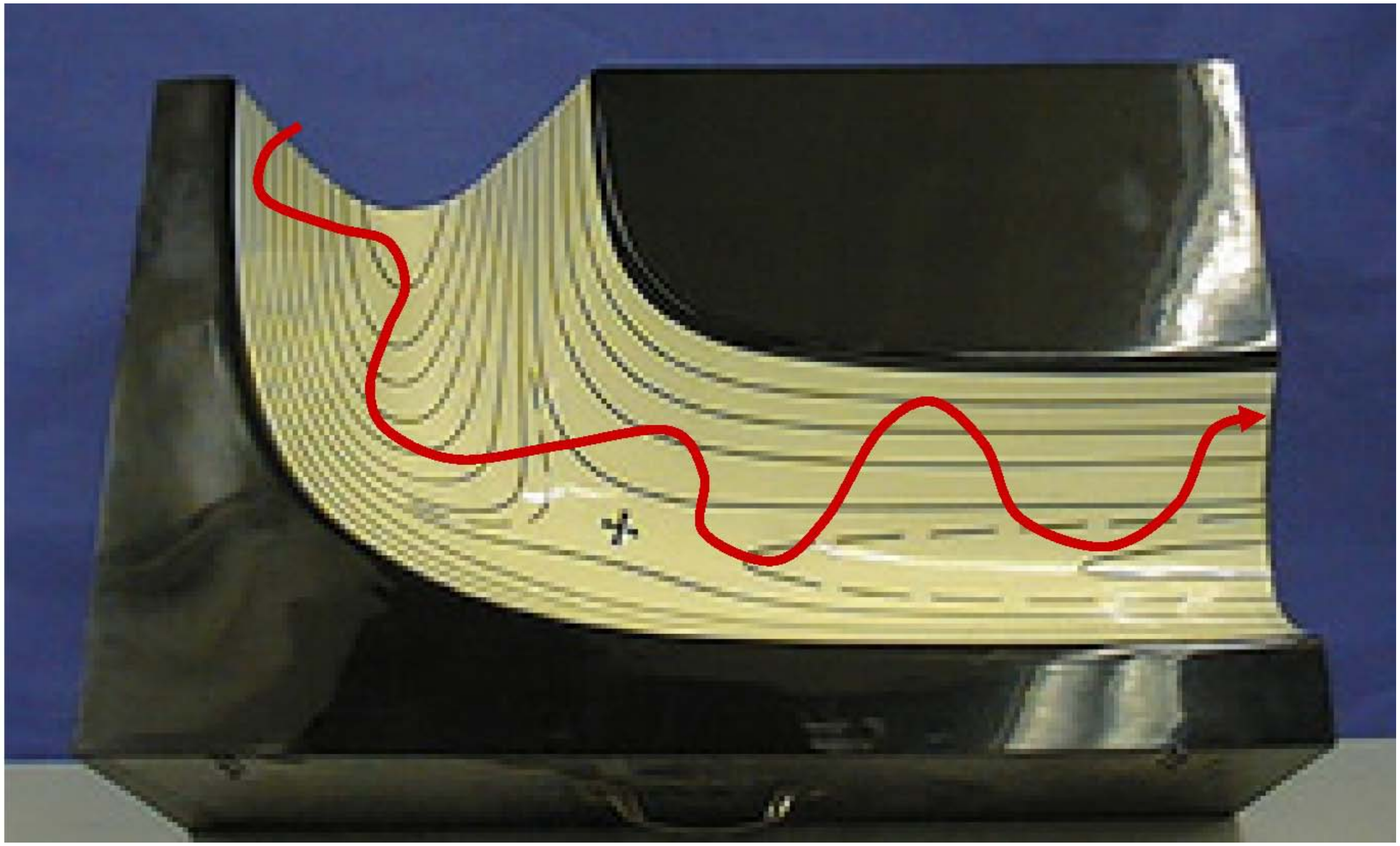
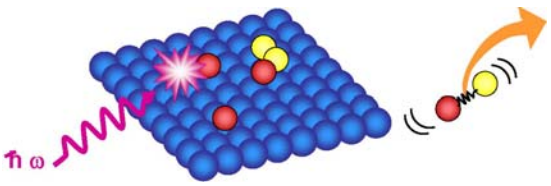
Chemical Dynamics

Telluride
July 2009
J. Tully





Time-dependent processes: $i\hbar \frac{\partial}{\partial t}\Psi(t) = \mathcal{H}\,\Psi(t)$

E. Schrödinger

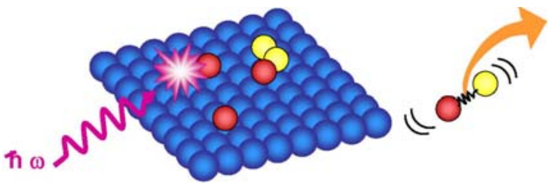
2 classes:

1. $\mathcal{H}$ depends on time
2. $\mathcal{H}$ independent of time

a. Initial state: let $\Psi(t_0) = \varphi_j$ where $\mathcal{H}\varphi_j = E_j\,\varphi_j$

$$i\hbar \frac{\partial}{\partial t}\Psi(t) = E_j\,\Psi(t) \longrightarrow \Psi(t) = \exp(-iE_j t/\hbar)\,\Psi(t_0)$$

$$\longrightarrow \left|\Psi(t)\right|^2 = \left|\Psi(t_0)\right|^2$$ time-independent



Time-dependent processes: $i\hbar \frac{\partial}{\partial t}\Psi(t) = \mathcal{H}\,\Psi(t)$

E. Schrödinger

2 classes:

1. $\mathcal{H}$ depends on time

→ 2. $\mathcal{H}$ independent of time

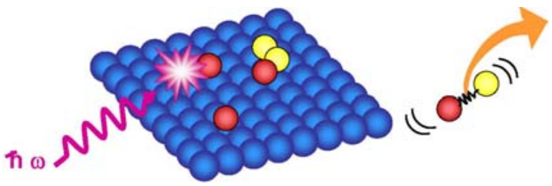
b. Initial state: let $\Psi(t_0) = \sum_j c_j \varphi_j$ where $\mathcal{H}\varphi_j = E_j\,\varphi_j$

$$\longrightarrow \Psi(t) = \sum_j c_j \exp(-iE_j t/\hbar)\,\varphi_j$$

$$\longrightarrow \left|\Psi(t)\right|^2 = \sum_j |c_j|^2\,|\varphi_j|^2 + \sum_{j\neq k} c_k^* c_j \exp\left[-i(E_j - E_k)t/\hbar\right]\varphi_k^*\varphi_j$$

time-dependent

<u>All Done!</u>



Chemical Dynamics

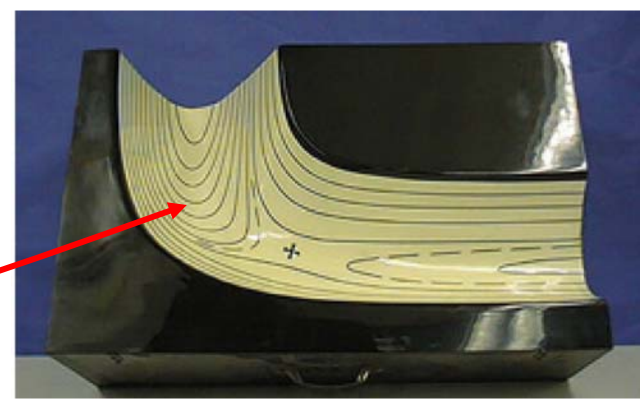
Objective: $$i\hbar \frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t) = \mathcal{H}(\mathbf{r},\mathbf{R})\Psi(\mathbf{r},\mathbf{R},t)$$

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

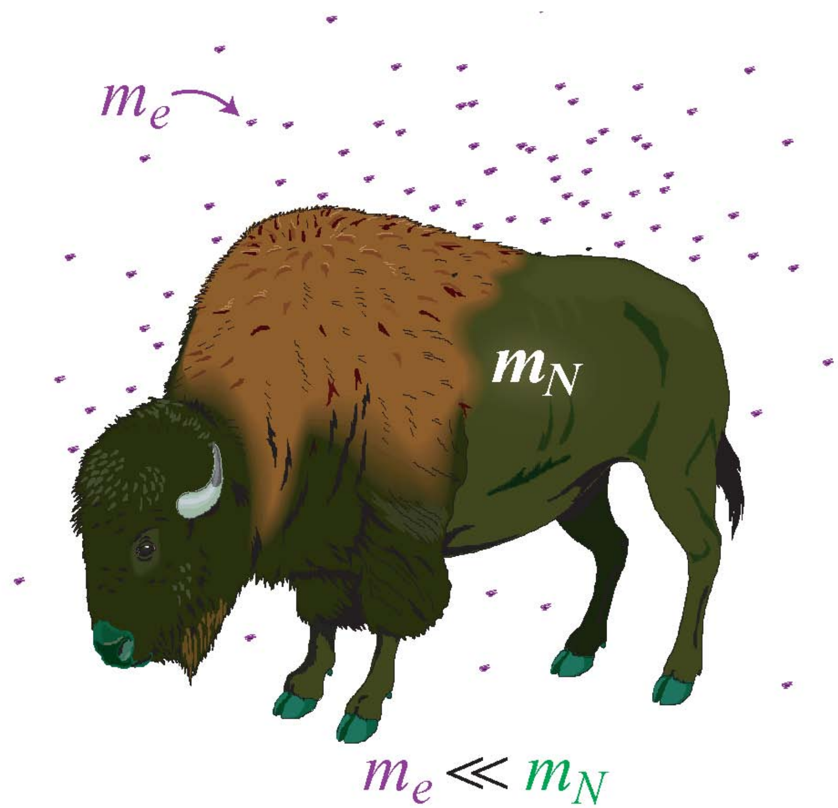
$$\mathcal{H} = -\sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla^2_{R_\alpha} - \sum_i \frac{\hbar^2}{2m_e}\nabla^2_r + V(\mathbf{r},\mathbf{R}) = -\sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla^2_{R_\alpha} + \mathcal{H}_{el}(\mathbf{r};\mathbf{R})$$

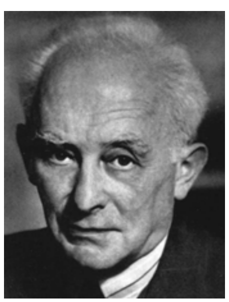
$$\mathcal{H}_{el}(\mathbf{r};\mathbf{R})\Phi_j(\mathbf{r};\mathbf{R}) = \mathcal{E}_j(\mathbf{R})\Phi_j(\mathbf{r};\mathbf{R})$$

Adiabatic (Born-Oppenheimer)
Potential Energy Surface



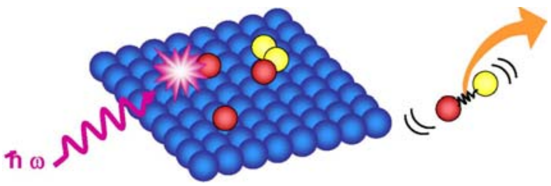
Born-Oppenheimer Approximation:





Max Born

J. Robert Oppenheimer



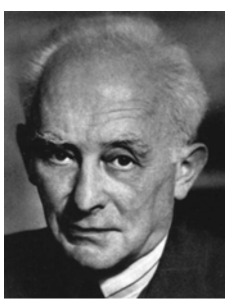
Born-Oppenheimer Approximation:

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

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

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

student problem: why is this not quite right?



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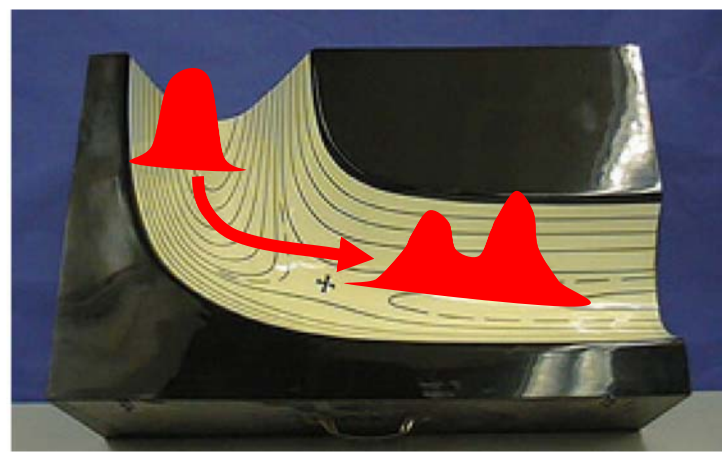

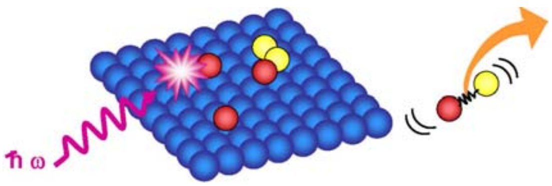

Chemical Dynamics

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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

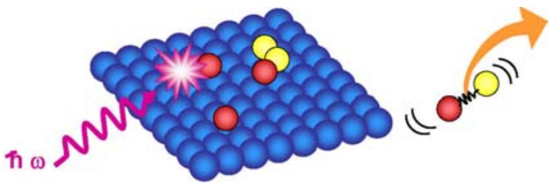
VIII. Beyond Born Oppenheimer

IX. Ehrenfest Dynamics

X. Surface Hopping

XI. Dynamics at Metal Surfaces

XII. Mixed Quantum-Classical Nuclear Dynamics



I. Quantum Dynamics

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

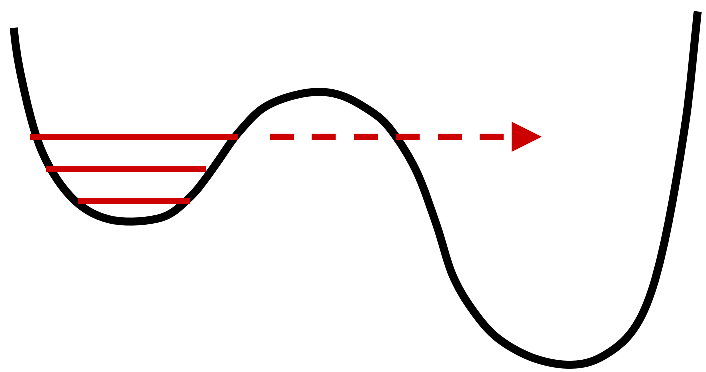
wavefunction for nuclear motion

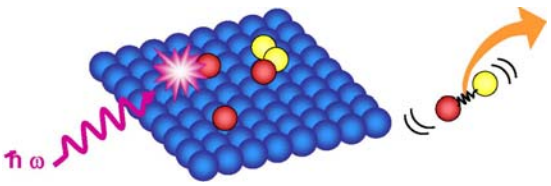
Born-Oppenheimer P.E.S

(or diabatic P. E. S.)

1. Zero-point energy
2. Quantized energy levels
3. Tunneling
4. Phase interference

   (coherence)





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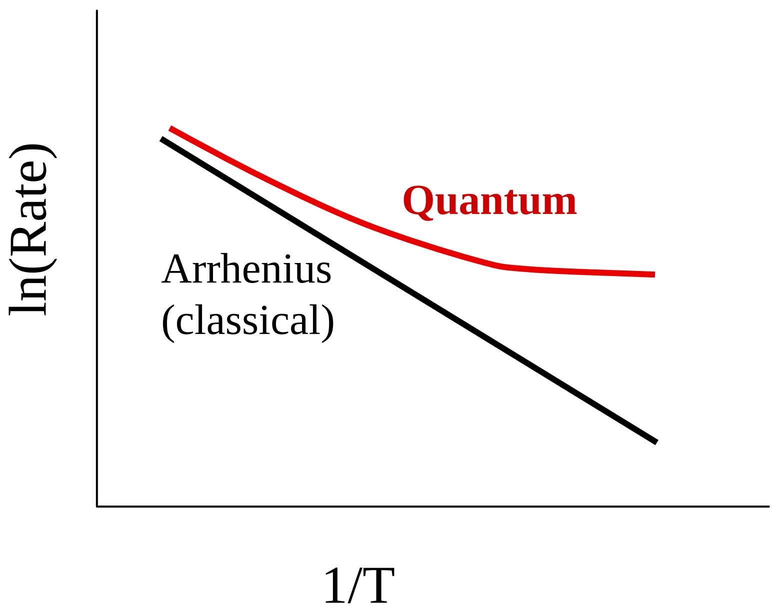
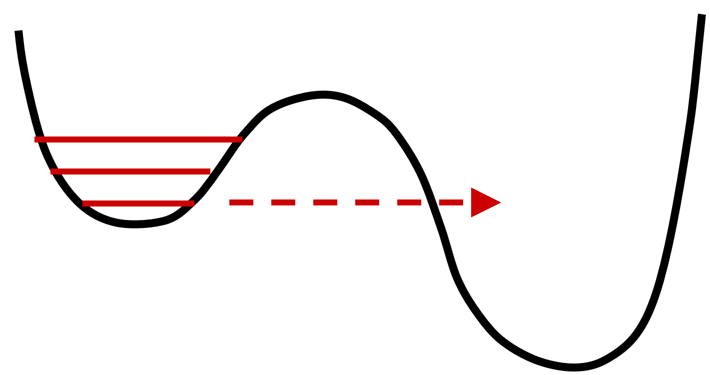
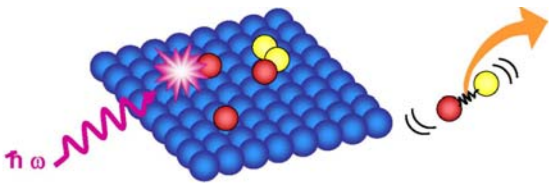
wavefunction for nuclear motion

Born-Oppenheimer P.E.S







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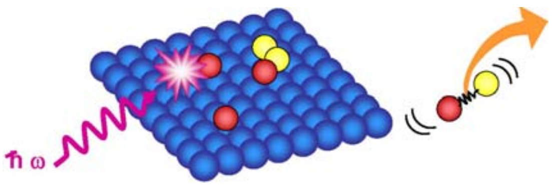
Wave packet methods: Initial wave function: Gaussian wave packet

$$\Omega(x,0) \;=\; \left(\frac{2}{\pi a^2}\right)^{1/4} \exp(ik_0 x)\,\exp[-(x-x_0)^2/a^2]$$

$$\hbar k_0 \;=\; p_0 \;=\; \text{initial avg momentum}$$

student problem: what is momentum distribution?



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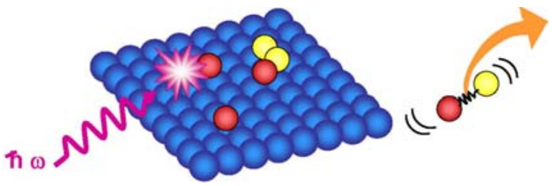
$\hbar k_0 = p_0 =$ initial avg momentum

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



I. Quantum Dynamics

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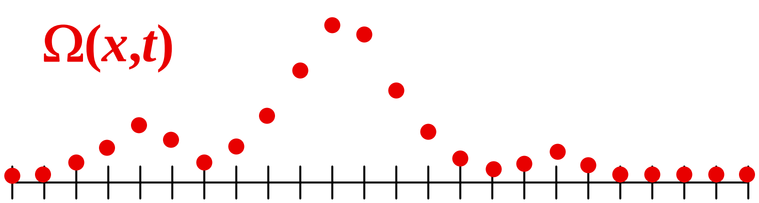
$$i\hbar \frac{\partial}{\partial t}\Omega(x,t) = \left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + \mathcal{E}(x) \right]\Omega(x,t)$$

Wave packet methods: Propagate wave function

$$\frac{i\hbar[\Omega(x,t+\delta)-\Omega(x,t)]}{\delta} \approx \left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + \mathcal{E}(x) \right]\Omega(x,t)$$

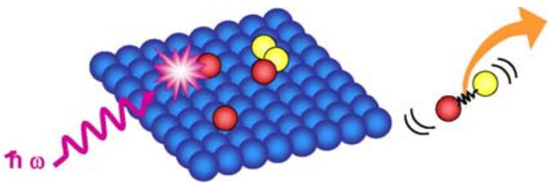
$$\longrightarrow \quad \Omega(x,t+\delta) = \Omega(x,t) - \frac{i\delta}{\hbar}\left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + \mathcal{E}(x) \right]\Omega(x,t)$$

crude!



$$\frac{d^2\Omega(x,t)}{dx^2} = \frac{\Omega(x+\Delta x,t)+\Omega(x-\Delta x,t)-2\Omega(x,t)}{(\Delta x)^2}$$

finite difference approximation ?



I. Quantum Dynamics

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$$i\hbar \frac{\partial}{\partial t}\Omega(x,t) \;=\; \left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + \mathcal{E}(x)\right]\Omega(x,t)$$

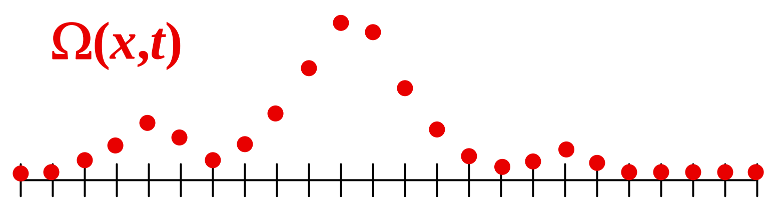
Wave packet methods: Propagate wave function: Fourier Transform method

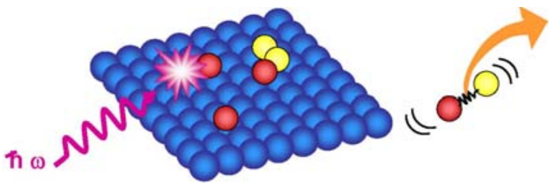
1. Compute F.T. $$\phi(p,t) = \frac{1}{\sqrt{2\pi}}\int \Omega(x,t)\, \mathrm{e}^{ipx/\hbar}\, dx$$

R. Kosloff

2. Inverse F.T. $$\frac{\hbar^2}{2M}\frac{d^2\Omega(x,t)}{dx^2} = \frac{1}{\sqrt{2\pi\hbar}}\int \frac{p^2}{2M}\phi(p,t)\, \mathrm{e}^{-ipx/\hbar}\, dp$$

student problem: derive Eq. 2





I. Quantum Dynamics

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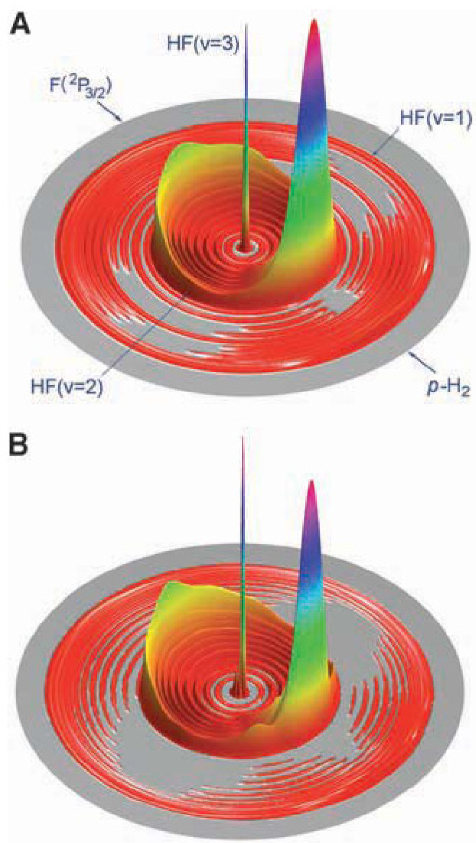
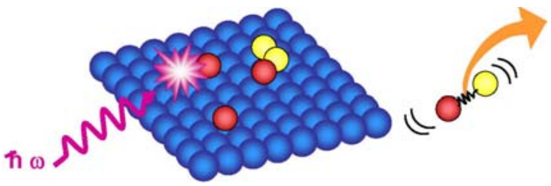
Experiment

Theory



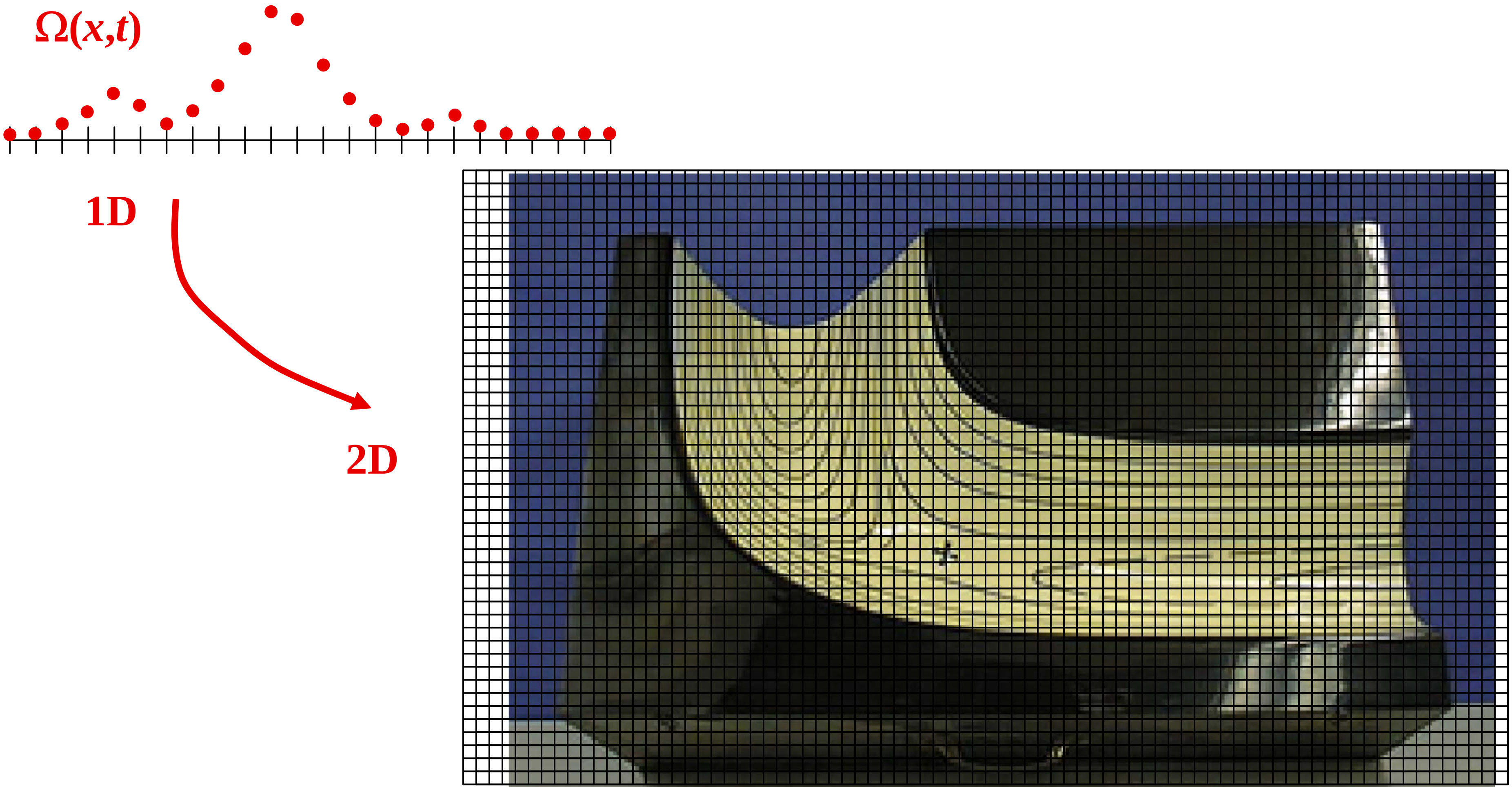
Angular and velocity distributions of the reaction $F + H_2 \rightarrow FH + H$

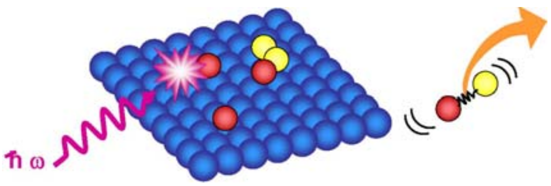
M. Qiu et al., *Science* **311**, 1440 (2006)



I. Quantum Dynamics

Problem: Scaling with Size is Prohibitive: $\mathbf{10^{3N-6}}$





Quantum Dynamics: Path Integrals

I. The Propagator

($\mathcal{H}$ indep of t)

$$i\hbar \frac{\partial \Psi}{\partial t} = \mathcal{H}\,\Psi \quad \Longleftrightarrow \quad \Psi(t) = \exp\left[-\frac{it}{\hbar}\mathcal{H}\right]\Psi(t=0)$$

Rewrite using *position representation*:

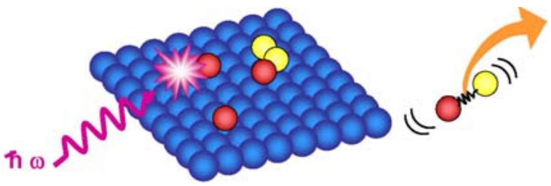
define: $|r_0> = \delta(r - r_0) \longrightarrow \Psi(r_0) = <r_0|\Psi(r)>$

and $\int dr_0 |r_0><r_0| = 1$

$$\Psi(x,t) = <x|e^{-\frac{it}{\hbar}\mathcal{H}}|\Psi(t=0)> = \int dy <x|e^{-\frac{it}{\hbar}\mathcal{H}}|y><y|\Psi(t=0)>$$

$$= \int dy \underbrace{<x|e^{-\frac{it}{\hbar}\mathcal{H}}|y>}_{\text{the propagator}} \Psi(y, t=0)$$

The contribution to the wave function at *x* and *t* from the wavefunction at *y* and *t*=0.



Quantum Dynamics: Path Integrals

II. Evaluating the Propagator $< x \,|\, e^{-\frac{it}{\hbar}\mathcal{H}} \,|\, y >$

$$e^A = [e^{A/N}]^N \quad \longrightarrow \quad \exp\left[-\frac{it}{\hbar}\mathcal{H}\right] = \prod_{k=1}^{N} \exp\left[-\frac{i\mathcal{H}}{\hbar}\Delta t\right], \text{ with } \Delta t = t/N$$

Aside: functions of operators? functions of matrices?

$$e^A \approx 1 + A + \frac{1}{2!}A^2 + \frac{1}{3!}A^3 + \cdots$$

$$e^{A+B} \approx 1 + A + B + \frac{1}{2!}(A^2 + AB + BA + B^2) + \frac{1}{3!}(A^3 + A^2B + ABA + \cdots$$

Student Problem: evaluate $\sin\begin{pmatrix} \pi/4 & -\pi/4 \\ -\pi/4 & \pi/4 \end{pmatrix}$

II. Evaluating the Propagator $< x | e^{-\frac{it}{\hbar}\mathcal{H}} | y >$

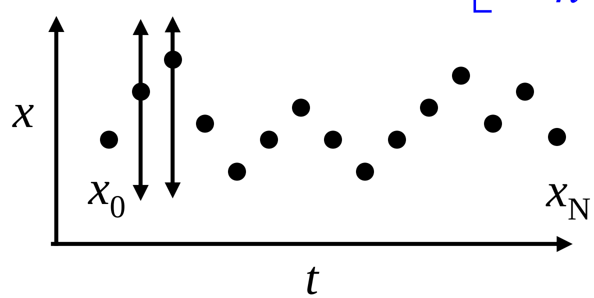
$$e^A = [e^{A/N}]^N \quad \longrightarrow \quad \exp\left[-\frac{it}{\hbar}\mathcal{H}\right] = \prod_{k=1}^{N} \exp\left[-\frac{i\mathcal{H}}{\hbar}\Delta t\right], \text{ with } \Delta t = t/N$$

$$\exp\left[-\frac{i\mathcal{H}}{\hbar}(t_{k+1}-t_k)\right]\exp\left[-\frac{i\mathcal{H}}{\hbar}(t_k-t_{k-1})\right]$$

$$= \int dx_k \exp\left[-\frac{i\mathcal{H}}{\hbar}(t_{k+1}-t_k)\right] | x_k >< x_k | \exp\left[-\frac{i\mathcal{H}}{\hbar}(t_k-t_{k-1})\right]$$

$$\longrightarrow < x_N | \exp\left[-\frac{i\mathcal{H}}{\hbar}t\right] | x_0 > \; = \; \int dx_1 \ldots \int dx_{N-1} \prod_{k=1}^{N} < x_k | \exp\left[-\frac{i\mathcal{H}}{\hbar}\Delta t\right] | x_{k-1} >$$

already looks like a path integral:



Quantum Dynamics: Path Integrals

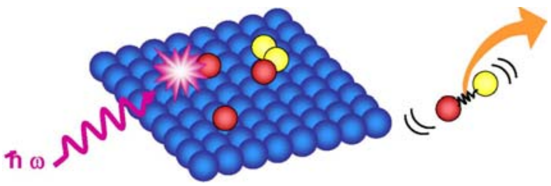
Split Operators: Trotter's formula

$$\mathcal{H}(x,p) = \frac{p^2}{2m} + V(x) = T + V$$

(T and V do not commute)

$$\exp\left[-\frac{i\mathcal{H}\Delta t}{\hbar}\right] \approx \exp\left[-\frac{iV\Delta t}{2\hbar}\right]\exp\left[-\frac{iT\Delta t}{\hbar}\right]\exp\left[-\frac{iV\Delta t}{2\hbar}\right]$$

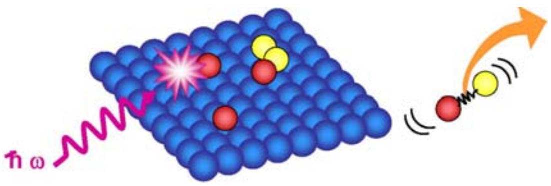
$$\longrightarrow \quad < x_k \,|\, e^{-\frac{i\mathcal{H}\Delta t}{\hbar}} \,|\, x_{k-1} > \approx < x_k \,|\, e^{-\frac{iT\Delta t}{\hbar}} \,|\, x_{k-1} > \exp\left[-\frac{i\Delta t}{2\hbar}(V_k + V_{k-1})\right]$$



Evaluate *T*-integral analytically:

$$< x_k | = \frac{1}{\sqrt{2\pi\hbar}} \int dp < p | \exp(-\frac{i}{\hbar} p x_k) \quad \text{and} \quad | x_{k-1} > = \frac{1}{\sqrt{2\pi\hbar}} \int dp' \exp(-\frac{i}{\hbar} p' x_{k-1}) | p' >$$

$$\longrightarrow \quad < x_k | e^{-\frac{iT\Delta t}{\hbar}} | x_{k-1} > = \sqrt{\frac{m}{2\pi i\hbar\Delta t}} \exp\left[\frac{i}{\hbar} \frac{m}{2\Delta t} (x_k - x_{k-1})^2 \right]$$



Quantum Dynamics: Path Integrals

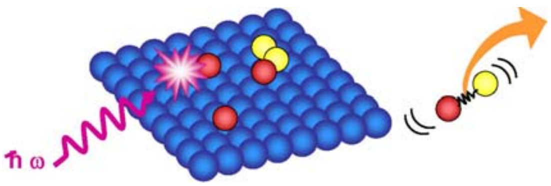
Put pieces back together:

$$< x_N \,|\, e^{-\frac{i\mathcal{H}t}{\hbar}} \,|\, x_0 > \approx C \int dx_1 \ldots \int dx_{N-1} \exp\left[\frac{i}{\hbar} \sum_{k=1}^{N} \left\{ \frac{mN}{2t}(x_k - x_{k-1})^2 - \frac{t}{2N}(V_k - V_{k-1}) \right\} \right]$$

The *Classical Action S* is the integral of the Lagrangian: $S \;=\; \int \mathcal{L}\, dt \;=\; \int (T - V)\, dt$

$$S \approx \sum_{k=1}^{N} \Delta t \left[\frac{m}{2\Delta t^2}(x_k - x_{k-1})^2 - V_k \right] = \sum_{k=1}^{N} \left[\frac{mN}{2t}(x_k - x_{k-1})^2 - \frac{t}{N} V_k \right]$$

remember Rig’s discussion of the classical action



Put pieces back together:

$$< x_N | e^{-\frac{i\mathcal{H}t}{\hbar}} | x_0 > \approx C\int dx_1 \ldots \int dx_{N-1} \exp\left[\frac{i}{\hbar}\sum_{k=1}^{N}\left\{\frac{mN}{2t}(x_k - x_{k-1})^2 - \frac{t}{2N}(V_k - V_{k-1})\right\}\right]$$

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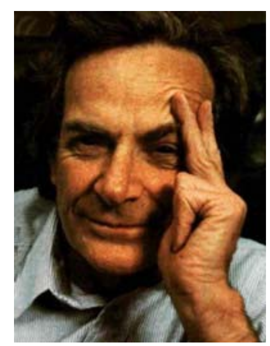
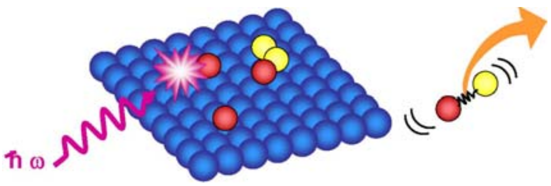
$$\Downarrow$$

Feynman Path Integral:

$$< x_N | e^{-\frac{i\mathcal{H}t}{\hbar}} | x_0 > \approx C\int dx_1 \ldots \int dx_{N-1} \exp\left[\frac{i}{\hbar} S(x_0, x_1, \ldots x_N)\right]$$



Richard Feynman



Quantum Dynamics: Path Integrals

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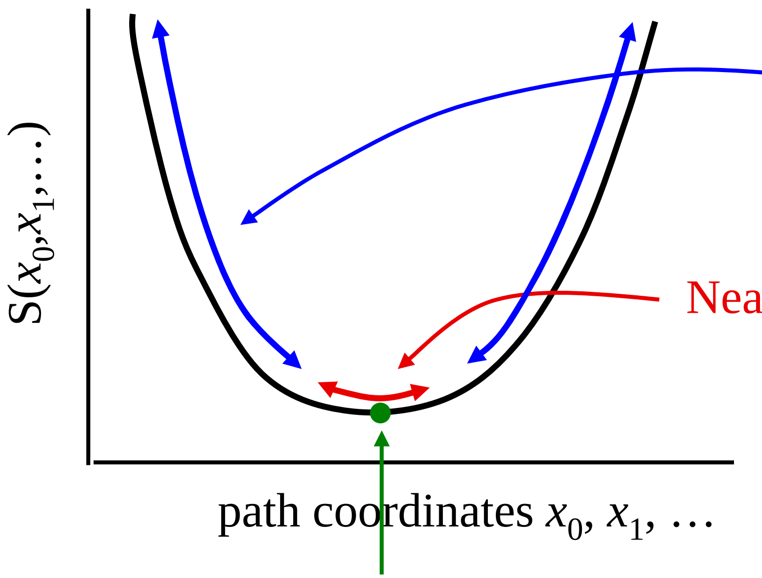
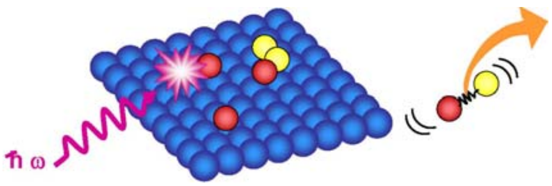


Far from classical path:
rapidly oscillating phases cancel

Near classical path: phases do not cancel

least action = stationary phase = classical path

Nancy Makri



Aside: Quantum Statistical Mechanics:

Canonical Partition Function: $Q = \sum_{\text{all states } n} e^{-E_n/kT} = \sum_n e^{-\beta E_n}$

Eigenstate representation: $< n | e^{-\beta E_n} | n > = < n | e^{-\beta \mathcal{H}} | n >$

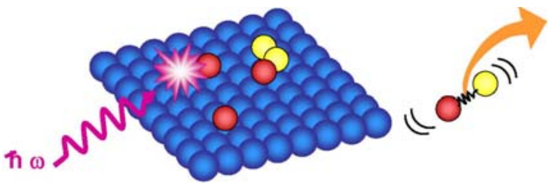
$\longrightarrow \quad Q = \sum_n < n | e^{-\beta \mathcal{H}} | n > = \mathrm{Tr}\left[e^{-\beta \mathcal{H}} \right]$ Valid for any representation

In particular, in position representation: $Q = \int dx < x | e^{-\beta \mathcal{H}} | x >$

Compare to path integral evaluation of propagator: $< x | e^{-i\mathcal{H}t/\hbar} | y >$

Set $t = -i\beta\hbar$ and $y = x$ (closed loop) $\longrightarrow \; < x | e^{-i\mathcal{H}t/\hbar} | x > = < x | e^{-\beta\mathcal{H}} | x >$

$\longrightarrow$ Evaluate Q via path integral in imaginary time



Aside: Quantum Statistical Mechanics:

$$< x_N \,|\, e^{-\frac{i\mathcal{H}t}{\hbar}} \,|\, x_0 > \approx C \int dx_1 \ldots \int dx_{N-1} \exp\left[\frac{i}{\hbar} S(x_0, x_1, \ldots x_N)\right]$$

where $$S = \sum_{k=1}^{N} \left[\frac{mN}{2t}(x_k - x_{k-1})^2 - \frac{t}{N} V_k\right]$$

now want:

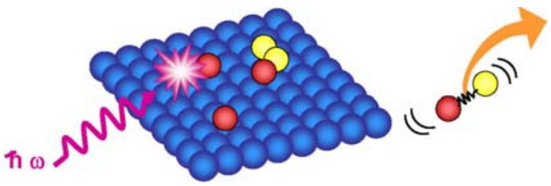
$$< x \,|\, e^{-\beta\mathcal{H}} \,|\, x > \approx C \int dx_1 \ldots \int dx_{N-1} \exp\left[\frac{i}{\hbar} S\right]$$

where path is specified by x, x_1, $\ldots x_{N-1}$, x

$$S(t = -i\beta\hbar) = i \sum_{k=1}^{N} \left[\frac{mN}{2\beta\hbar}(x_k - x_{k-1})^2 + \frac{\beta\hbar}{N} V_k\right] = i\, S_R$$

where S_R is real

Necklace of Classical Beads



Aside: Quantum Statistical Mechanics:

Necklace of Classical Beads

$$< x \,|\, e^{-\beta\mathcal{H}} \,|\, x > \approx C \int dx_1 \ldots \int dx_{N-1} \exp\left[\frac{i}{\hbar} S\right]$$

where path is specified by x, x_1, …x_{N-1}, x

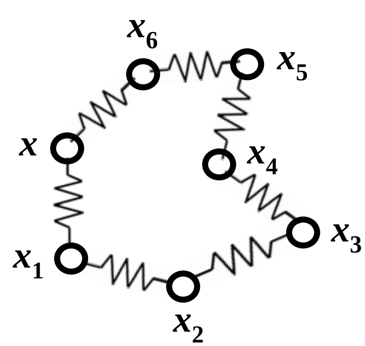
$$S(t = -i\beta\hbar) = i \sum_{k=1}^{N} \left[\frac{mN}{2\beta\hbar}(x_k - x_{k-1})^2 + \frac{\beta\hbar}{N} V_k \right] = i\, S_R$$

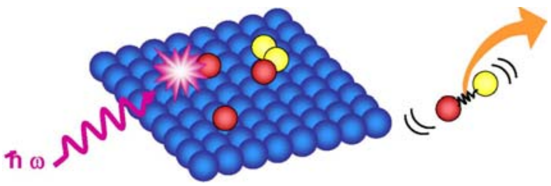
where S_R is real

$$\longrightarrow \quad Q = C \int dx \oint_{\text{all loop paths}} \exp\left[-\frac{S_R(\text{path})}{\hbar} \right]$$

decaying: no phase cancellation problems

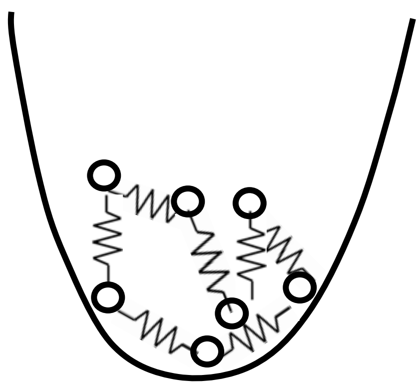
potential energy function for a classical mechanical "ring polymer"



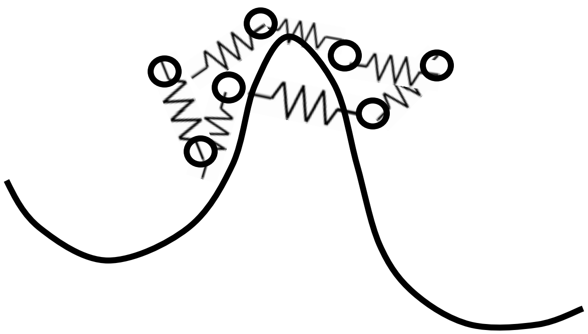


Aside: Quantum Statistical Mechanics:

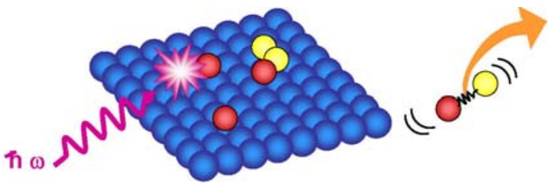
How does a purely classical mechanical formalism introduce quantum effects like zero-point energy and tunneling?



zero-point energy

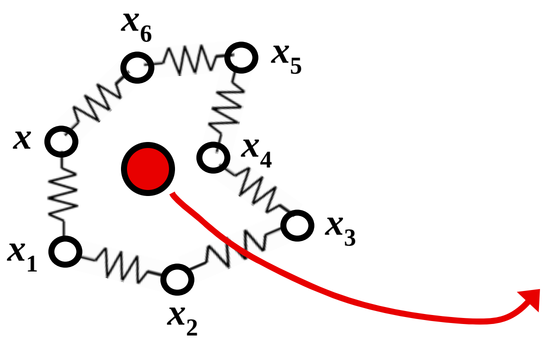


tunneling

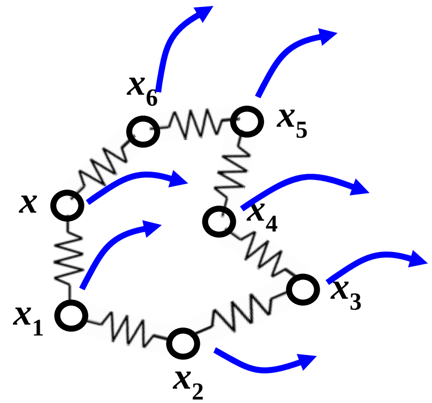


Quantum Dynamics: Path Integrals

***CMD*: Centroid Variable Molecular Dynamics**



***RPMD*: Ring Polymer Molecular Dynamics**

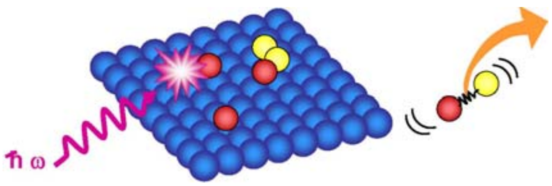


Greg Voth

solves scaling problem

but: short times only

David Manolopoulos



Chemical Dynamics

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

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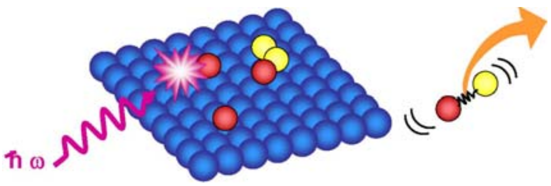
X. Surface Hopping

XI. Dynamics at Metal Surfaces

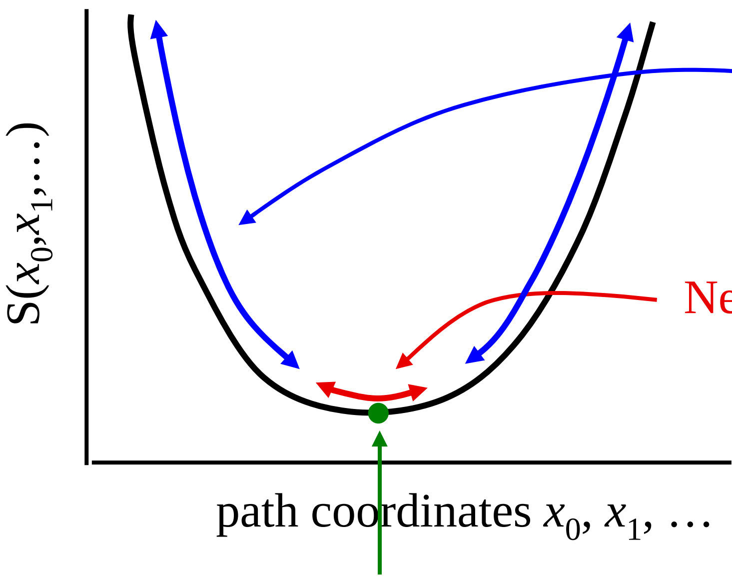
XII. Mixed Quantum-Classical Nuclear Dynamics



II. Semiclassical Dynamics

Semiclassical Path Integral Approach:

$$< x_N \,|\, e^{-\frac{i\mathcal{H}t}{\hbar}} \,|\, x_0 > \approx C\int dx_1 \ldots \int dx_{N-1} \exp\left[\frac{i}{\hbar} S(x_0, x_1, \ldots x_N)\right]$$

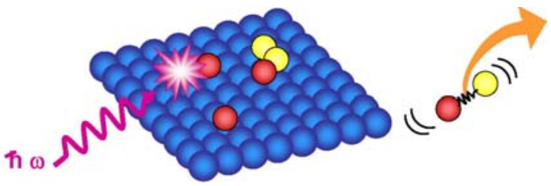


Far from classical path:
rapidly oscillating phases cancel

Near classical path: phases do not cancel

least action = stationary phase = classical path

Bill Miller



II. Semiclassical Dynamics

Frozen Gaussian:

$$\Omega(x,0) \;=\; \left(\frac{2}{\pi \mathbf{a}^2}\right)^{1/4} \exp(ik_0 x)\,\exp[-(x-x_0)^2/\mathbf{a}^2]$$

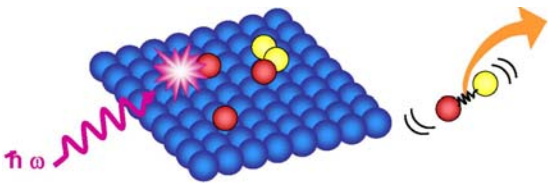
fixed

⟶ Center of Gaussian, x_0, follows classical trajectory

Advantages:

1. Simple
2. Includes delocalization of wavepacket
3. Includes quantum interference effects (add amplitudes, not probabilities)

Rick Heller



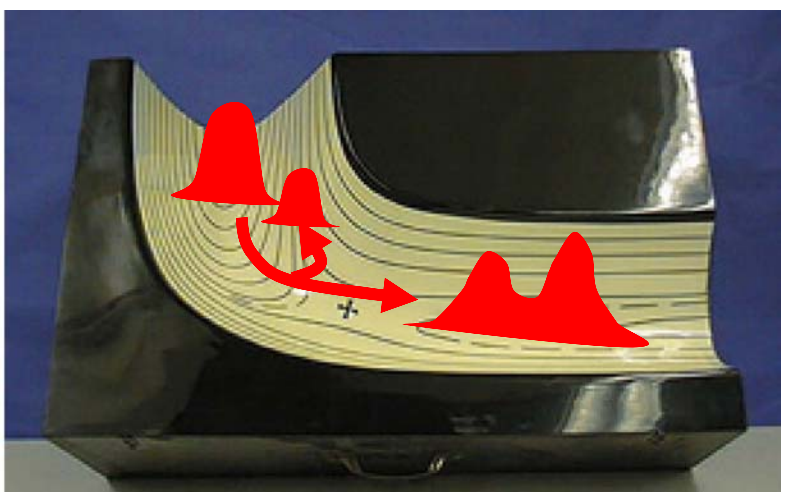
II. Semiclassical Dynamics

Frozen Gaussian (E. J. Heller)

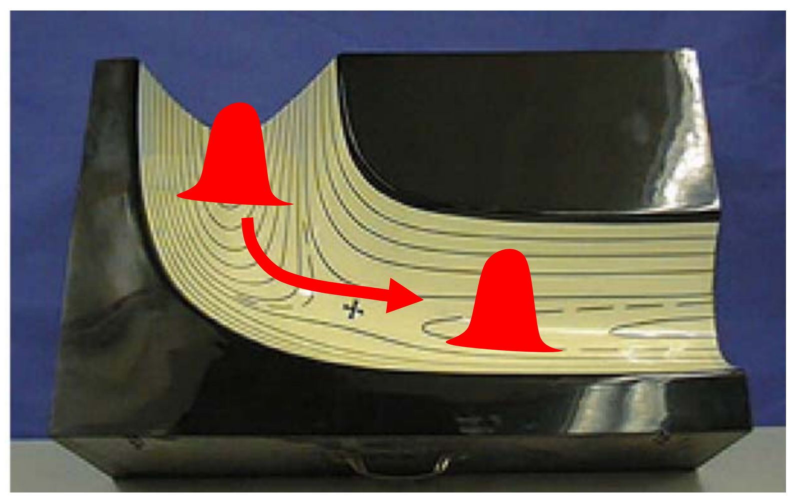
$$\Omega(x,0) = \left(\frac{2}{\pi \mathbf{a}^2}\right)^{1/4} \exp(ik_0 x)\exp[-(x-x_0)^2/\mathbf{a}^2]$$

→ Center of Gaussian, x_0, follows classical trajectory

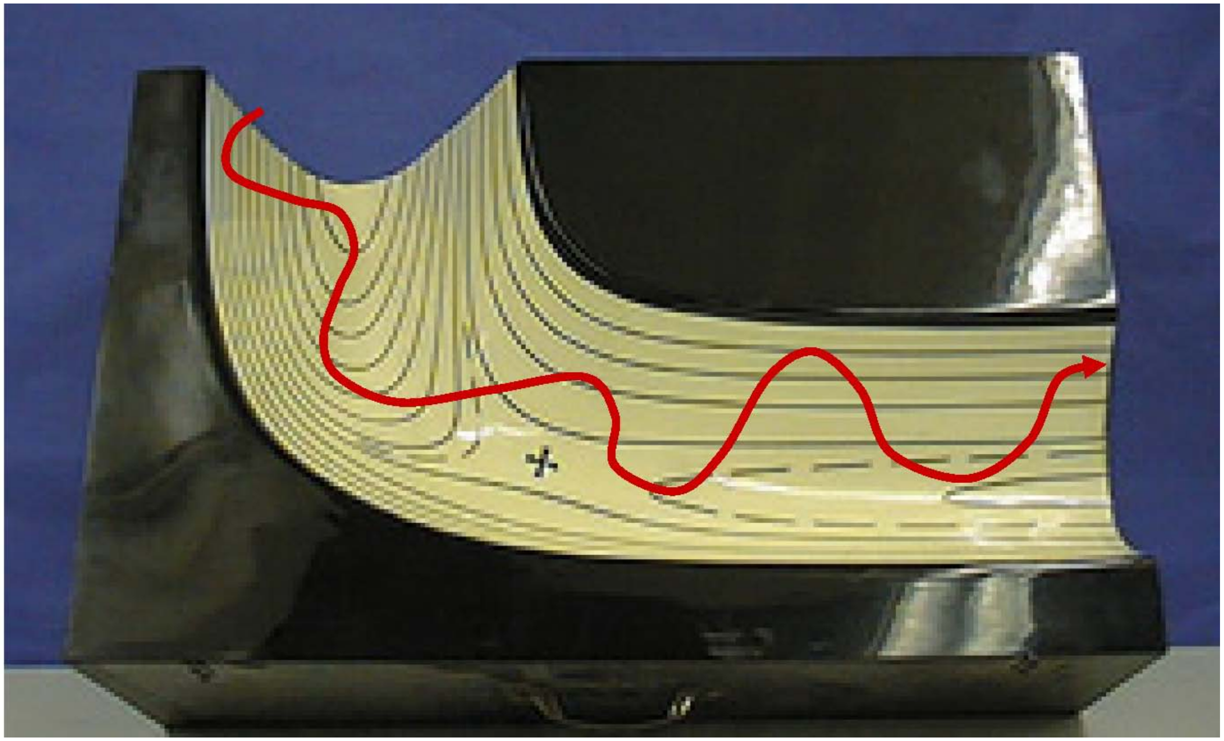
Disadvantages:



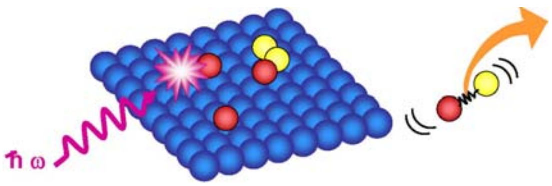
→



Classical Molecular Dynamics:



Aside: brief tutorial on classical mechanics



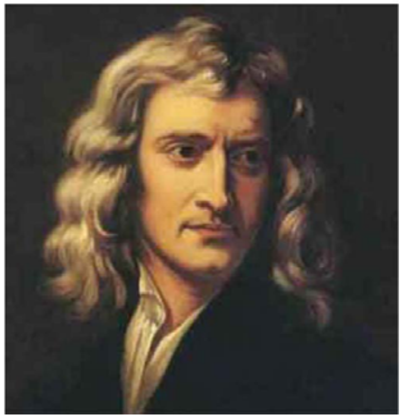
Chemical Dynamics

Telluride
July 2009
J. Tully

Newton's equations:

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

Isaac Newton

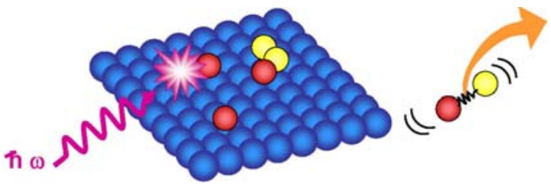


Force is the gradient of the potential:

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

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

Newton's Equations



Tutorial on Classical Mechanics

Hamilton's equations:

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

$$\dot{q} = \partial\mathcal{H}(p,q)/\partial p$$

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

Hamilton's Equations

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

$\longrightarrow$

$$\dot{q} = p/m$$

$$\dot{p} = -\partial V(q)/\partial q$$

William Rowan Hamilton.

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

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

Joseph-Louis Lagrange

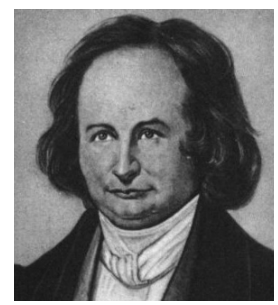
Hamilton-Jacobi Equation:

Define *Hamilton's Principle Function S*:

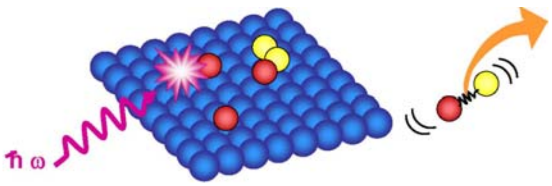
$$S = \int p\, dq$$

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

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



Karl Gustav Jacob Jacobi



Chemical Dynamics

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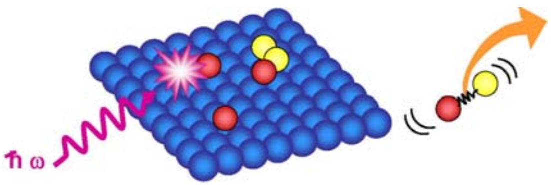


III. Classical Limit via Bohm Eqs.

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

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

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

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

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

III. Classical Limit via Bohm Eqs.

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

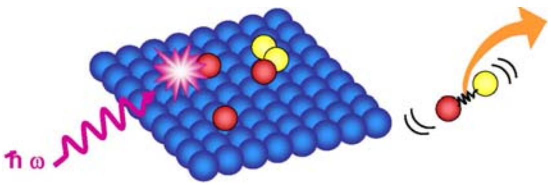
$$\frac{\partial S}{\partial t} = -\mathcal{H}\left(q, \frac{\partial S}{\partial q}\right) \qquad \text{where} \qquad \frac{\partial S}{\partial q} = p$$

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

the "quantum potential"

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

David Bohm



Chemical Dynamics

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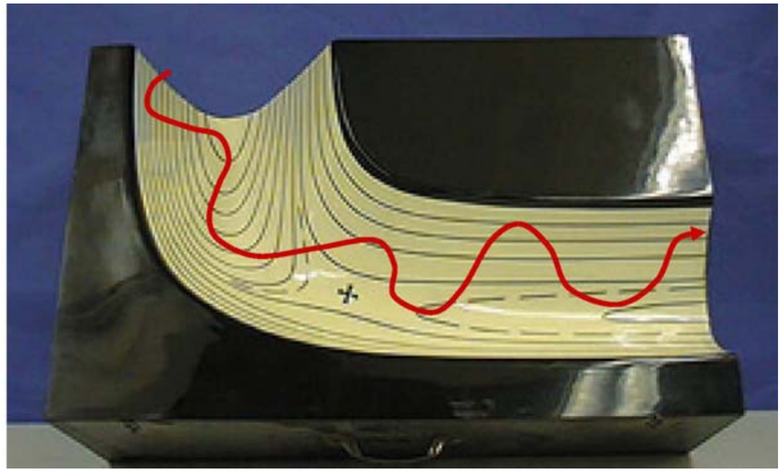
IV. Classical Molecular Dynamics

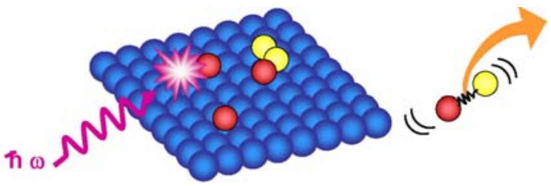


Basic Assumptions:

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



IV. Classical Molecular Dynamics

Numerical propagation of equations of motion:

Assume we know $x(t)$ and $v(t)$ at some time t.

How do we find $x(t+\delta)$ and $v(t+\delta)$ at later time $t+\delta$?

Taylor's series:

$$x(t+\delta) = x(t) + \frac{dx}{dt}\delta + \frac{d^2x}{2dt^2}\delta^2 + \frac{d^3x}{3!dt^3}\delta^3 + \ldots$$

$$= x(t) + v(t)\delta + \frac{1}{2}a(t)\delta^2 + \frac{d^3x}{3!dt^3}\delta^3 + \ldots$$

$$x(t-\delta) = x(t) - v(t)\delta + \frac{1}{2}a(t)\delta^2 - \frac{d^3x}{3!dt^3}\delta^3 + \ldots$$

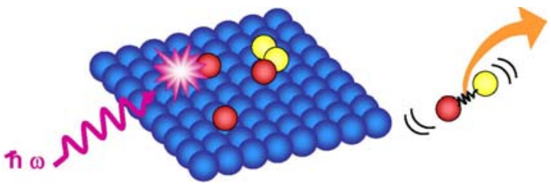
Add →

$$x(t+\delta) \cong 2x(t) - x(t-\delta) + a(t)\delta^2 + O(\delta^4)$$

where

$$Ma(t) = -\partial \mathcal{E}(x)/\partial x$$

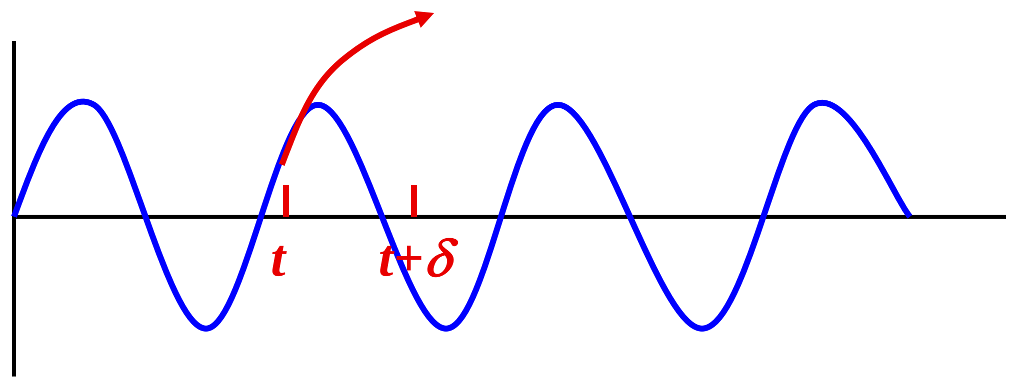
Verlet algorithm



IV. Classical Molecular Dynamics

Choice of time step δ:

The highest frequency (fastest)
Motions are stiff vibrational modes

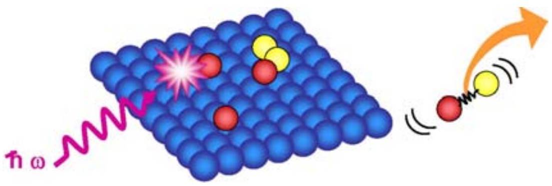


⟶ $\delta \ll$ **1/ω**

e.g, O-H stretch: 3700 cm-1 → $\omega = 1\text{x}10^{14}\ s^{-1}$

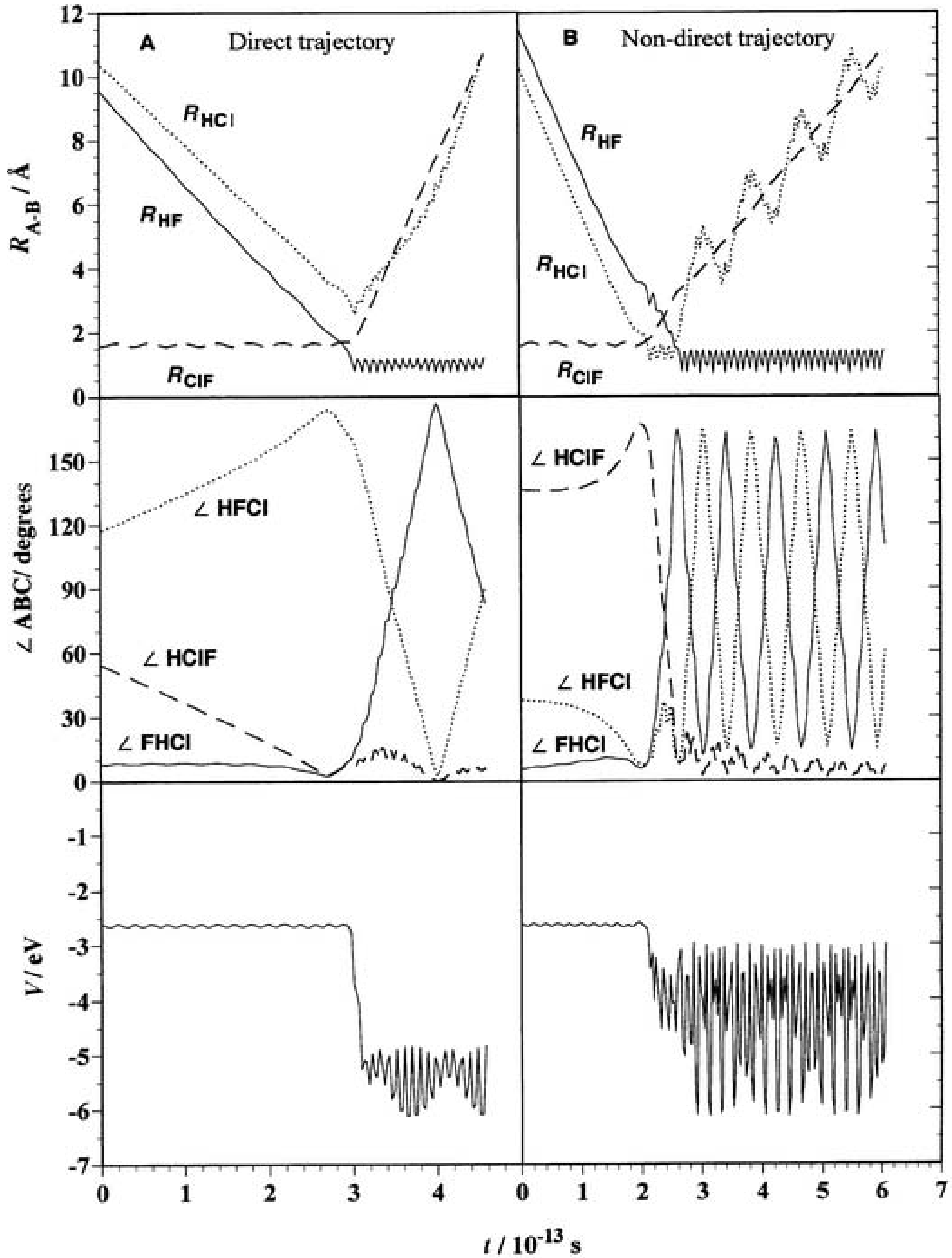
Test: Energy Conservation

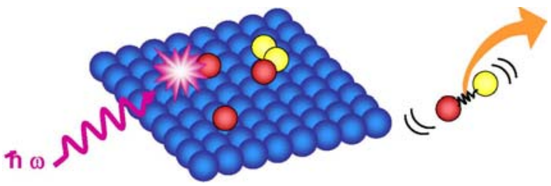
remember Rig: “weak test”


ħ ω

H + ClF

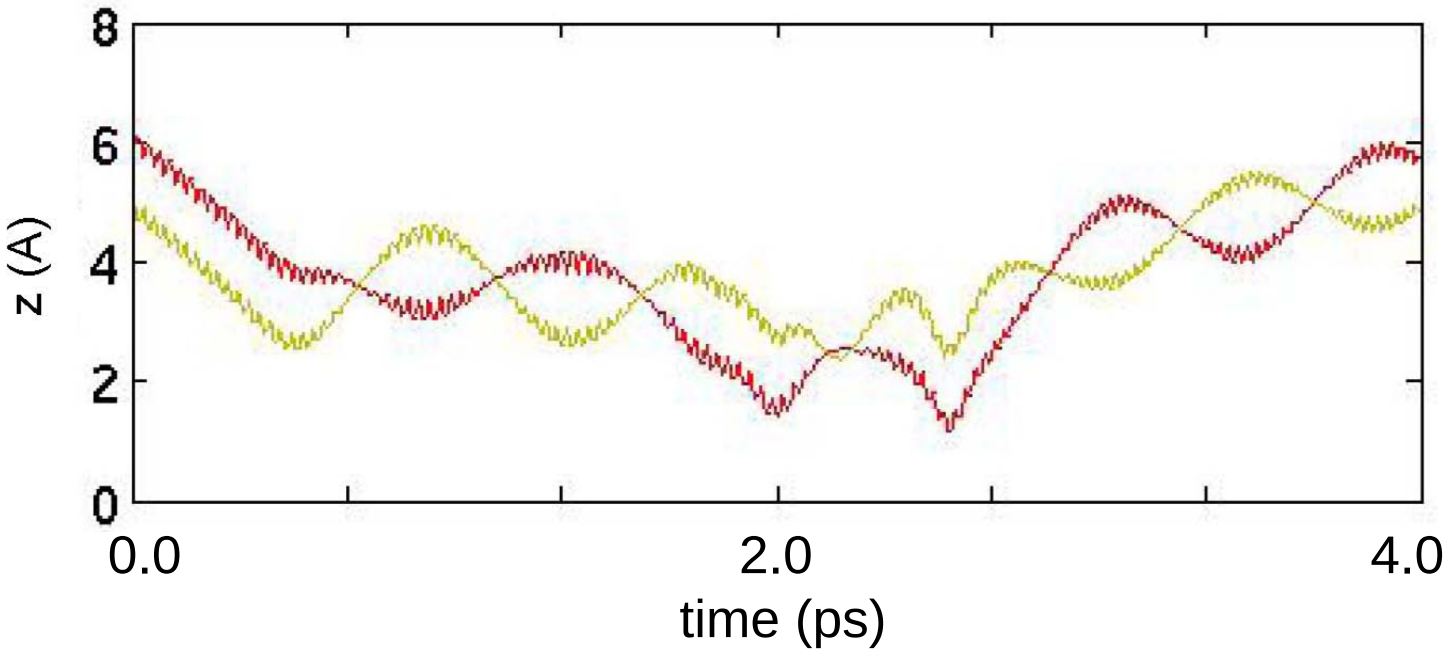
→ HF + Cl


A
Direct trajectory
B
Non-direct trajectory
R_{HCl}
R_{HF}
R_{ClF}
R_{A-B} / Å
∠ HFCl
∠ HClF
∠ FHCl
∠ ABC/ degrees
V / eV
t / 10^-13 s



IV. Classical Molecular Dynamics

Inelastic scattering of NO molecules from a gold surface



IV. Classical Molecular Dynamics

Protein in water

do we need all of these water molecules?

dielectric continuum approximation