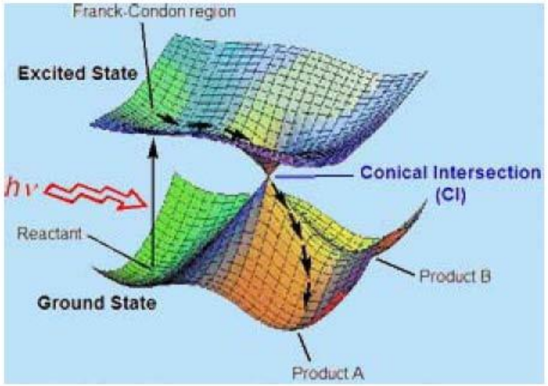
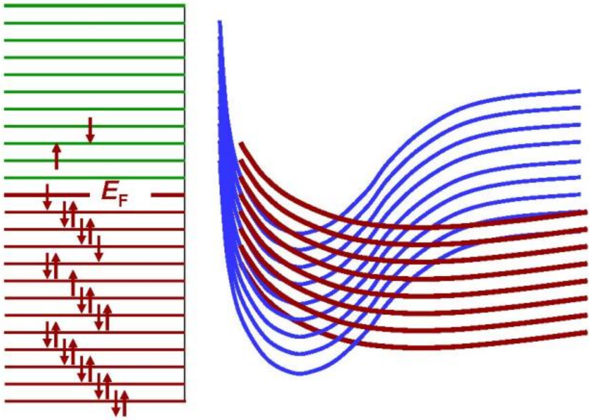
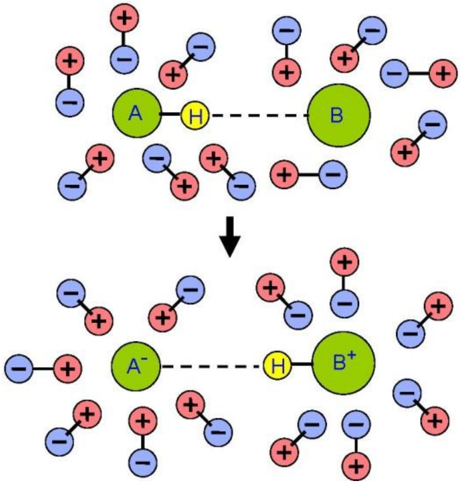
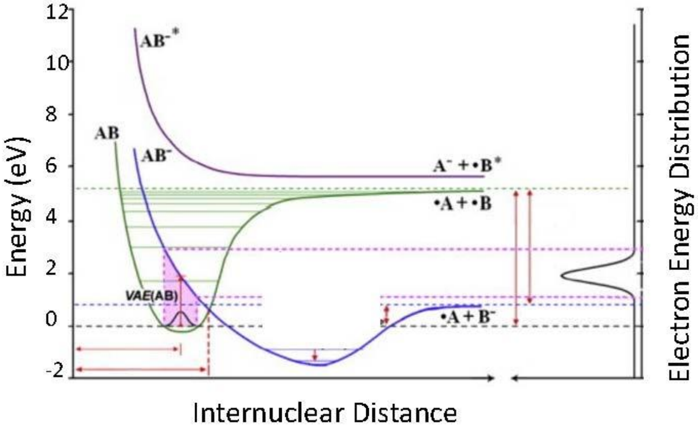
VISTA: Virtual International Seminar on Theoretical Advancements

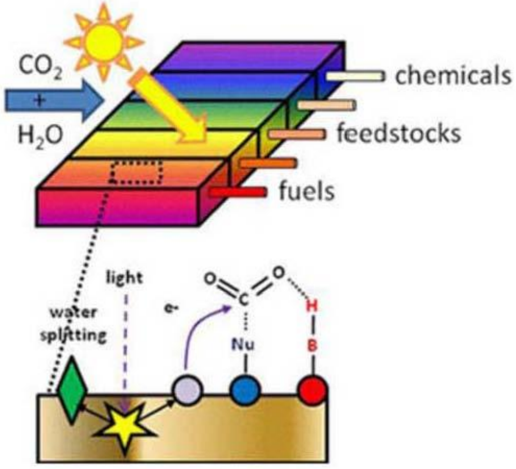
Adventures with Surface Hopping

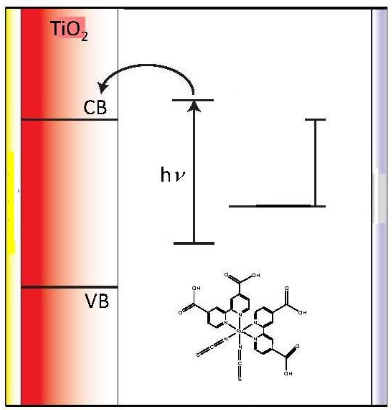












Adventures with Surface Hopping

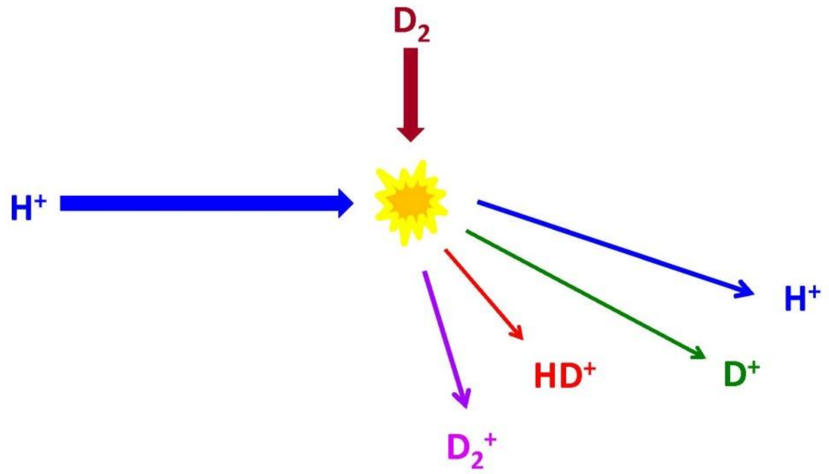
A historical view of my role in some of the
origins and developments of surface hopping

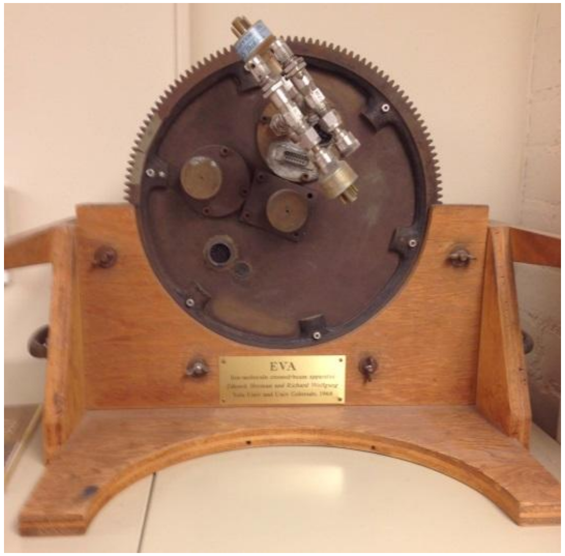
This will not be a scholarly review:
I will omit many important contributions by others

Molecular Beam Experiments of the Reaction of H^+ with D_2

Collaboration with Zdenek Herman, Richard Wolfgang, …

1969 Univ Colorado Boulder





Detect the angular and velocity distributions of ions

Theory: How hard can it be?

H_3^+ : 3 nuclei, 2 electrons

simplest chemical reaction ?

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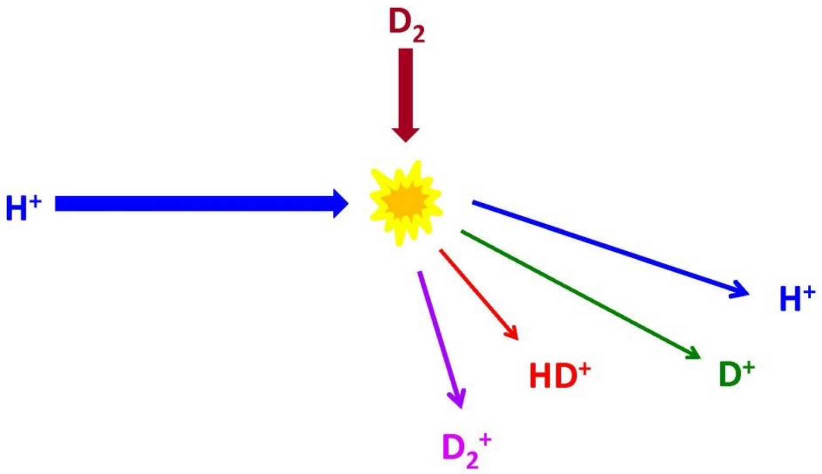
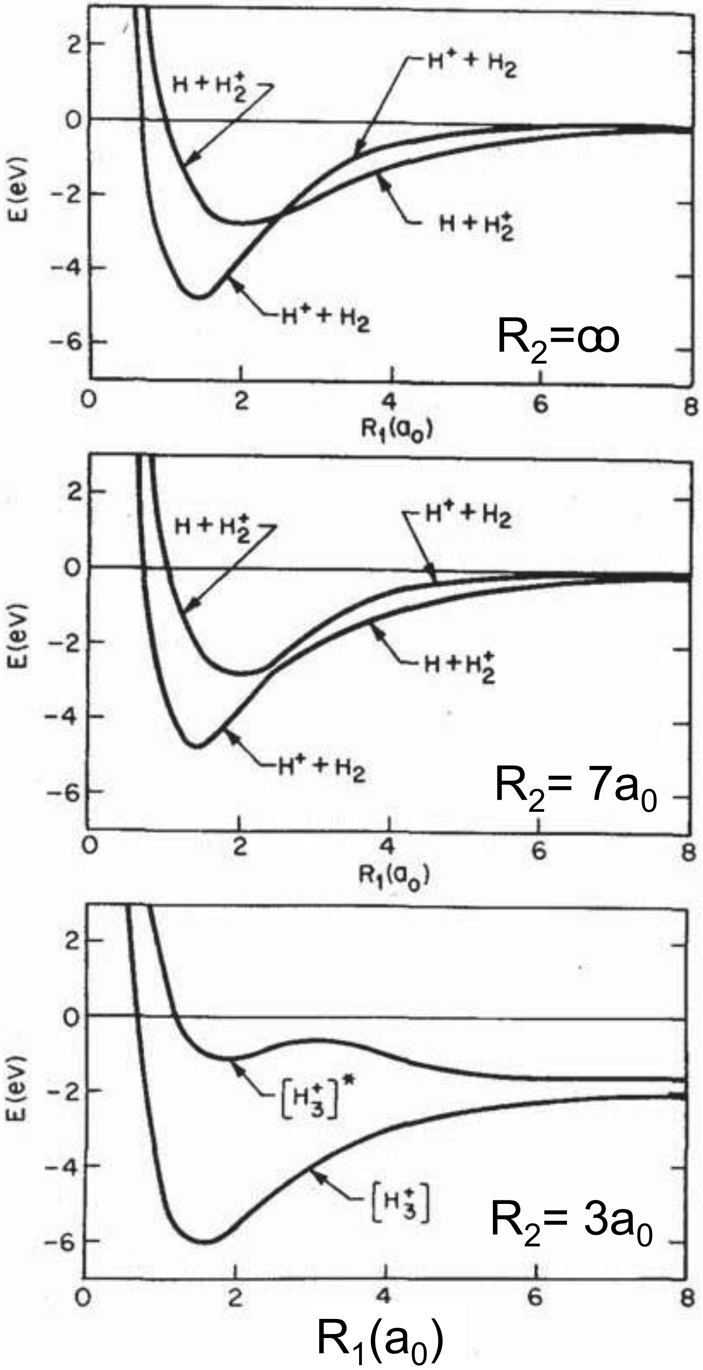
simplest chemical reaction ?

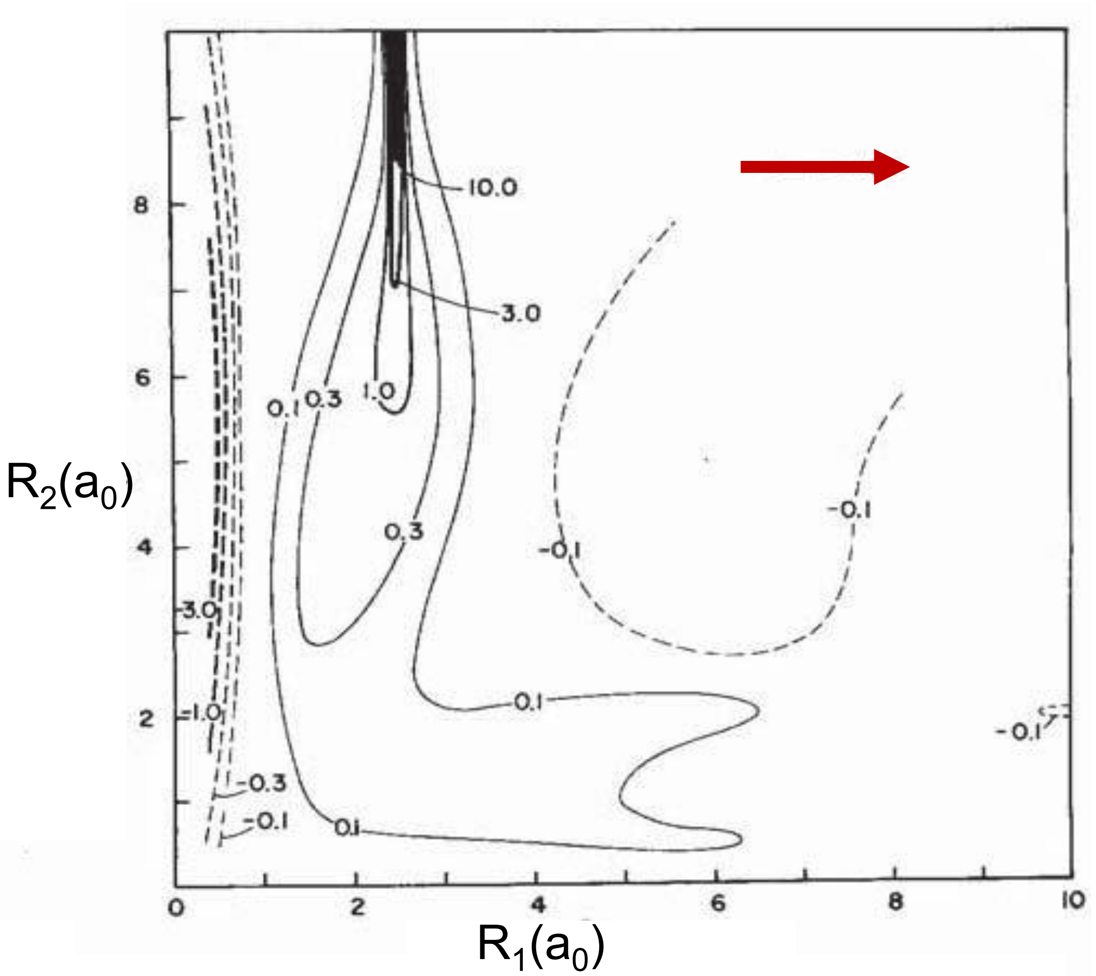
However: 2 potential energy surfaces !



Compute Potential Energy Surfaces and Nonadiabatic Coupling Vectors

Semiempirical *Diatomics in Molecules*

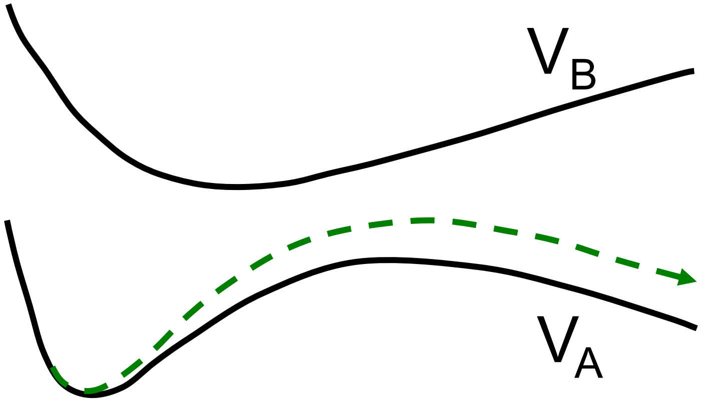




Nonadiabatic coupling vector

January 14, 2026

MIXED QUANTUM-CLASSICAL STRATEGIES
FOR NONADIABATIC DYNAMICS



Ehrenfest

(self-consistent field)

e.g., A. D. McLachlan, *Mol. Phys*. 1964

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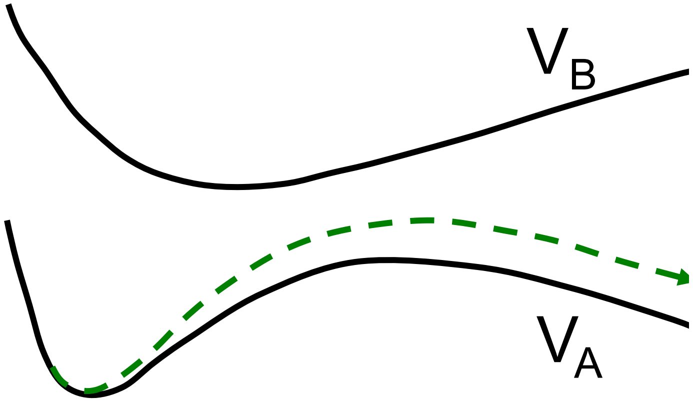

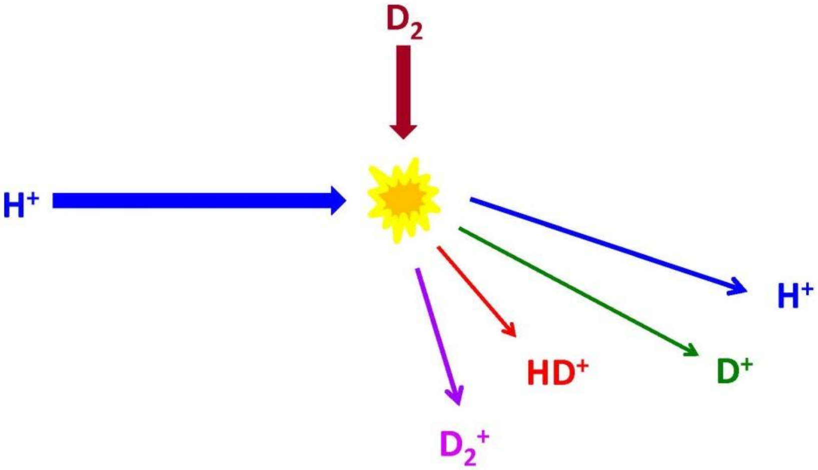

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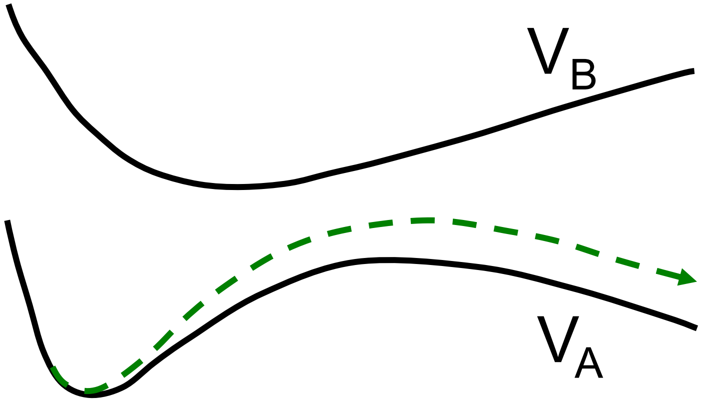

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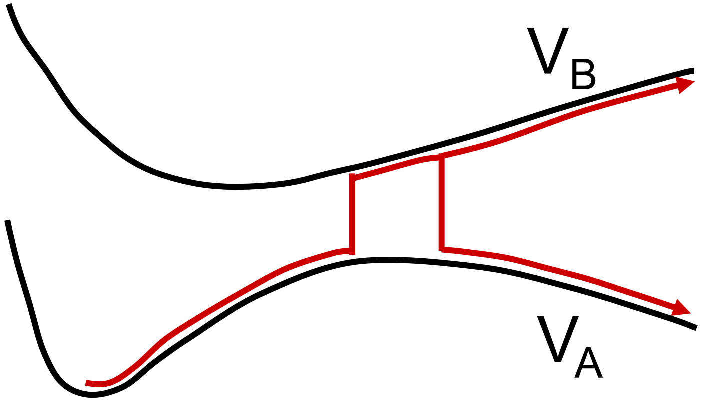

Trajectory Surface-Hopping

↓

motion on individual
potential energy surfaces

Surface Hopping (1971 Version)

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

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2] Electronic amplitudes along path: $dc_j/dt = -\frac{i}{\hbar}V_{jj}c_j - \dot{R}\cdot\sum_i < \varphi_j \,|\, \nabla_R \varphi_i > c_i$

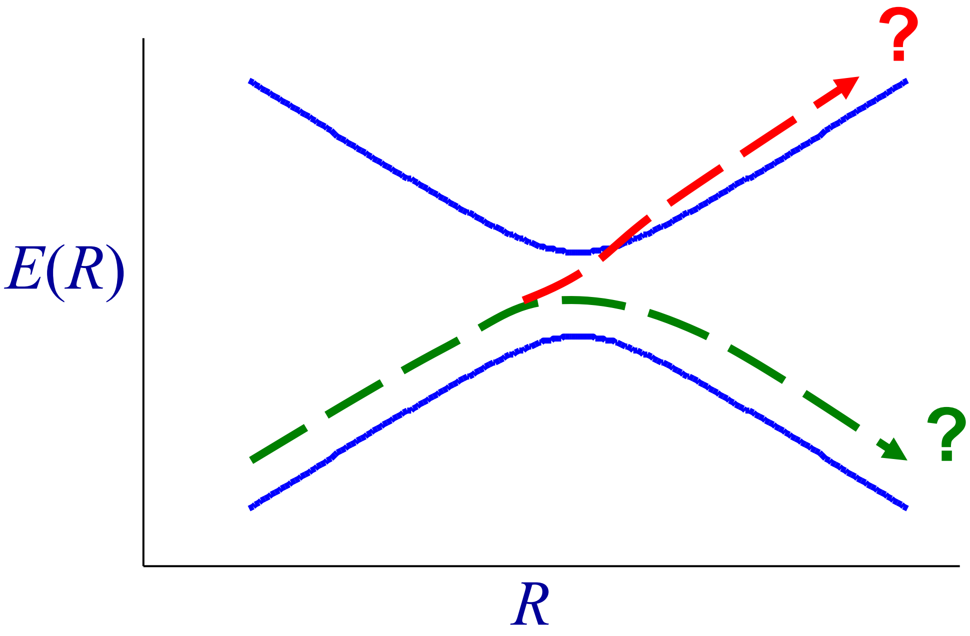
Approximate $|c_k|^2$ by Landau-Zener formula

Landau-Zener Approximation: 1932

2 x 2 Hamiltonian matrix

Assumptions:

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



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

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Approximate $|c_k|^2$ by Landau-Zener formula

3] Select electronic state by random number according to $|c_k|^2$

Hops occur only at crossing points

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Approximate $|c_k|^2$ *by Landau-Zener formula*

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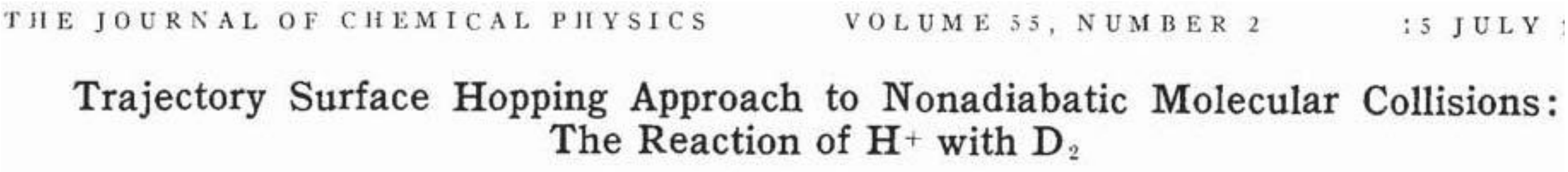
Hops occur only at crossing points

4] Scale momentum in *direction of coupling vector* to conserve energy

P. Pechukas, Phys. Rev., 1969

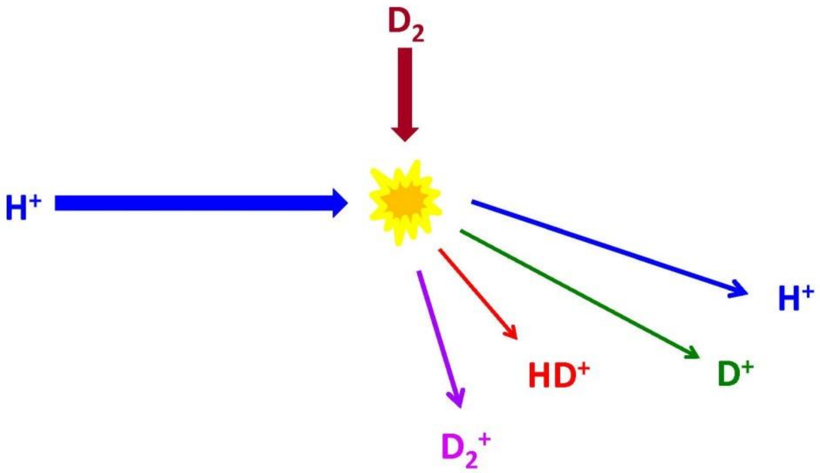


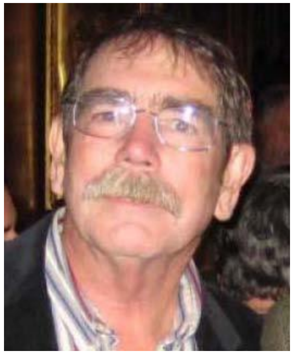
THE JOURNAL OF CHEMICAL PHYSICS VOLUME 55, NUMBER 2 15 JULY

Trajectory Surface Hopping Approach to Nonadiabatic Molecular Collisions: The Reaction of H^+ with D_2

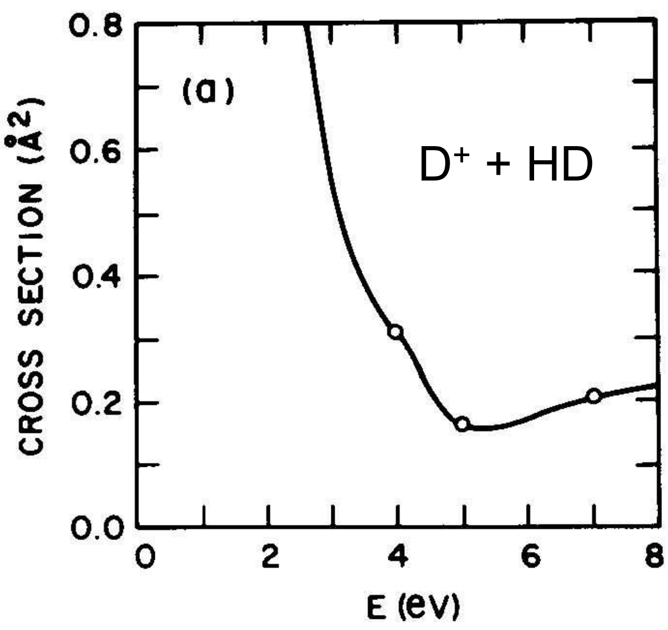
1971 with graduate student Richard Preston

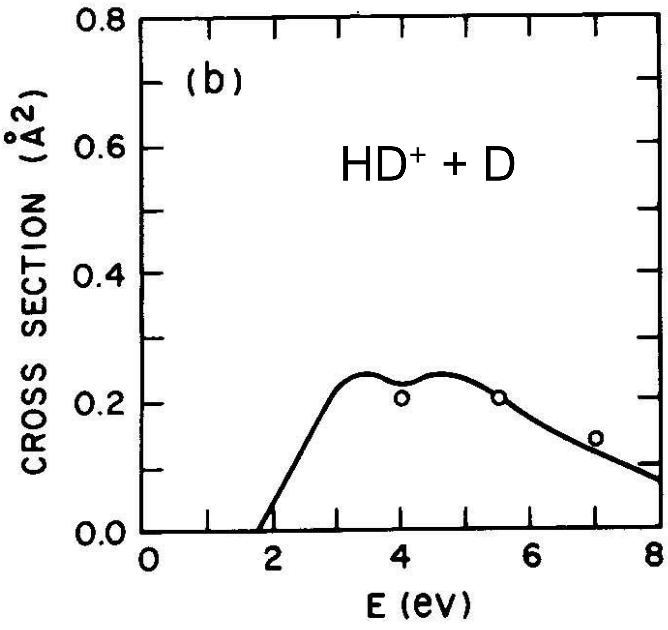
Used Brookhaven National Labs CDC 6600 supercomputer

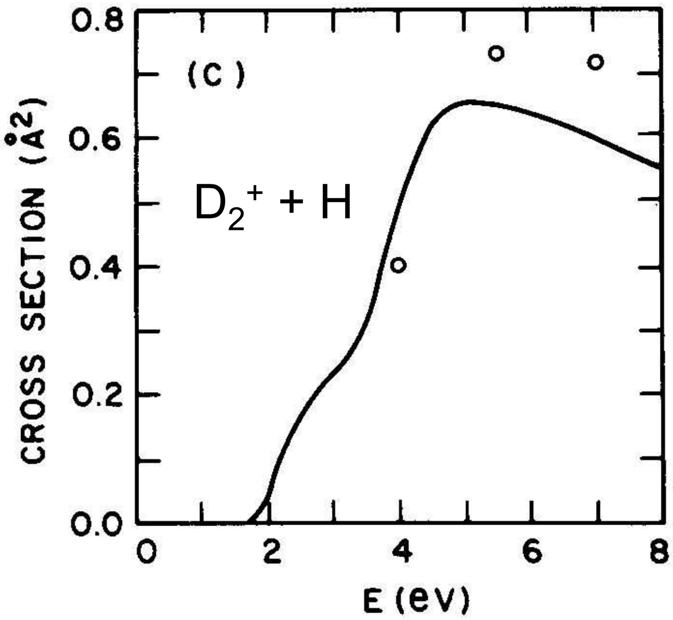




“It takes a laser physicist to be a farmer” Richard Preston, 2010





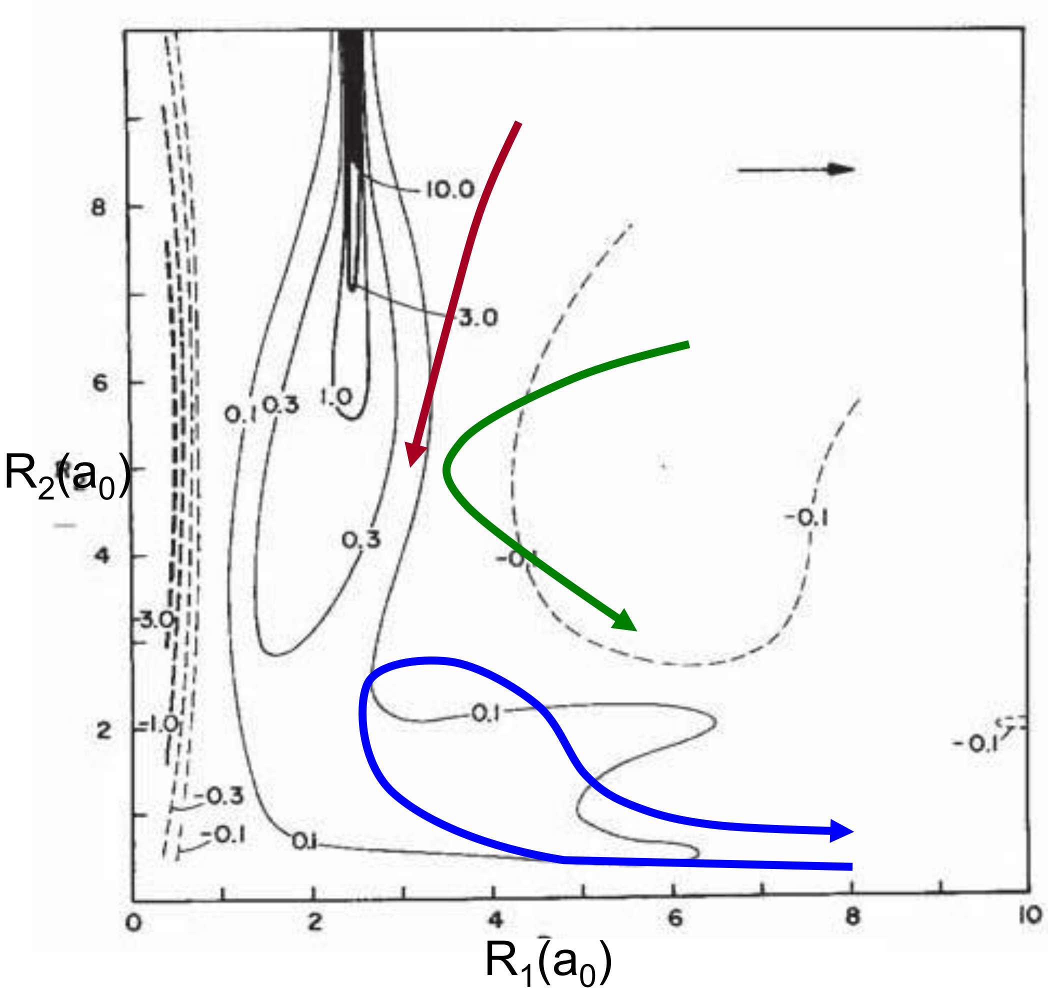


Absolute cross sections for the reaction of H^+ with D_2 as a function of incident energy

Points: surface hopping,
Tully - Preston, 1971

Solid curves: experiment,
Ochs -Teloy, 1974

Fast Forward to 1990, Bell Labs:



Nonadabatic coupling vector

Turning points

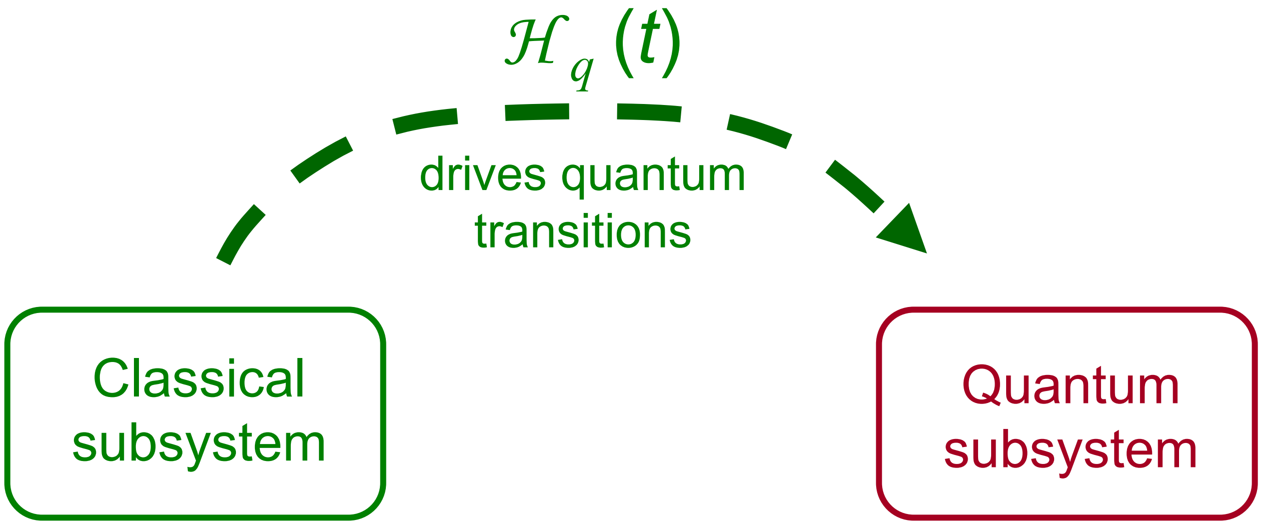
No distinct crossing points

Nearly parallel surfaces

Many electronic states

Broad coupling region

→ *Need to go beyond 1971 assumption of hopping only at crossing points*



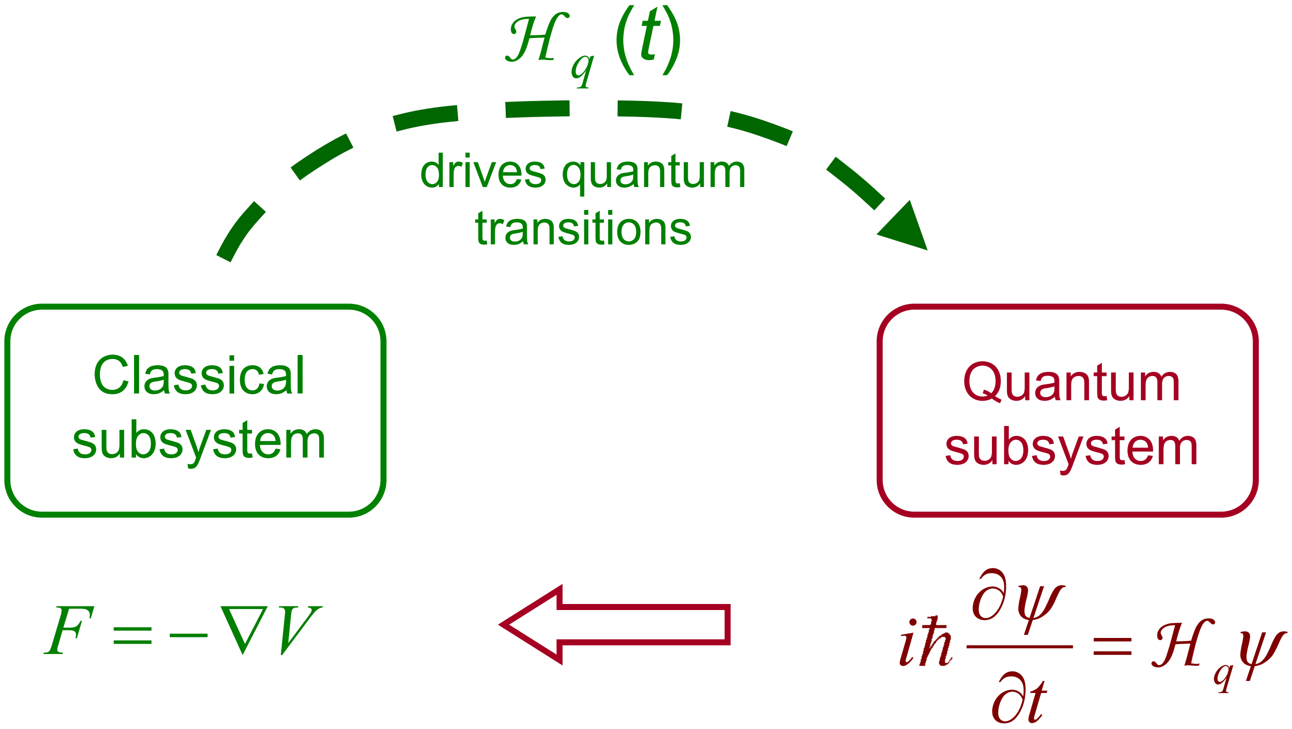
$\mathcal{H}_q(t)$

drives quantum transitions

Classical subsystem

Quantum subsystem

$$F = -\nabla V$$



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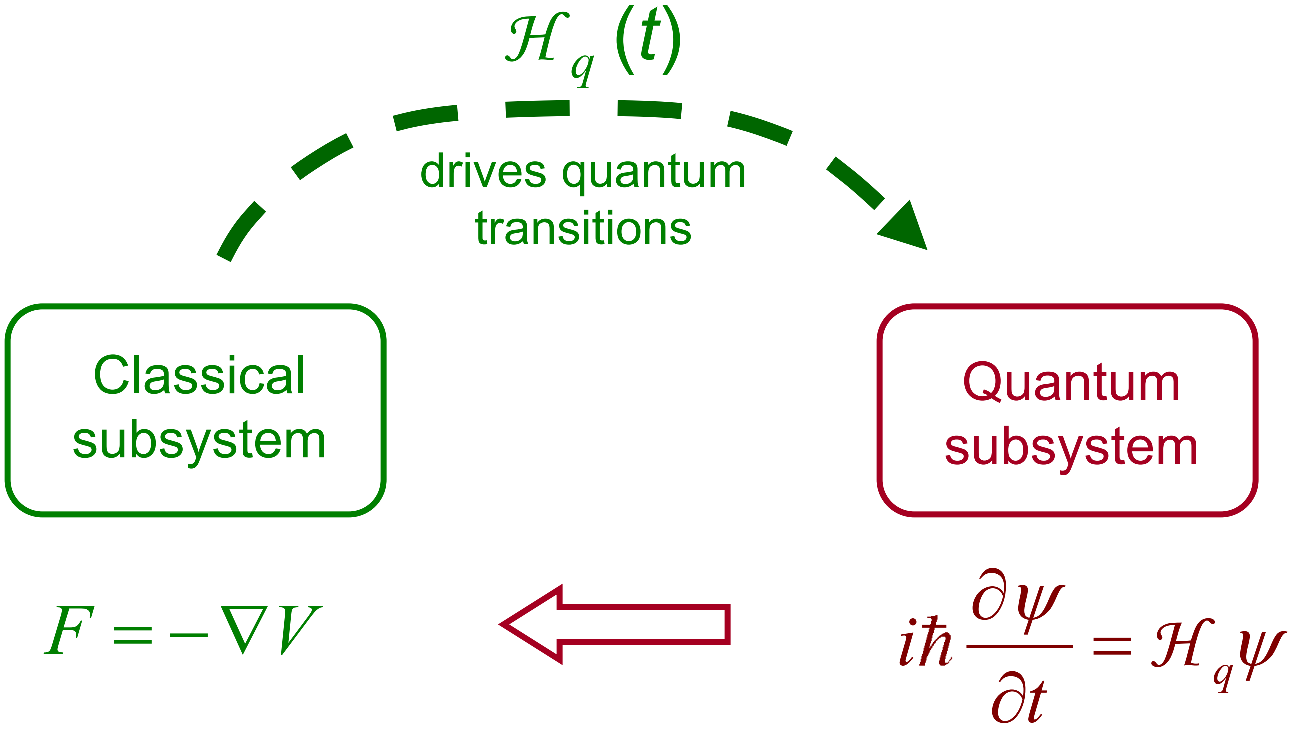
$$F = -\nabla V$$

$$i\hbar \frac{\partial \psi}{\partial t} = \mathcal{H}_q \psi$$



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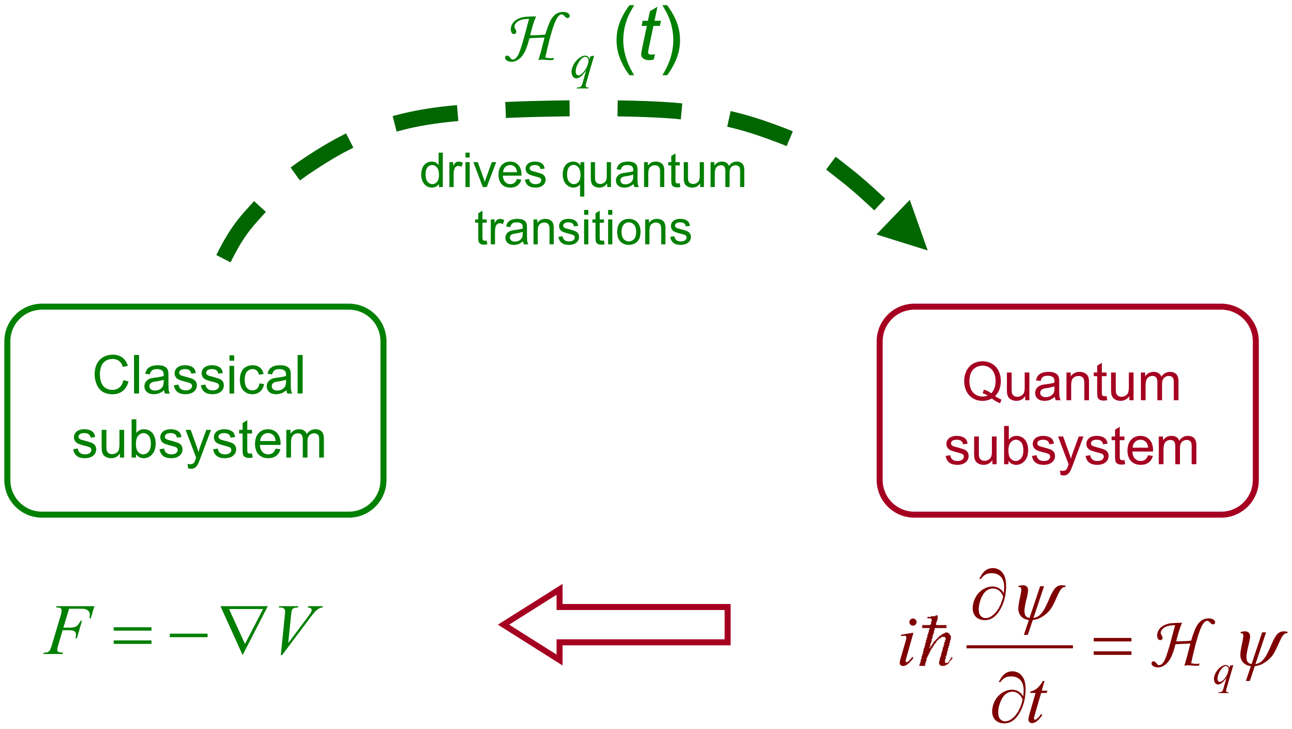
Key: quantum force: “*back-reaction*”

How do quantum transitions effect classical path?



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Key: quantum force: “*back-reaction*”

How do quantum transitions effect classical path?

How can we treat back-reaction more accurately, and yet retain the feature that trajectories end up in distinct states rather than mixtures?

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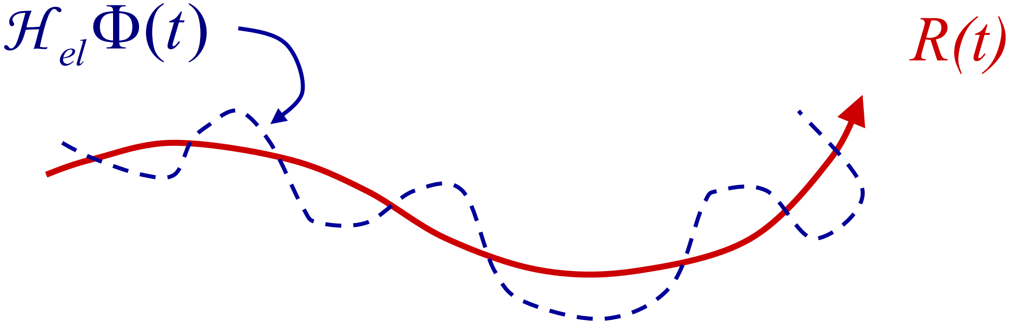
$$i\hbar\frac{\partial\Phi(t)}{\partial t} = \mathcal{H}_{el}\Phi(t)$$



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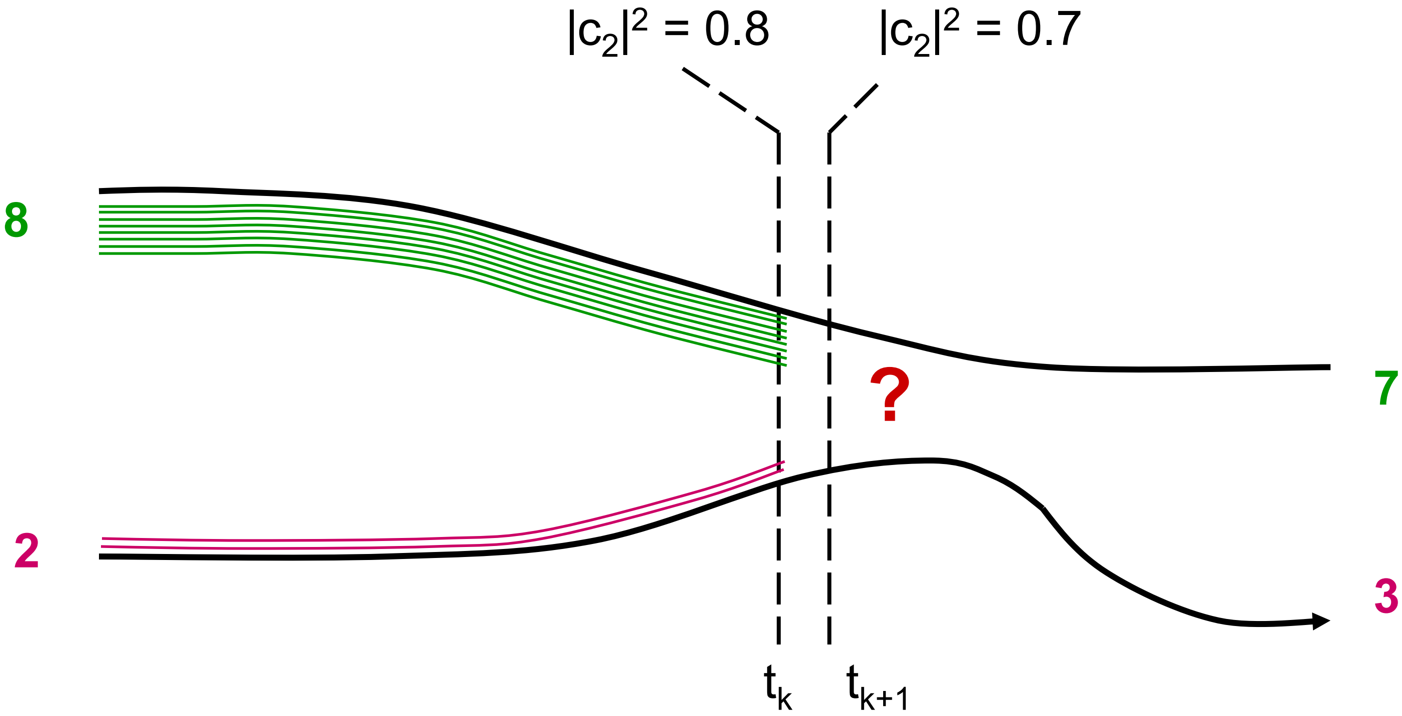
3] Stochastic “hops” between states so that avg probability = $|c_k(t)|^2$

“fewest switches”

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



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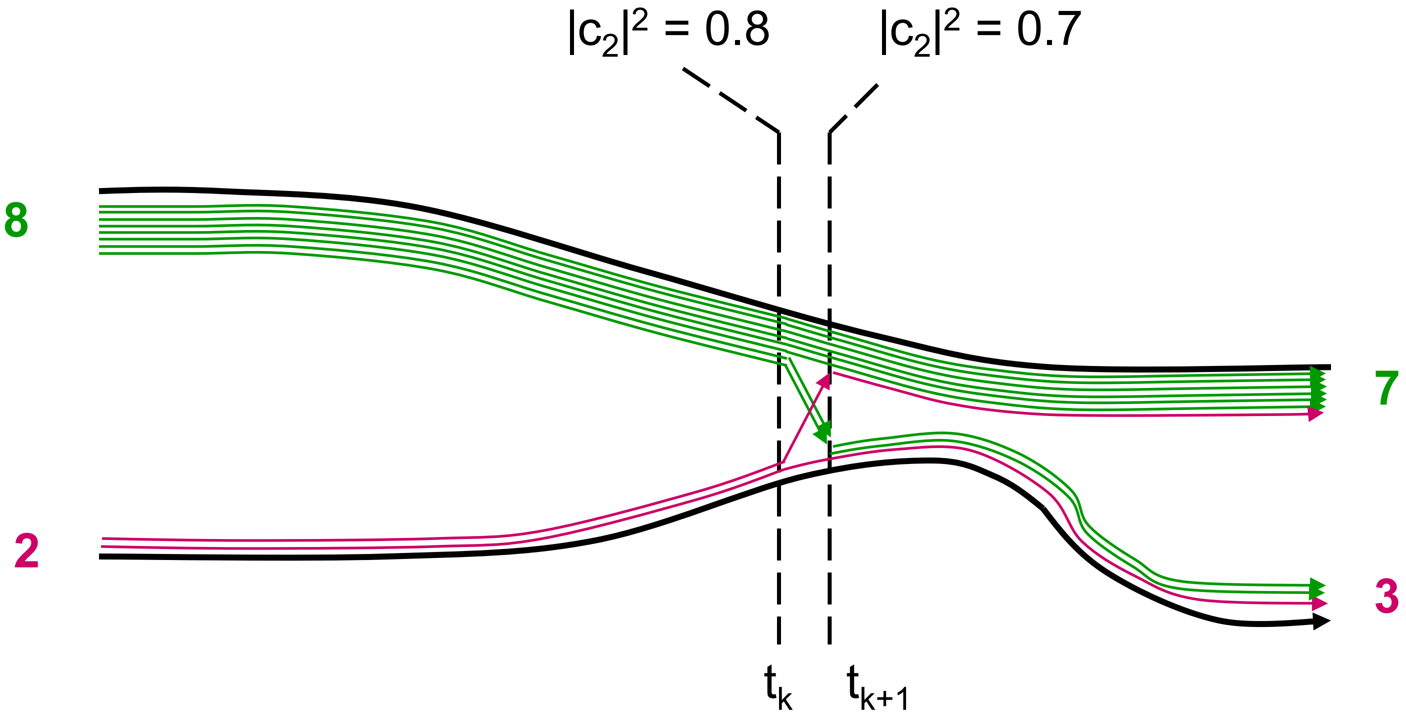

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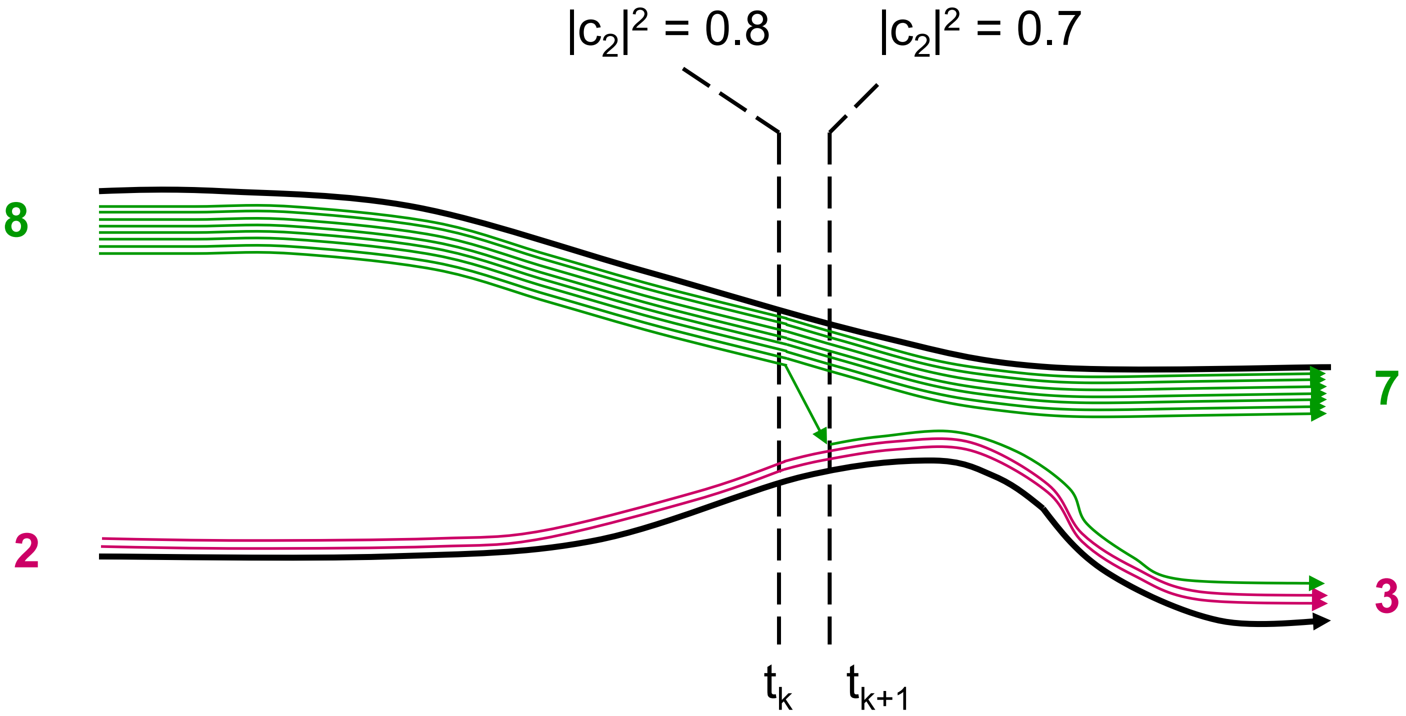

$$P_{2\to 1} = \begin{cases} \dfrac{|c_2(k)|^2 - |c_2(k+1)|^2}{|c_2(k)|^2}, & |c_2(k)|^2 > |c_2(k+1)|^2 \\ 0, & |c_2(k)|^2 \le |c_2(k+1)|^2 \end{cases}$$

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“Pechukas Force”

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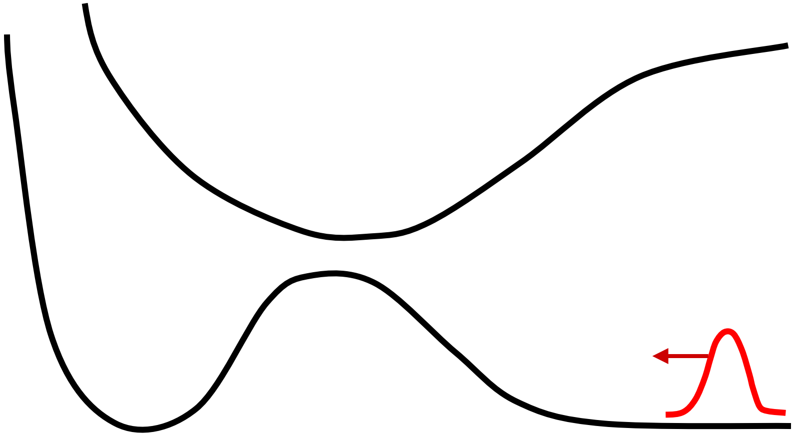
Decoherence



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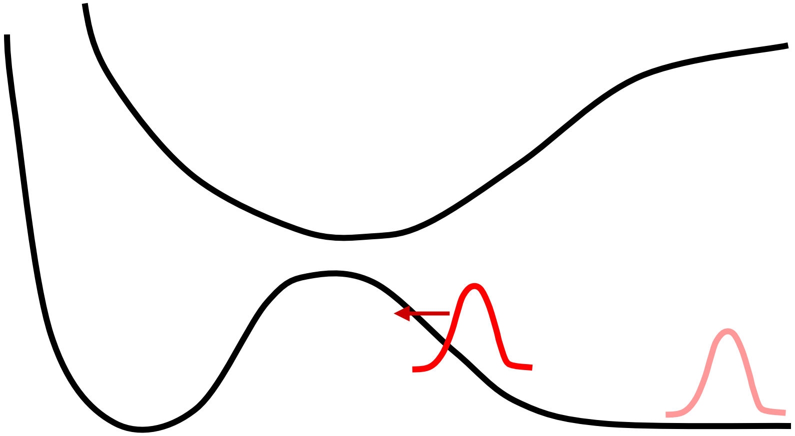

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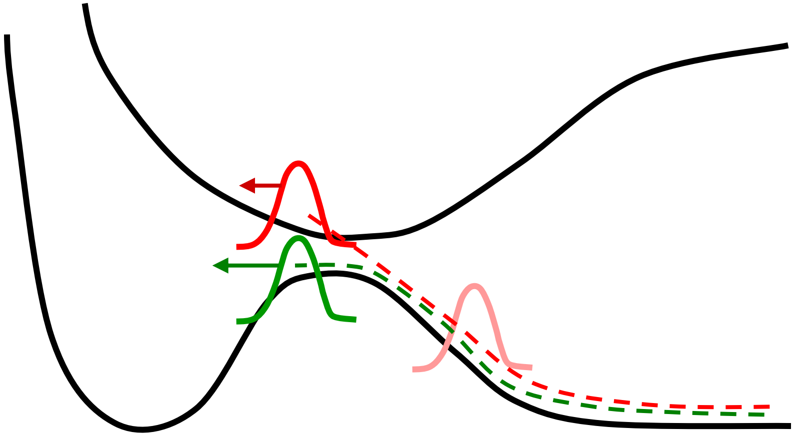

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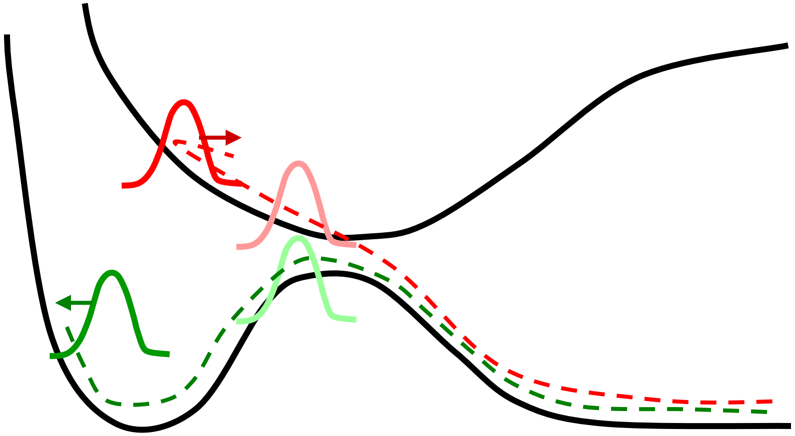

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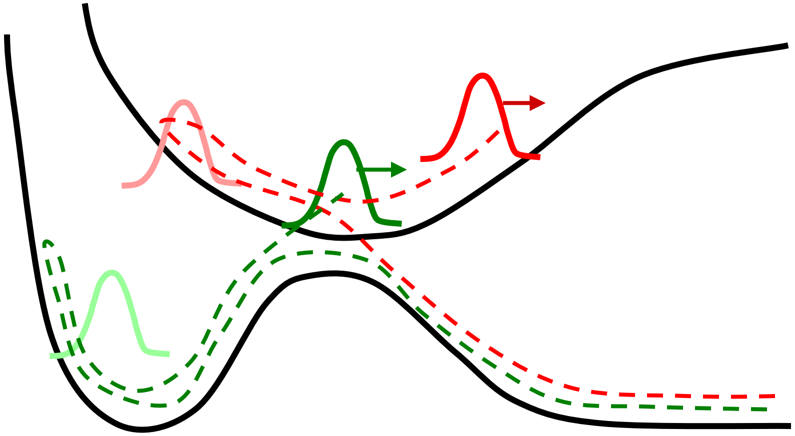

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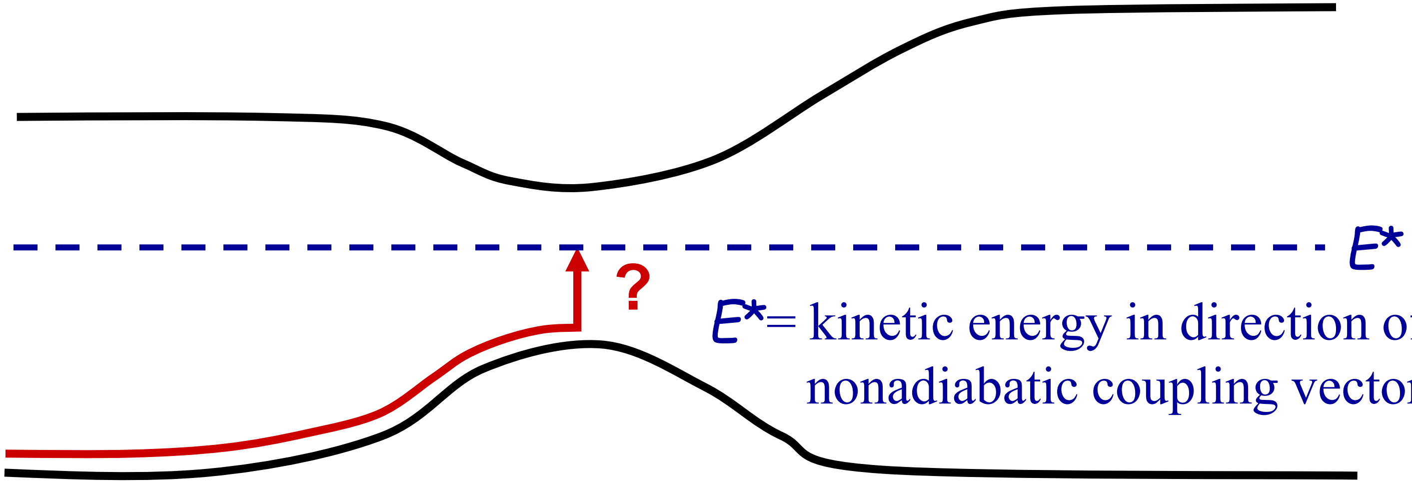


E^*= kinetic energy in direction of the nonadiabatic coupling vector

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

Critical element of Surface Hopping: Branching probabilities are determined not by $|c_k|^2$, but by the fraction of trajectories on each state.

Frustrated Hops and Detailed Balance

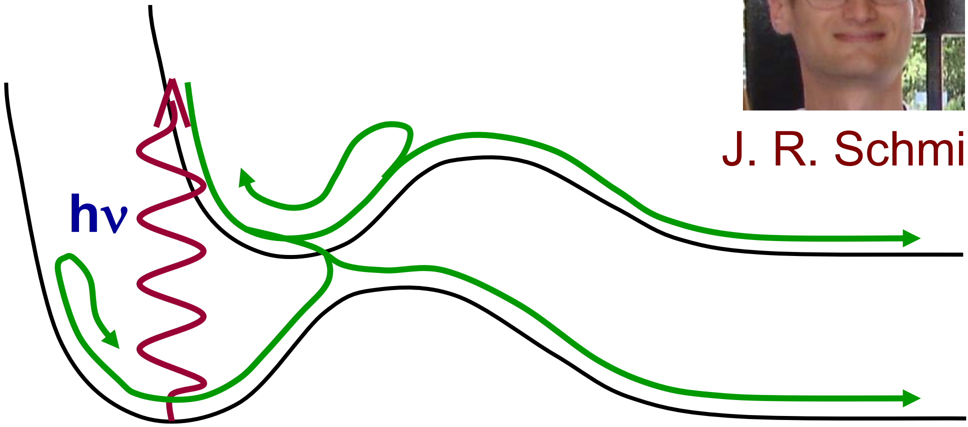
Priya Parandekar

Detailed Balance:

$\mathcal{N}_1 \, P_{1\rightarrow2} \;=\; \mathcal{N}_2 \, P_{2\rightarrow1} \;\rightarrow$ **Equilibrium**

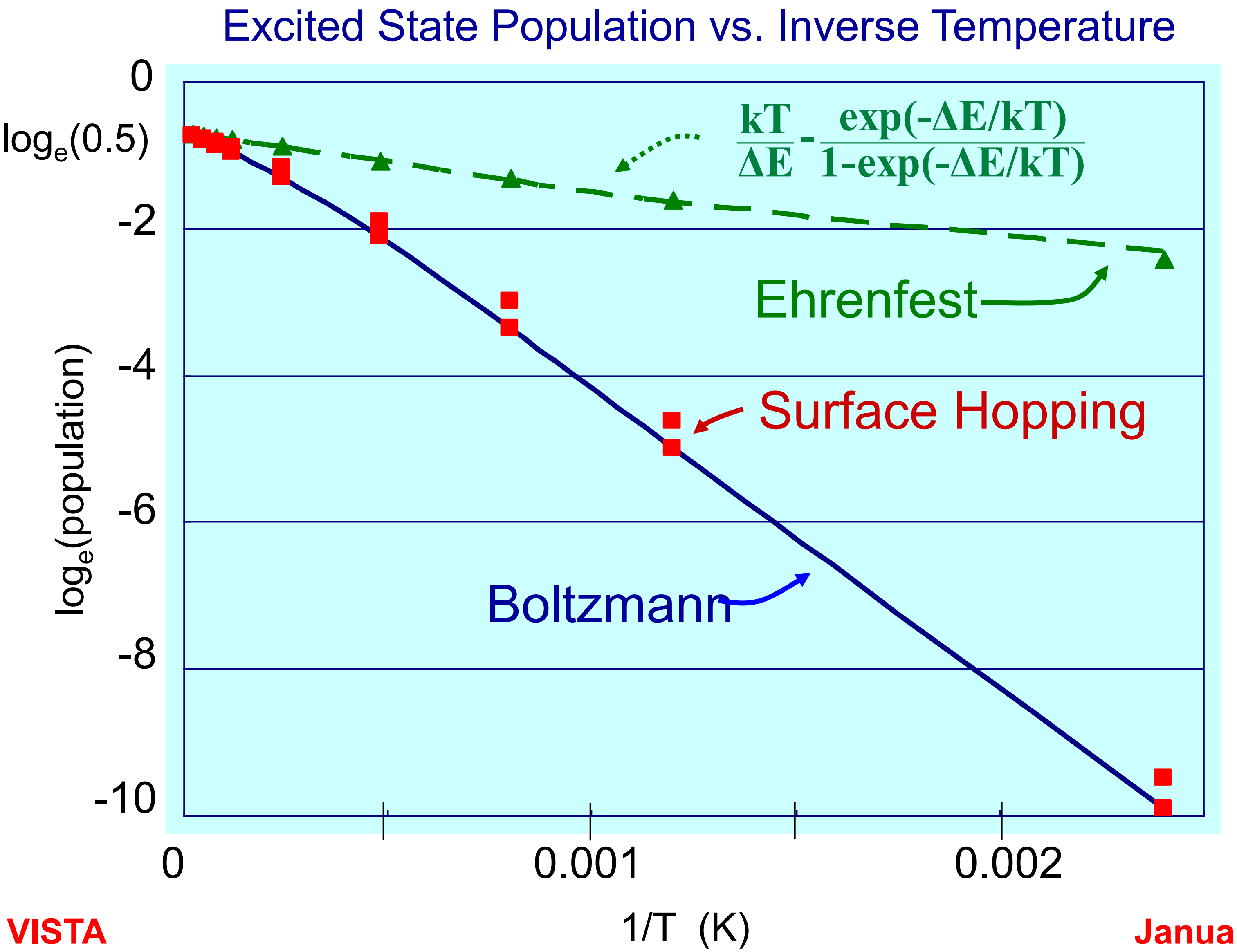
J. R. Schmidt

- Multiple Transitions
- Relaxation Processes
- Infrequent events
- Condensed Phases
- *Long Timescales*



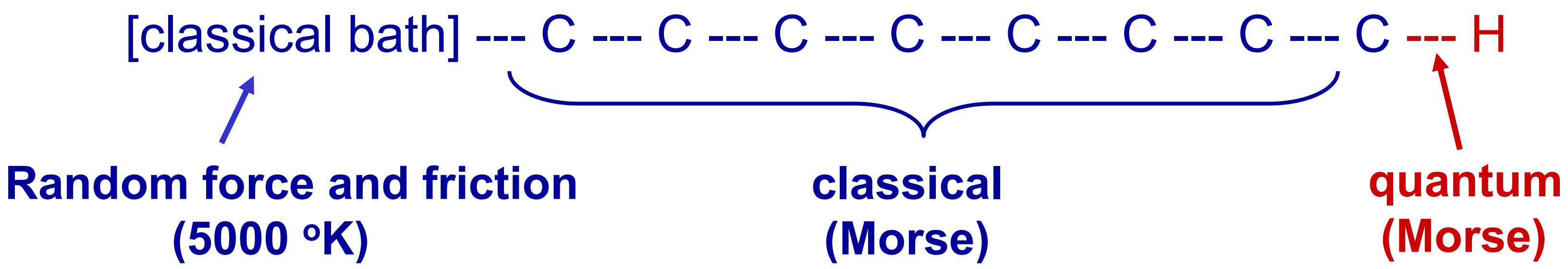
e.g., nonradiative transition
vs. reaction on excited state

2-Electronic State Model $\Delta E = 34.6$ kJ/mole



$$\frac{kT}{\Delta E} - \frac{\exp(-\Delta E/kT)}{1-\exp(-\Delta E/kT)}$$

Many Quantum States 2005 Priya Parandekar

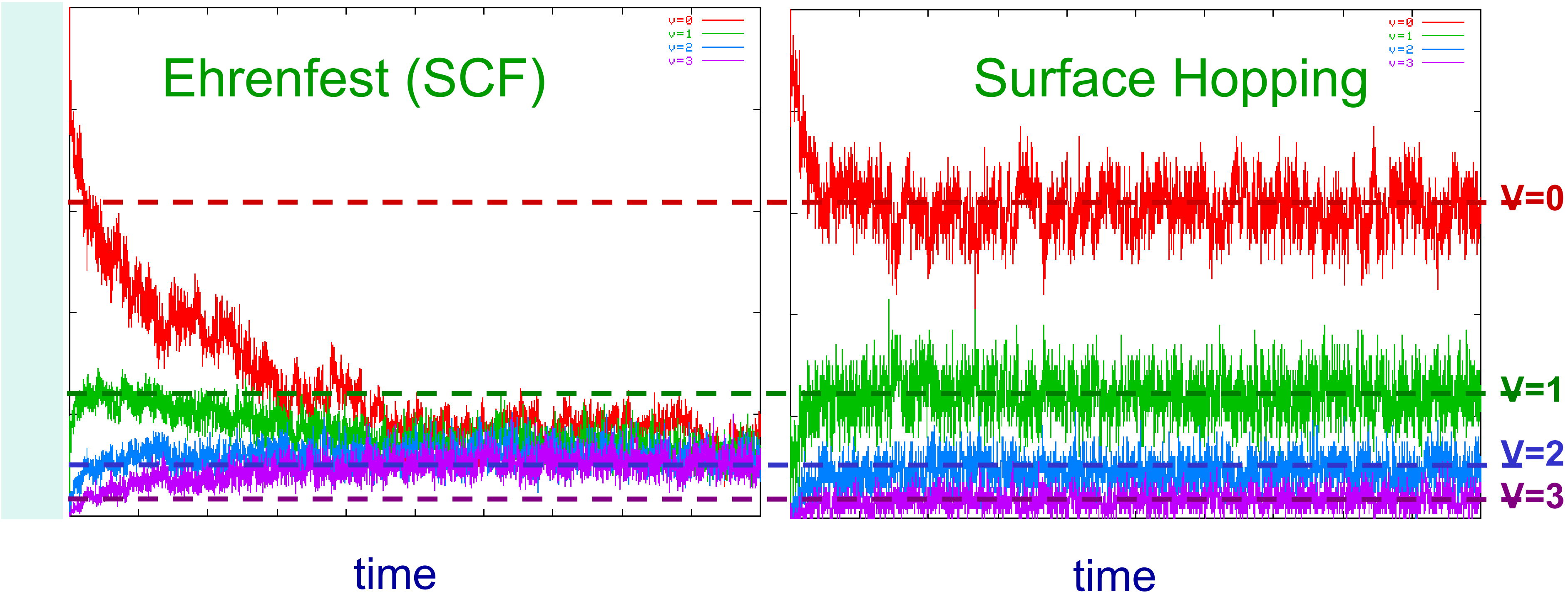


[classical bath] --- C --- C --- C --- C --- C --- C --- C --- C --- H

Random force and friction (5000 °K)

classical (Morse)

quantum (Morse)



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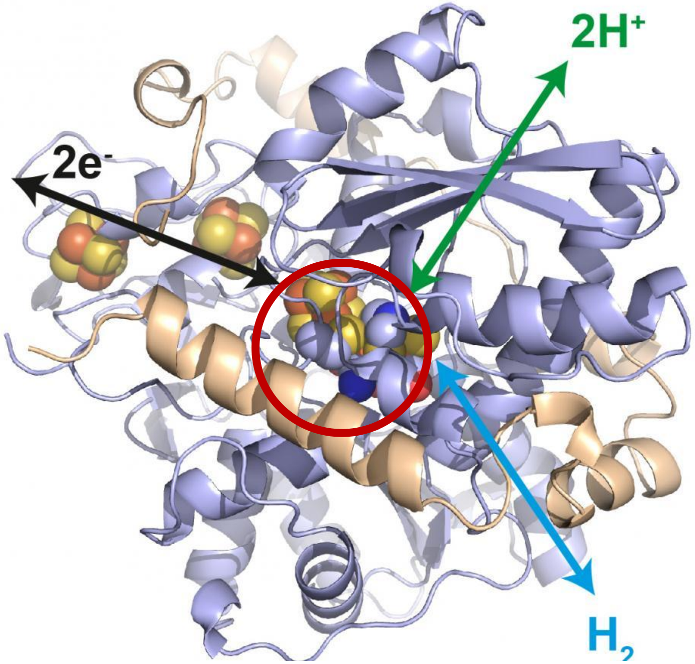
Treat Nuclear Motion by Quantum Mechanics:

- tunneling
- zero-point motion
- quantized energy levels

Prohibitive for large number of nuclei

Compromise strategy: a few quantum nuclei, the rest classical



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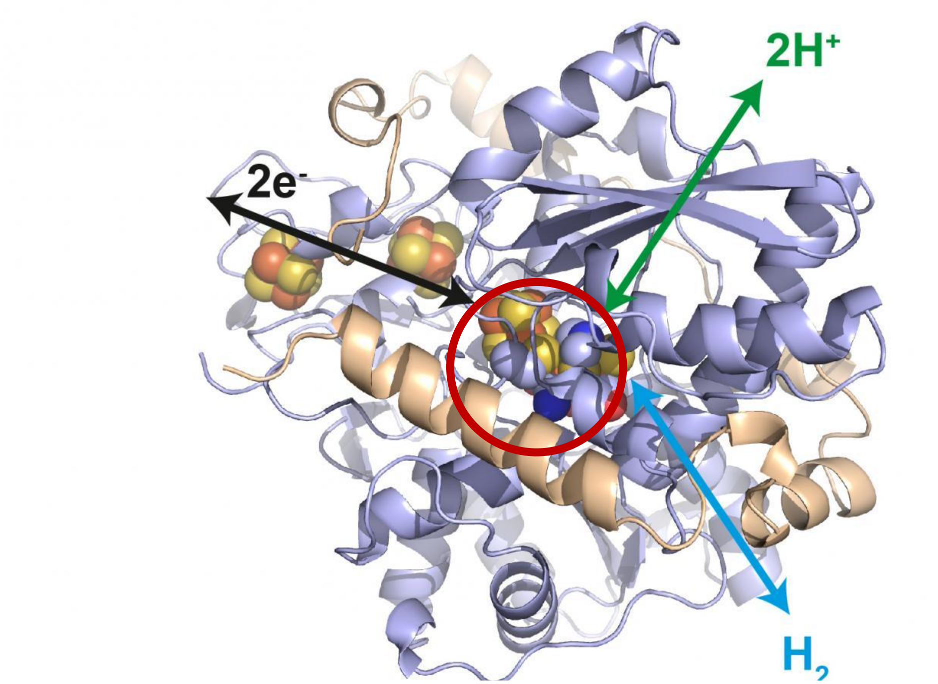
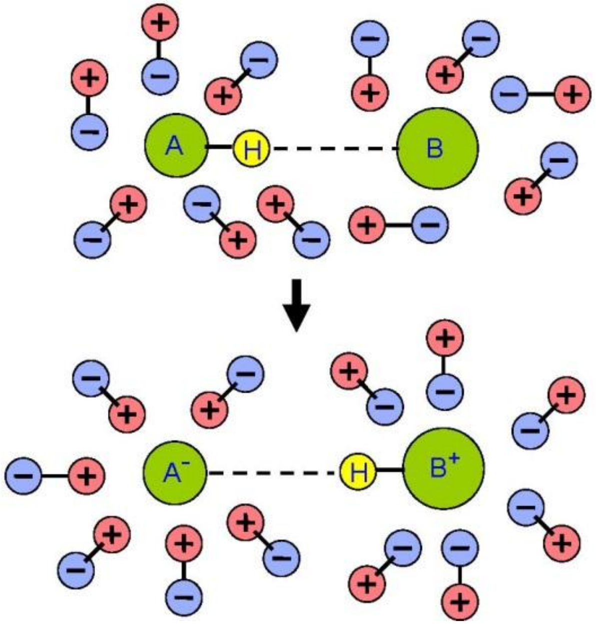


However:
justification of the
Born-Oppenheimer
approximation ???

Mixed Quantum-Classical Nuclear Motion

Sharon Hammes-Schiffer and JCT, *J. Chem. Phys*. **101**, 4657 (1994)



Quantum Effects:

- *Zero-Point Energy*
- *Quantized Energy Levels*
- *Tunneling*

Mixed Quantum-Classical Nuclear Motion

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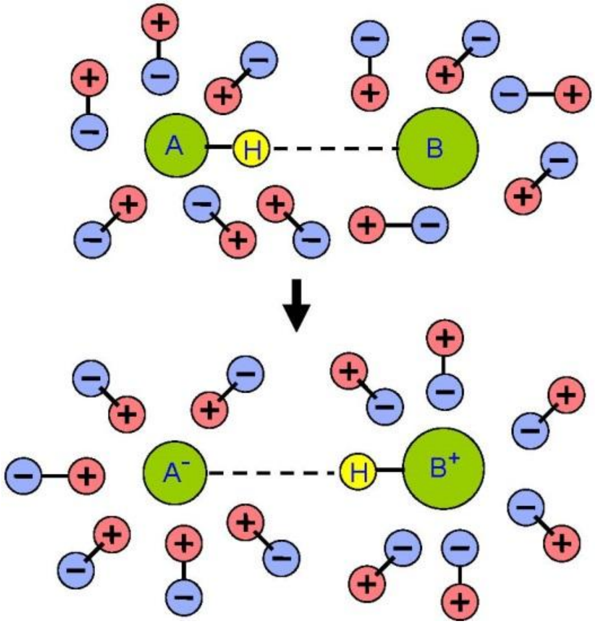
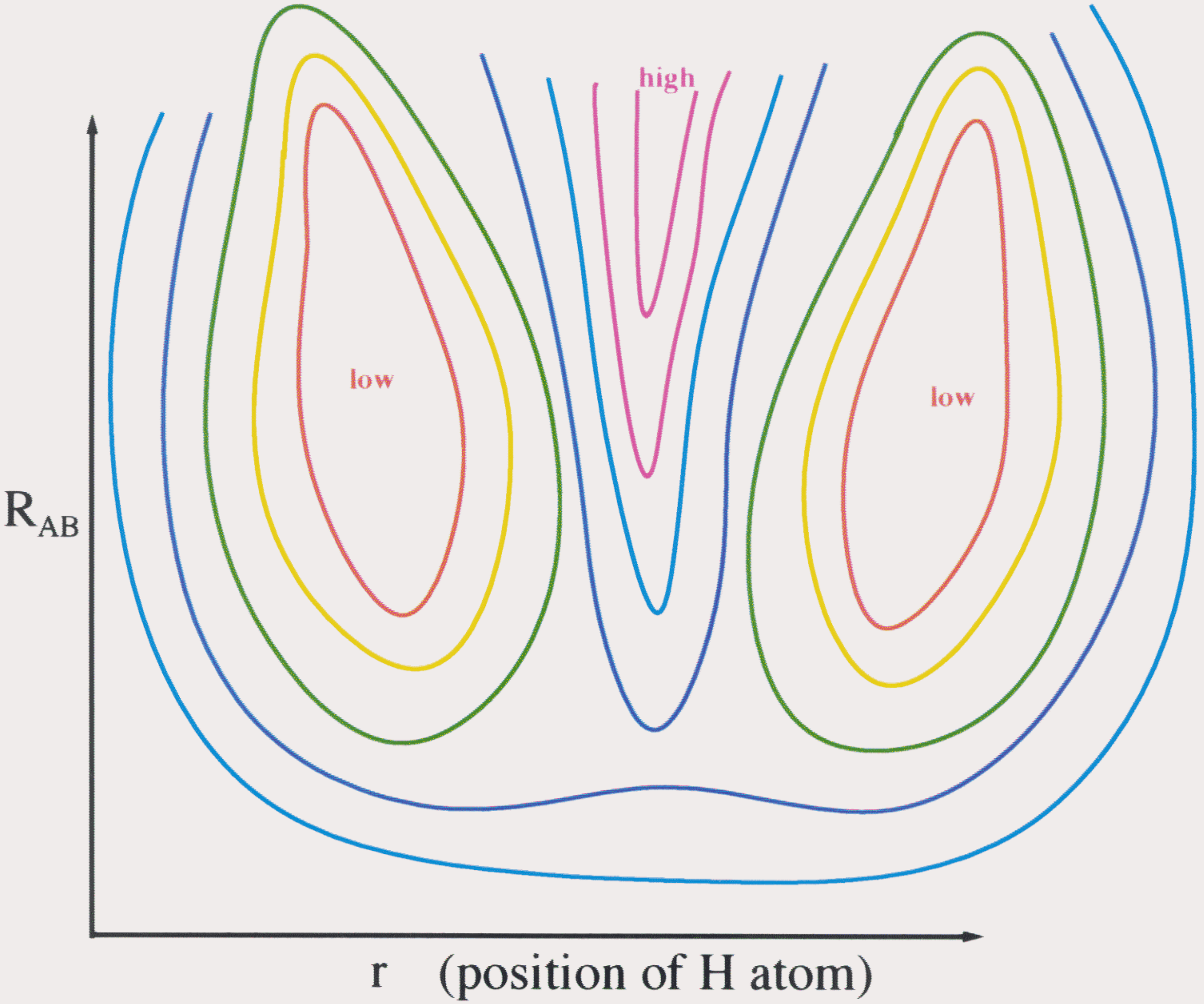


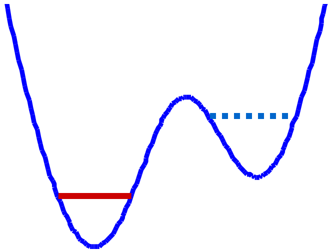
Quantum Effects:

- *Zero-Point Energy*
- *Quantized Energy Levels*
- ***Tunneling***

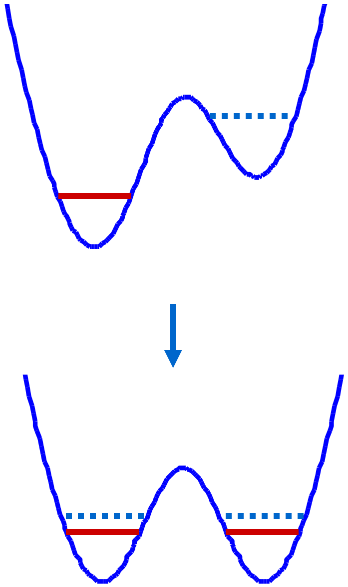
CONTOUR PLOT OF FREE ENERGY



Adiabatic vs. Nonadiabatic (Sharon Hammes-Schiffer, JCT)

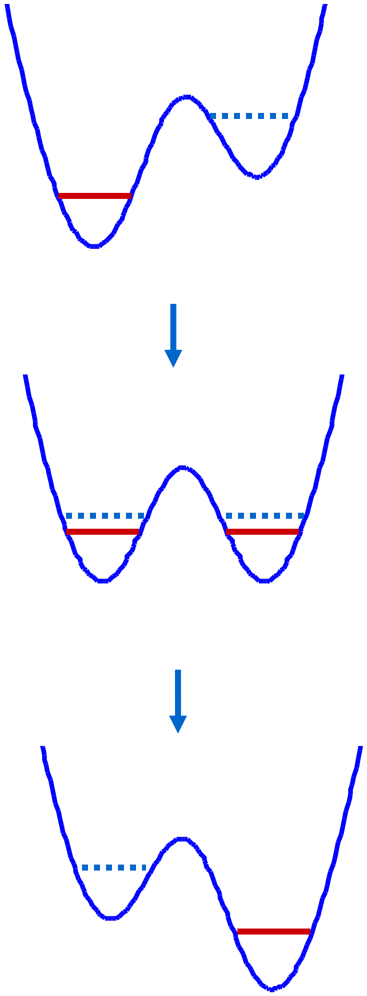


Adiabatic vs. Nonadiabatic (Sharon Hammes-Schiffer, JCT)



Solvent
Fluctuation

Adiabatic vs. Nonadiabatic (Sharon Hammes-Schiffer, JCT)

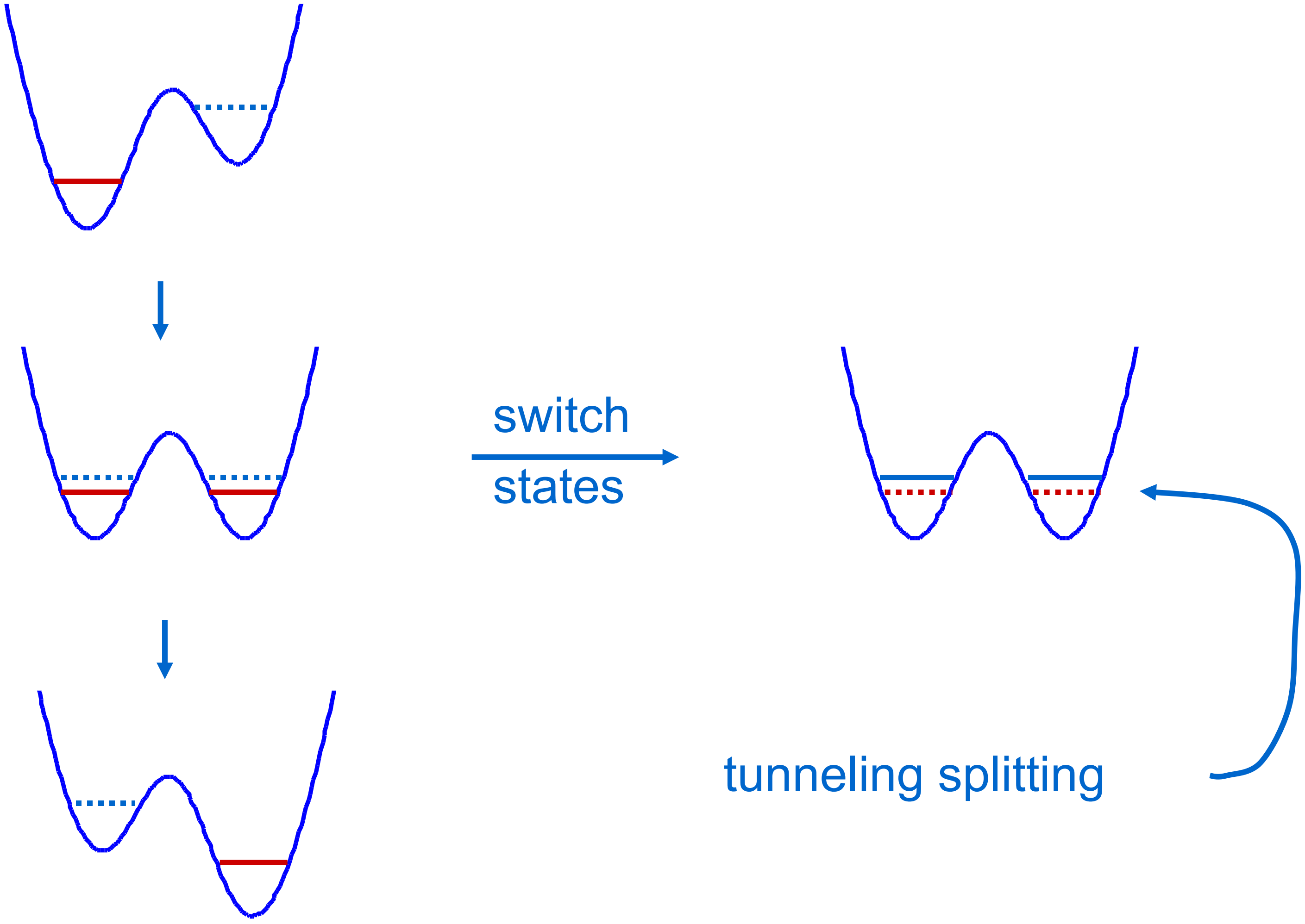


Solvent
Fluctuation

Solvent
Fluctuation

Adiabatic → Reaction

Adiabatic vs. Nonadiabatic (Sharon Hammes-Schiffer, JCT)

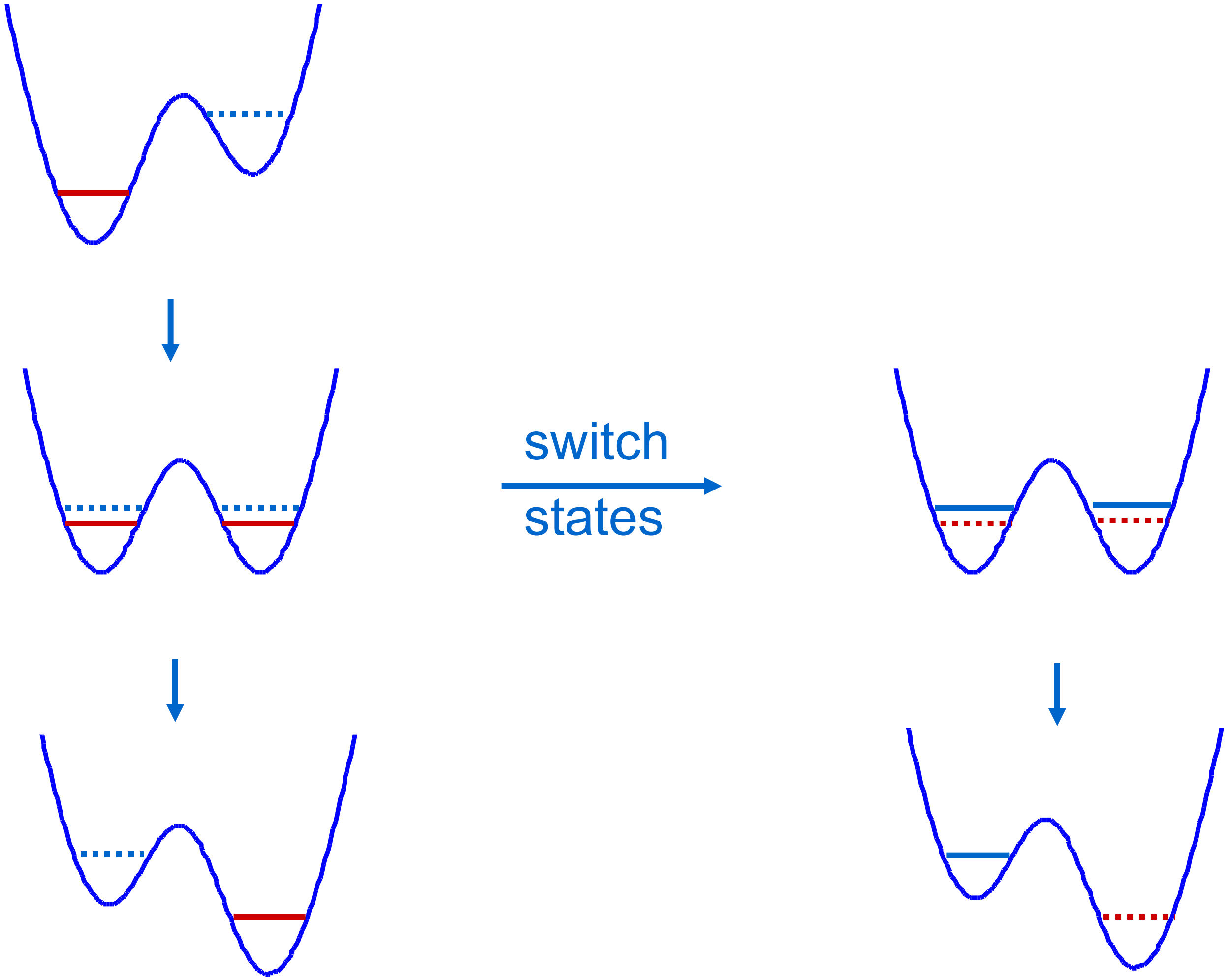


switch states

tunneling splitting

Adiabatic → Reaction

Adiabatic vs. Nonadiabatic (Sharon Hammes-Schiffer, JCT)



switch

states

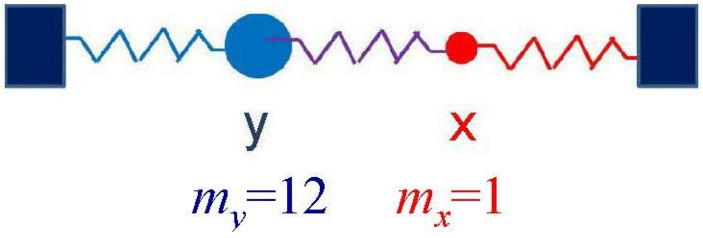
Adiabatic → Reaction

Nonadiabatic → No Reaction

Mixed Quantum-Classical Nuclear Motion

Vibrational Spectra ? JCT, *J. Chem. Phys.* 2023

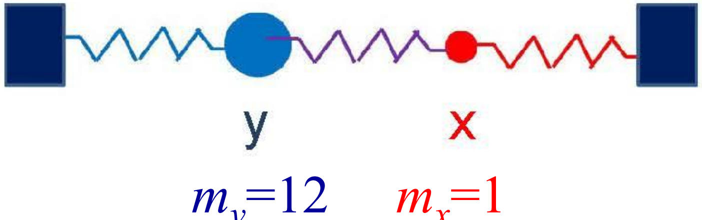
Simple 2 atom linear model



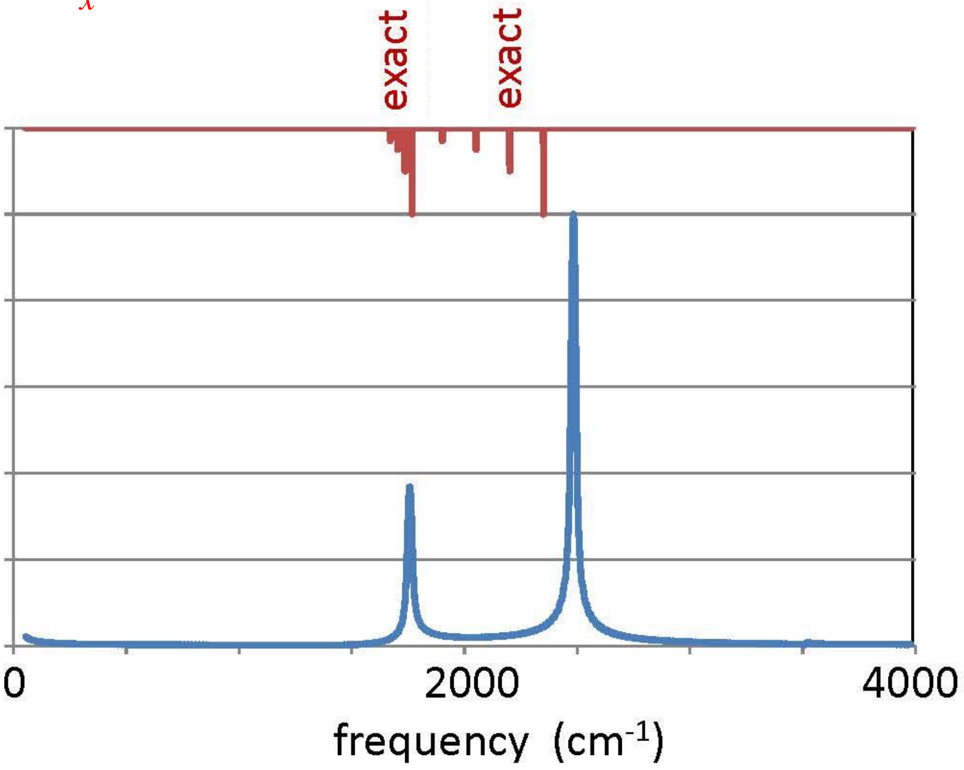
Compute spectra by Fourier Transform

of Dipole Moment Correlation Function

Morse Potentials

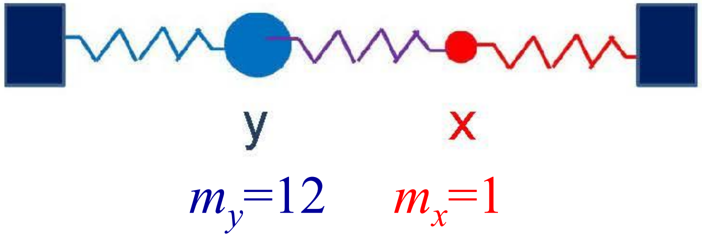


Both atoms classical

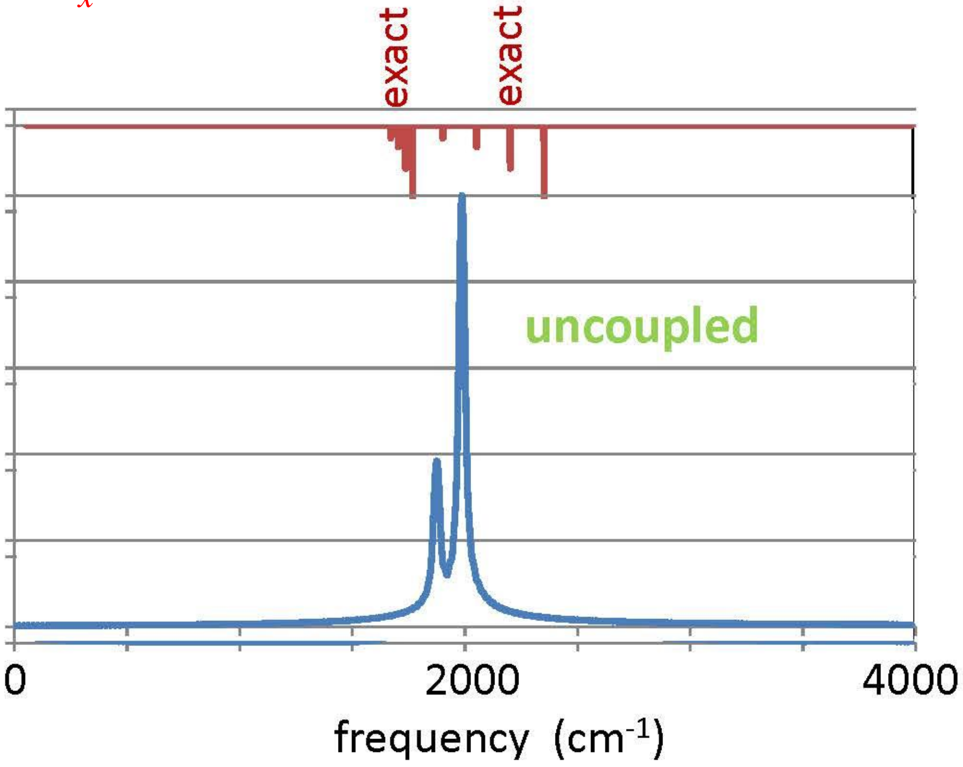


Fourier transform of dipole moment autocorrelation function

Morse Potentials

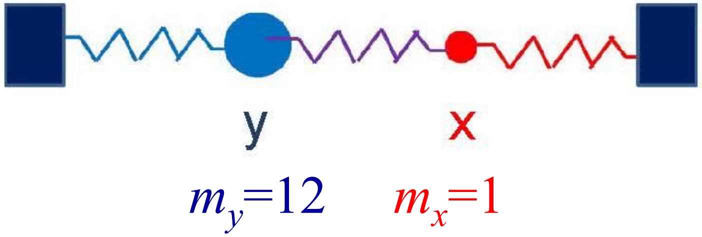


Light atom quantum: Adiabatic

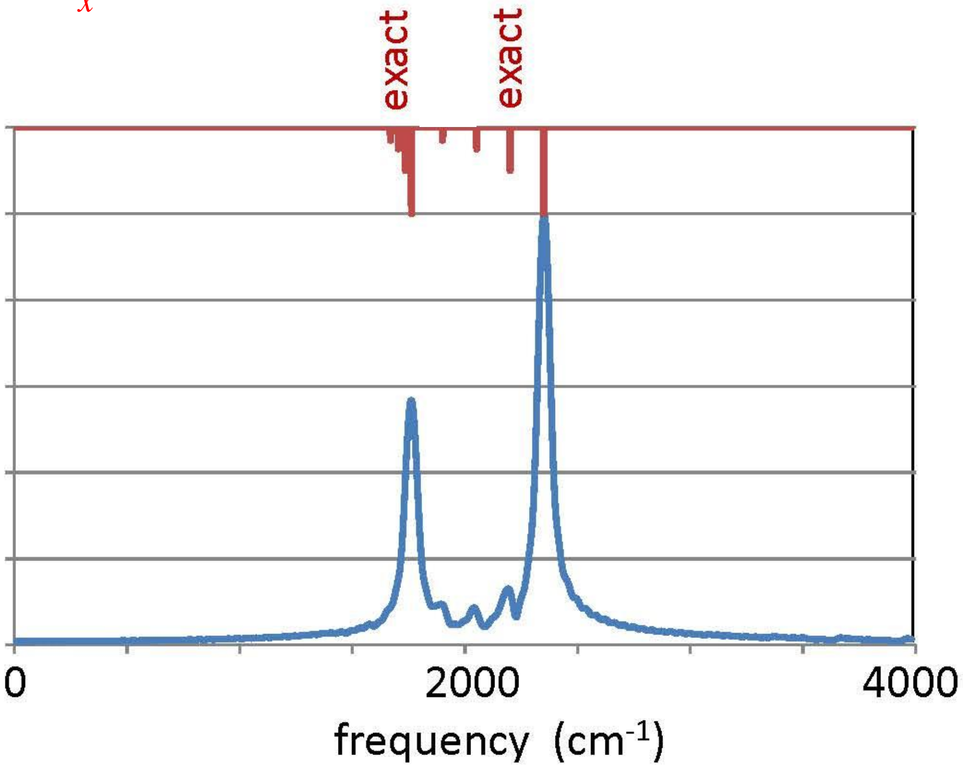


Fourier transform of dipole moment autocorrelation function

Morse Potentials



Light atom quantum: Ehrenfest



Fourier transform of dipole moment autocorrelation function

Conclusions about treating some nuclei quantum, others classical

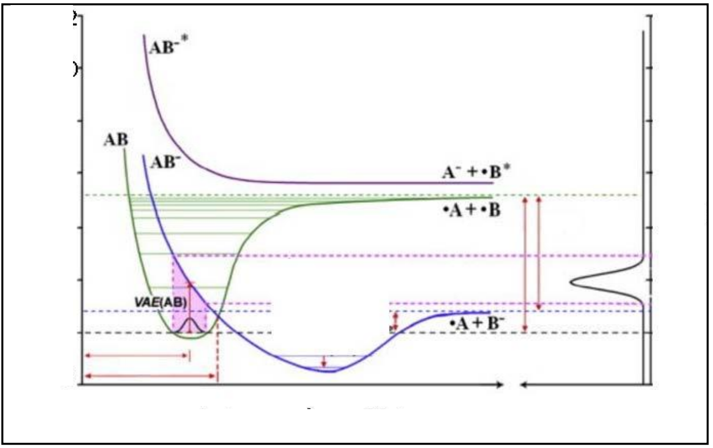
1. Requires nonadiabaticity to achieve coupled motions
   (e.g., normal modes)

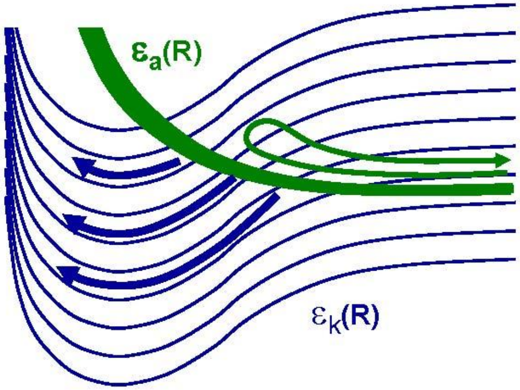
2. True also for electron-nuclear coupled motion, but less
   dramatic because of mass disparities

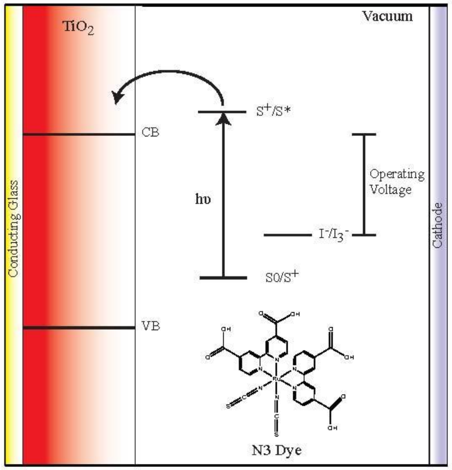
3. Ehrenfest incorporates coupled motion

4. *Surface Hopping is problematical*

electronic continuum ?





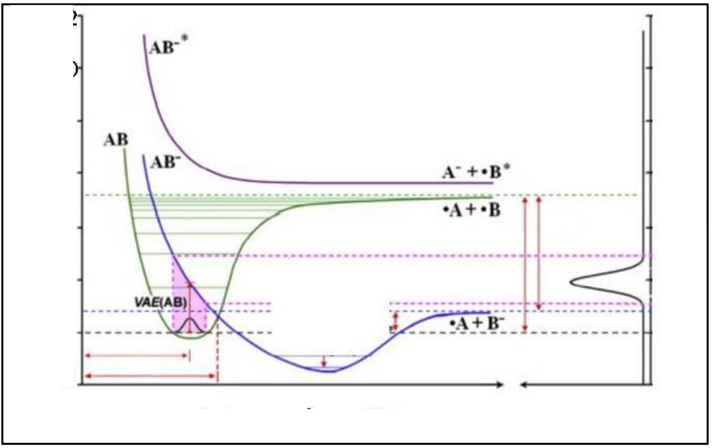


ionization

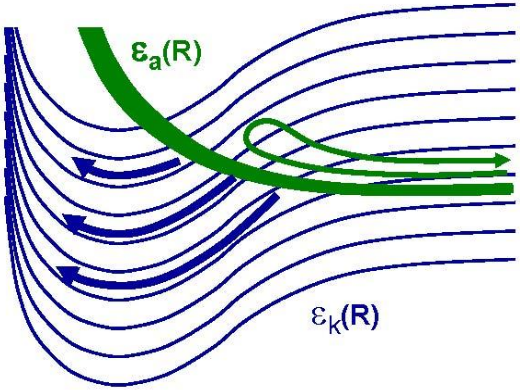
metals

semiconductors

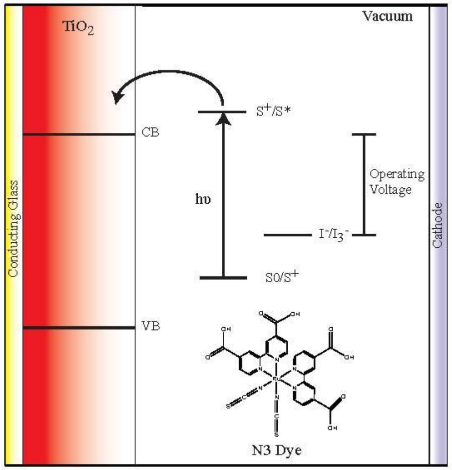
electronic continuum ?



ionization



metals

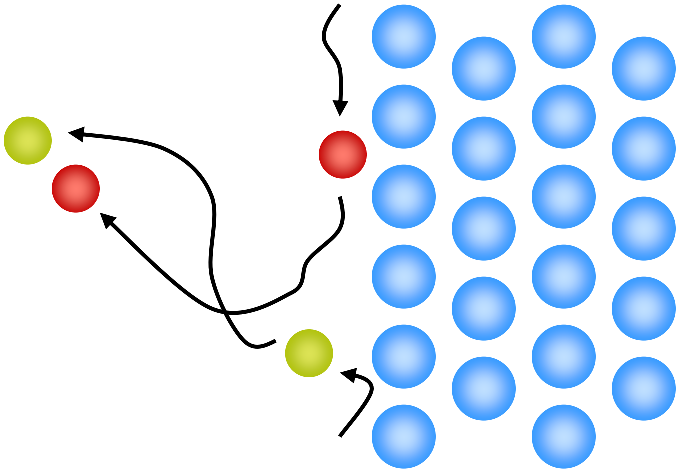


semiconductors

Nonadiabatic dissipation at metal surfaces

Weak Coupling Approx to Ehrenfest:

Molecular Dynamics with Electronic Friction, Martin Head-Gordon, JCT, *J. Chem. Phys*. **103**, 10137 (1995)



$$M\ddot{x} = -\nabla V(x) - \int_0^t dt'\Lambda(t,t')\dot{x}(t') + R(t),$$

friction kernal

fluctuating force

VIBRATIONAL LIFETIME: CO on Cu(100) (ps.)

MODE	**EXPERIMENT**	**CALC (0K)** (*Phonons*)	**CALC(0K)** (*Electrons*)
C – O stretch	2.5 +/- 0.5 (A. Harris et al.)	>100000	3.3 +/- 0.5

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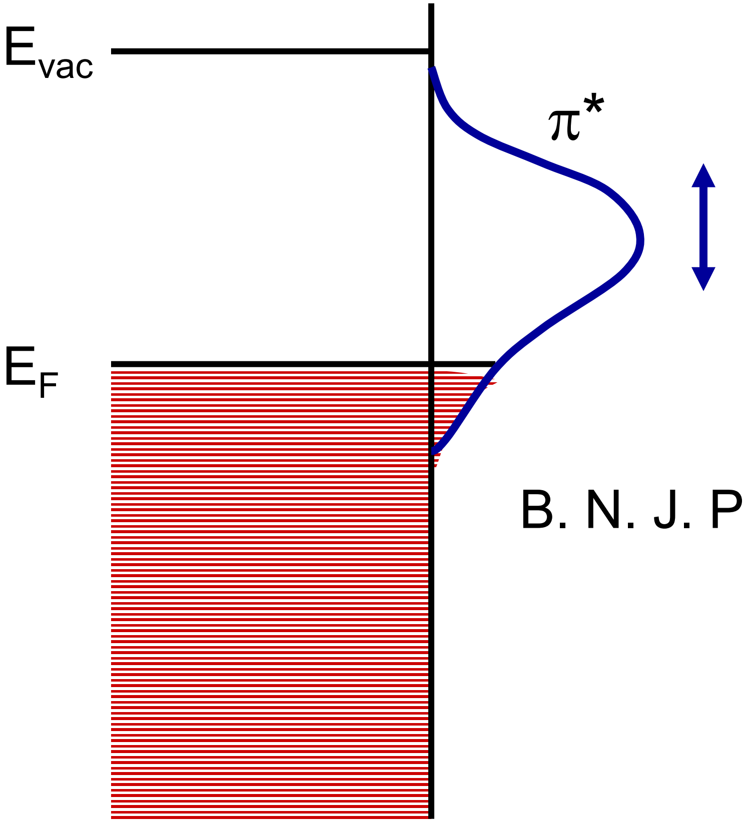
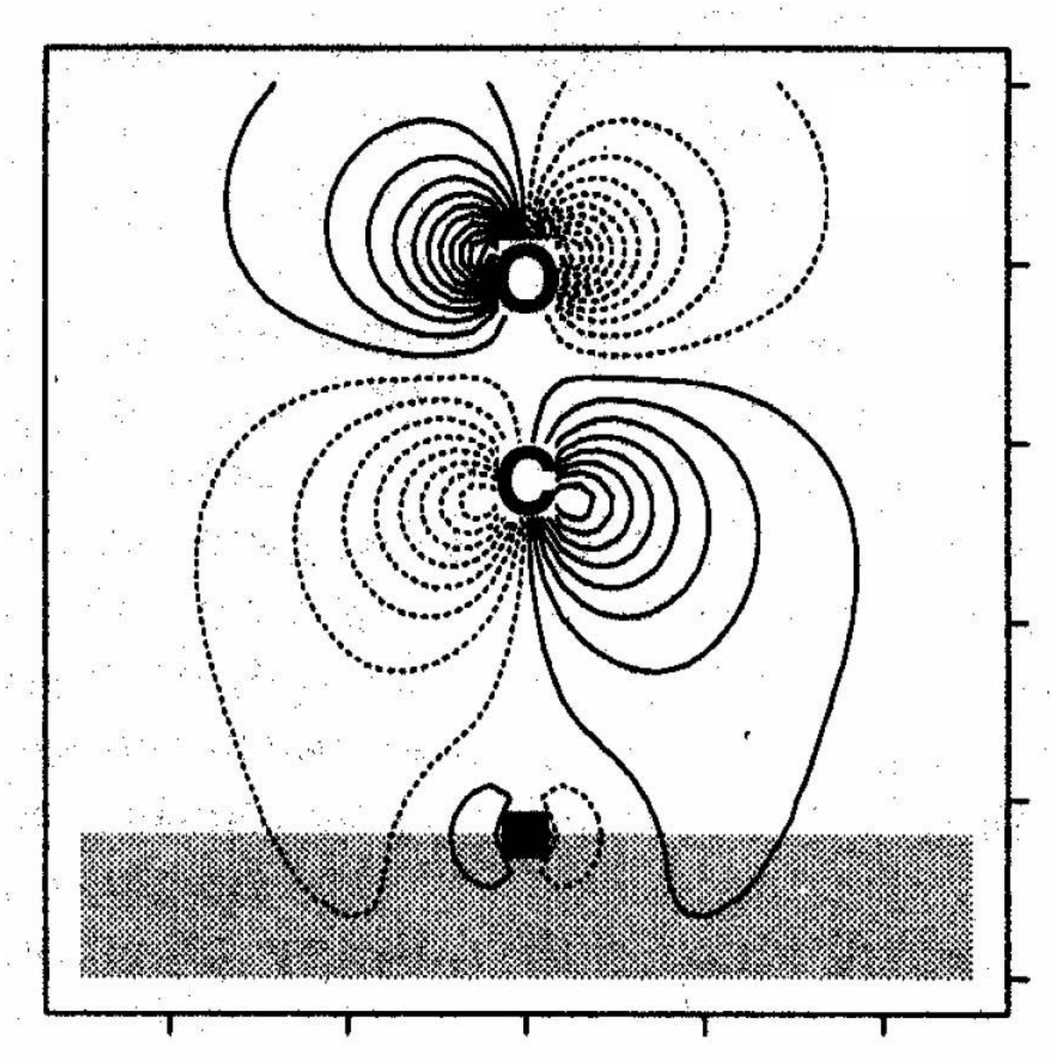


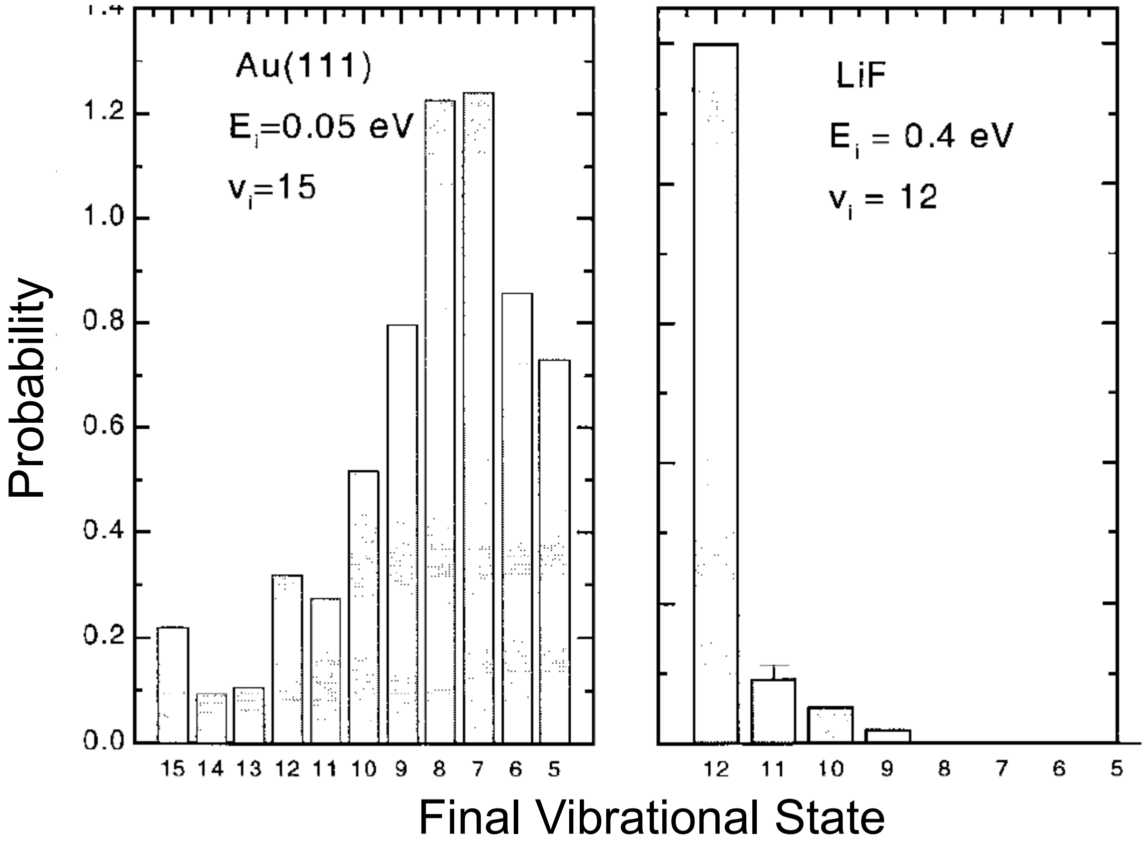
B. N. J. Persson and M. Persson, (1980)

$d\Psi_{HOMO}/dR$ (C -- O Stretch)



Scattering of vibrationally excited NO from Au(111)

electron transfer: strong coupling



Huang, Rettner, Auerbach, Wodtke,*Science* **2000**, *290*, 111.

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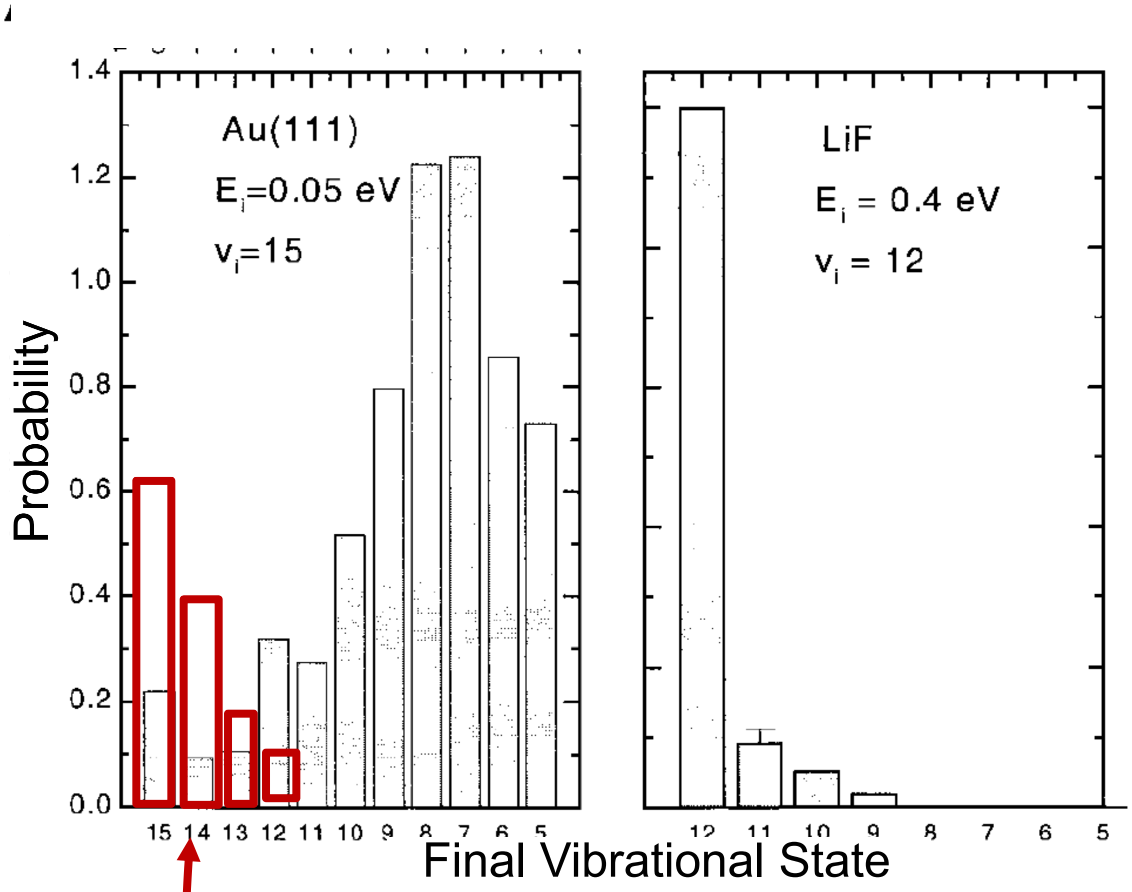


Friction: from my memory !

Friction:

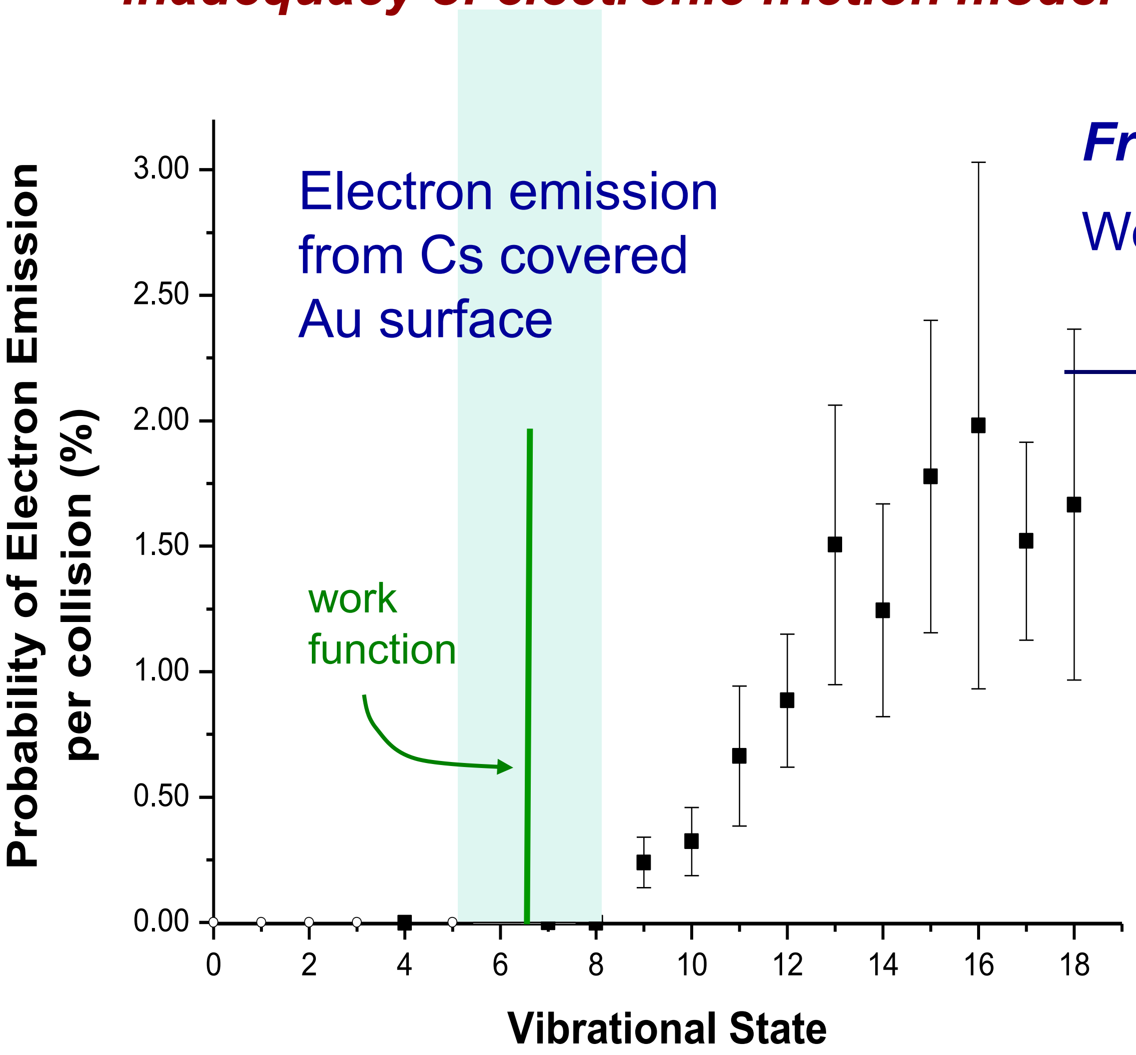
Weak Coupling:

→ Δv □ ± 1

Electronic Friction cannot account for the observed huge energy transfer

Electron Emission:

→ *inadequacy of electronic friction model*



Electron emission from Cs covered Au surface

White, J. D.; Chen, J.; Auerbach, D. J.; Wodtke, A. M. *Nature* **2005**, *433*, 503.

Friction:

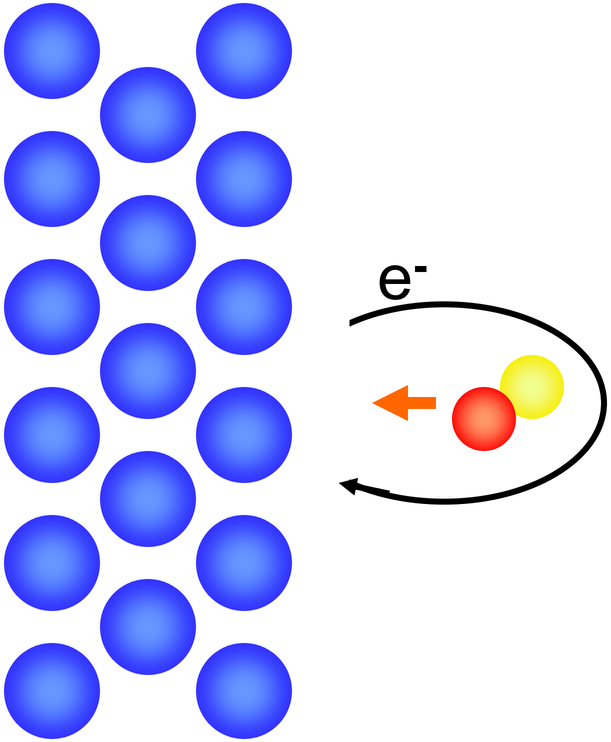
Weak Coupling:

→ $\Delta \nu$ ▯ ± 1

Electronic excitations at metal surfaces?

Inelastic Electron Scattering Picture:

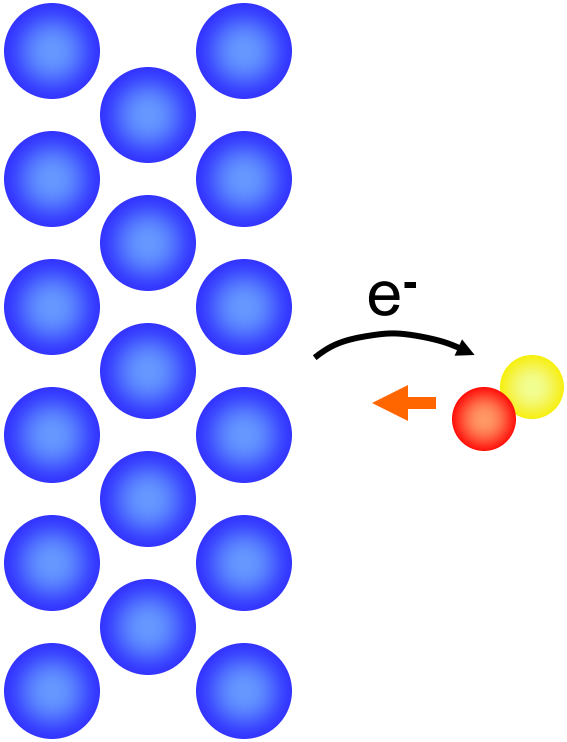
a. Non-Resonant → *friction model*

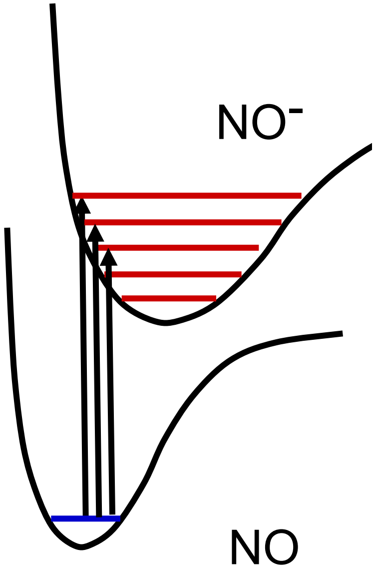


Electronic excitations at metal surfaces?

Inelastic Electron Scattering Picture:

b. Resonant → *transient negative ion*





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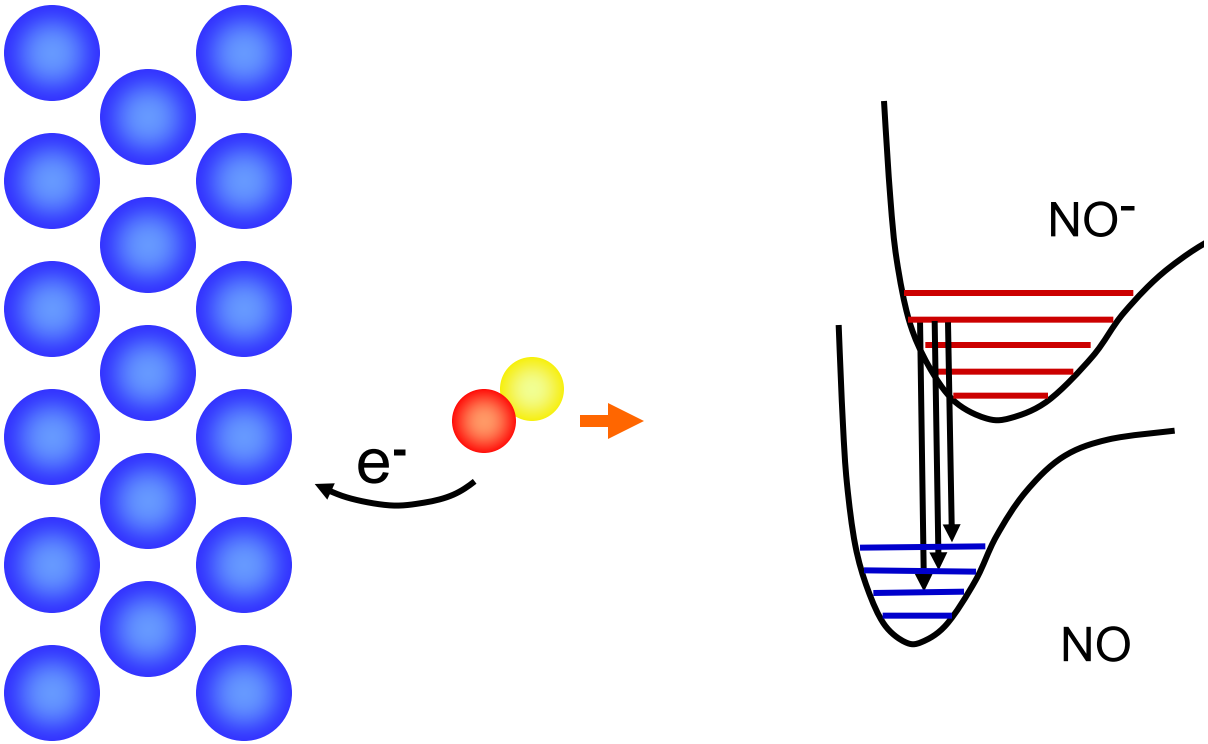
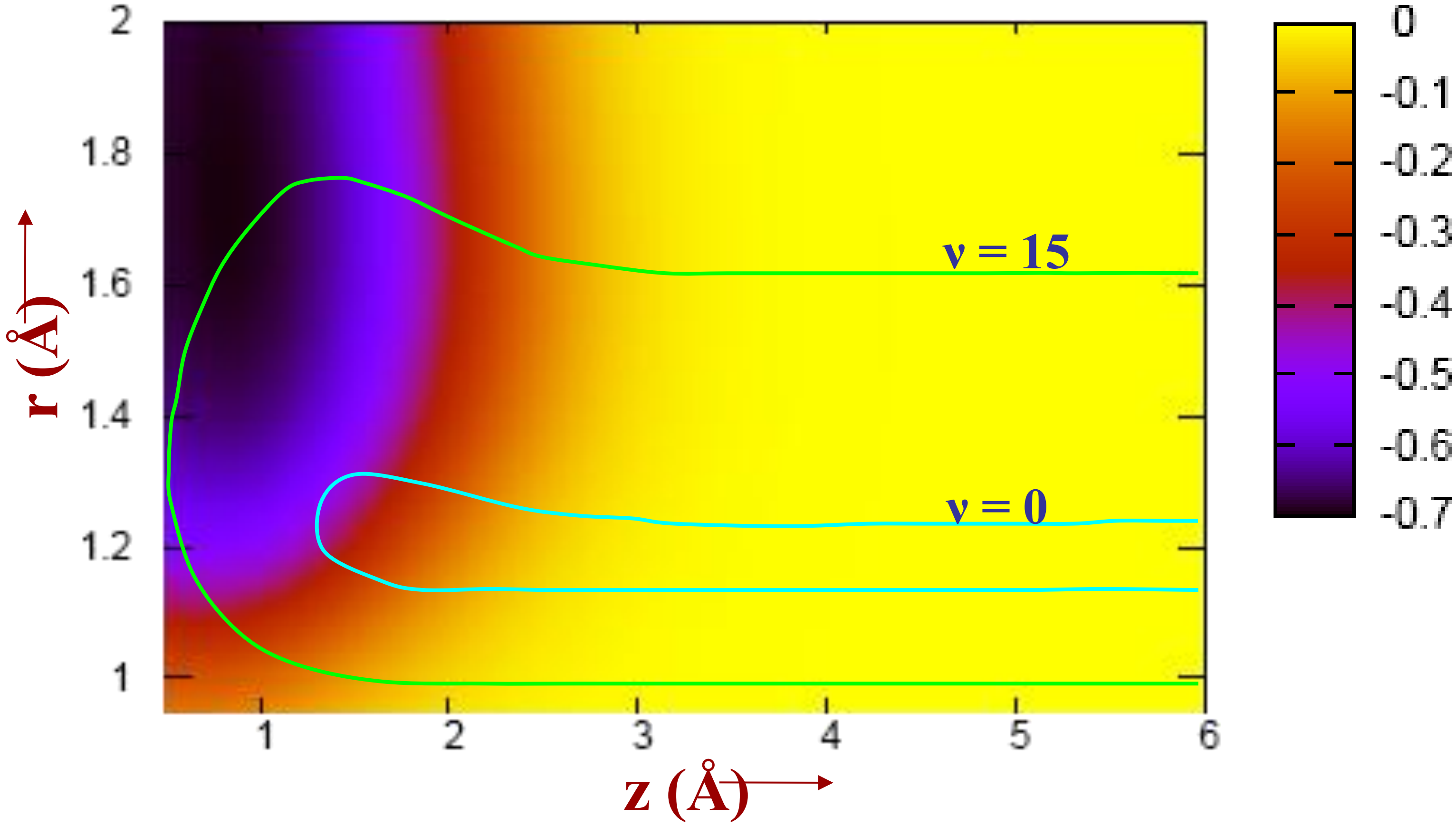


Franck-Condon picture (J. W. Gadzuk)

NO approaching a three-fold site on Au(111)

Ground state charge on NO

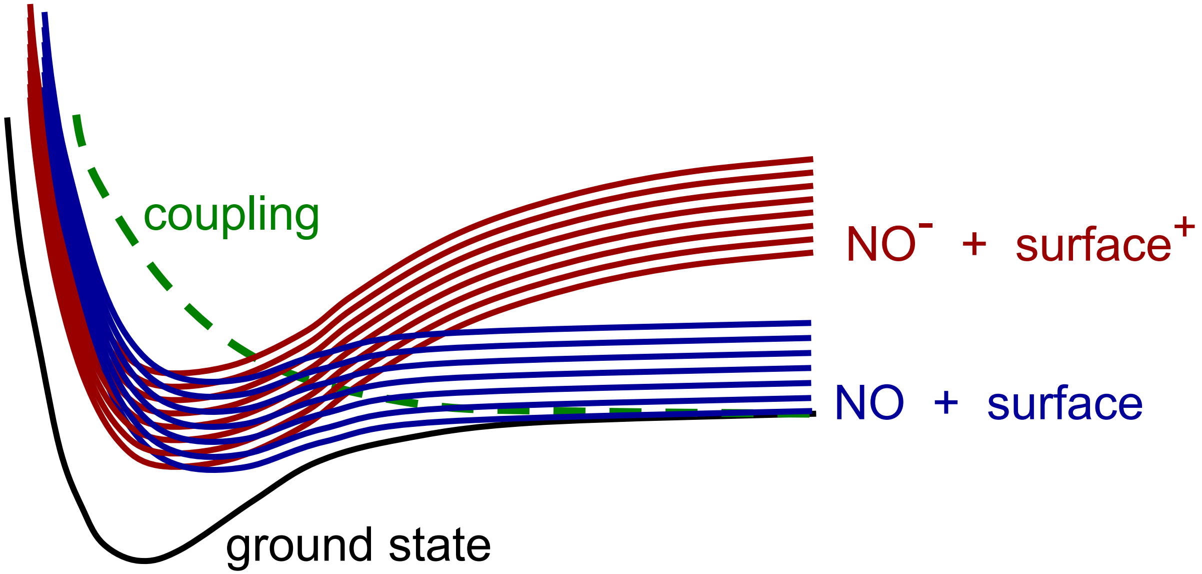
DFT (VASP, PW91)

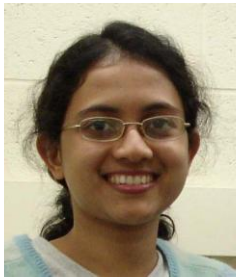


Scattering of Nitric Oxide from a Metal Surface (Gold)

1. Calculations of potential energy surfaces and nonadiabatic couplings? *Newns-Anderson Hamiltonian*
2. Propagation of surface hopping trajectories?

Independent Electron Surface Hopping (IESH)

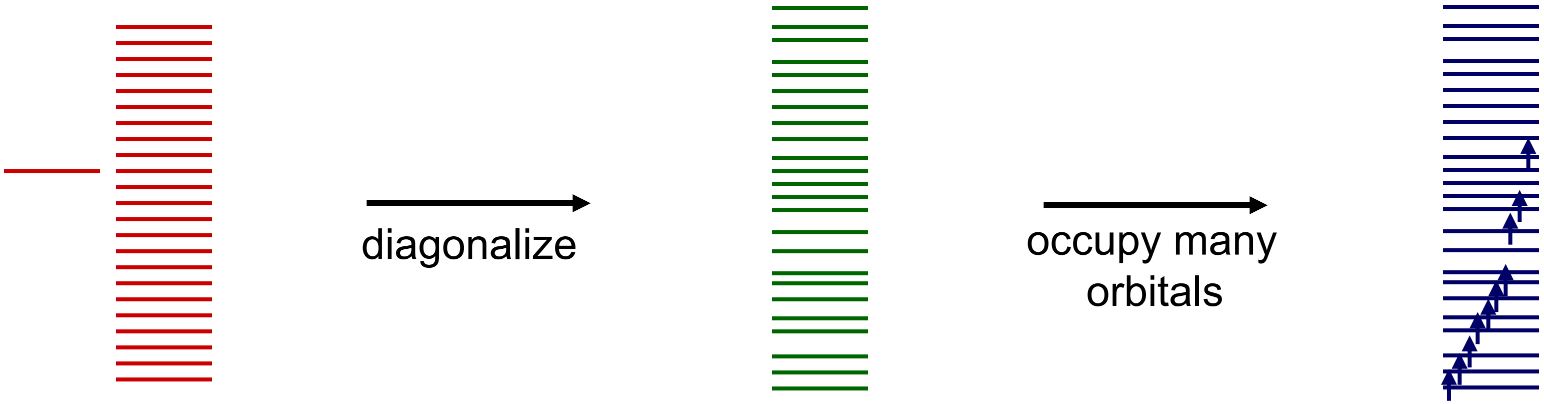




Sharani Roy

Neil Shenvi

1. Map onto Anderson-Newns (tight binding) picture:



diagonalize

occupy many orbitals

1-el diabatic orbitals

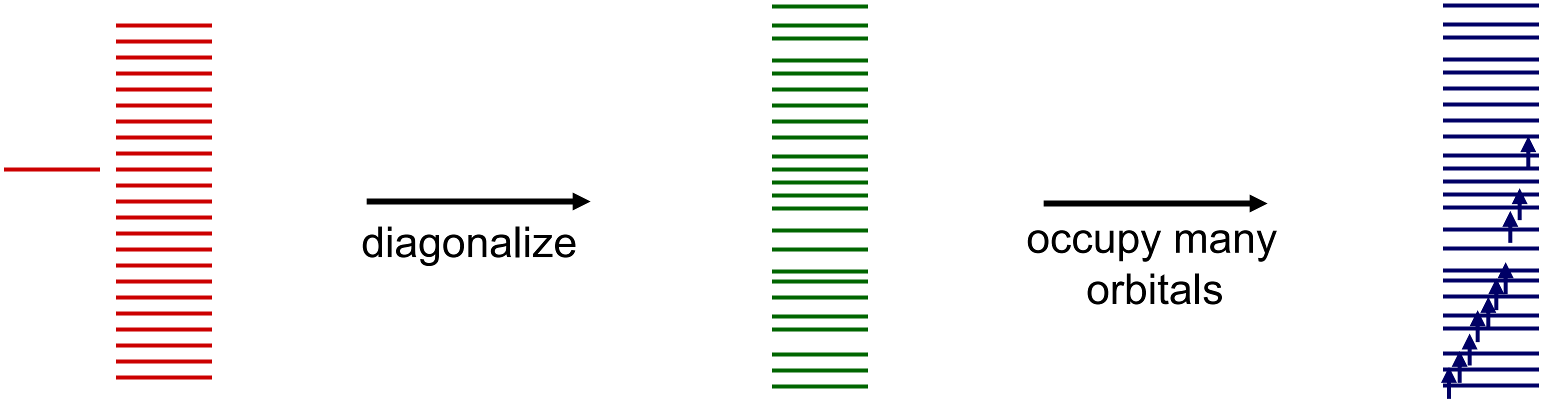
$1 + 60$

1-el adiabatic orbitals

61

many-el product wave fn.

1. Map onto Anderson-Newns (tight binding) picture:



diagonalize

occupy many orbitals

1-el diabatic orbitals

1 + 60

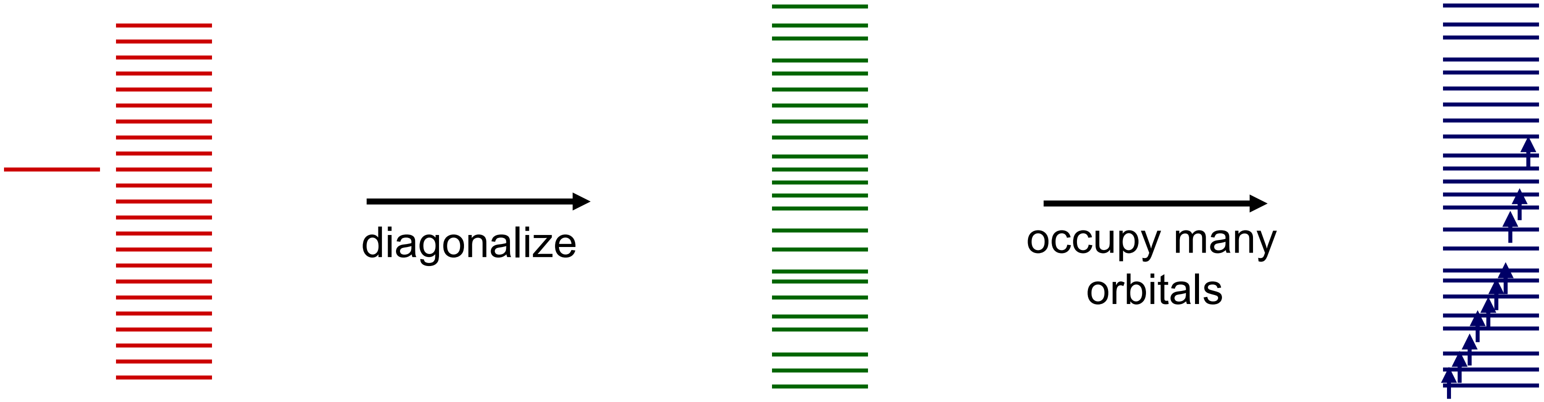
1-el adiabatic orbitals

61

many-el product wave fn.

30 electrons → ~ 10^{17} states

1. Map onto Anderson-Newns picture:



diagonalize

occupy many orbitals

1-el diabatic orbitals

1-el adiabatic orbitals

many-el product wave fn.

2. Evolve many-electron wave function along trajectory:

initial many -electron wave fn (eg, ground state)

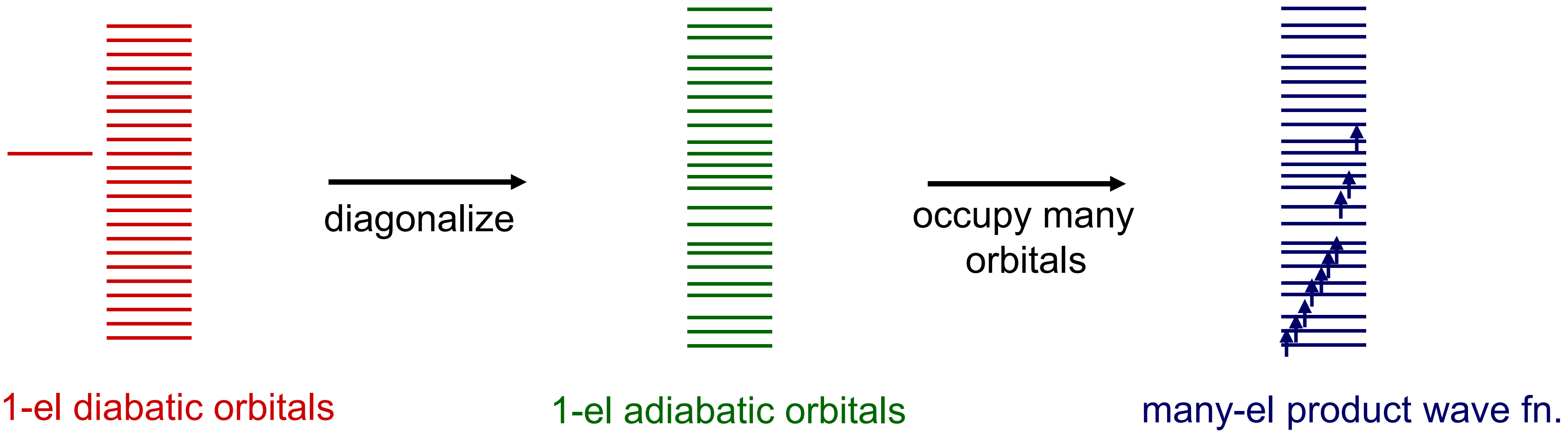
→

each orbital evolves into linear combination of adiabatic orbitals

→

many-el wave fn at any time is a specific occupation of these evolving mixed orbitals

1. Map onto Anderson-Newns picture:



2. Evolve many-electron wave function along trajectory:

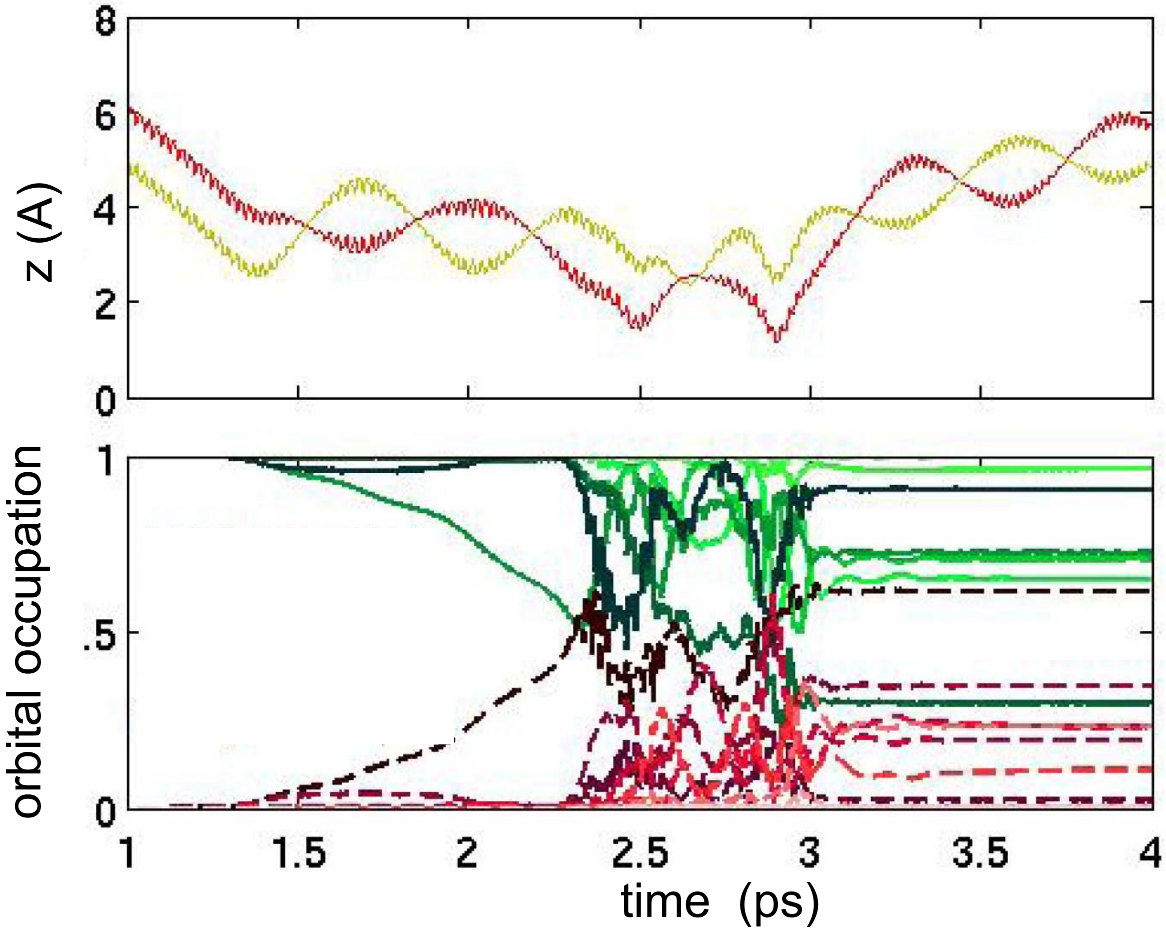
initial many -electron wave fn (eg, ground state) → each orbital evolves into linear combination of adiabatic orbitals → many-el wave fn at any time is a specific occupation of these evolving mixed orbitals

3. Fewest Switches Surface Hop among adiabatic orbitals

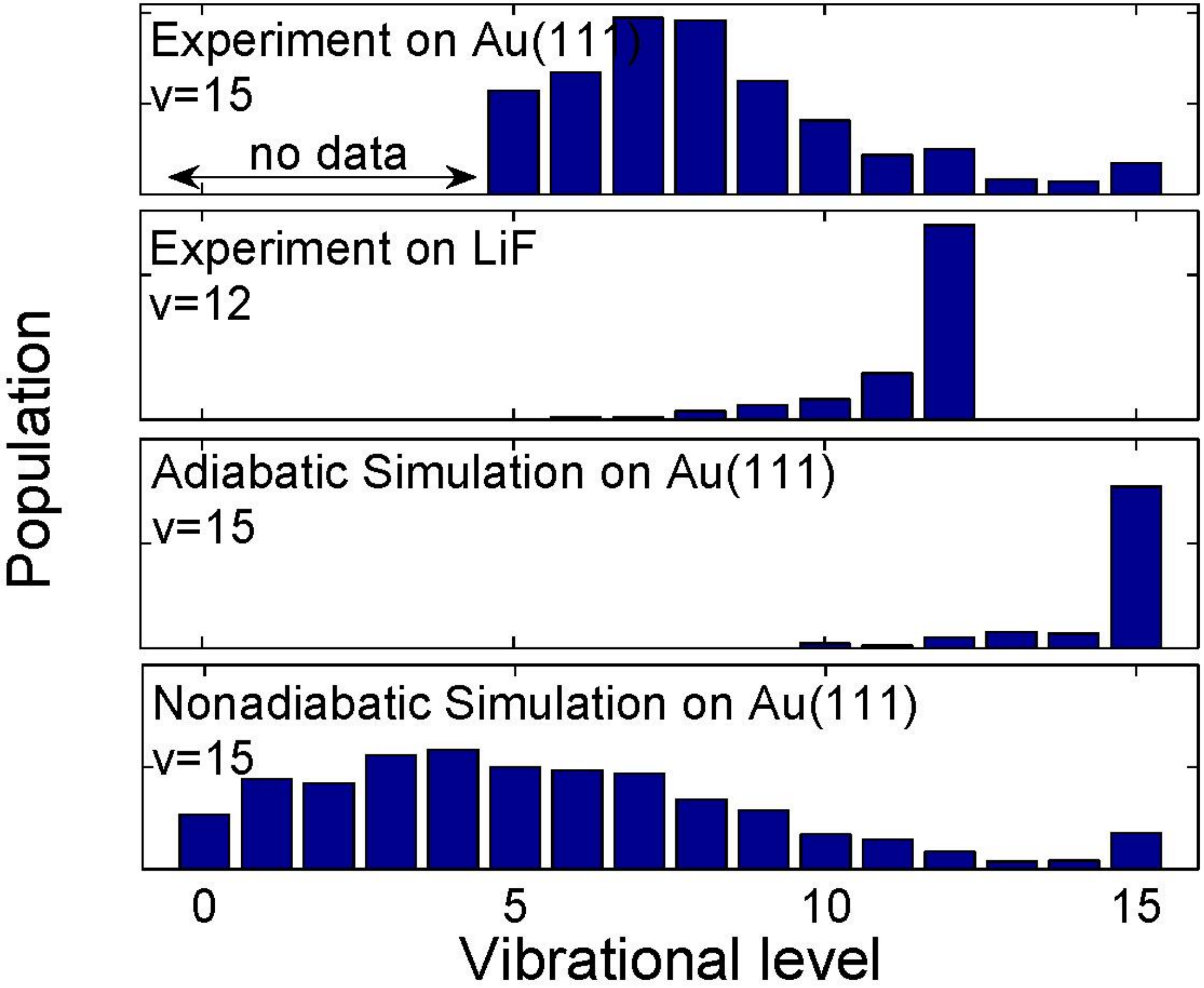
each electron independently

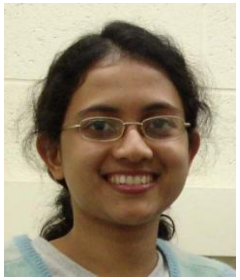
NO(v=15) scattered from Au(111) (*surface hopping trajectory*)

132 moving Au atoms, accurate phonon spectrum, periodic boundaries, etc.



~ 100 surface hops typically encountered

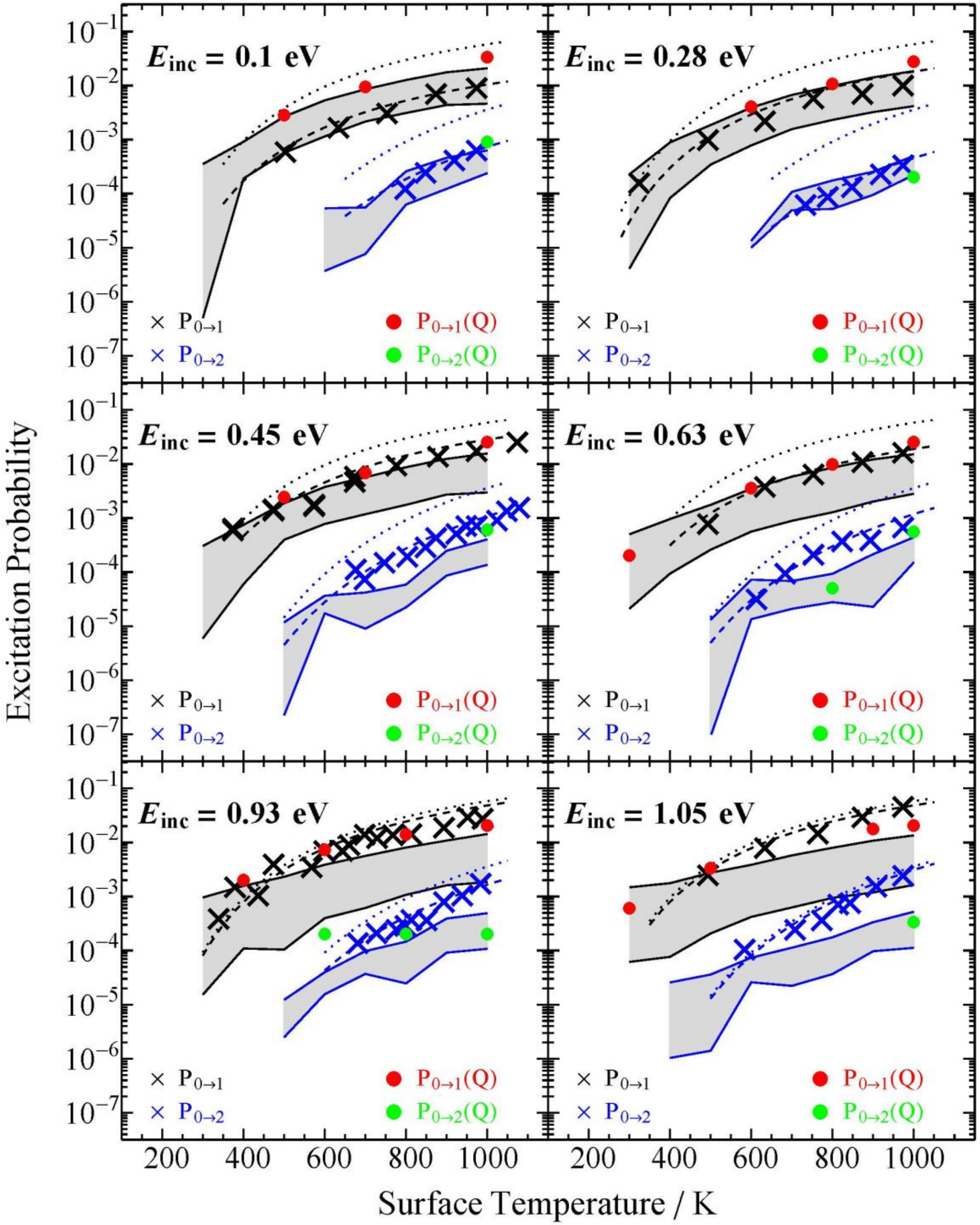




Sharani Roy

Neil Shenvi

Expts: Huang, Rettner, Auerbach, Wodtke,
Science **2000**, *290*, 111.



NO(v=0) scattered from Au(111)

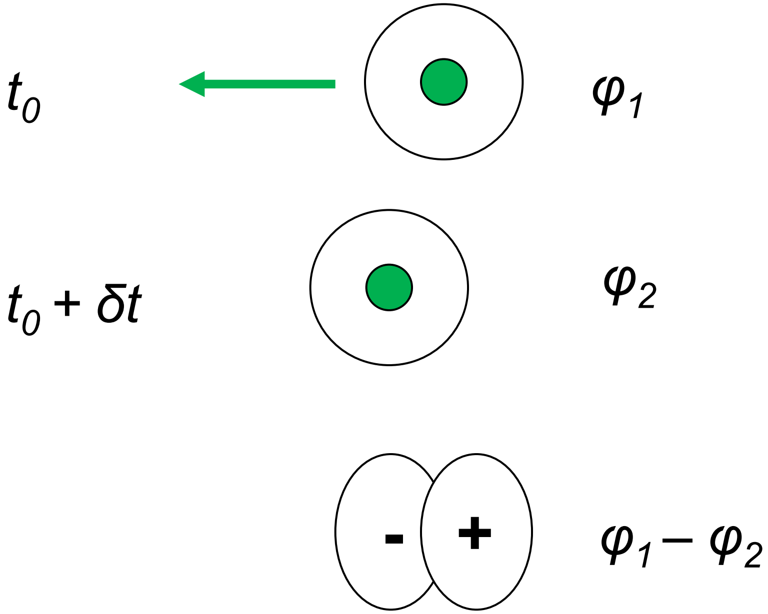
xxxx $P_{0 \to 1}$

xxxx $P_{0 \to 2}$

Sascha
Kandratsenka

January 14, 2026

Translational and Angular Momentum Conservation ?



moving nucleus but
stationary electron

$$\varphi(z) \longrightarrow \varphi(z)\exp(i\, k_e\, z)$$

Translational and Angular Momentum Conservation ?

Direct Dynamics in Cartesian coordinates:

E_{trans}* and *J are not conserved

This is true for all nonadiabatic (Cartesian) direct dynamics methods that are based on separation of “fast” and “slow” particles, where energies and couplings of the fast particles are computed at fixed positions of the slow particles, and motion of the slow coordinates is governed by nonadiabatic coupling.

Examples:

Ehrenfest (mean field)

Surface Hopping

Exact Factorization

Nonadiabatic wave packet evolution

Translational and Angular Momentum Conservation ?

Some Strategies:

- Electron translational factors (Subotnik et al. 2023)

$$\varphi\,(z) \longrightarrow \varphi(z)\,\mathrm{exp}(\,i\,k_e\,z)$$

- Direct Dynamics with approximations to nonadiabatic couplings that depend only on internal coordinates
- Projection Operator to remove overall translation and rotation from nonadiabatic couplings (Truhlar et al. 2020)
- Fitted potentials and nonadiabatic couplings that depend only on internal coordinates. e.g., machine learning

VISTA: Virtual International Seminar on Theoretical Advancements

Thanks to **Alexey Akimov** for inaugurating and leading ***VISTA***:

100 Seminars!!