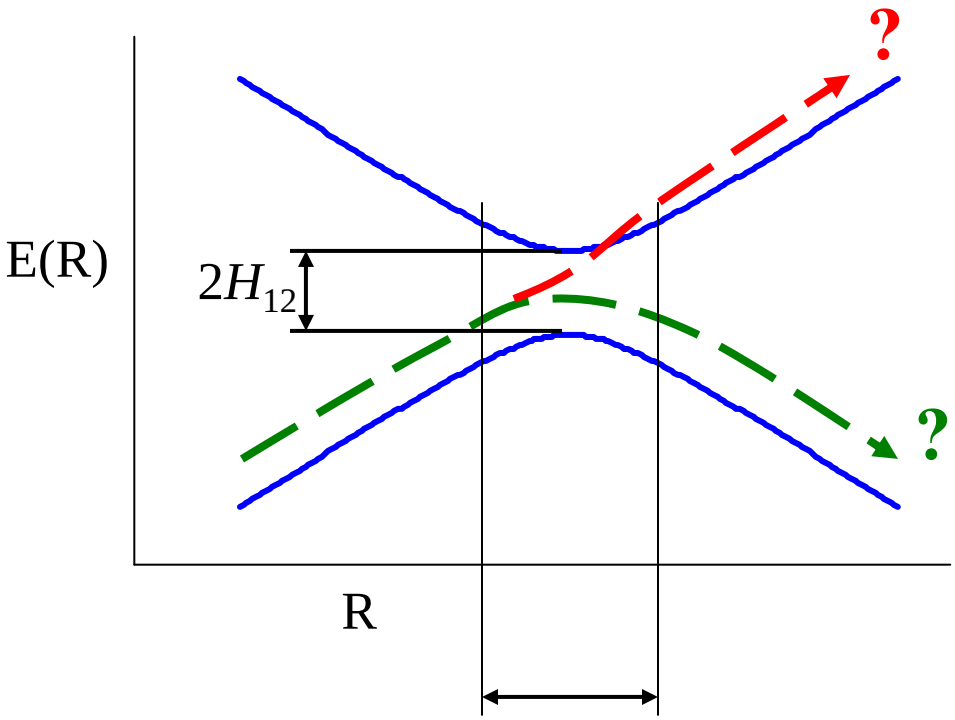


$$\approx \quad 2H_{12} / |\partial(H_{11} - H_{22}) / \partial R|$$

The Massey Criterion:

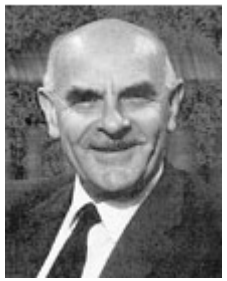
$$\Delta\mathcal{E}\,\Delta t \quad \gg \quad \hbar$$

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

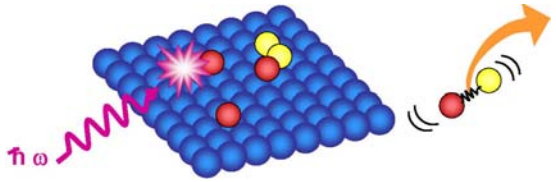
$$\Delta t \quad \approx \quad \text{distance/velocity}$$

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

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



H. S. W. Massey



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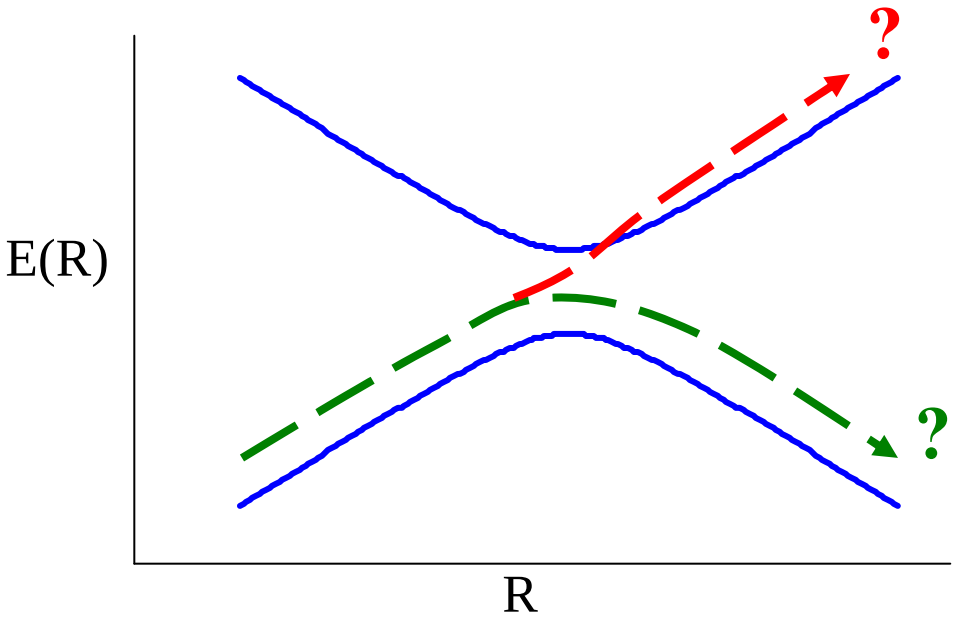
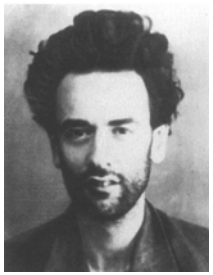


Landau-Zener Approximation

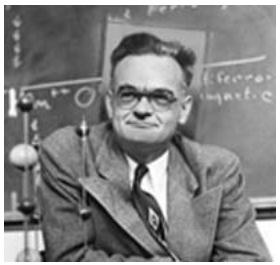
Assumptions:

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

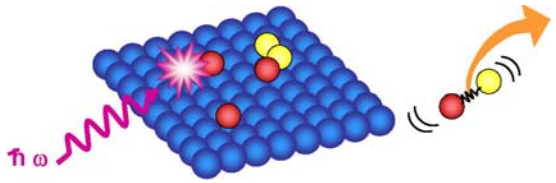
$$P_{nonad} \approx \exp\left[\frac{-2\pi H_{12}^2}{\hbar \dot{R} \left| \partial (H_{11} - H_{22}) / \partial R \right|}\right]$$



L. D. Landau



C. M. Zener



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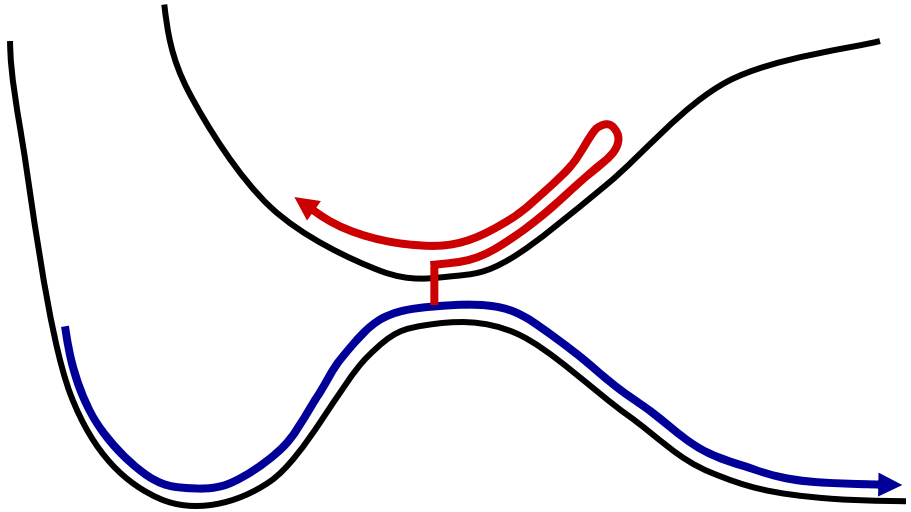
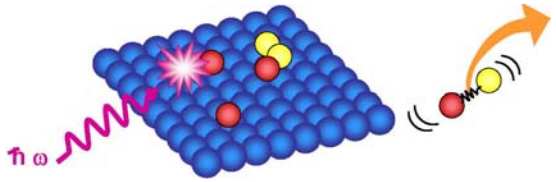
How do we simulate dynamics?



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

→ Quantum – Classical Feedback: Self-Consistency



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

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

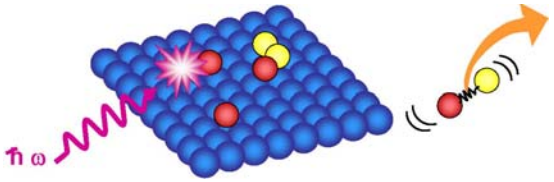
$$-\frac{\hbar^2}{2}\sum_\alpha M_\alpha^{-1}\nabla^2_{R_\alpha}\Omega_j(\mathbf{R}) + \mathcal{E}_j(\mathbf{R})\,\Omega_j(\mathbf{R}) - E\,\Omega_j(\mathbf{R}) \;=$$

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

Wave packet methods: Initial wave function: Gaussian wave packet

$$\Omega_i(x,0) \;=\; \left(\frac{2}{\pi a^2}\right)^{1/4}\exp(ik_0x)\exp[-(x-x_0)^2/a^2]$$

$$\Omega_j(x,0) \;=\; 0\,, \qquad j\neq i$$



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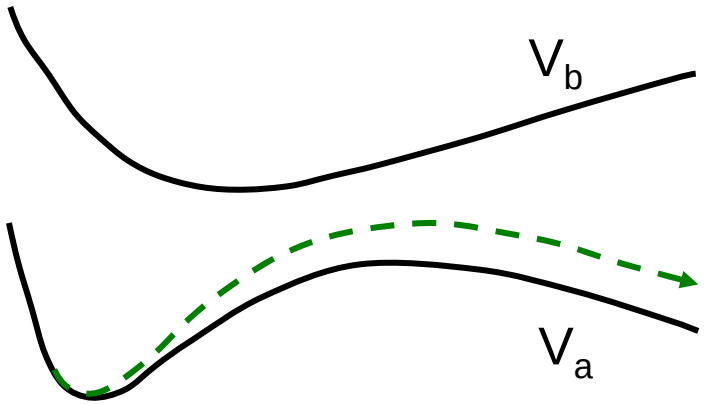
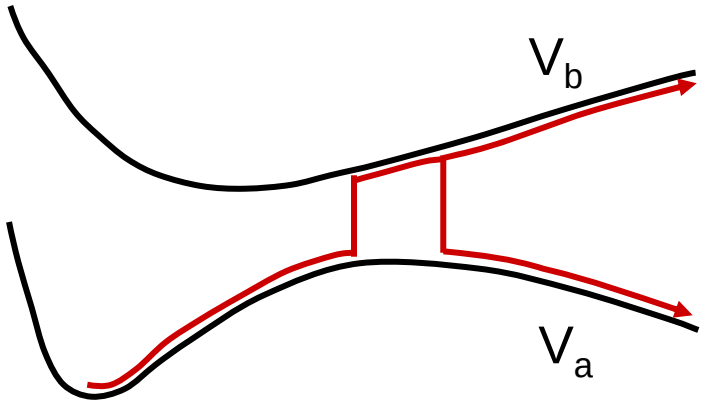
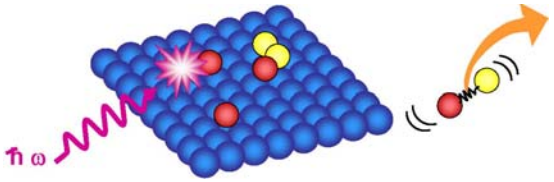
TWO GENERAL MIXED QUANTUM-CLASSICAL APPROACHES FOR INCLUDING FEEDBACK



Ehrenfest (SCF)



Surface-Hopping



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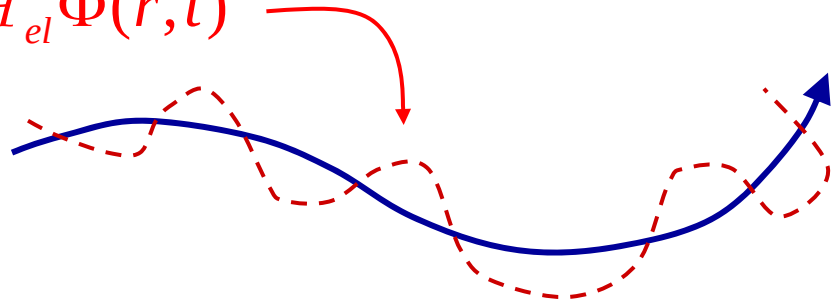
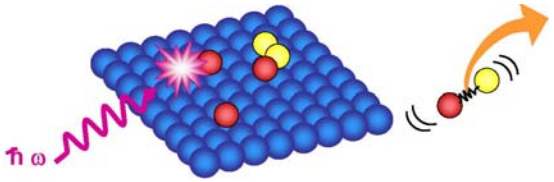
$$i\hbar \frac{\partial \Phi(r,t)}{\partial t} = \mathcal{H}_{el} \Phi(r,t)$$



$$\Phi(r,t) = \sum_i c_i(t)\ \phi_i(r;R)$$

(adiabatic states)

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



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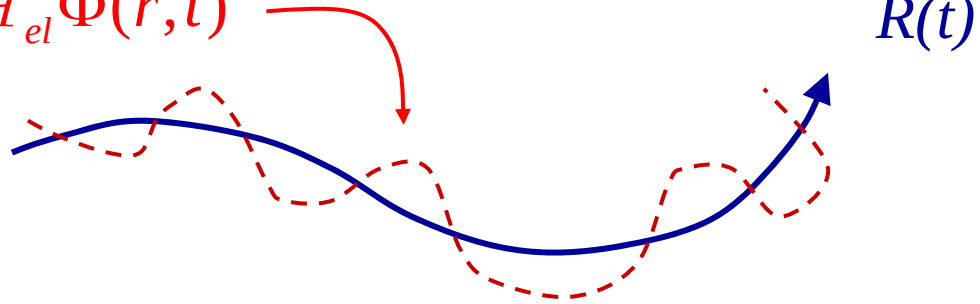
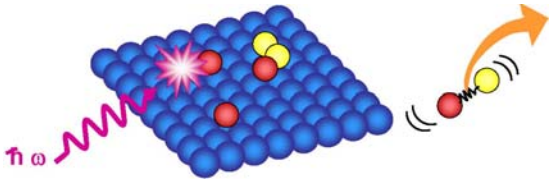
$$i\hbar \frac{\partial \Phi(r,t)}{\partial t} = \mathcal{H}_{el}\Phi(r,t)$$



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

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



Chemical Dynamics

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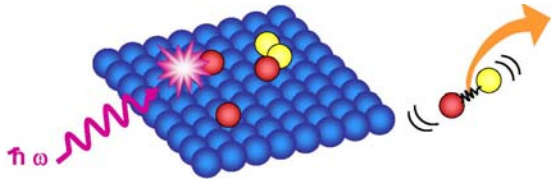
Paul Ehrenfest



IX. Ehrenfest Dynamics

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

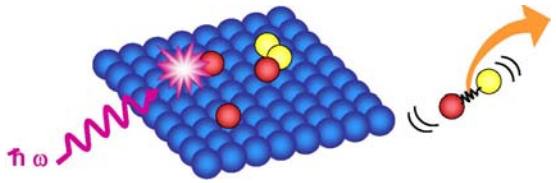
Self-consistent Field Approximation (fully quantum):

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

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

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

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



IX. Ehrenfest Dynamics

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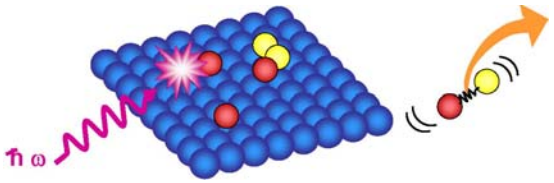
Substituting (2) into (1), multiplying on the left by $\Xi(\mathbf{r},t)$ and integrating over **r** gives the equivalent SCF equation for the nuclear wave function $\Omega(\mathbf{R},t)$:

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

Thus, the potential energy function governing the nuclei becomes

$\int\Phi^*(\mathbf{r},t)\,\mathcal{H}_{el}(\mathbf{r},\mathbf{R})\,\Phi(\mathbf{r},t)\,d\mathbf{r}$ instead of the adiabatic energy $E_j(\mathbf{R})$.

The Ehrenfest method consists of taking classical limit of Eq. 5,
i.e., running classical trajectories subject to this potential function



IX. Ehrenfest Dynamics

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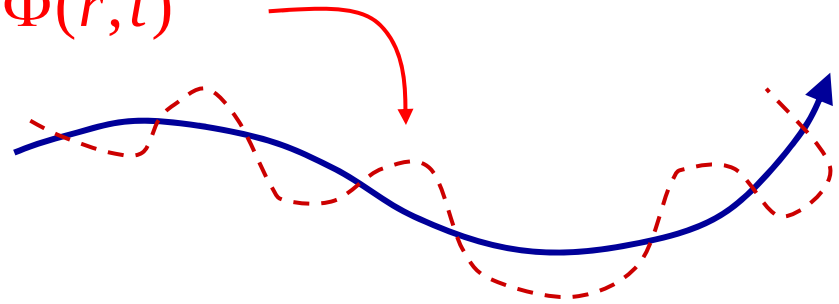
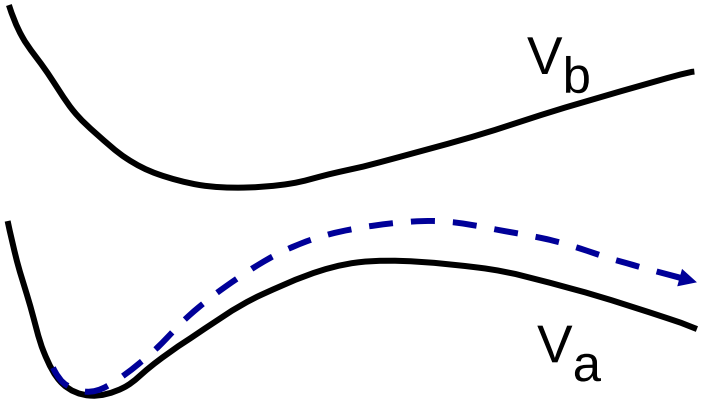
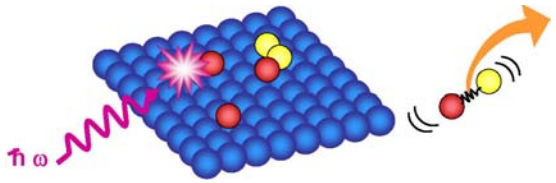
$$i\hbar \frac{\partial \Phi(r,t)}{\partial t} = \mathcal{H}_{el}\Phi(r,t)$$



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





IX. Ehrenfest Dynamics

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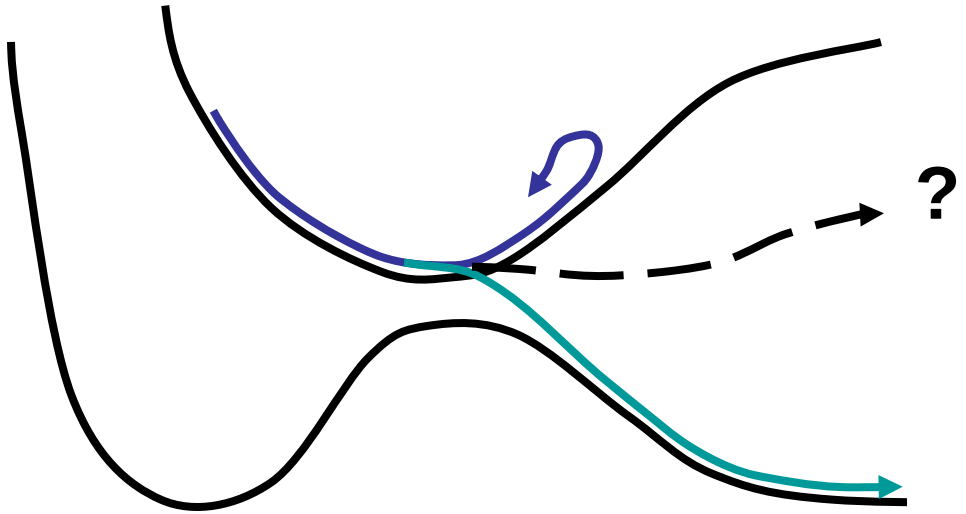
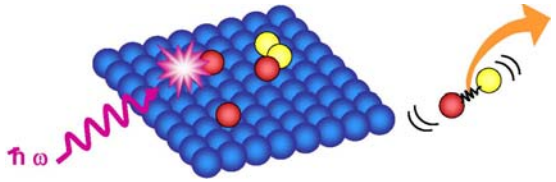
$$M\,\ddot{R}(t) \;=\; -\nabla_R < \Phi(t) \,|\, \mathcal{H}_{el} \,|\, \Phi(t) >$$



Problem:
single configuration
→ average path



Chemical Dynamics

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I. Quantum Dynamics

II. Semiclassical Dynamics

aside: tutorial on classical mechanics

III. The Classical Limit via the Bohm Equations

IV. Classical Molecular Dynamics

V. Adiabatic "on-the-fly" Dynamics

VI. Car-Parrinello Dynamics

VII. Infrequent Events

aside: transition state theory and re-crossing

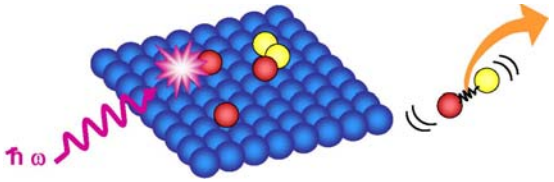
VIII. Beyond Born Oppenheimer

IX. Ehrenfest Dynamics

X. Surface Hopping

XI. Dynamics at Metal Surfaces

XII. Mixed Quantum-Classical Nuclear Dynamics



X. Surface Hopping

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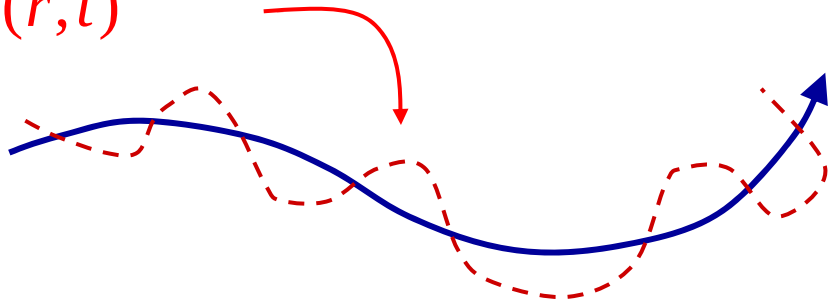
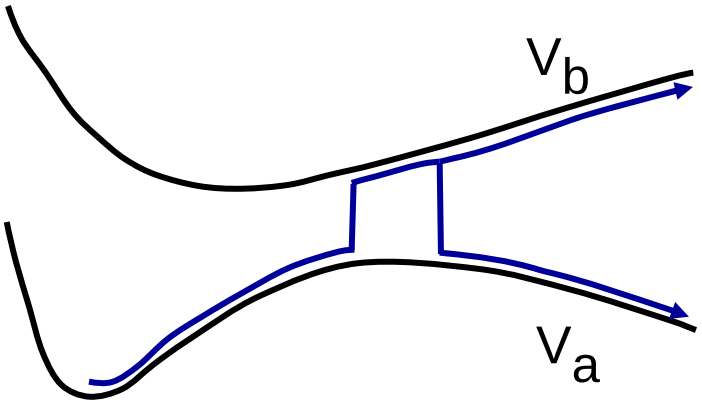
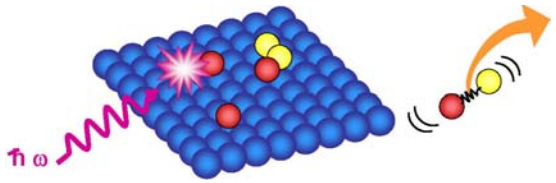
$$i\hbar \frac{\partial \Phi(r,t)}{\partial t} = \mathcal{H}_{el}\Phi(r,t)$$







X. Surface Hopping

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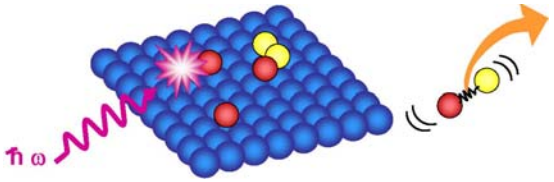
Multi-Configuration Wave Function:

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

Substitute into Schrodinger Eq and take classical limit:

→ Surface Hopping

However, a rigorous classical limit has not been achieved !



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One Approach: Multi-Configuration Bohm Equations:

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

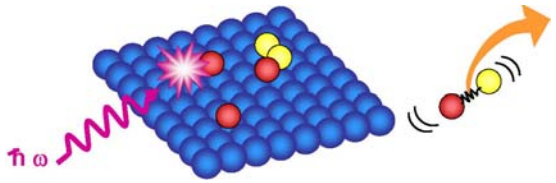
$$\Omega_j(\mathbf{R},t) = A_j(\mathbf{R},t)\exp\left[\tfrac{i}{\hbar}S_j(\mathbf{R},t)\right]$$

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

small ħ →

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

→ motion on potential energy surface *j*



X. Surface Hopping

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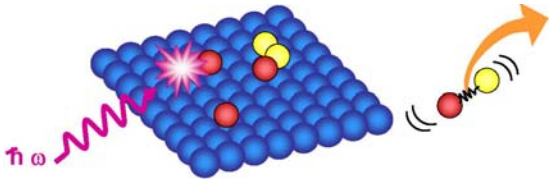
$$\dot{A}_n = \nabla_R A_n \bullet \dot{\mathbf{R}} - \frac{1}{2M} A_n \nabla_R^2 S_n - \sum_m A_m \langle \Phi_n \nabla_R \Phi_m \rangle \bullet \dot{\mathbf{R}} \exp\left[\frac{i}{\hbar}(S_m - S_n)\right]$$

Surface Hopping:

- Evaluate all quantities along a single path
- Sum over many stochastic paths



X. Surface Hopping

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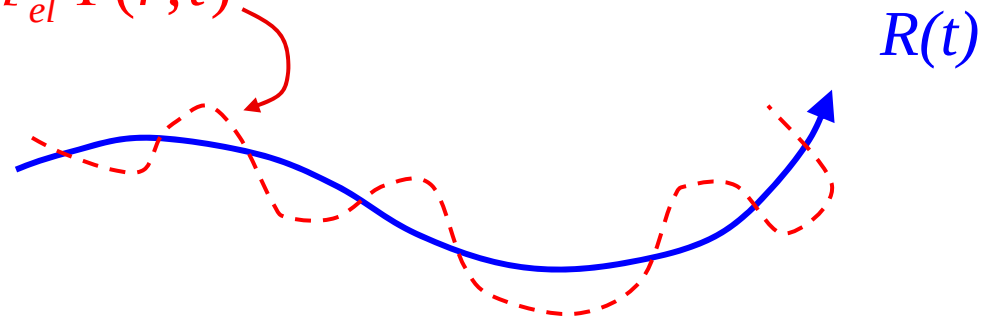
Multi-Configuration Theory: *Surface Hopping*

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

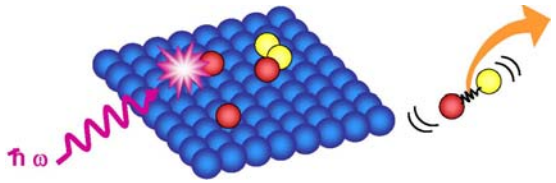


1] $M\ddot{R}(t) = -\nabla_R \mathcal{E}_k$, i.e., motion on single p.e.s.

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:



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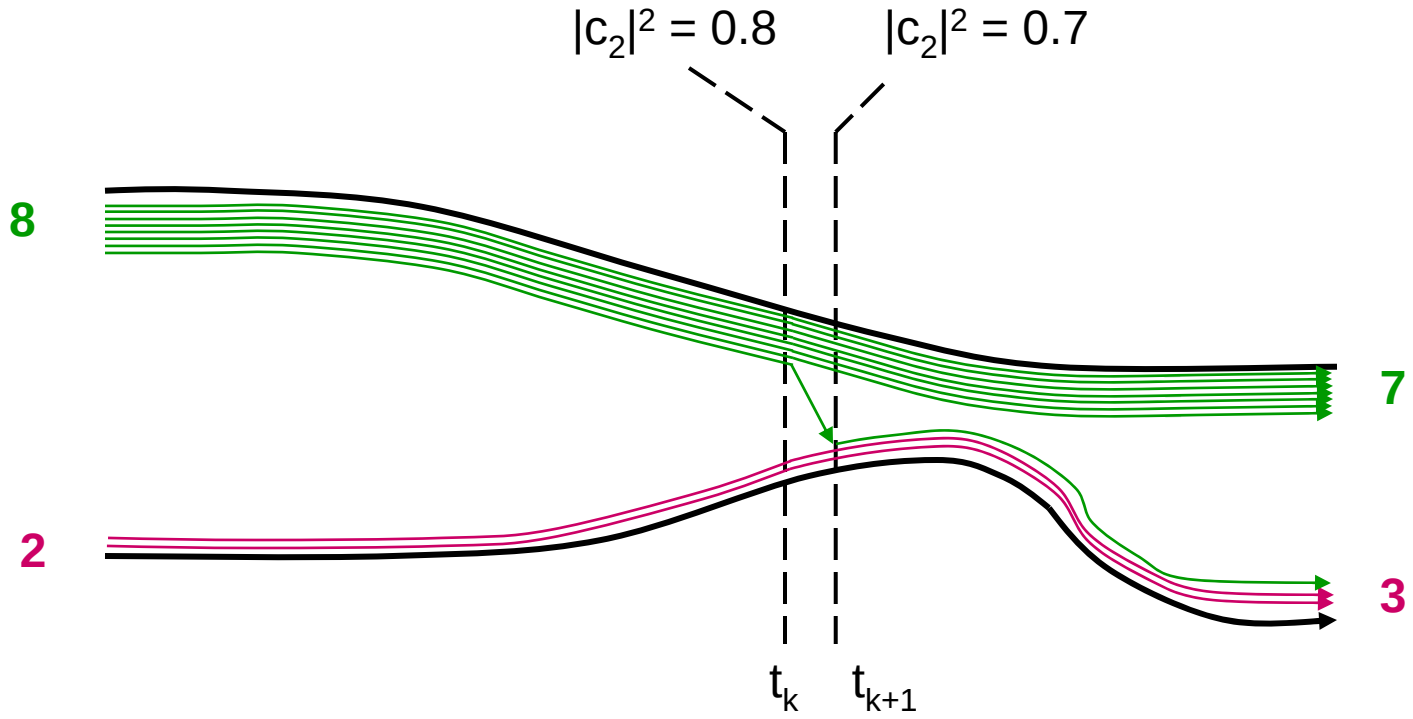
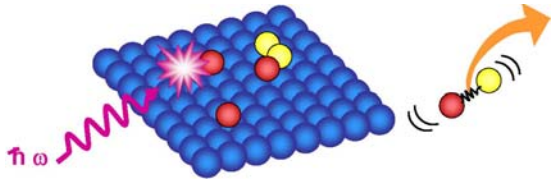


Stochastic *Fewest Switches* algorithm (2-state):

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



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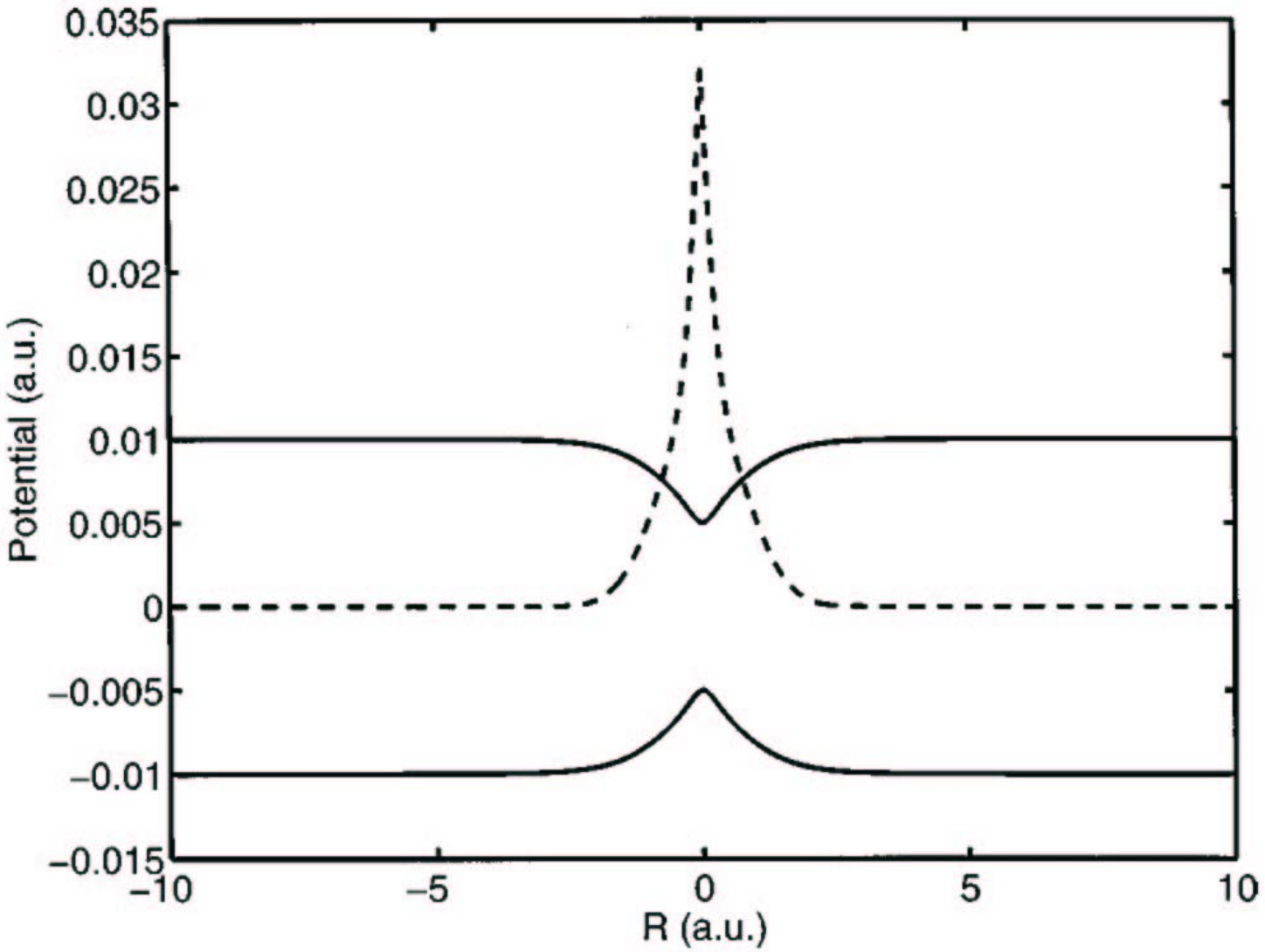

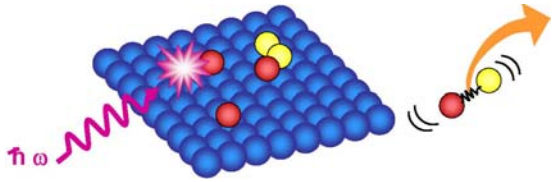

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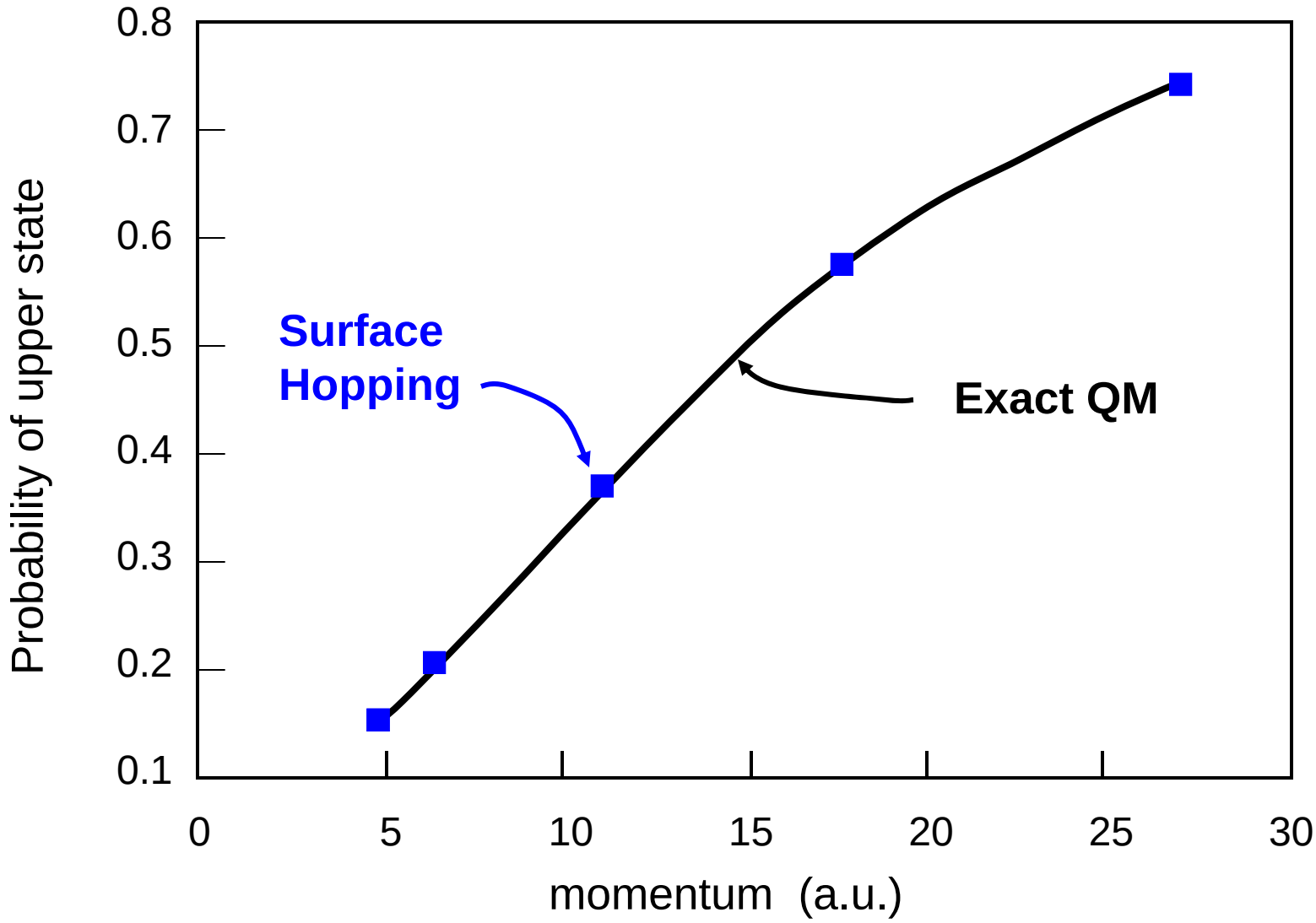

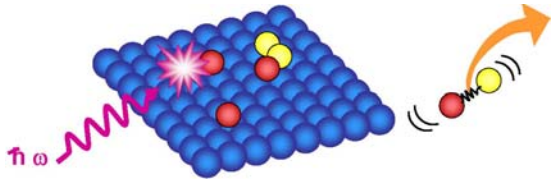

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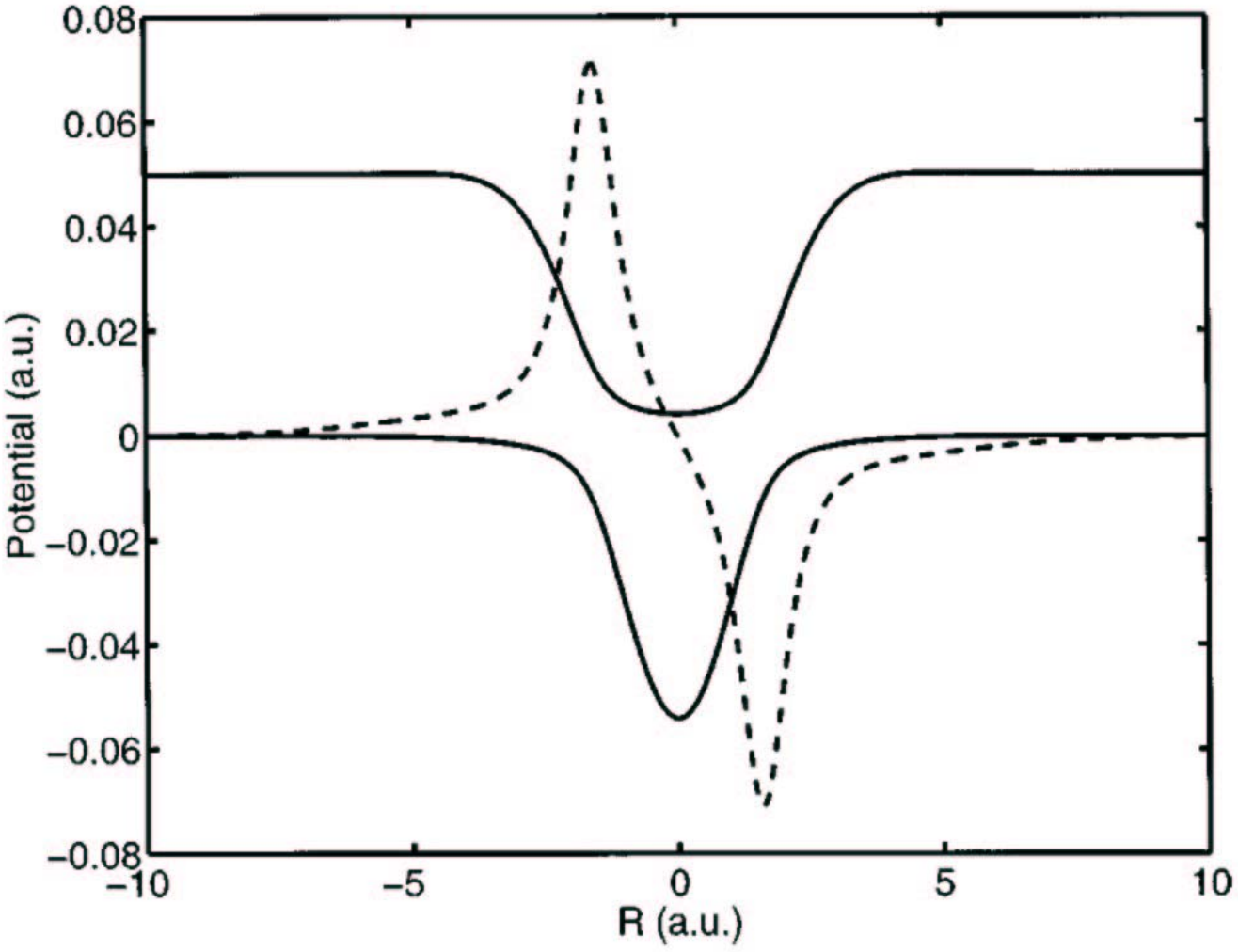

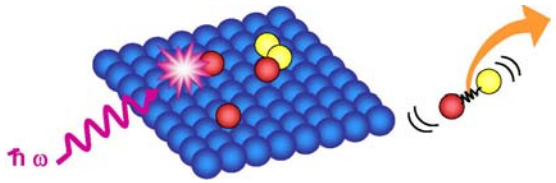

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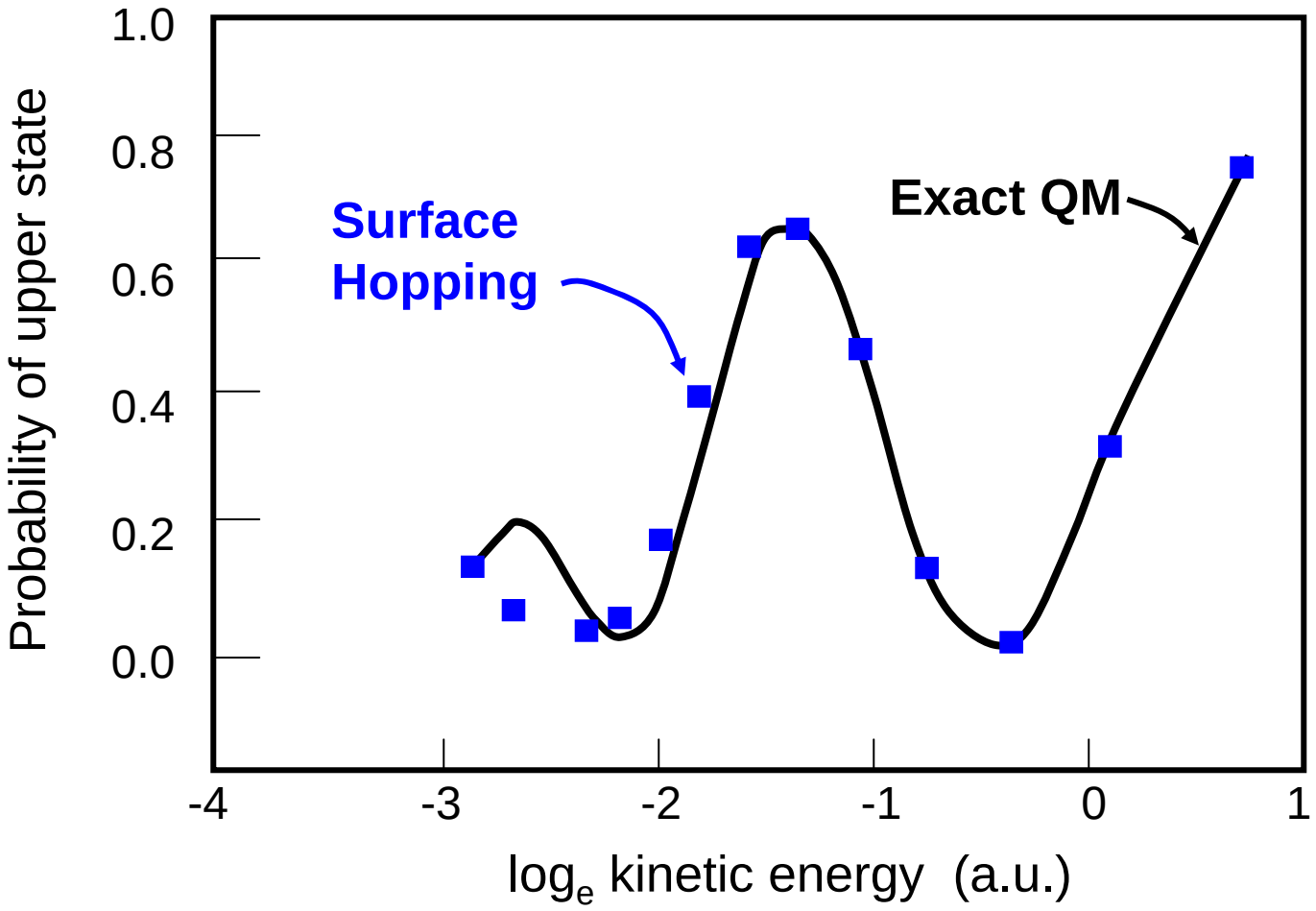

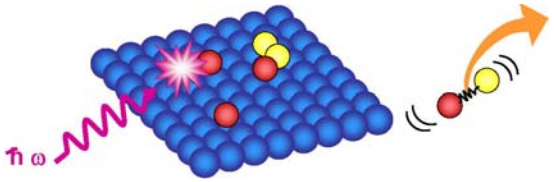

X. Surface Hopping

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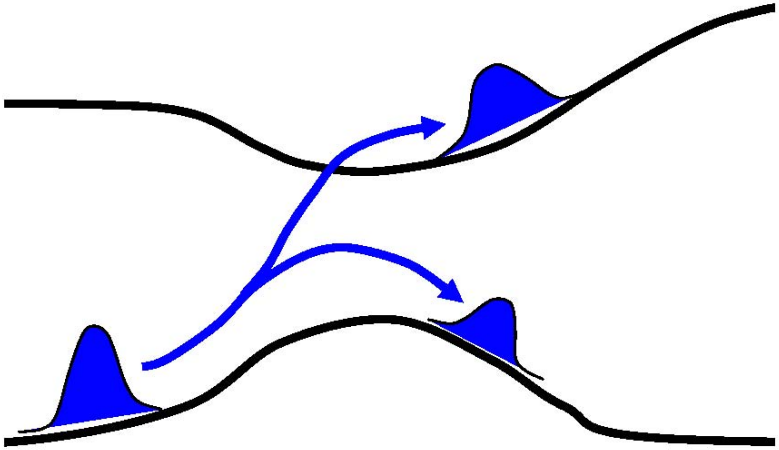
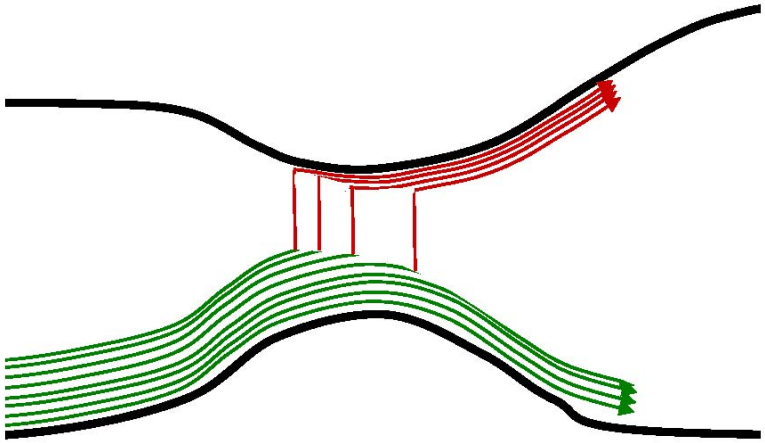
SHORTCOMINGS OF SURFACE HOPPING

1] Trajectories are independent

Trajectories should talk to each other

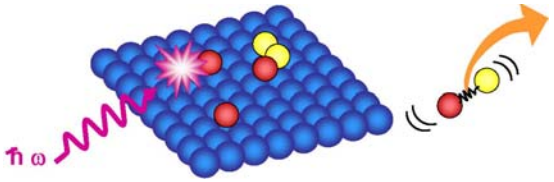


quantum wave packet



surface hopping

Fundamental approximation, but required to make practical



X. Surface Hopping

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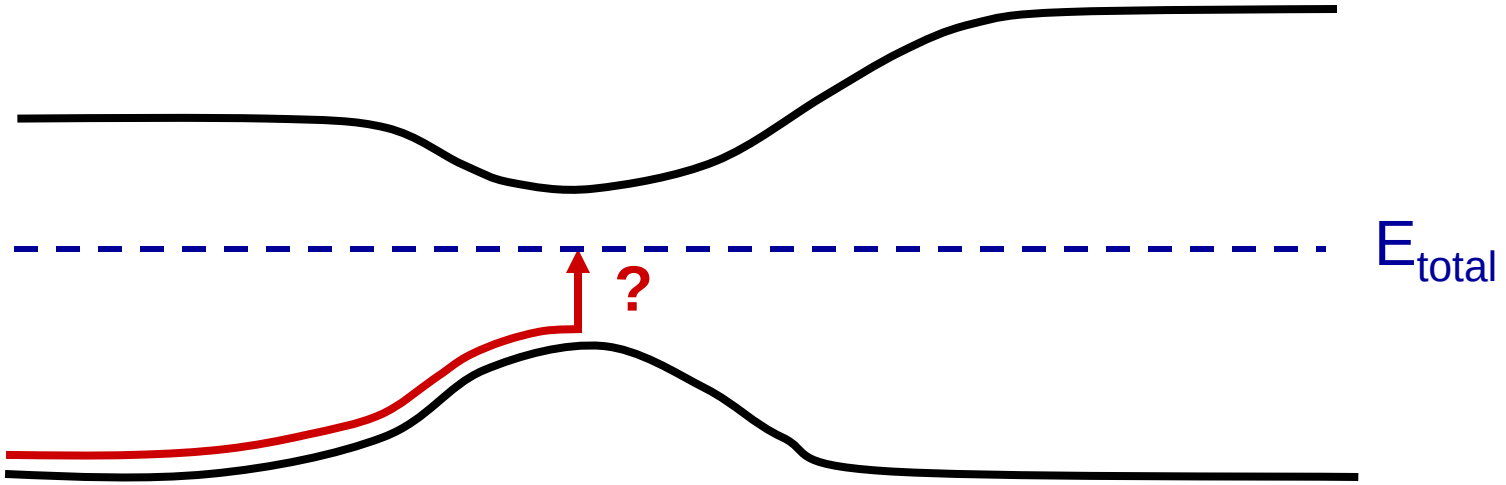
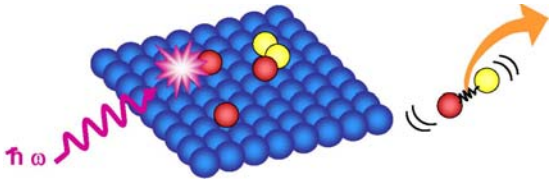
SHORTCOMINGS OF SURFACE HOPPING

2] Forbidden Hops (or *frustrated hops*)

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



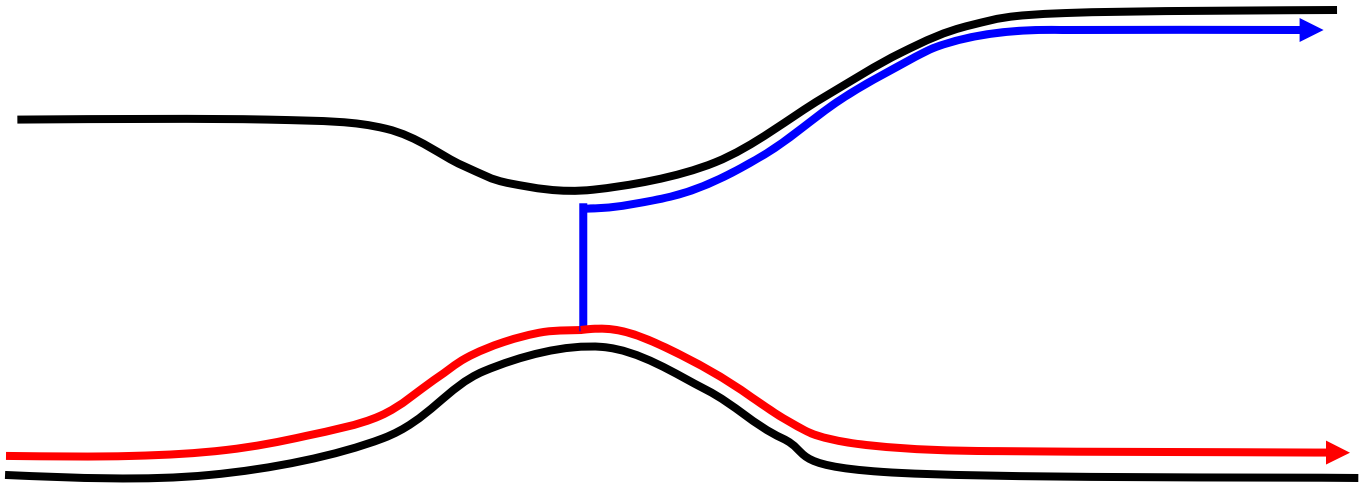
→ probability on state k ≠ $|c_k|^2$

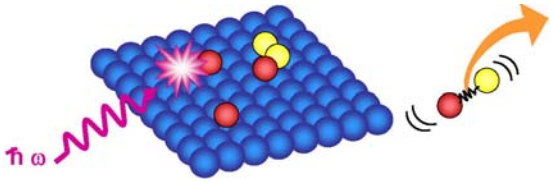


SHORTCOMINGS OF SURFACE HOPPING

3] Detailed Balance?

What are the populations of the quantum states at equilibrium?





X. Surface Hopping

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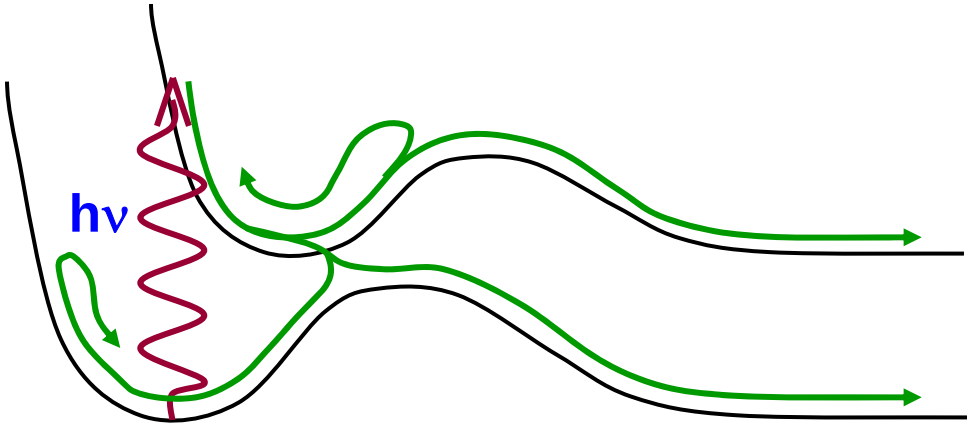
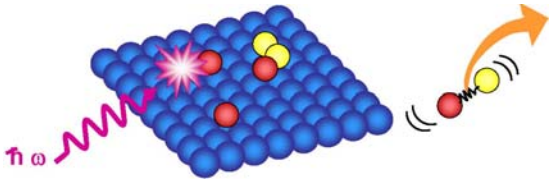
Detailed Balance: $\mathcal{N}_1 P_{1\to2} = \mathcal{N}_2 P_{2\to1} \rightarrow$ **Equilibrium**

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



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

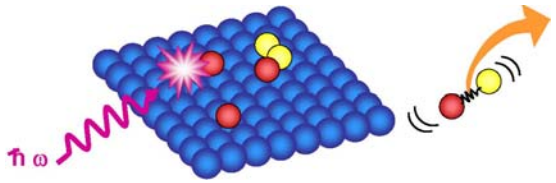


X. Surface Hopping

"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



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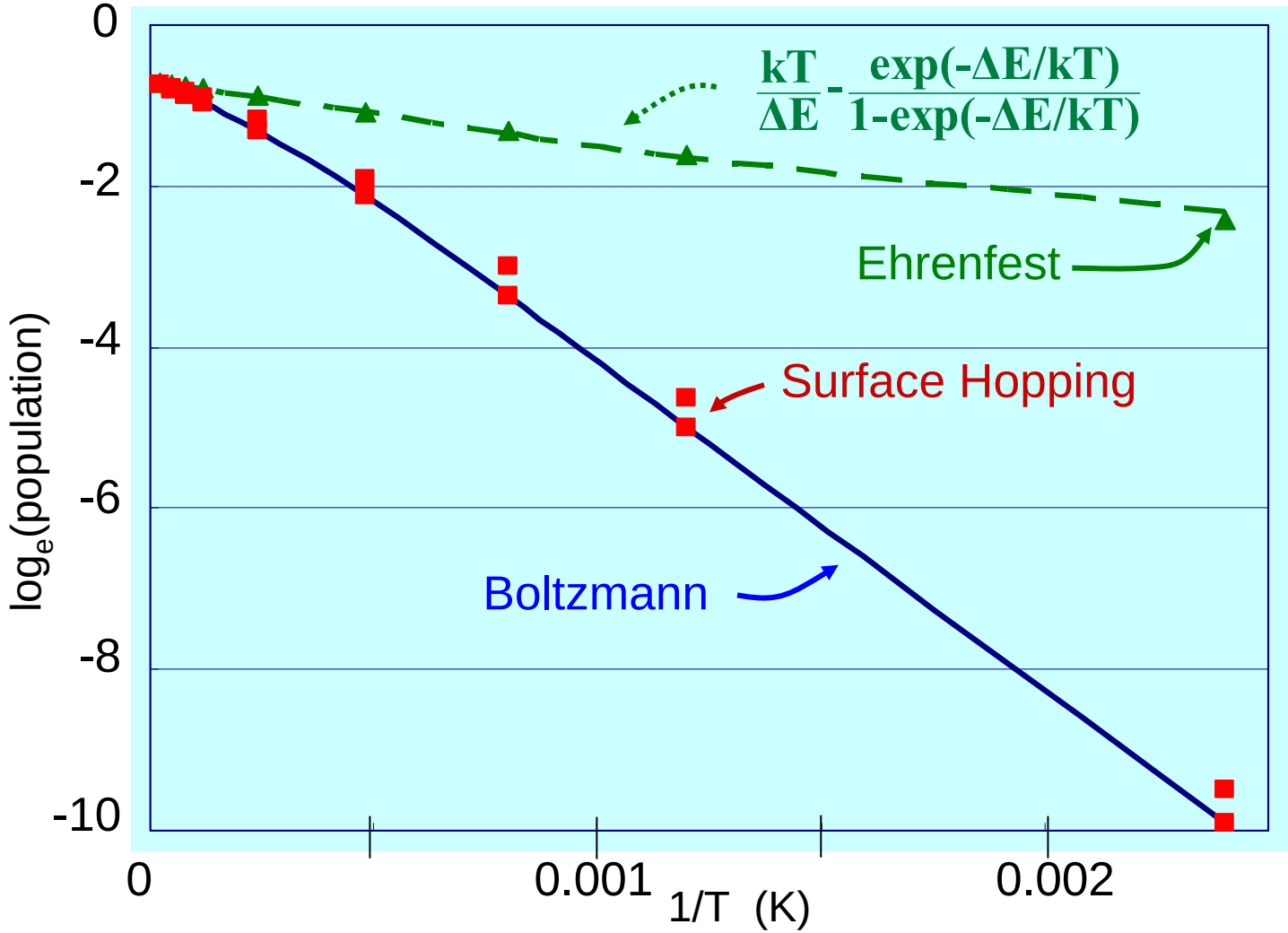
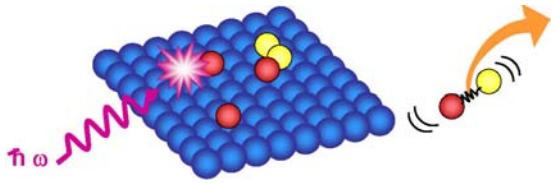
Excited State Population vs. Inverse Temperature



2-State System

ΔE = 34.6 kJ/mole



X. Surface Hopping

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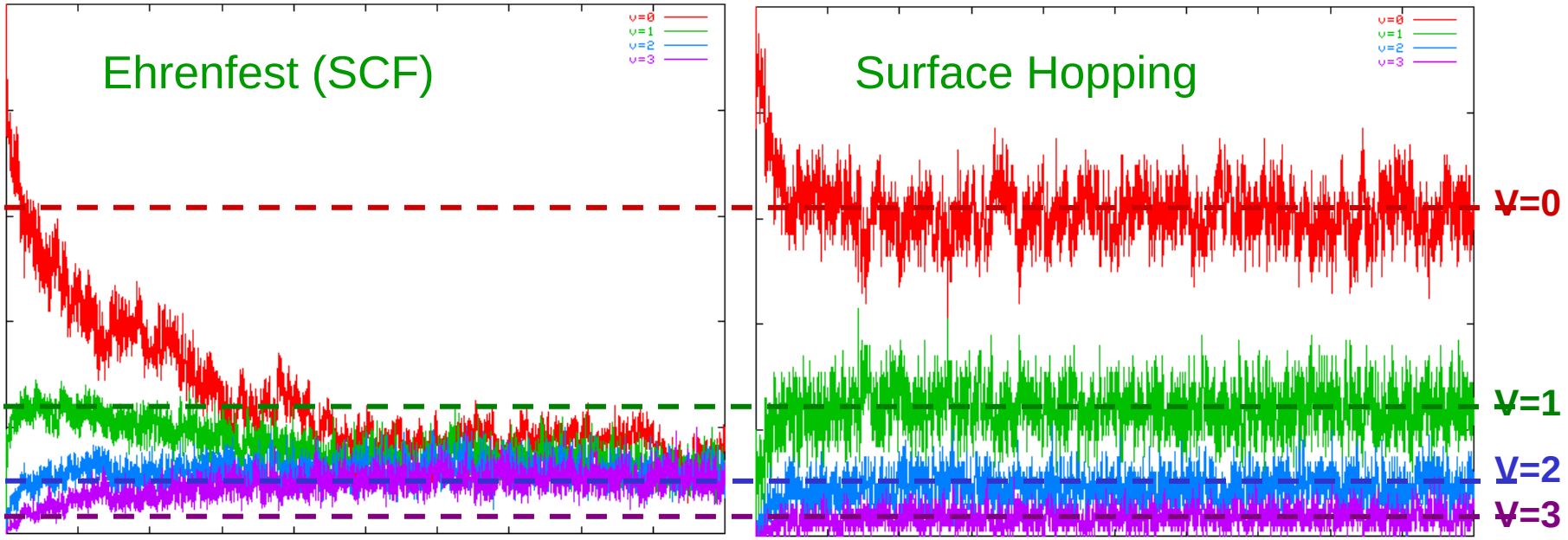
Many Quantum States

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

Random force and friction (5000 ºK)

classical (Morse)

quantum (Morse)



Priya Parandekar