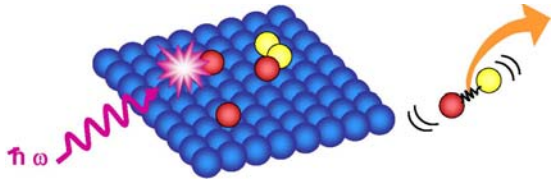


Chemical Dynamics

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

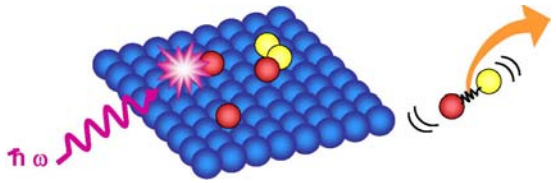
VIII. Beyond Born Oppenheimer

IX. Ehrenfest Dynamics

X. Surface Hopping

XI. Dynamics at Metal Surfaces

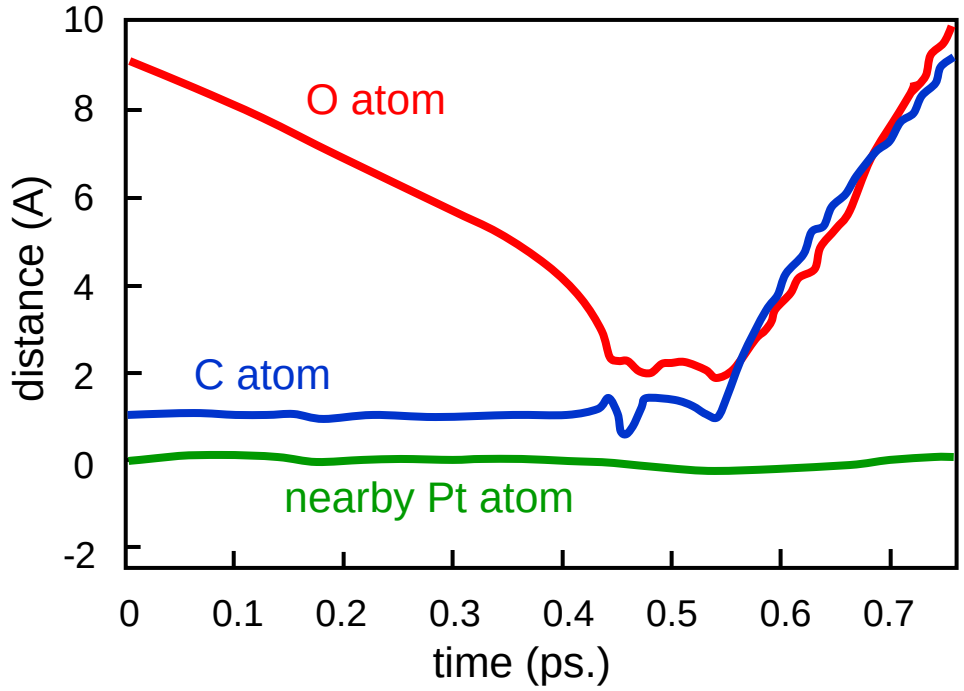
XII. Mixed Quantum-Classical Nuclear Dynamics

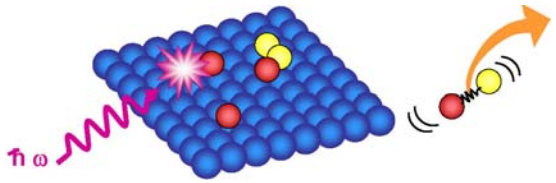


XI. Dynamics at Metal Surfaces

Molecular dynamics simulation of the reaction of a gas-phase oxygen atom with a carbon atom adsorbed on platinum (111)

$$O_{(gas)} + C_{(ads)} \longrightarrow CO_{(gas)}$$





XI. Dynamics at Metal Surfaces

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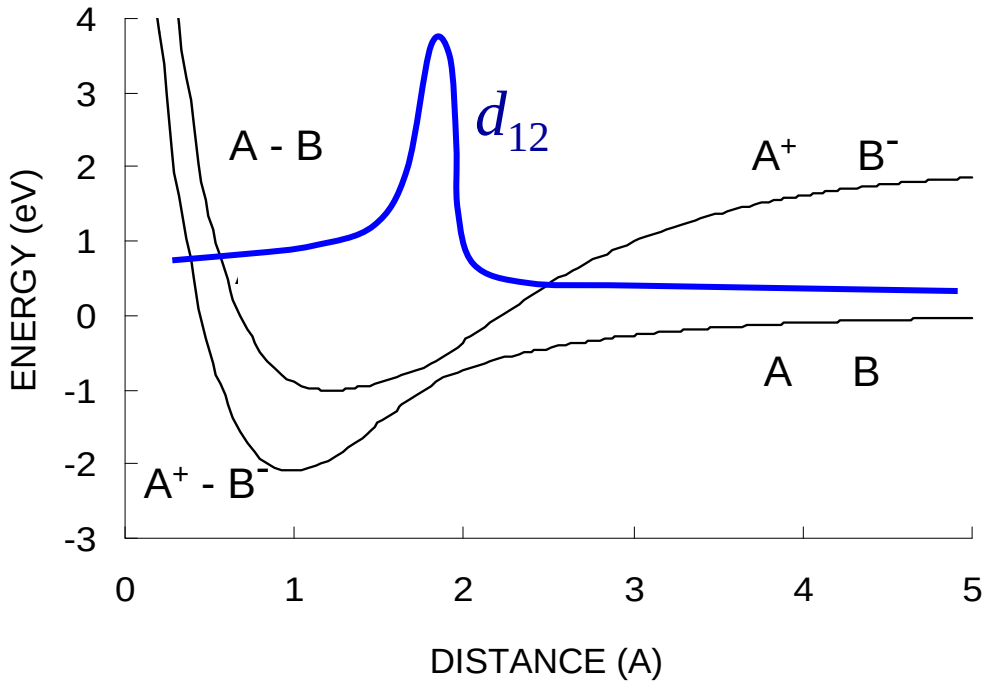
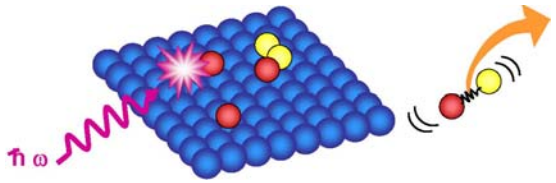
Gas Phase
Molecular Collisions



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

Massey Criterion: $\frac{|\hbar \dot{x} d_{12}|}{|E_2 - E_1|} << 1$ → Adiabatic



XI. Dynamics at Metal Surfaces

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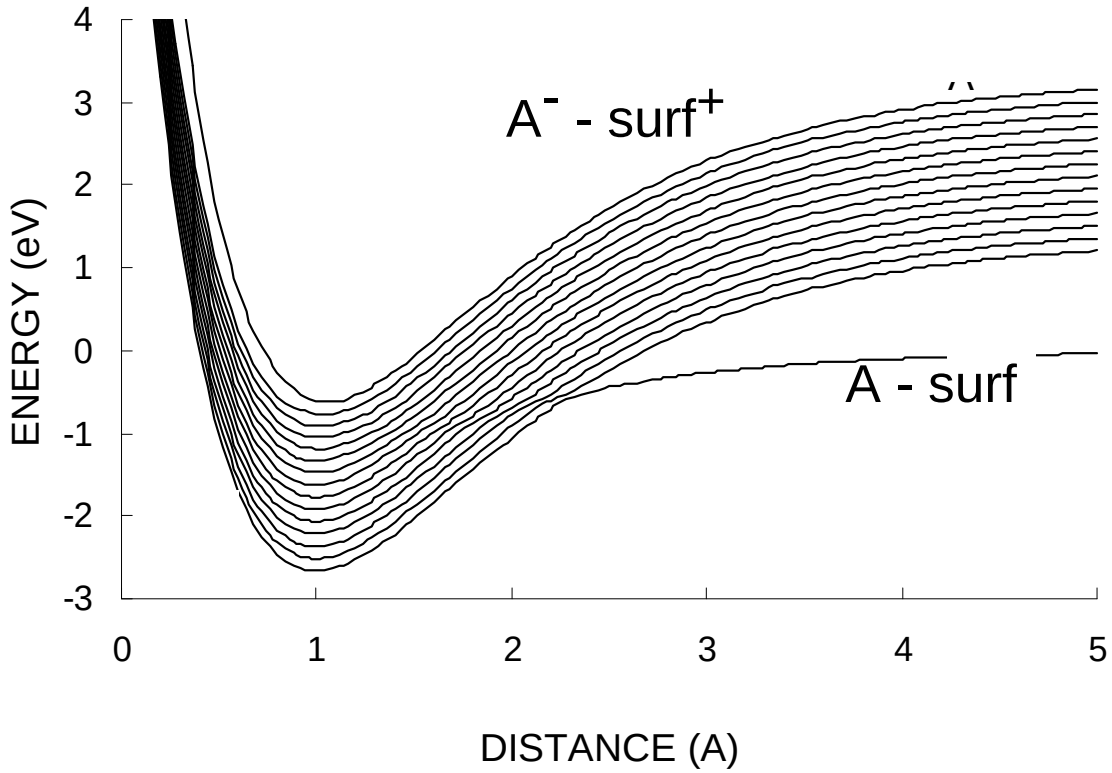
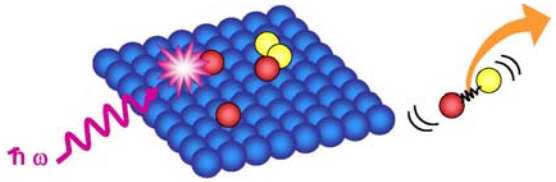
Molecule at Metal Surface:



Massey Criterion:

$$\frac{|\hbar \dot{x} d_{12}|}{|E_2 - E_1|} << 1$$

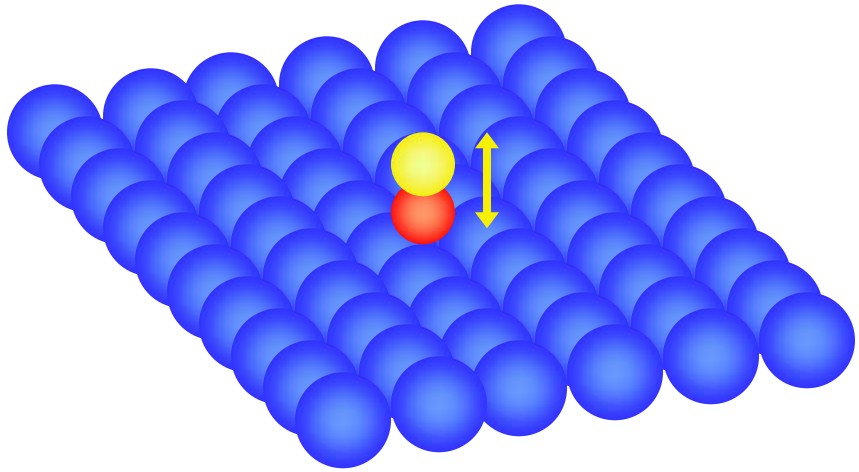
→ Adiabatic



XI. Dynamics at Metal Surfaces

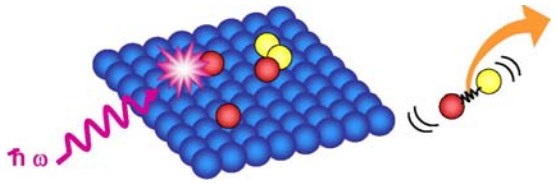
Vibrational Lifetime of CO on Cu(100)

$v = 1 \longrightarrow v = 0$



Classical Molecular Dynamics: $\tau \geq 10^{-3}\ s.$

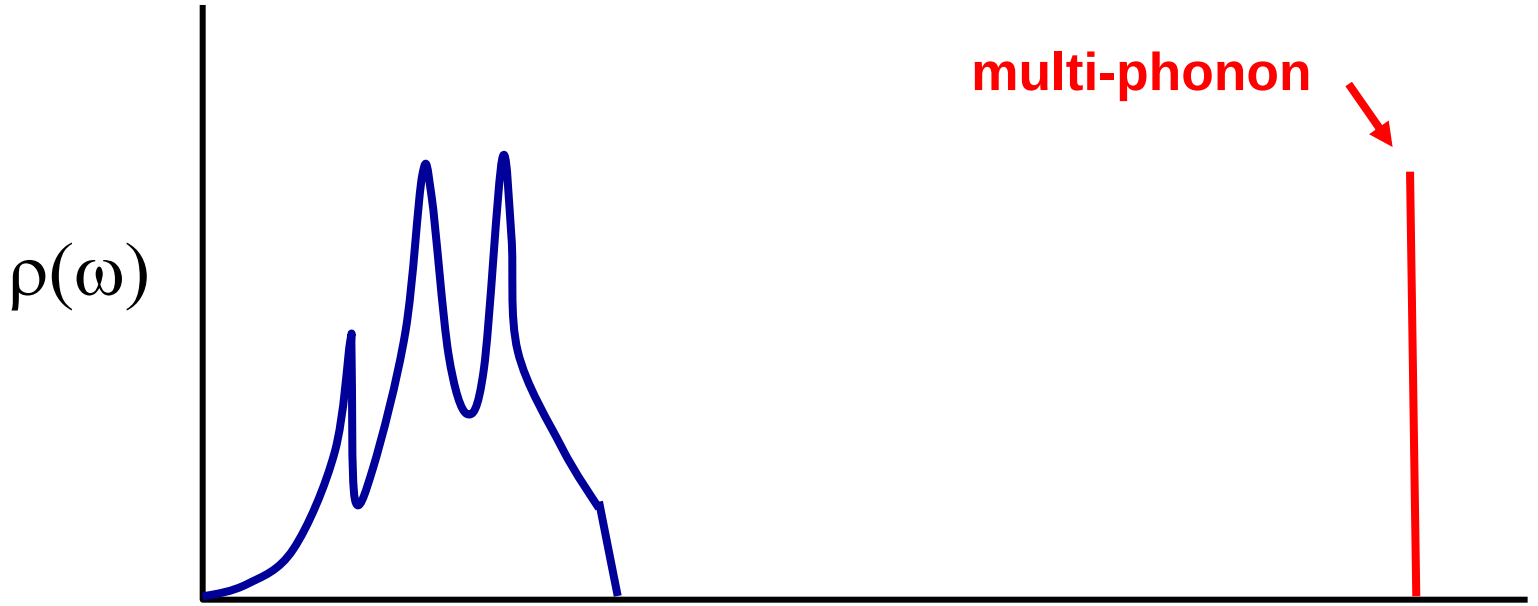
QM Perturbation Theory: $\tau \approx 10^{-3}\ s.$



XI. Dynamics at Metal Surfaces

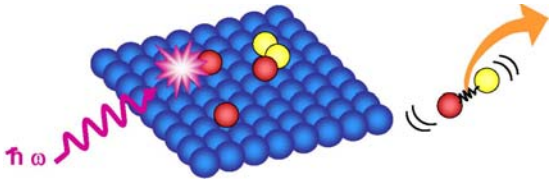
Vibrational Relaxation: T_1

$v = 1 \rightarrow v = 0$



CO: ω = 2107 cm^{-1}

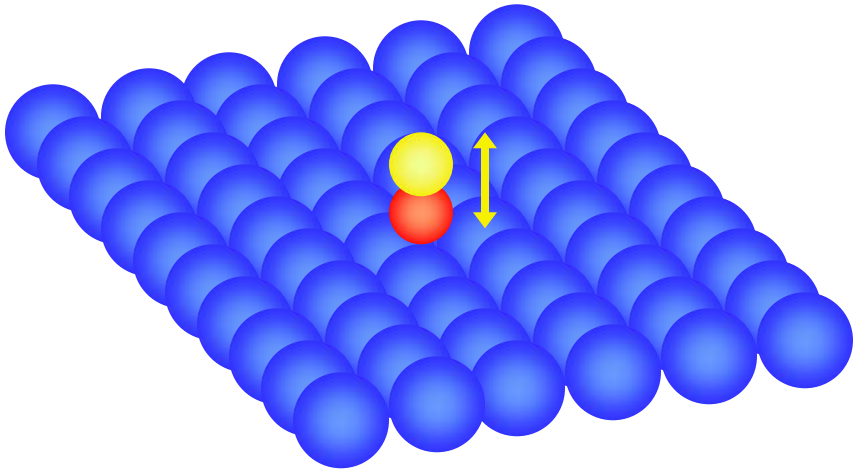
Cu: ω_D = 239 cm^{-1}



XI. Dynamics at Metal Surfaces

Vibrational Lifetime of CO on Cu(100)

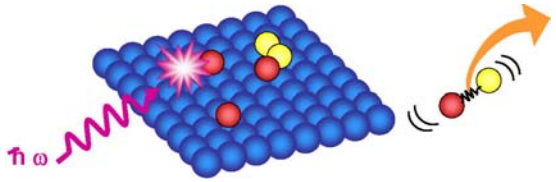
$v = 1 \longrightarrow v = 0$



Classical Molecular Dynamics: $\tau \geq 10^{-3}\ s.$

QM Perturbation Theory: $\tau \approx 10^{-3}\ s.$

Experiment (A. Harris et al.): $\tau = 2.5 \text{x} 10^{-12}\ s.$



XI. Dynamics at Metal Surfaces

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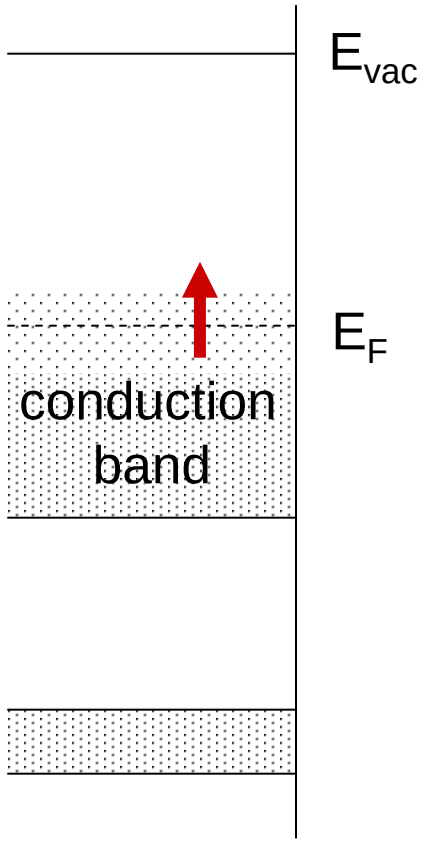
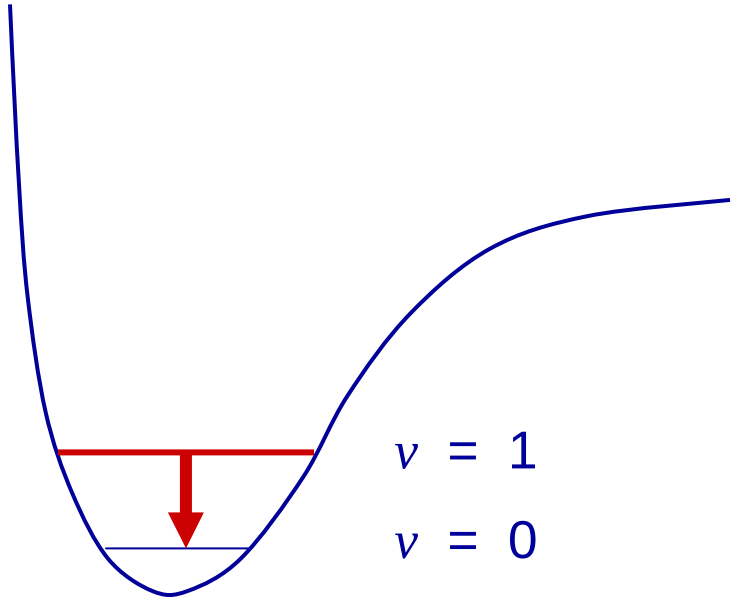
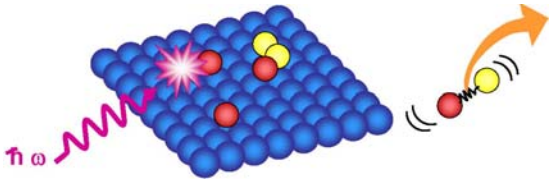
Vibrational De-excitation via Electron-Hole Pairs

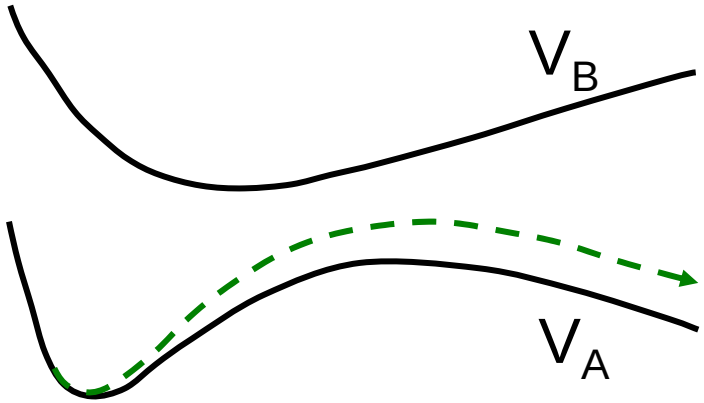






XI. Dynamics at Metal Surfaces

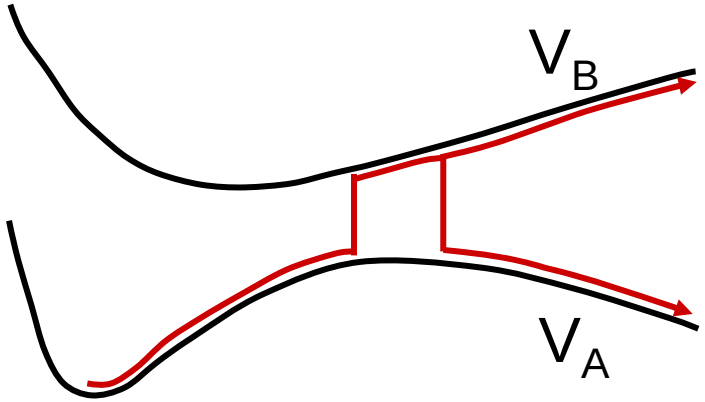
MIXED QUANTUM-CLASSICAL STRATEGIES FOR INCLUDING QUANTUM BACK-REACTION



Ehrenfest

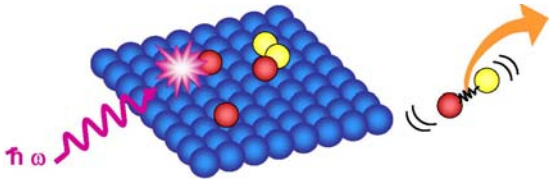
(self-consistent field)

electronic friction



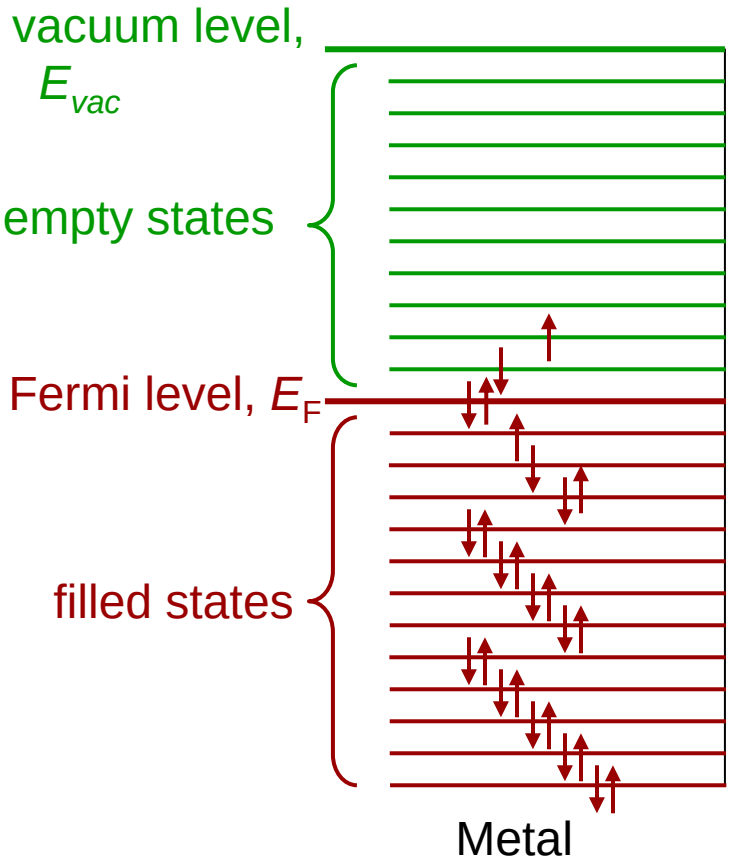
Surface-Hopping

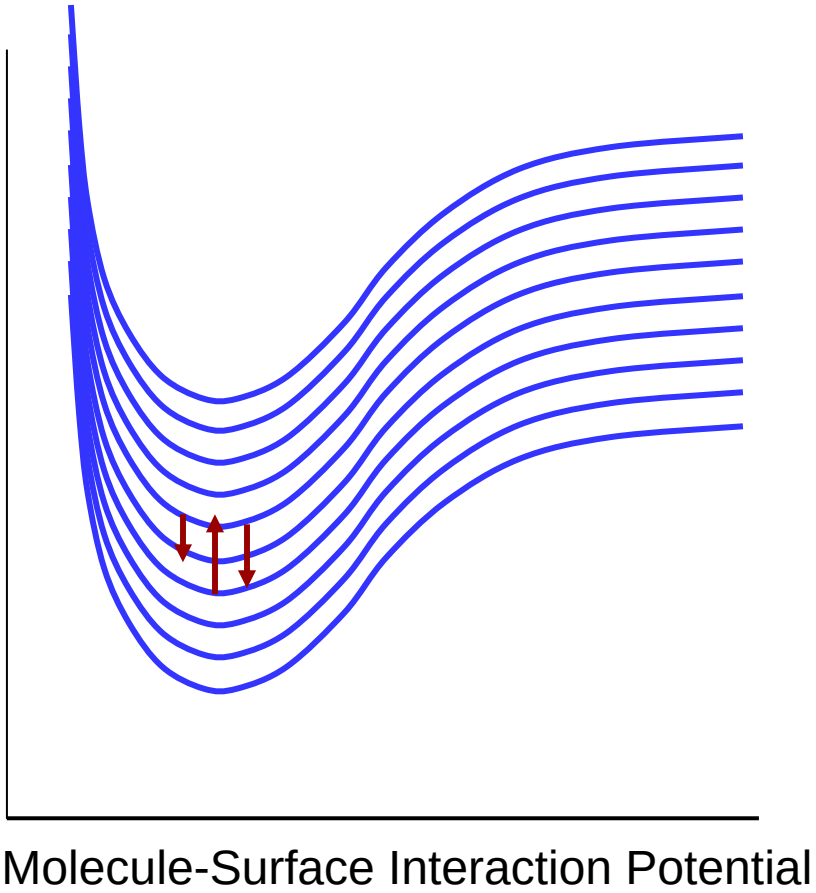
(stochastic)

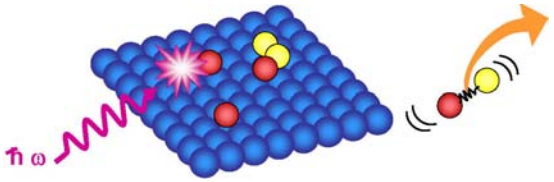


XI. Dynamics at Metal Surfaces

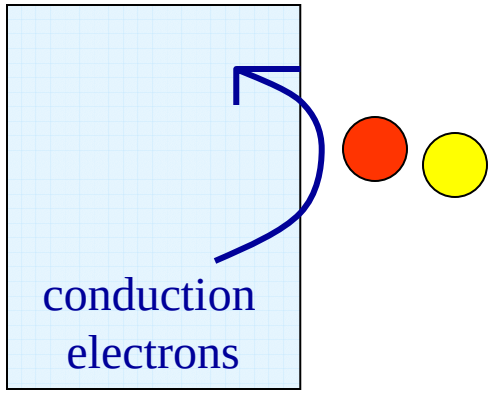
Electronic Friction: M. Head-Gordon and J C Tully, *J. Chem. Phys*. **103**, 10137 (1995).
V. Krishna and J C Tully, *J. Chem. Phys.* **125**, 054706 (2006).







XI. Dynamics at Metal Surfaces

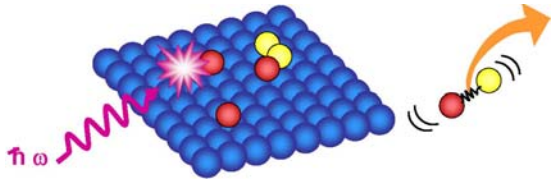


$$\frac{d\phi}{dx}$$

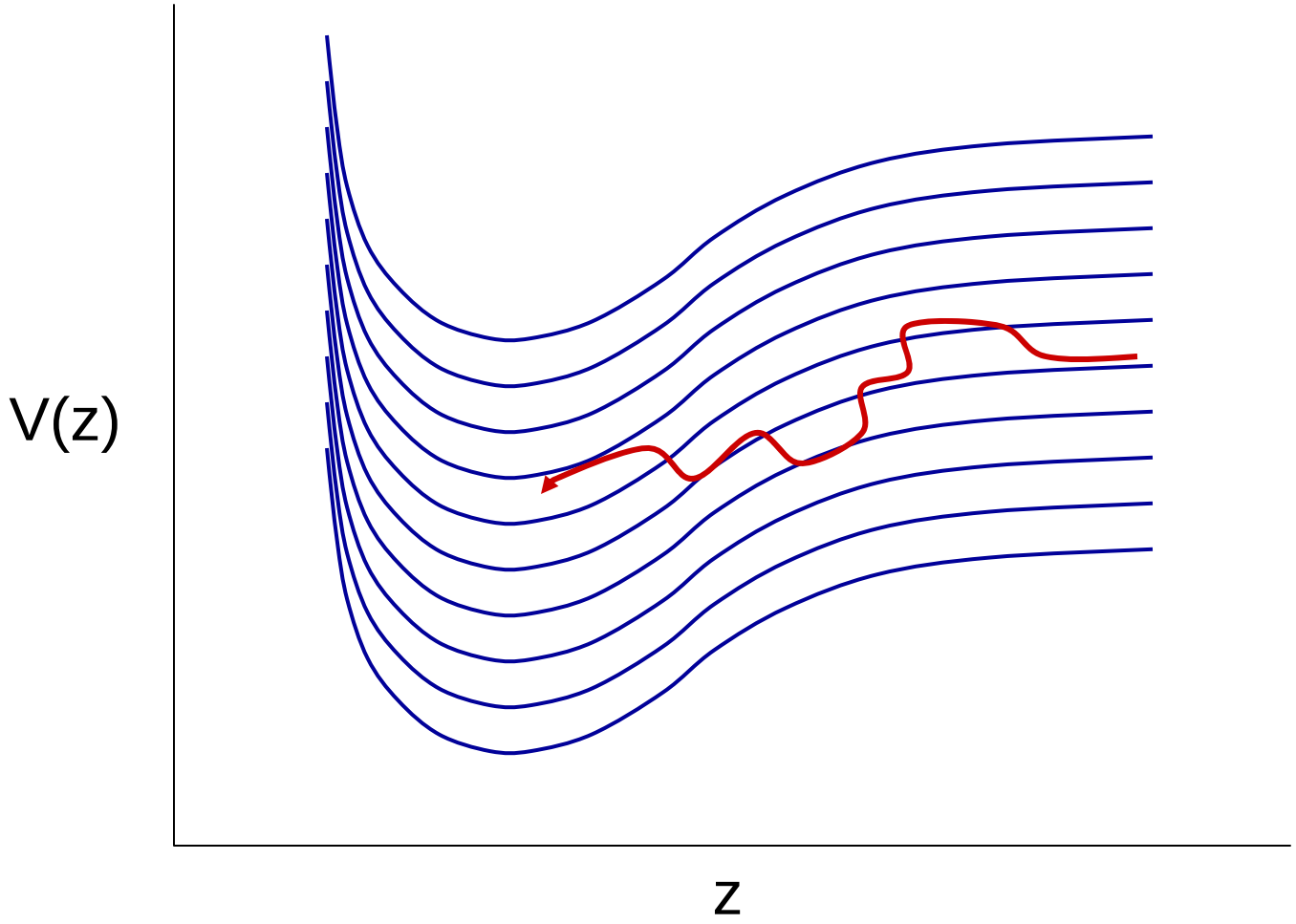
"Molecular Dynamics with Electronic Frictions"

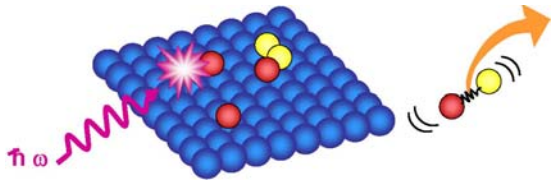
1. *Ehrenfest* Mixed Quantum-Classical SCF Approach

However:
many coupled electronic states, rapidly oscillating phases

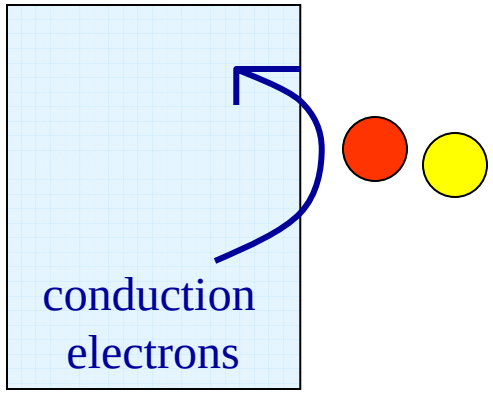


XI. Dynamics at Metal Surfaces





XI. Dynamics at Metal Surfaces

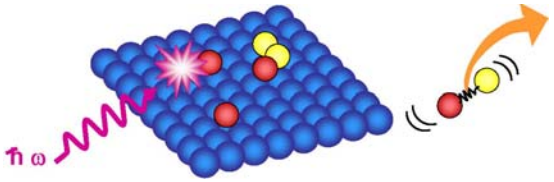


$$\frac{d\phi}{dx}$$

"Molecular Dynamics with Electronic Frictions"

1. *Ehrenfest* Mixed Quantum-Classical SCF Approach

2. Transform electronic transitions to frictions and fluctuating forces (weak coupling)



VIII. Beyond Born-Oppenheimer

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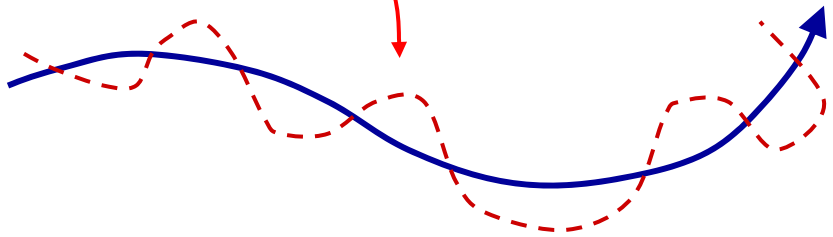
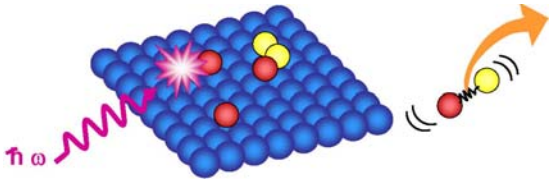
$$i\hbar \frac{\partial \Phi(r,t)}{\partial t} = \mathcal{H}_{el}\Phi(r,t)$$



$R(t)$

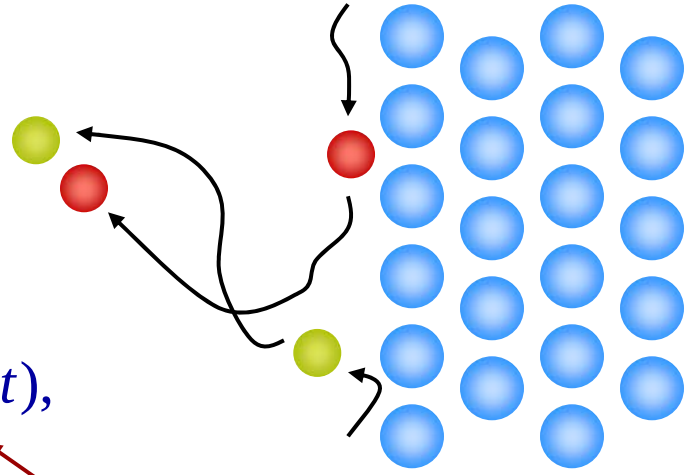
$$\Phi(r,t) = \sum_i c_i(t)\ \phi_i(r;R)$$ (adiabatic states)

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



XI. Dynamics at Metal Surfaces

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



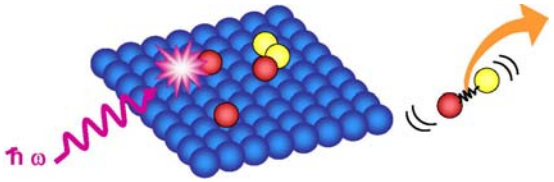
$$M\ddot{x} = -\nabla V(x) - \int_0^t dt'\,\Lambda(t,t')\,\dot{x}(t') + R(t),$$

friction kernal

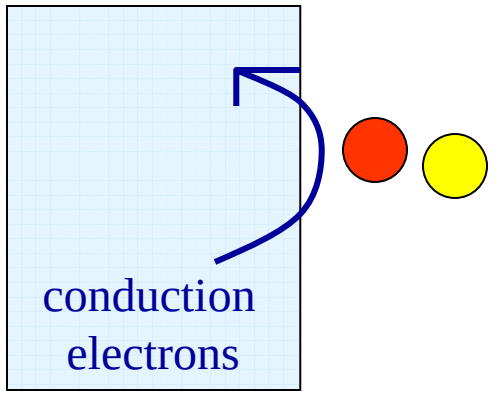
fluctuating force

2nd fluctuation-dissipation theorem:

$$\langle R(t)\,R(t')\rangle = kT\,\Lambda(t,t')$$



XI. Dynamics at Metal Surfaces



$$\frac{d\phi}{dx}$$

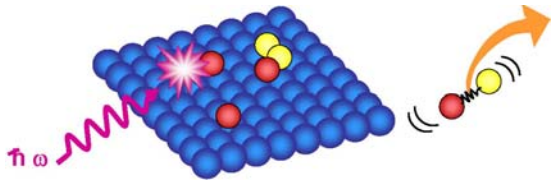
"Molecular Dynamics with Electronic Frictions"

1. *Ehrenfest* Mixed Quantum-Classical SCF Approach

2. Transform electronic transitions to frictions and fluctuating forces

3. Develop *ab initio* methods to compute $\frac{d\phi}{dx}$

DFT method: *Vinod Krishna and JCT, J. Chem. Phys. 125, 054706 (2006)*



XI. Dynamics at Metal Surfaces

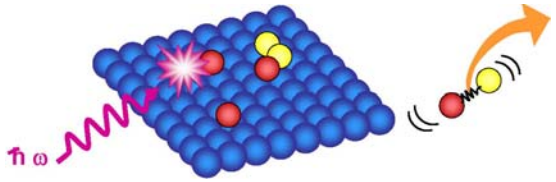
Illustrate with Golden Rule expression for vibrational lifetime:

$$\Gamma = \frac{n\pi\hbar\Delta}{M}\sum_{\alpha\alpha'}|\langle 00|\frac{\partial}{\partial Q}|\alpha\alpha'\rangle|^2\ \delta(E_{\alpha'}-E_{\alpha}-\Delta)$$

occupied unoccupied ħω

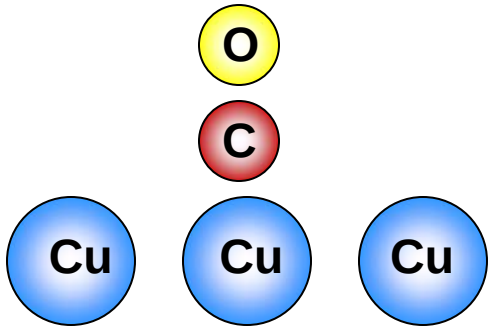
Problem 1: non-adiabatic couplings

Problem 2: delta function



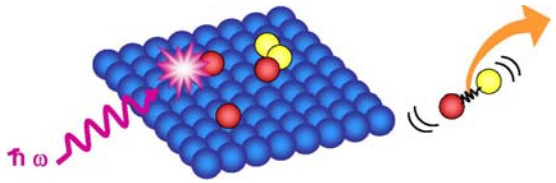
XI. Dynamics at Metal Surfaces

CO - Cu(100) Potential Energy Hypersurface



Binding Energy: 0.59 eV (expt: 0.59 eV, J. C. Tracy)

Vibrational Frequencies:	**calc.**	**expt.**
C - O stretch:	2118 cm^{-1}	2085 cm^{-1}
CO – surface stretch:	372 cm^{-1}	345 cm^{-1}
Bending mode:	357 cm^{-1}	285 cm^{-1}
Frustrated Translation:	31 cm^{-1}	30 cm^{-1}

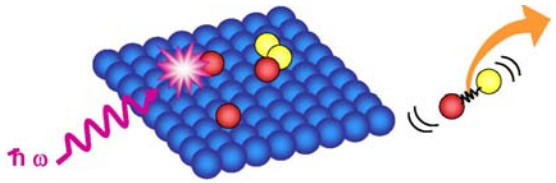


XI. Dynamics at Metal Surfaces

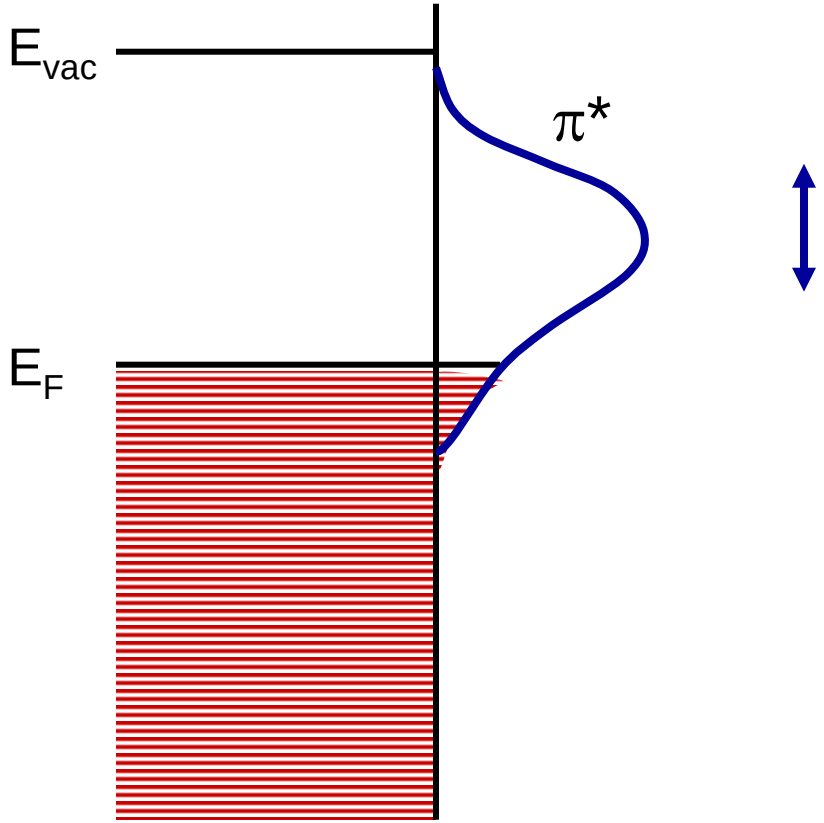
VIBRATIONAL LIFETIMES: CO on Cu(100) (ps.)

Vinod Krishna and JCT, J. Chem. Phys. ***125****, 054706 (2006)*

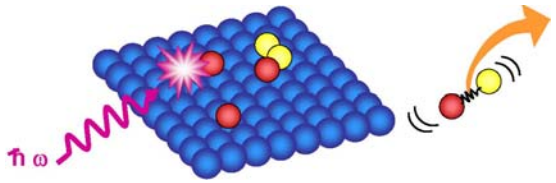
MODE	EXPERIMENT	CALC (0K) (*Phonons*)	CALC(0K) (*Electrons*)
C – O stretch	2.5 +/- 0.5 (A. Harris et al.)	>100000	3.3 +/- 0.5
CO - Cu stretch	23 +/- 8 (Ryberg et al, CO-Pt)	26 +/- 6	33.7 +/- 3.0
CO bend	1.5 +/- 0.5 (Hirschmugl et al)	>50	3.8 +/- 0.5
CO frust. transl.	6.0 +/- 2.0 (Germer et al)	17 +/- 6	19.5 +/- 4.0



XI. Dynamics at Metal Surfaces



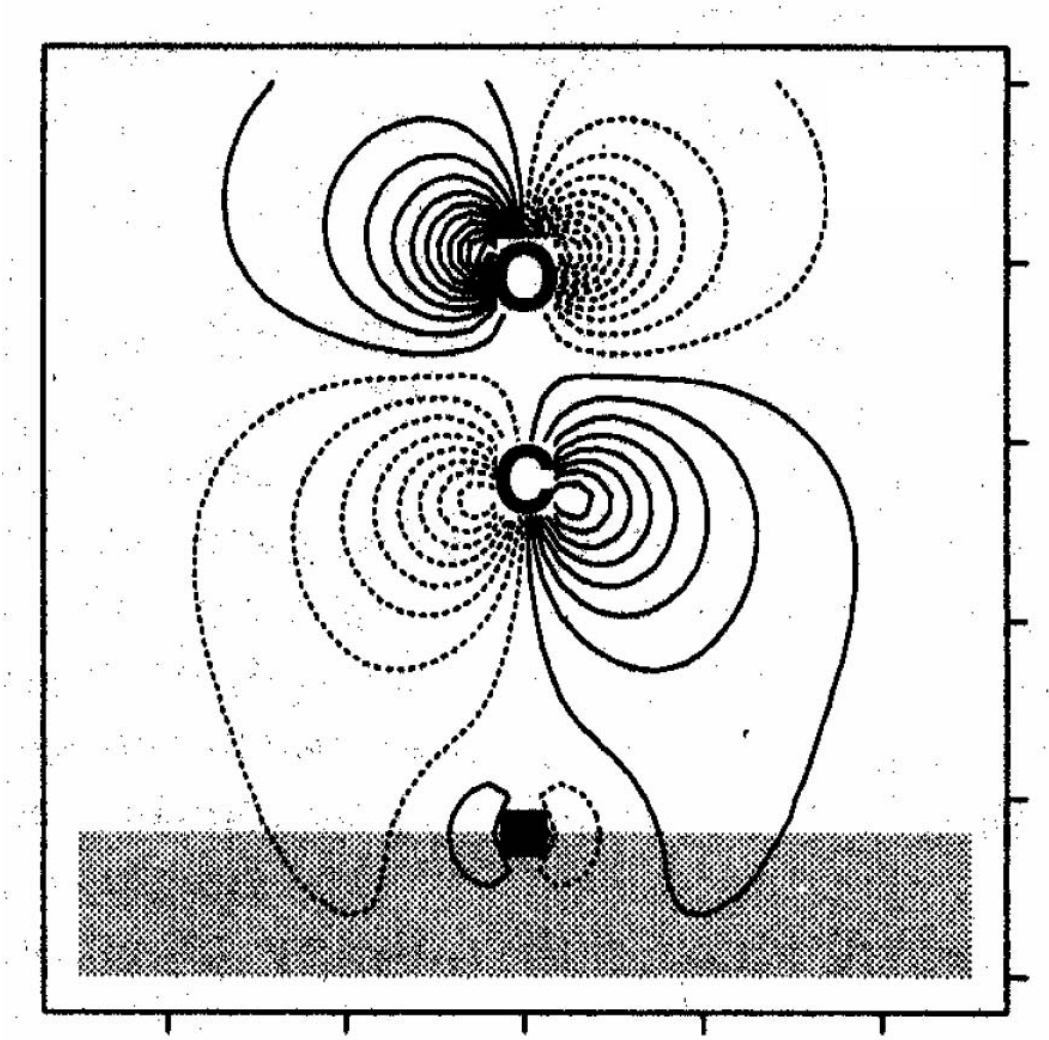
B. N. J. Persson and M. Persson, *Solid State Commun*. **36**, 175 (1980)

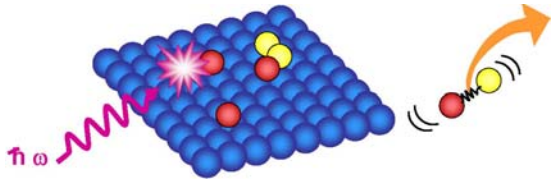


XI. Dynamics at Metal Surfaces

$d\Psi_{HOMO}/dR$

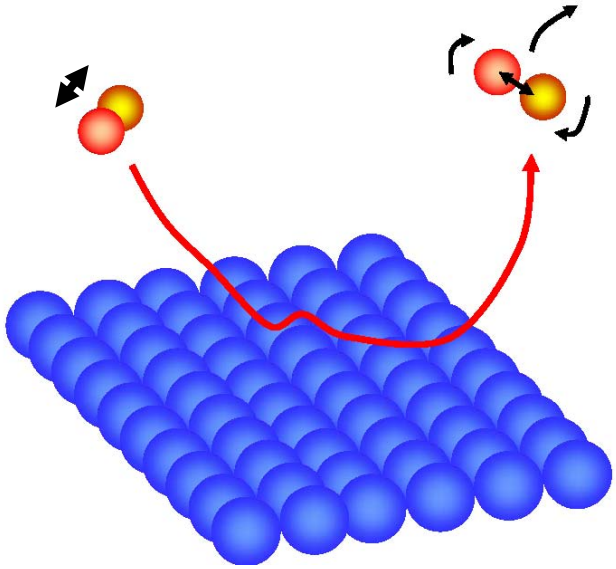
(C -- O Stretch)

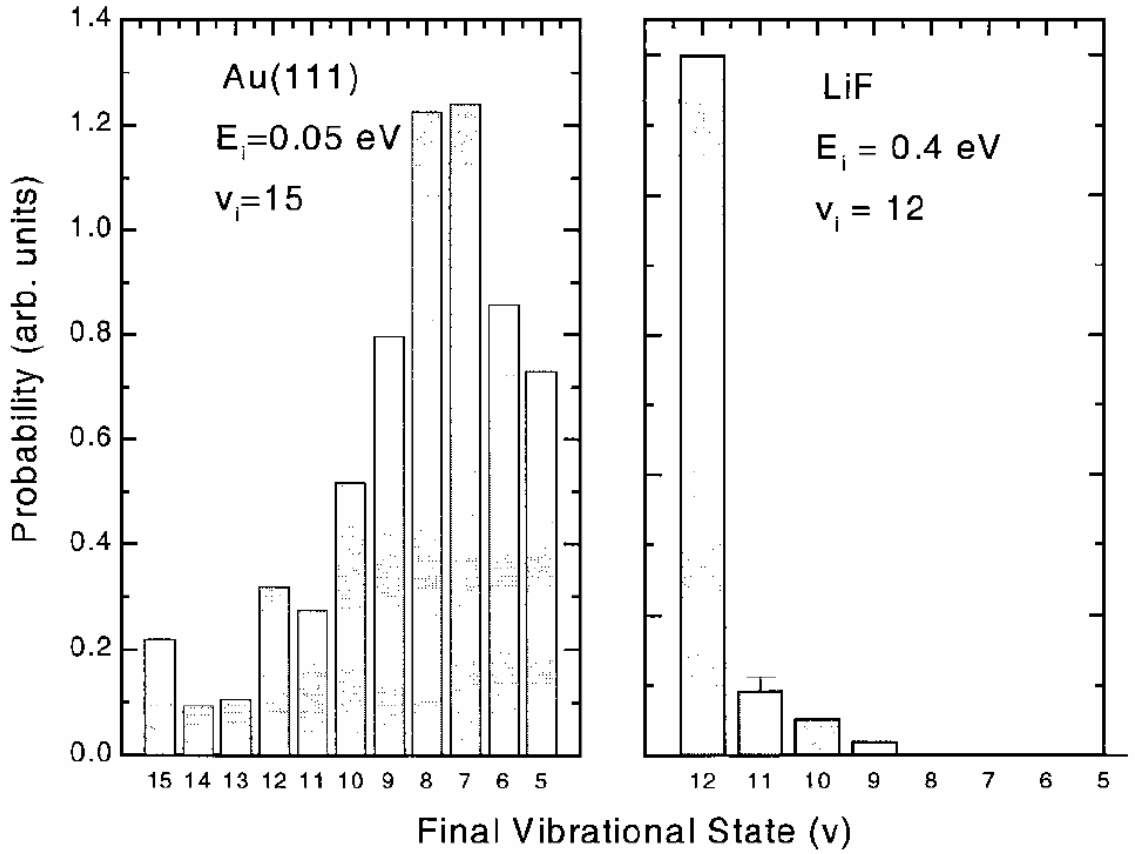




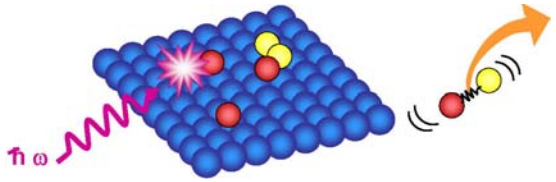
XI. Dynamics at Metal Surfaces

Multi-Quantum Transitions: → *inadequacy of friction model ?*



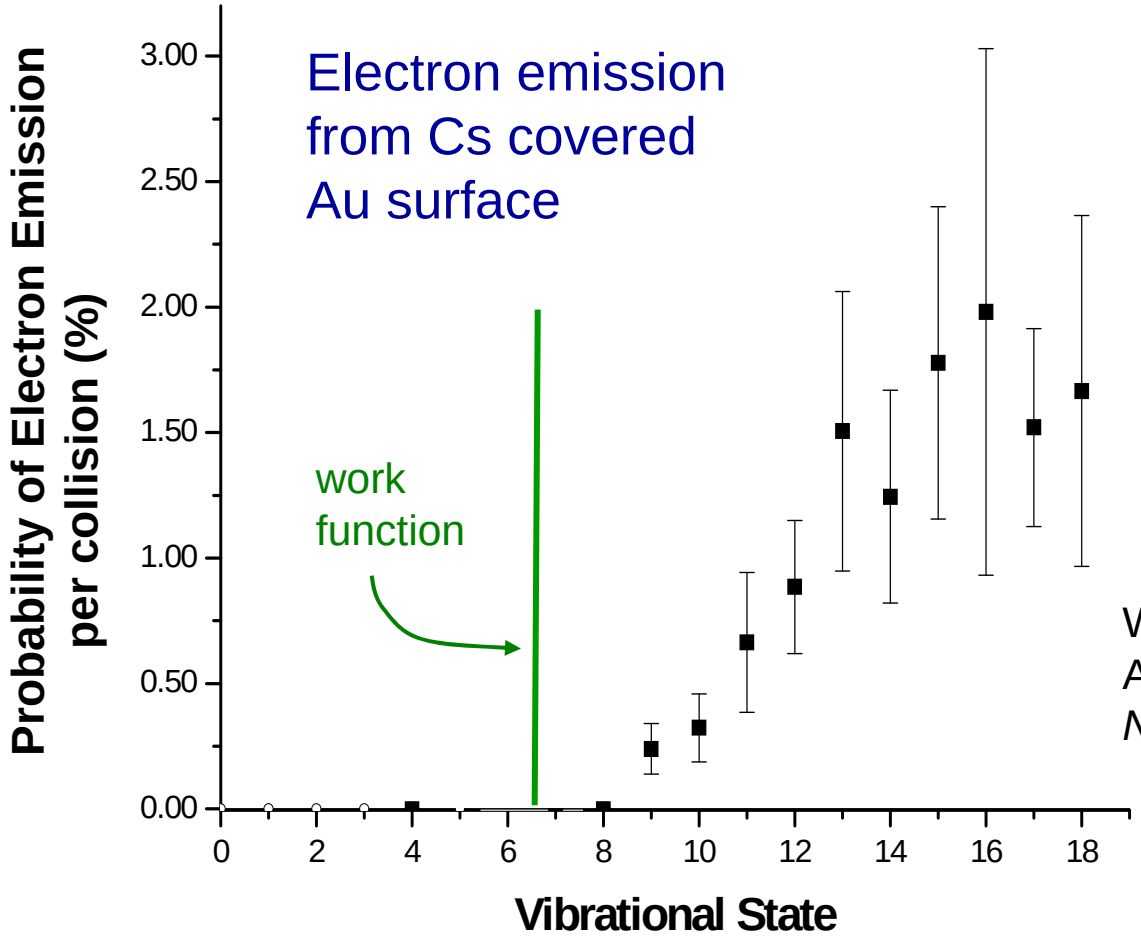


Huang, Rettner, Auerbach, Wodtke,*Science* **2000**, *290*, 111.

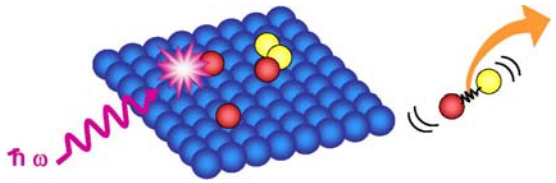


XI. Dynamics at Metal Surfaces

Electron Emission: → *inadequacy of electronic friction model ?*



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



XI. Dynamics at Metal Surfaces

Electron Emission:
→*inadequacy of electronic friction model ?*

"Chemically Induced Electronic Excitations at Metal Surfaces,"
B. Gergen, H. Nienhaus, W.H. Weinberg, and E.W. McFarland,
Science **294** (5551) 2521-2523 (2001)

"Electronic excitations induced by surface reactions of H and D on gold",
B. Mildner, E. Hasseklbrink, D. Diesing, *Chem. Phys. Lett*. **432**, 132 (2006)

"The Catalytic Nanodiode: Gas Phase Catalytic Reaction Generated Electron Flow Using Nanoscale Platinum Titanium Oxide Schottky Diodes",
X. Ji, A. Zuppero, J. M. Gidwani, G. A. Somorjai, *Nano Letters* **5**, 2557, (2005)

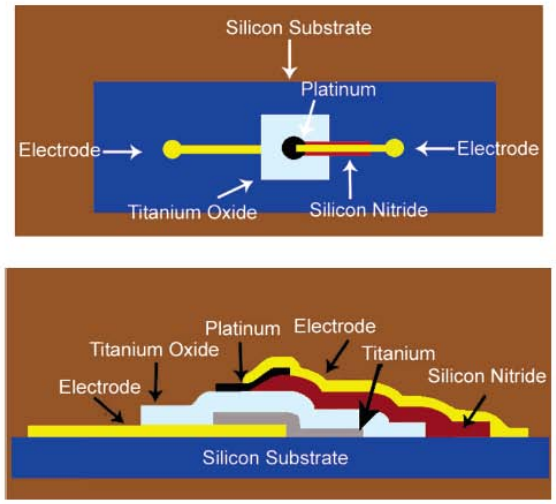


Figure 1. The top view and the cross-section of the platinum/*n*-titanium oxide Schottky diode.

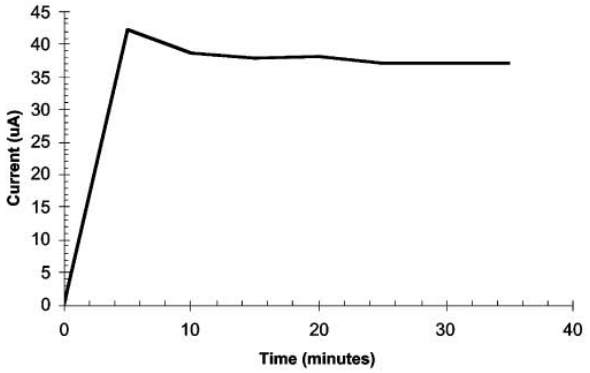
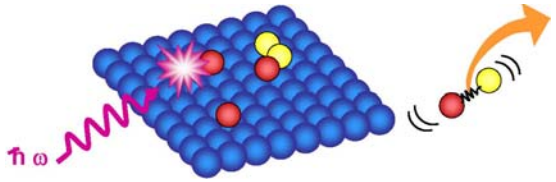


Figure 3. Gas-phase catalytic oxidation of carbon monoxide on 5 nm platinum/150 nm *n*-titanium oxide Schottky diode generates a steady-state electron flow of 37 microampere for over half an hour.



XI. Dynamics at Metal Surfaces

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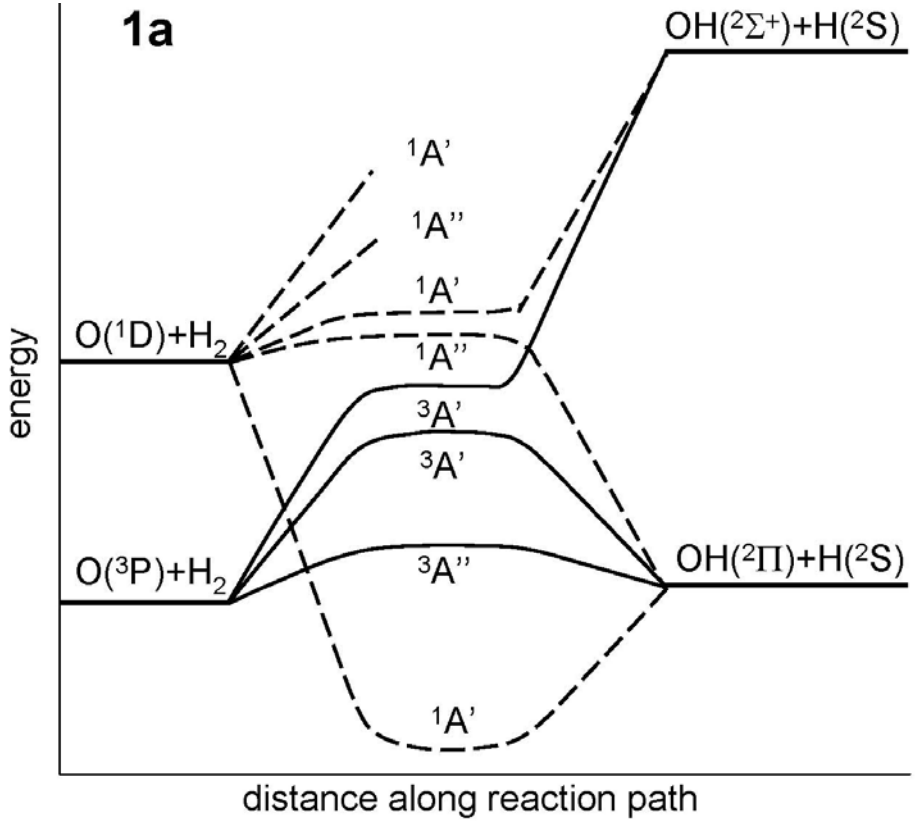
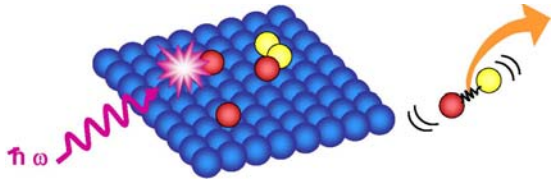
Reactions of open shell atoms and molecules in the gas phase

Gas Phase



$O(^3P) + H_2 \rightarrow OH + H$



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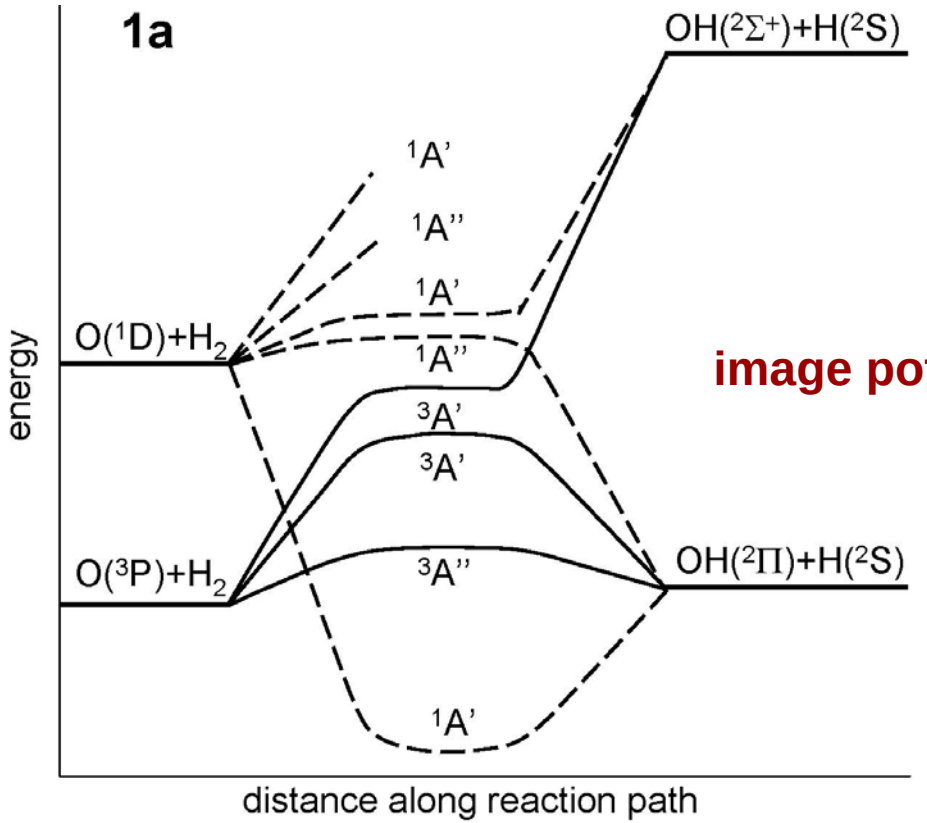
Reactions of open shell atoms and molecules at surfaces

Gas Phase



Gas-Surface

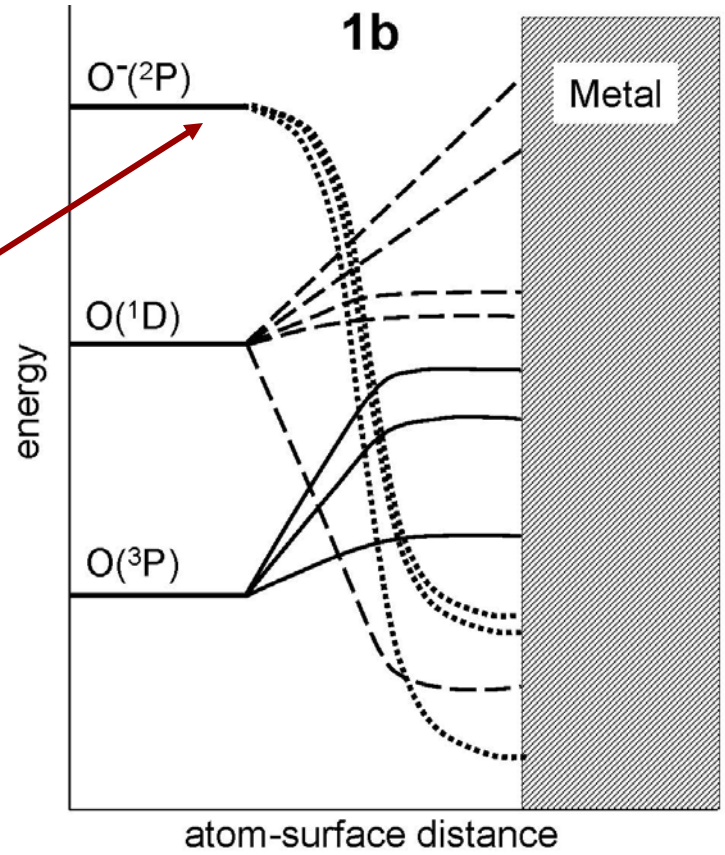
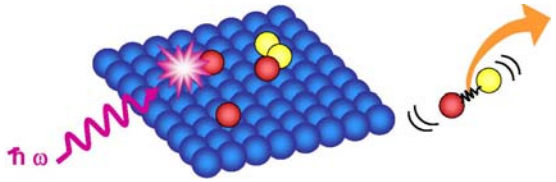


image potential



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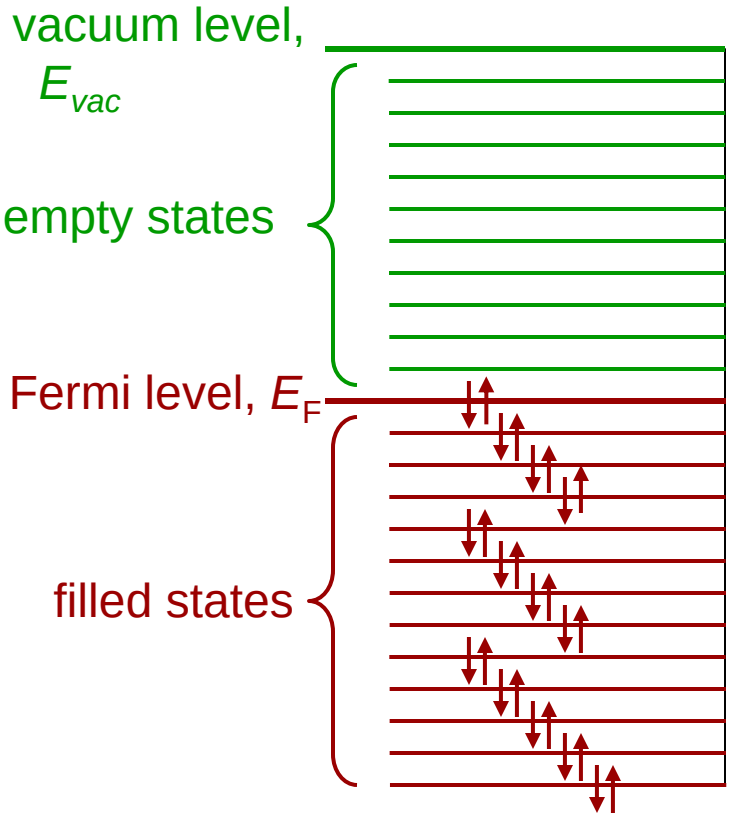
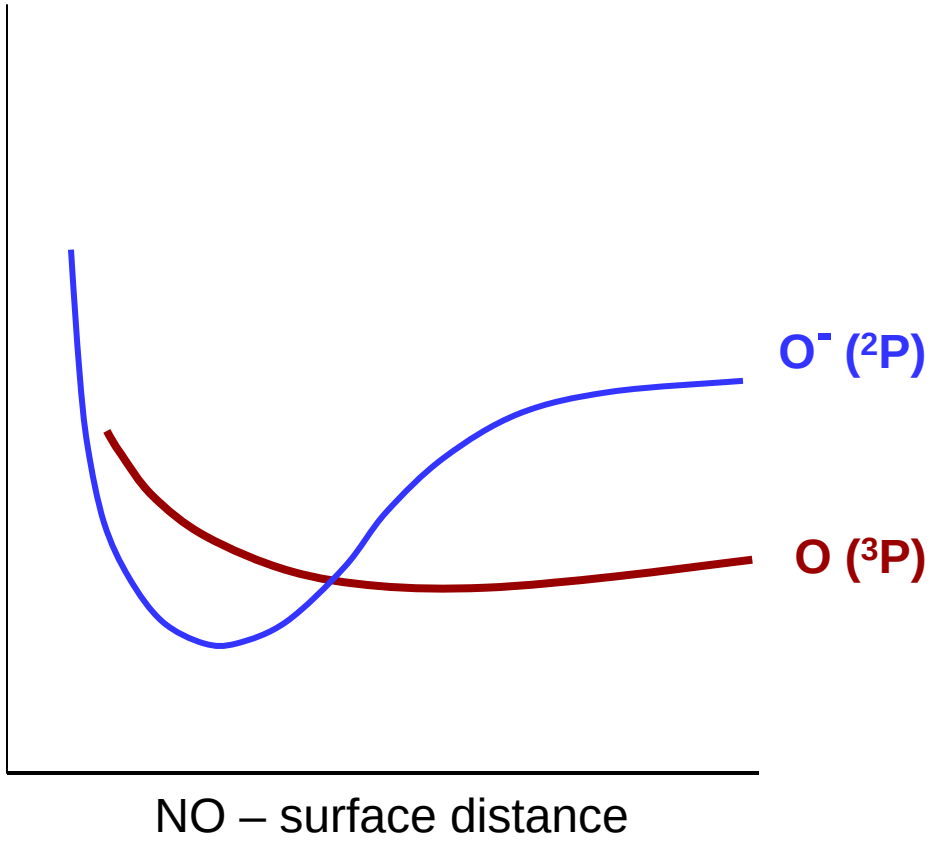
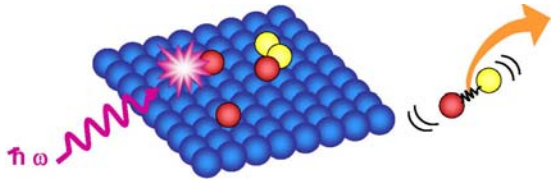
Metal







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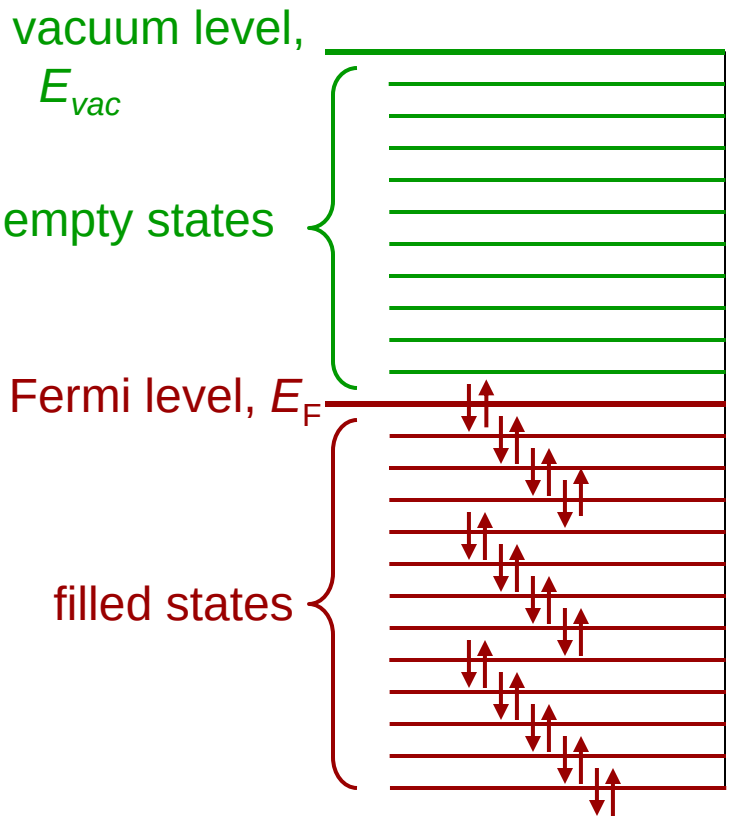
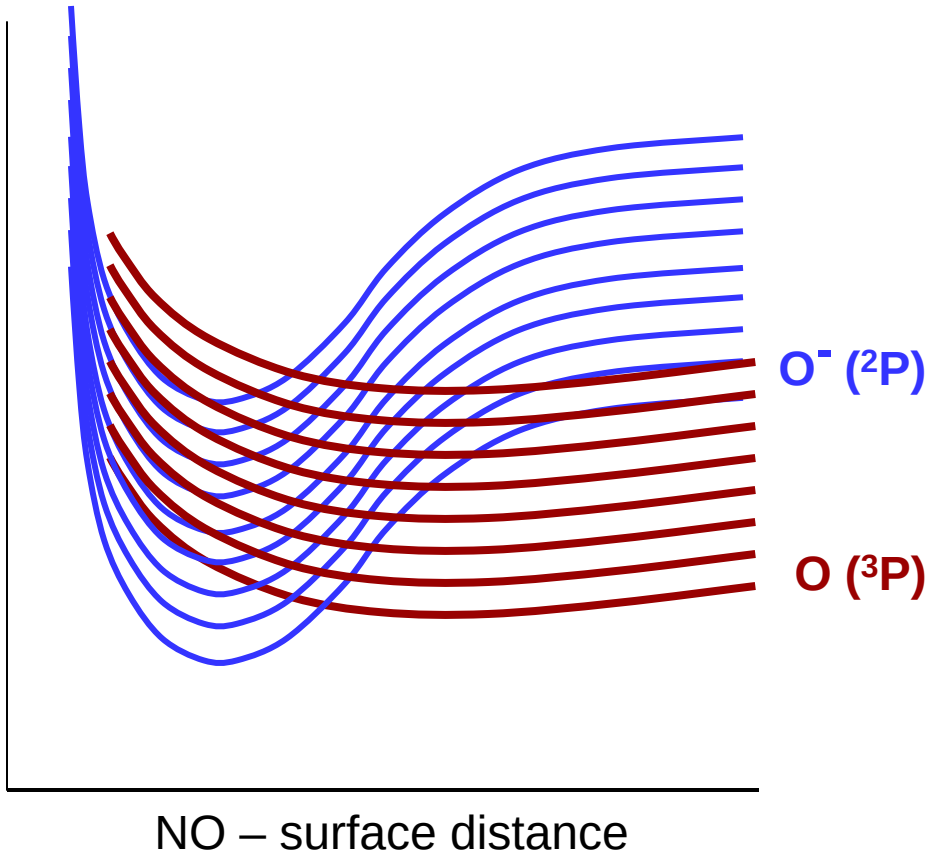
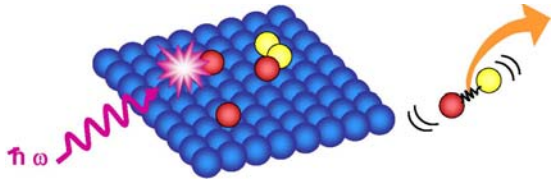
Metal







XI. Dynamics at Metal Surfaces

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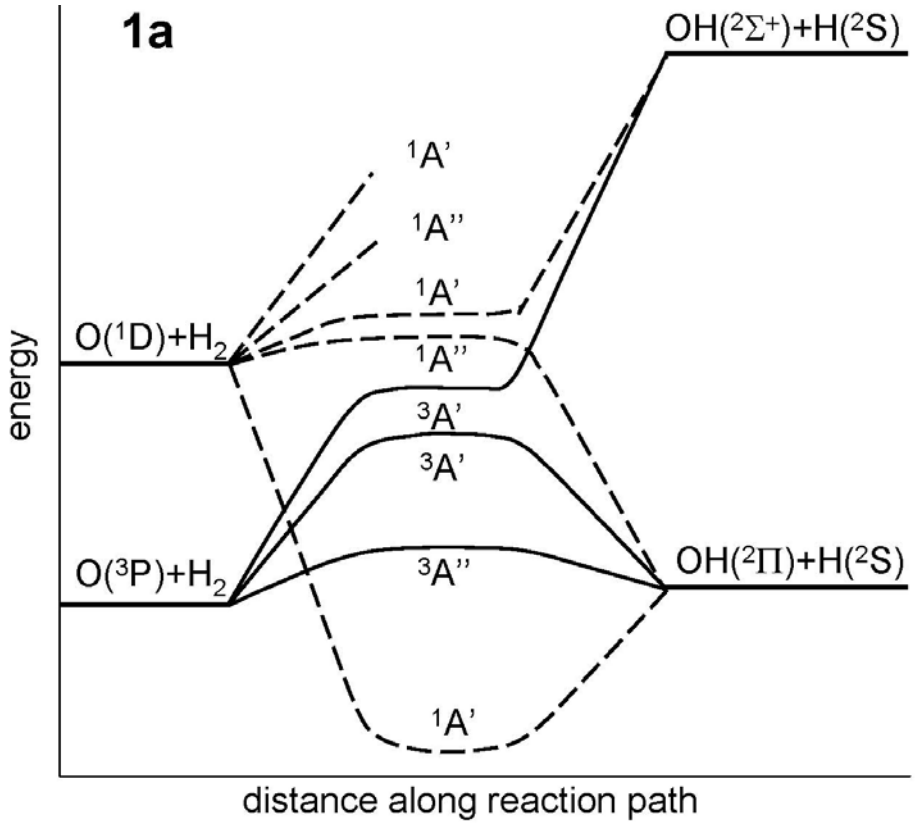
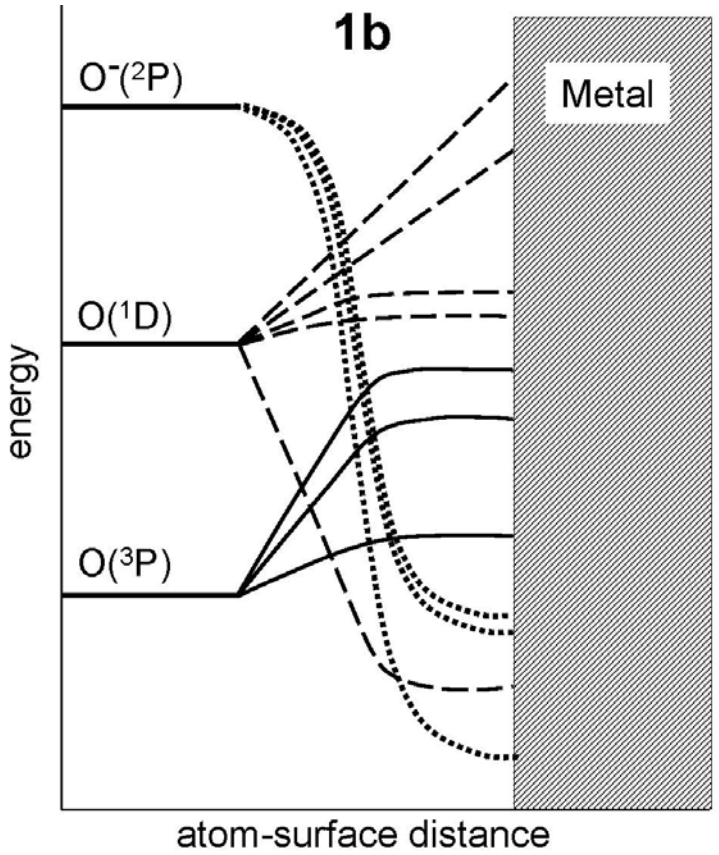
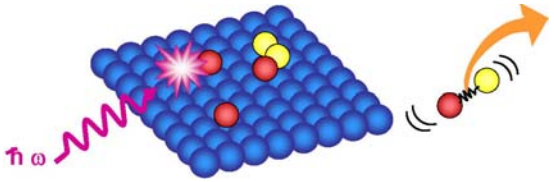
Reactions of open shell atoms and molecules at surfaces

Gas Phase



Gas-Surface





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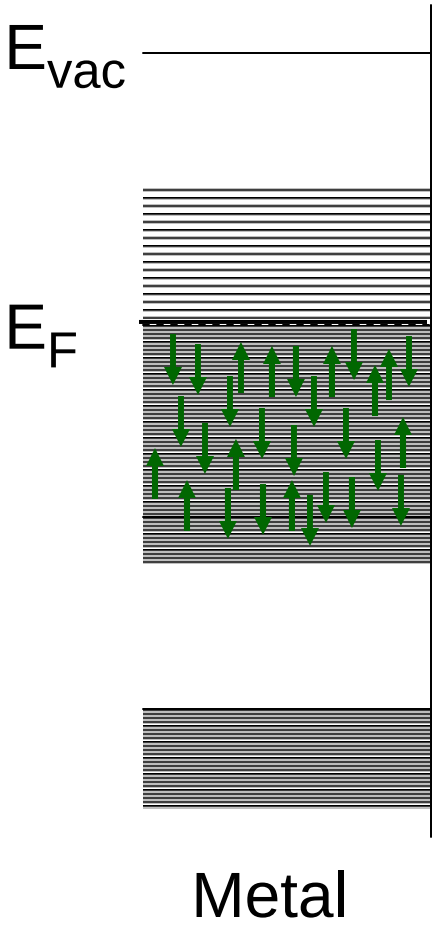
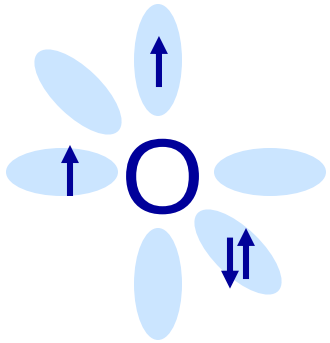
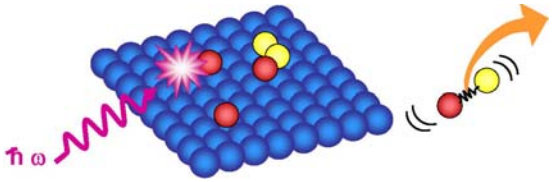




^3P



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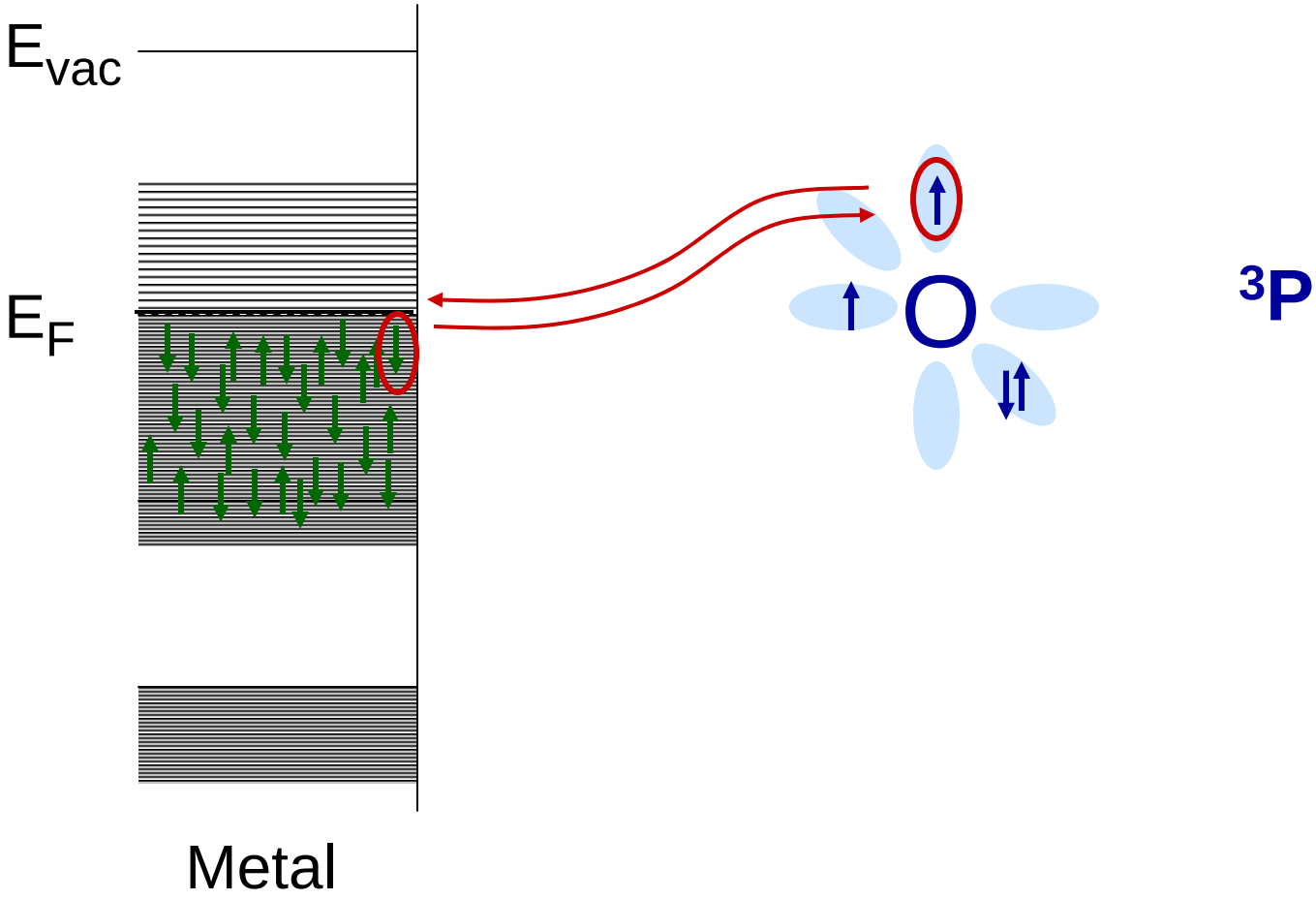
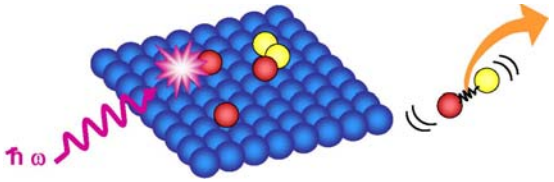
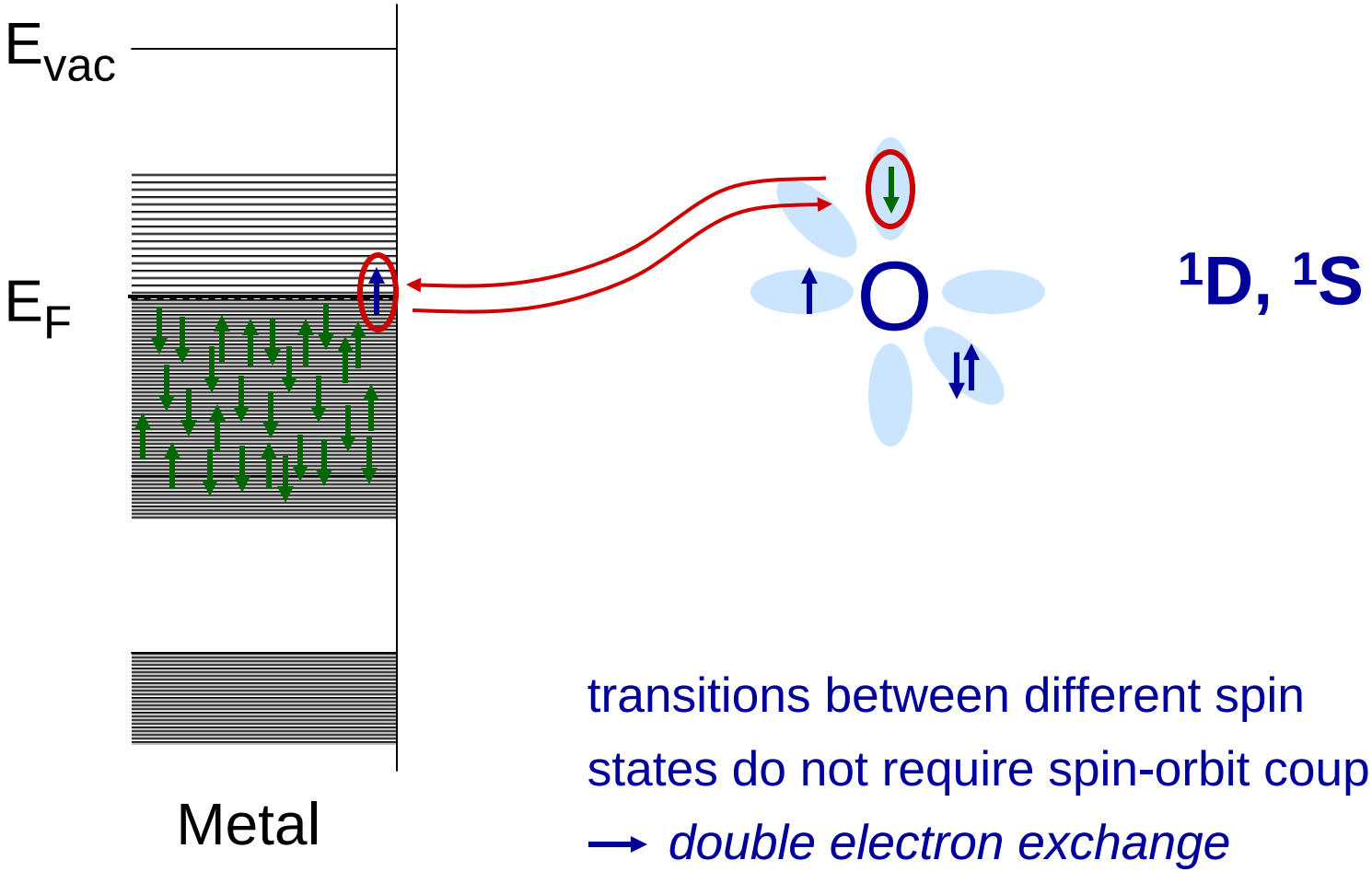


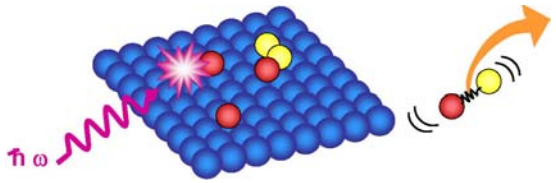


XI. Dynamics at Metal Surfaces



transitions between different spin states do not require spin-orbit coupling:

→ *double electron exchange*



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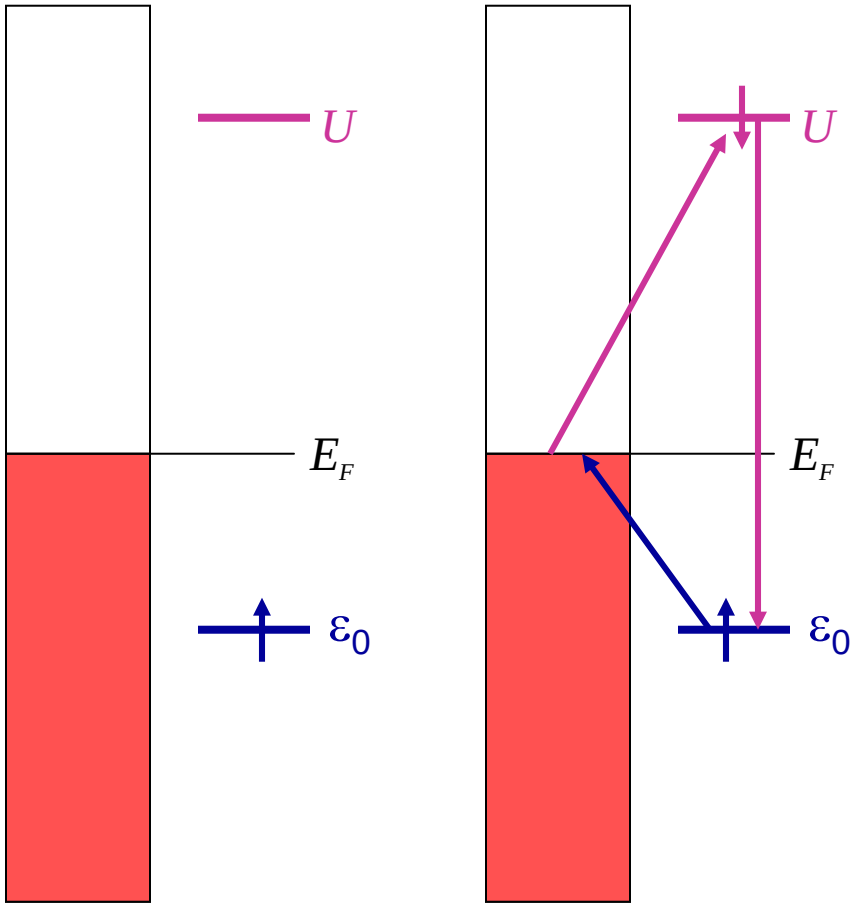
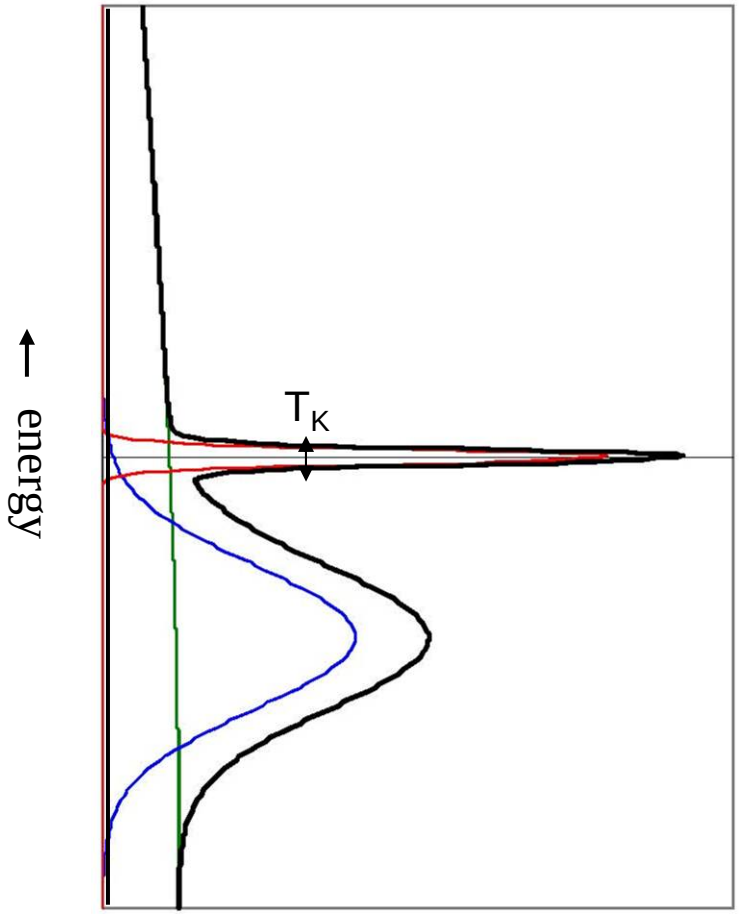
Kondo Effect:



Spin flip



density of states

Nano Lett., **6** (6), 1146 -1150, 2006. 10.1021/nl0602847
Web Release Date: March 21, 2006

Local Electronic Structure around a Single Kondo Impurity

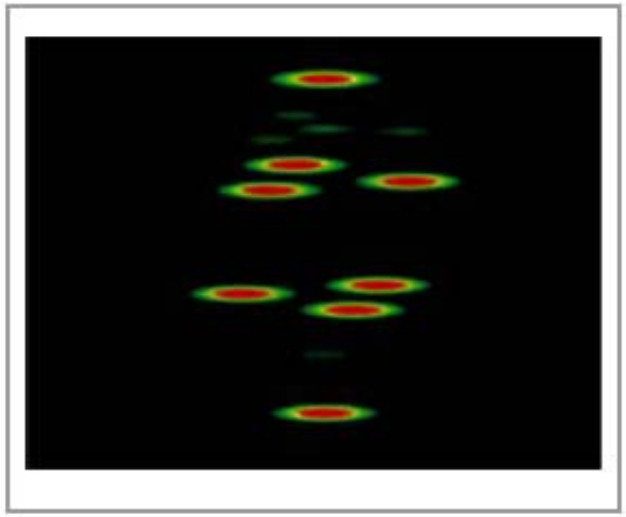
Patrick Huang and Emily A. Carter*

Department of Mechanical & Aerospace Engineering and Program in Applied & Computational Mathematics, Princeton University, Princeton, New Jersey 08544-5263

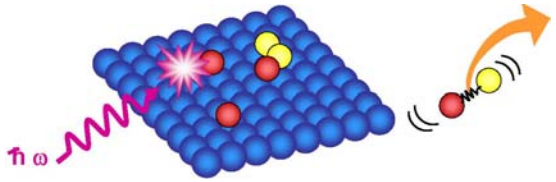
Received February 7, 2006

Revised March 7, 2006

Abstract:



The local electronic structure due to the adsorption of Co on Cu(111) is studied using an embedded cluster model, in which the crystal background is taken into account via an effective density functional theory (DFT)-based potential. This approach goes beyond the usual single-impurity Anderson model, where the ground state consists of a singly occupied impurity whose moment is compensated by the background conduction electrons. Ab initio correlated wave function calculations for the embedded cluster provide an alternative picture for this ground state and indicate that the quenching of the Co magnetic moment is due to the formation of metal-metal bonds with the Cu substrate. Low-lying excitations are also studied within the embedding model, and our results are discussed in the context of scanning tunneling microscopy experiments (Manoharan, H. C.; Lutz, C. P.; Eigler, D. M. *Nature* **2000**, *403*, 512), which find a sharp tunneling resonance localized in the vicinity of the Co adatom.



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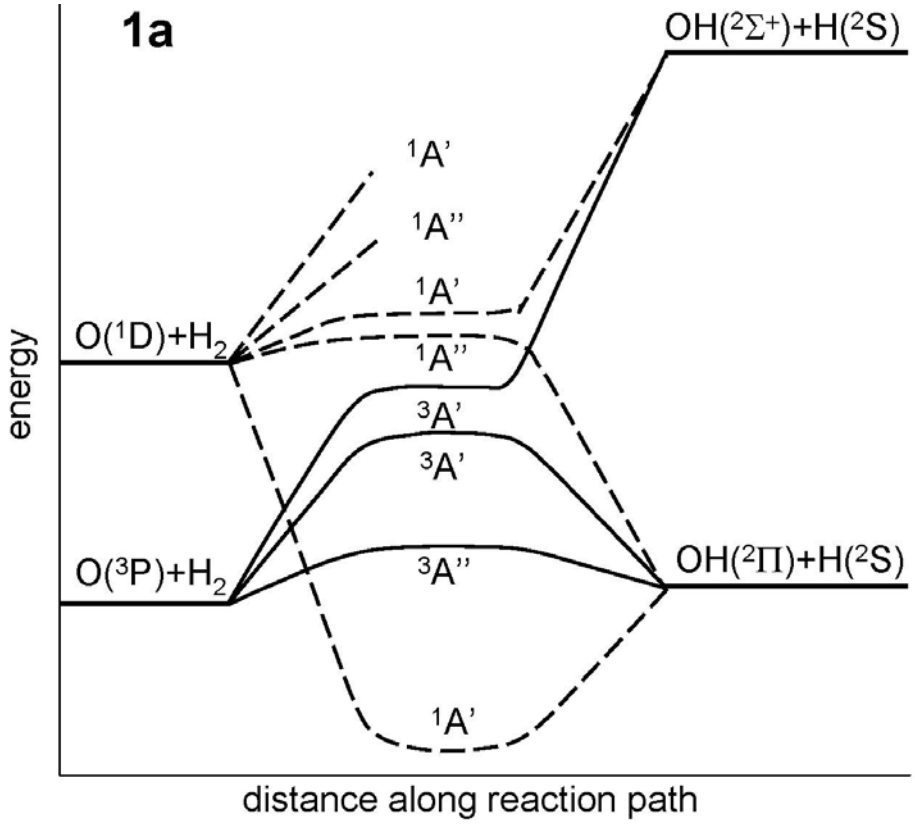
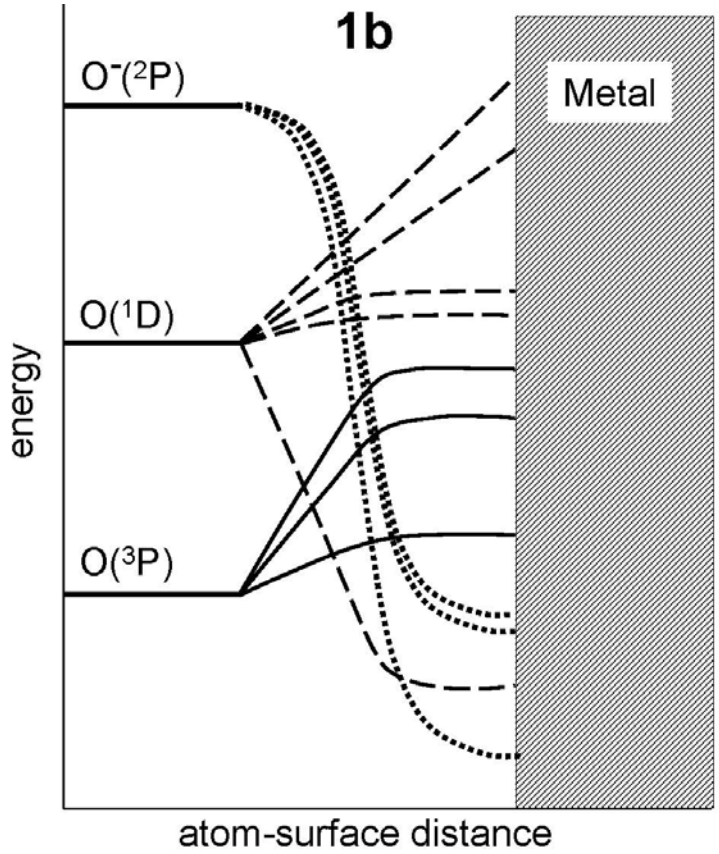
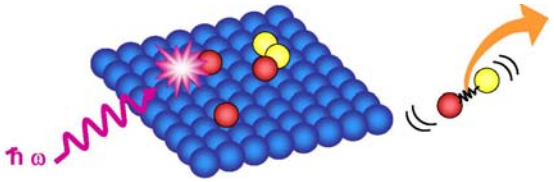
Open shell molecules at surfaces:
more complicated than a spin ½ Kondo impurity

Gas Phase



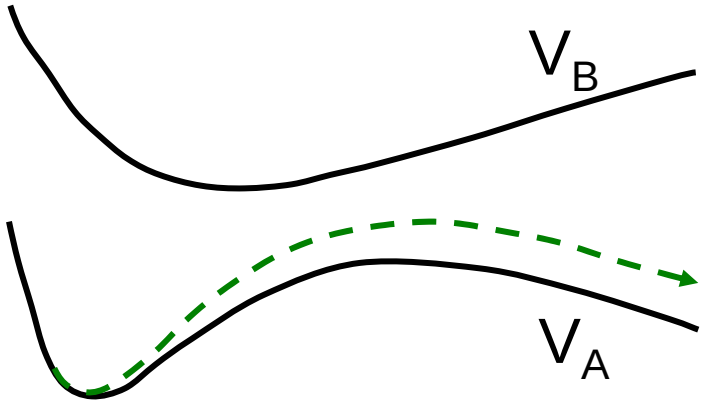
Gas-Surface





XI. Dynamics at Metal Surfaces

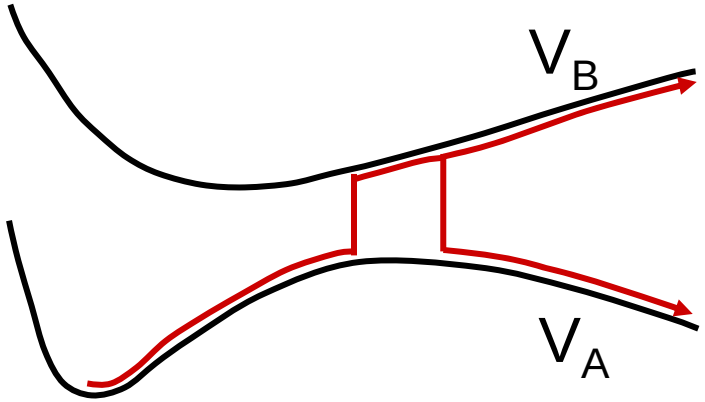
MIXED QUANTUM-CLASSICAL STRATEGIES FOR INCLUDING QUANTUM BACK-REACTION



Ehrenfest

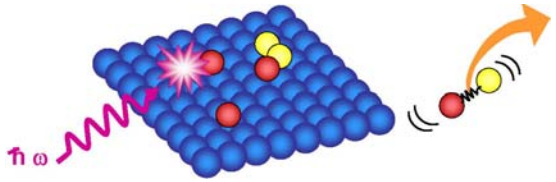
(self-consistent field)

electronic friction



Surface-Hopping

(stochastic)



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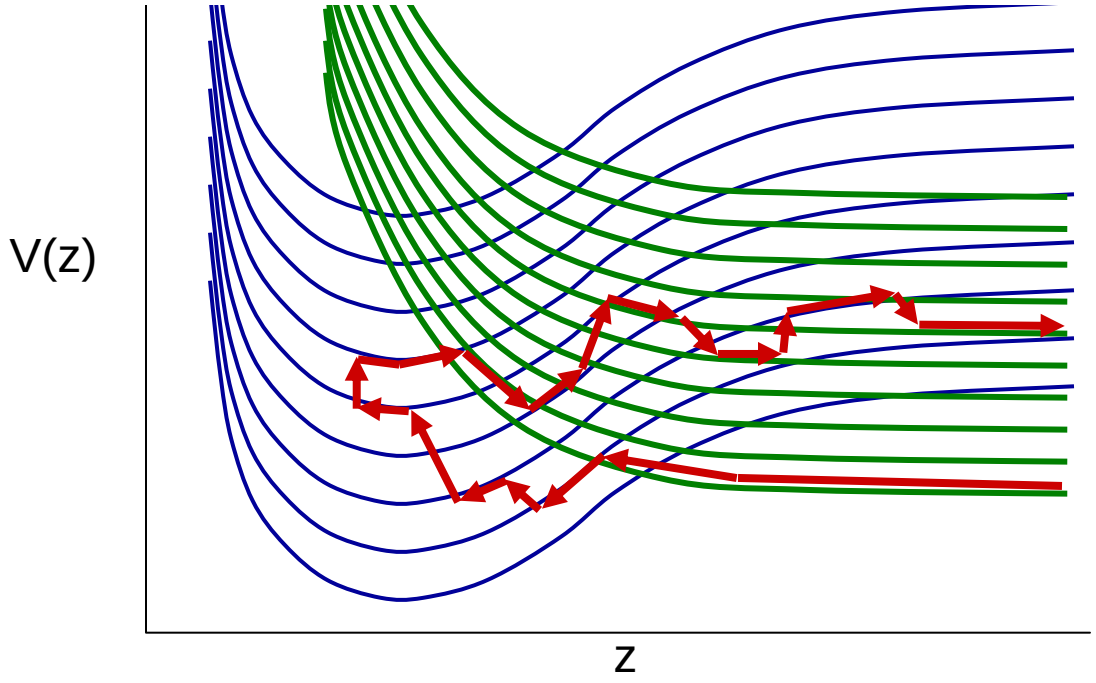
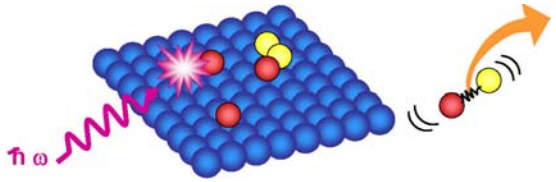
How do we do surface hopping among **huge** numbers of potential energy surfaces?

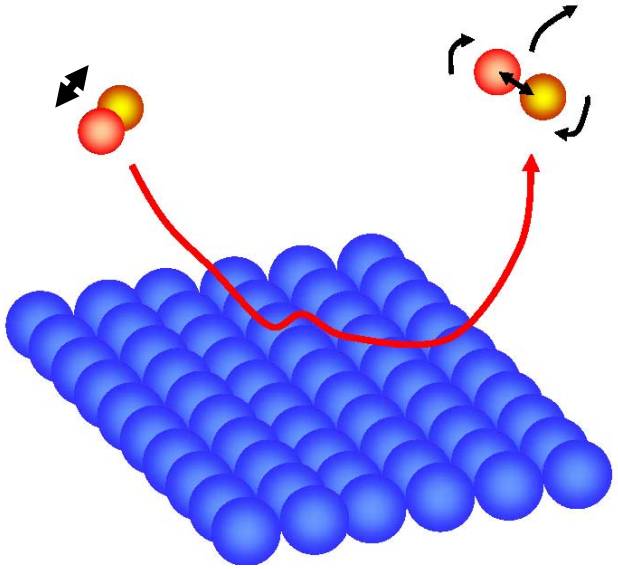
1. How do we compute **adiabatic** potential energy surfaces and nonadiabatic couplings? *Newns-Anderson Hamiltonian*

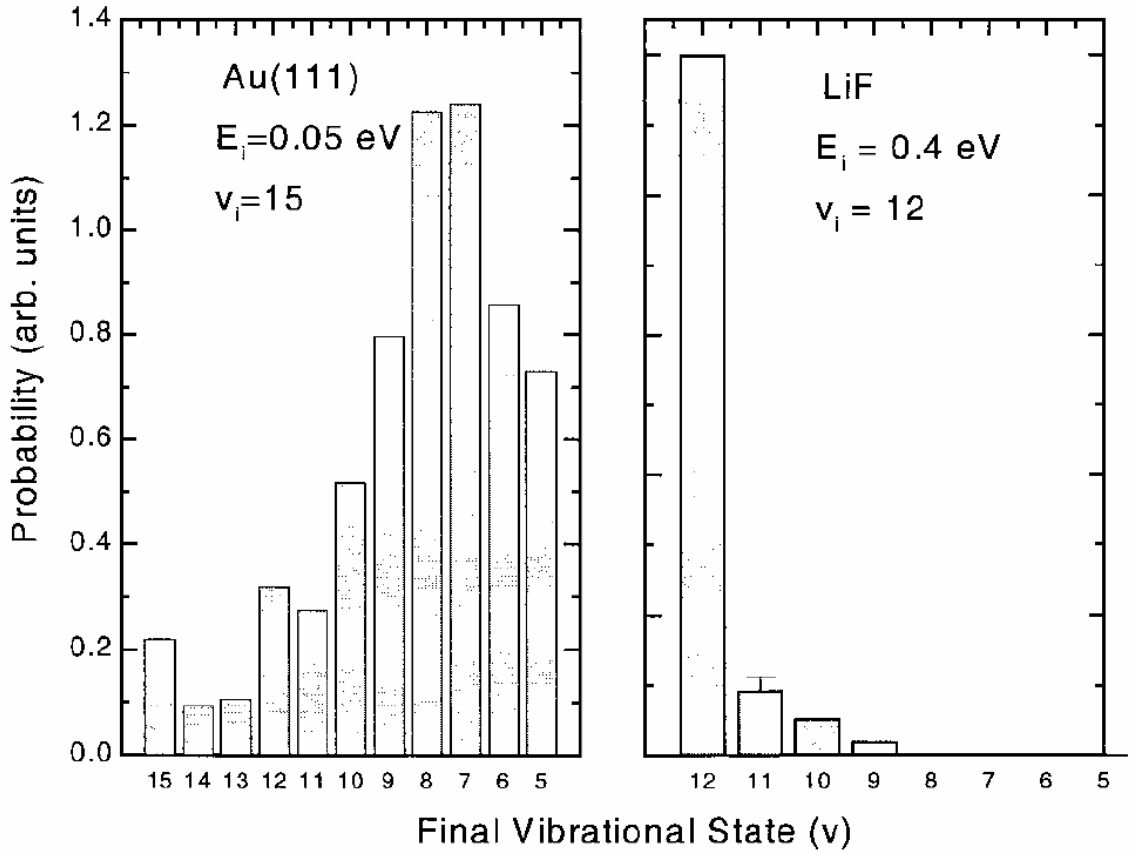
2. How do we integrate surface hopping trajectories? *Independent Electron Surface Hopping*



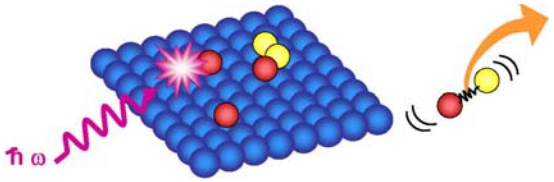


XI. Dynamics at Metal Surfaces



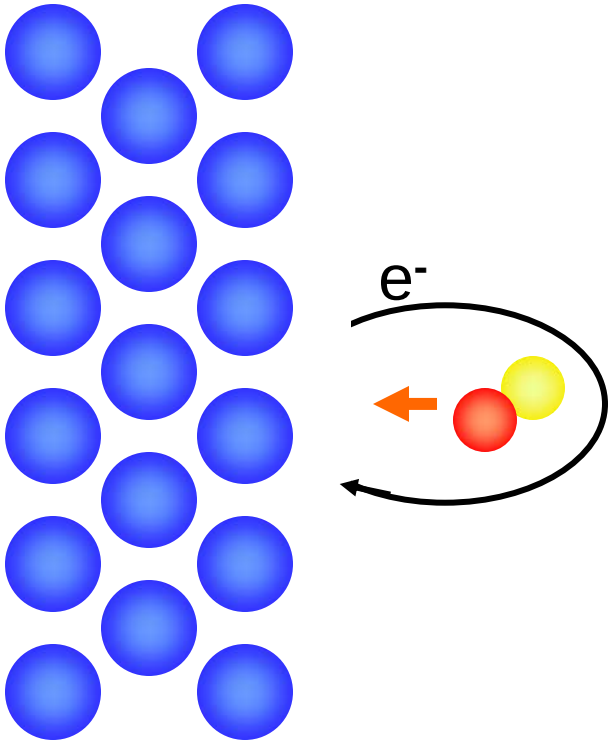


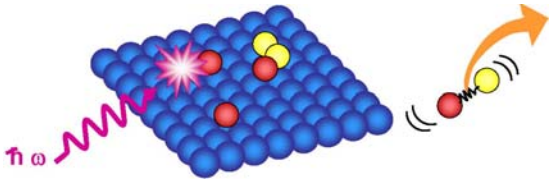
Huang, Rettner, Auerbach, Wodtke,*Science* **2000**, *290*, 111.



XI. Dynamics at Metal Surfaces

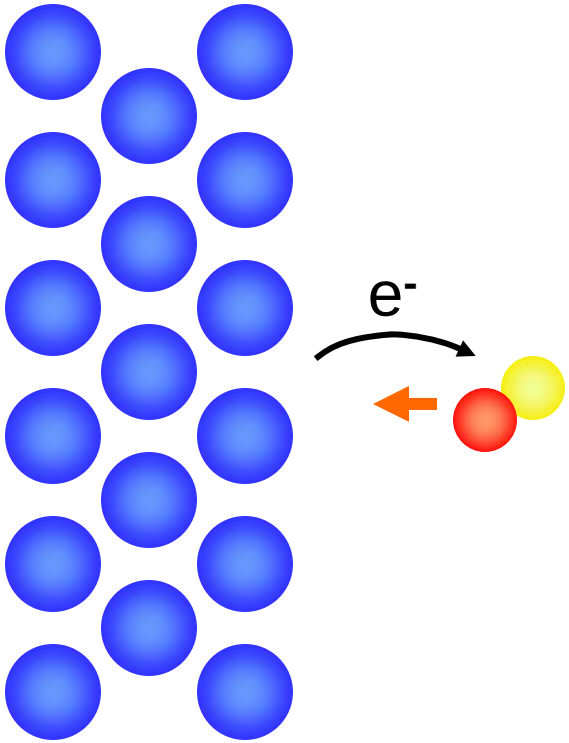
a. Non-Resonant → *friction model*

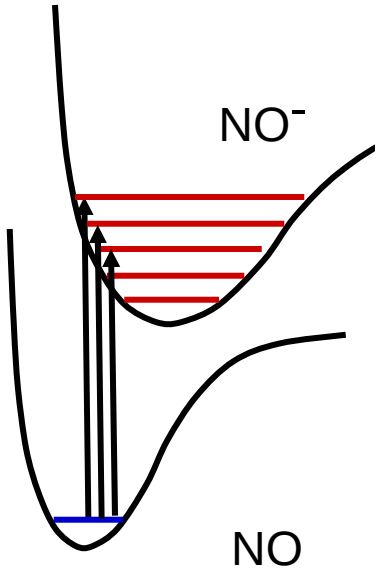


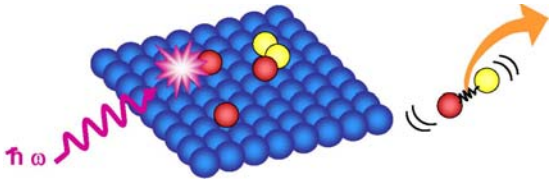


XI. Dynamics at Metal Surfaces

b. Resonant → *transient negative ion*

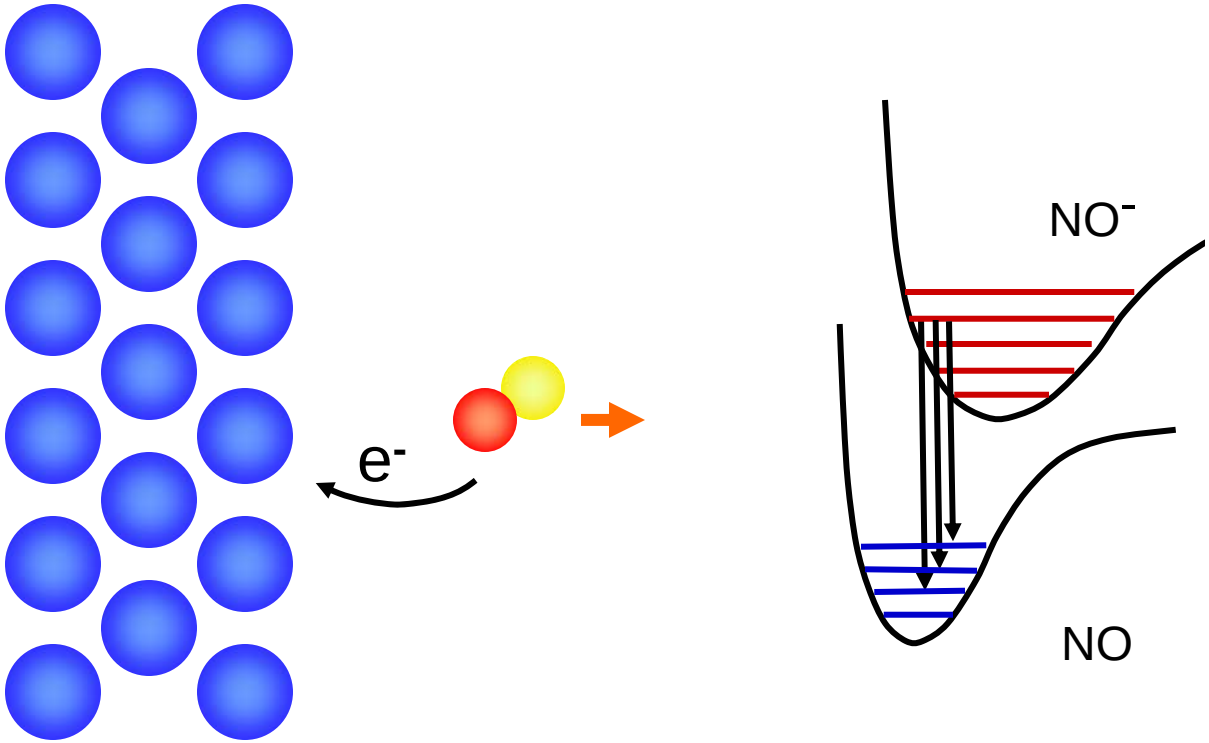


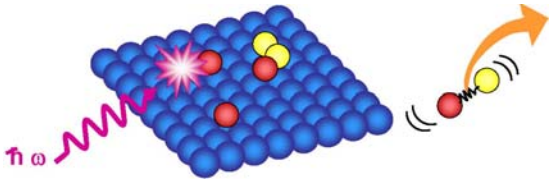




XI. Dynamics at Metal Surfaces

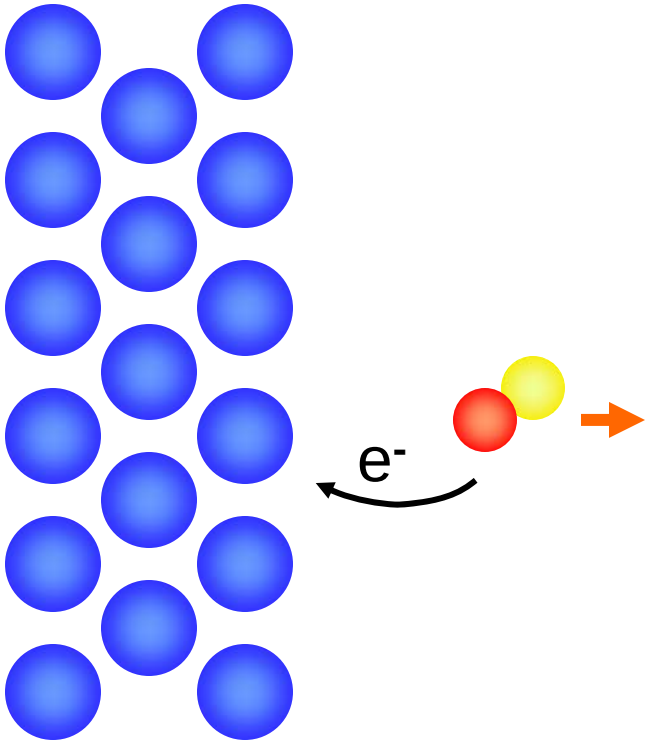
b. Resonant → *transient negative ion*





XI. Dynamics at Metal Surfaces

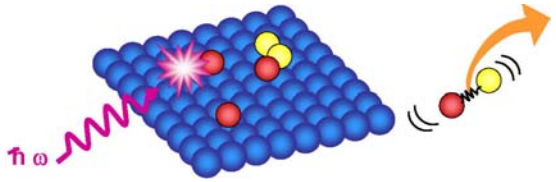
b. Resonant → *transient negative ion*



See:

J. W. Gadzuk

Can we unify friction and resonance models?



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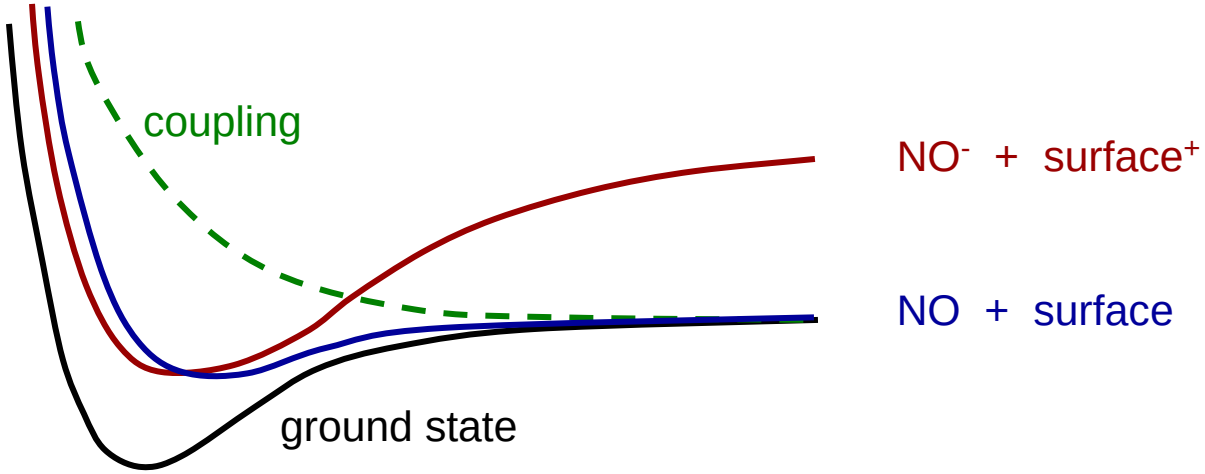
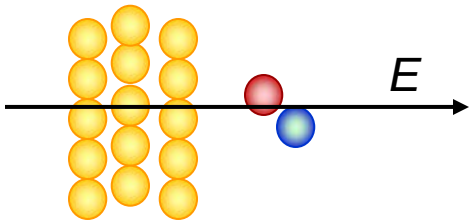
Nitric Oxide on Gold:
Diabatic Description

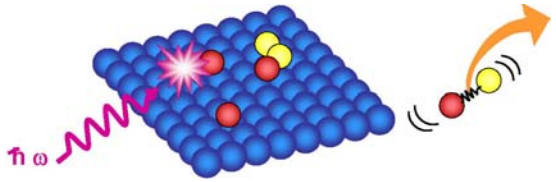


$$\begin{bmatrix} E_{ionic}(\mathbf{R}) & V(\mathbf{R}) \\ V(\mathbf{R}) & E_{neutral}(\mathbf{R}) \end{bmatrix} \longrightarrow$$ 3 unknowns

DFT calculation → ground state energy
effective charge on NO

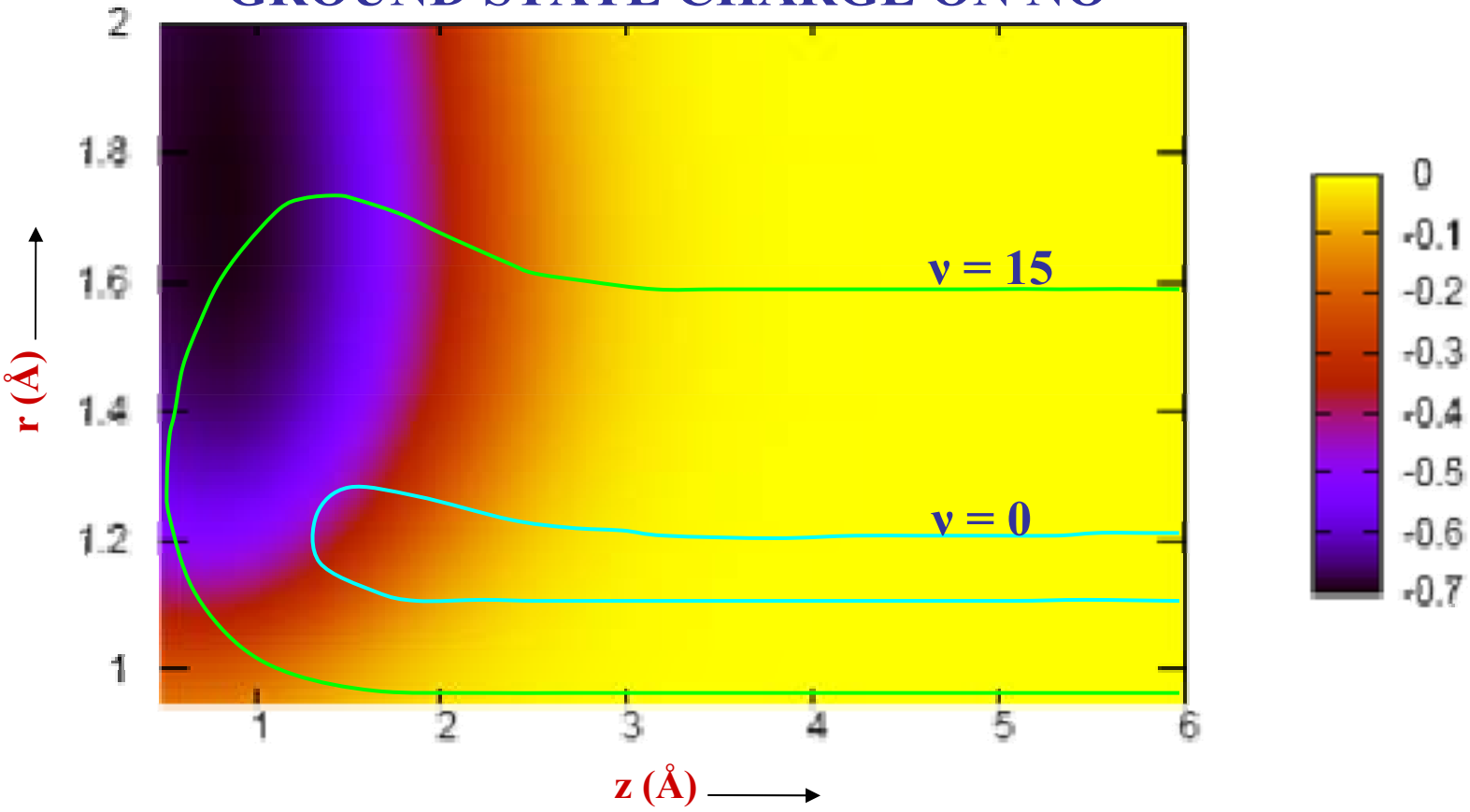


add small electric field → 3^d quantity

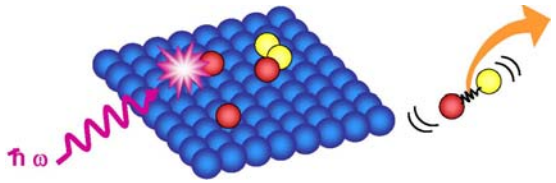


XI. Dynamics at Metal Surfaces

GROUND STATE CHARGE ON NO



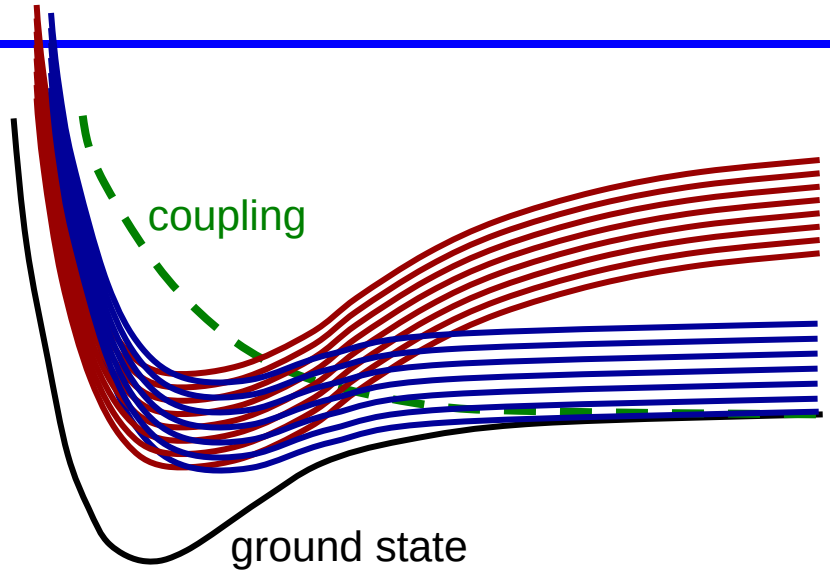
NO significantly charged when close to Au(111) and stretched to long bond lengths



XI. Dynamics at Metal Surfaces

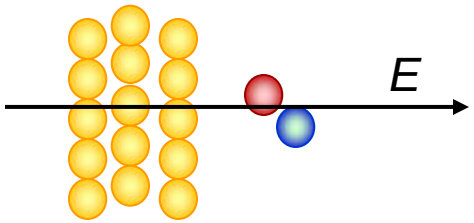
Park City
June 2005
Tully

Nitric Oxide on Gold:
Diabatic Description

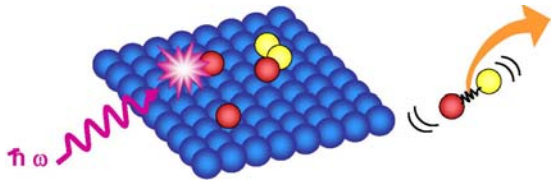


$$\begin{bmatrix} E_{ionic}(\mathbf{R}) & V(\mathbf{R}) \\ V(\mathbf{R}) & E_{neutral}(\mathbf{R}) \end{bmatrix} \longrightarrow$$ 3 unknowns

DFT calculation → ground state energy
effective charge on NO



add small electric field → 3^d quantity



XI. Dynamics at Metal Surfaces

Park City
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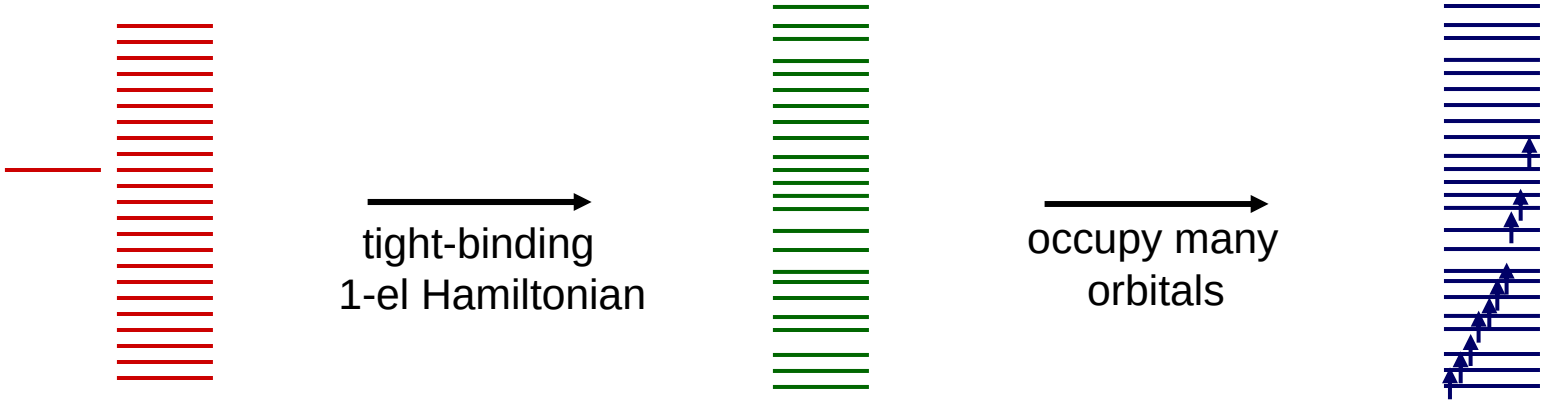
1. Map onto Anderson-Newns picture:



1-el diabatic orbitals

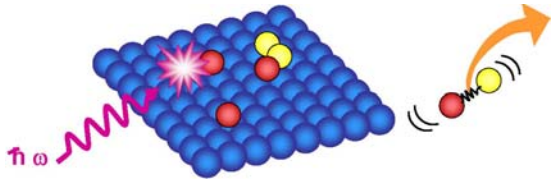
1-el adiabatic orbitals

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 comb of diabatic (or adiabatic) orbitals → many-el wave fn at any time is a specific occupation of these evolving mixed orbitals

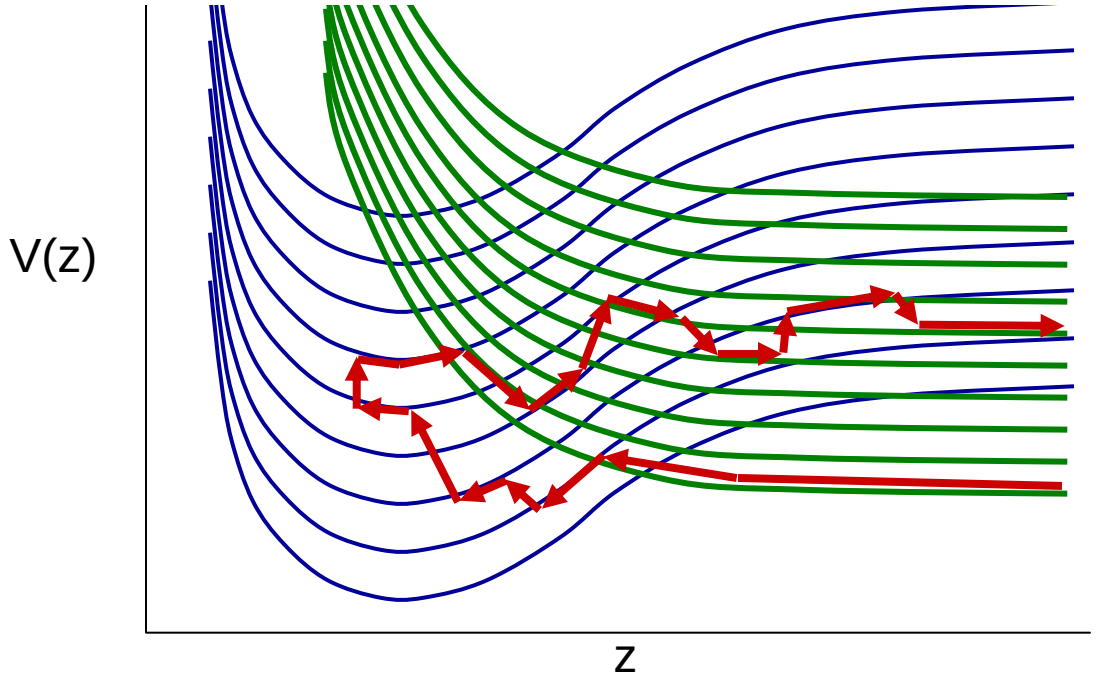
3. Surface Hop among adiabatic potential energy surfaces

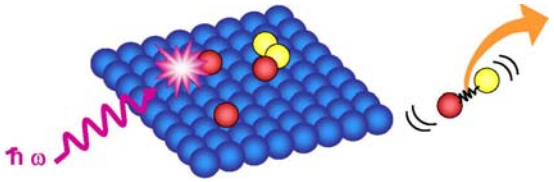


XI. Dynamics at Metal Surfaces

SIMULATIONS: NO on Au(111)

1. Adiabatic
2. Nonadiabatic: Electronic Friction
3. Nonadiabatic: Surface Hopping among myriads of ***adiabatic*** potential energy surfaces

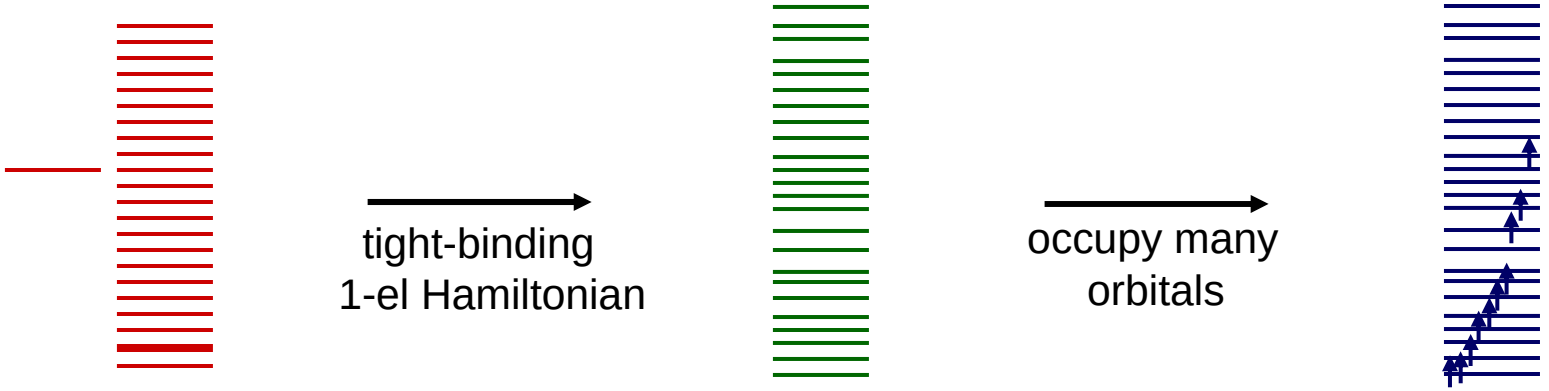




XI. Dynamics at Metal Surfaces

Park City
June 2005
Tully

1. Map onto Anderson-Newns picture:



1-el diabatic orbitals
1 + 40

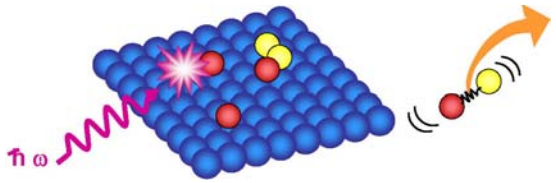
1-el adiabatic orbitals
41

many-el product wave fn.
20 electrons → ~ 10^{11} states

2. Evolve many-electron wave function along trajectory:

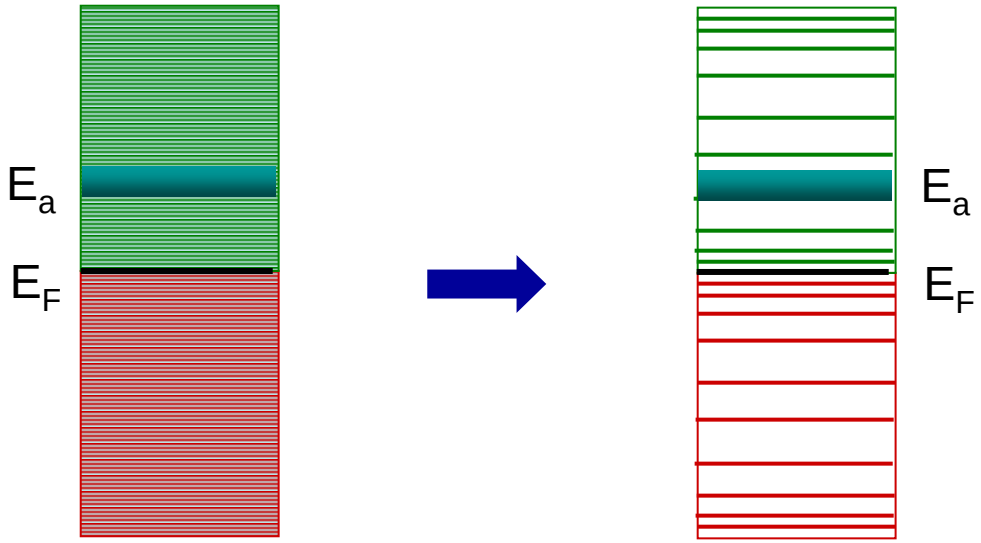
initial many -electron wave fn (eg, ground state) → each orbital evolves into linear comb of diabatic (or adiabatic) orbitals → many-el wave fn at any time is a specific occupation of these evolving mixed orbitals

3. Surface Hop among adiabatic potential energy surfaces



XI. Dynamics at Metal Surfaces

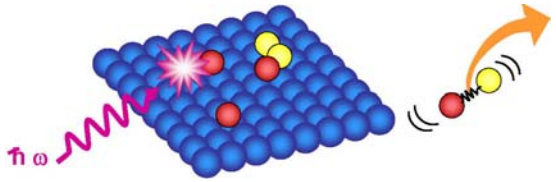
Discretization of the Continuum:



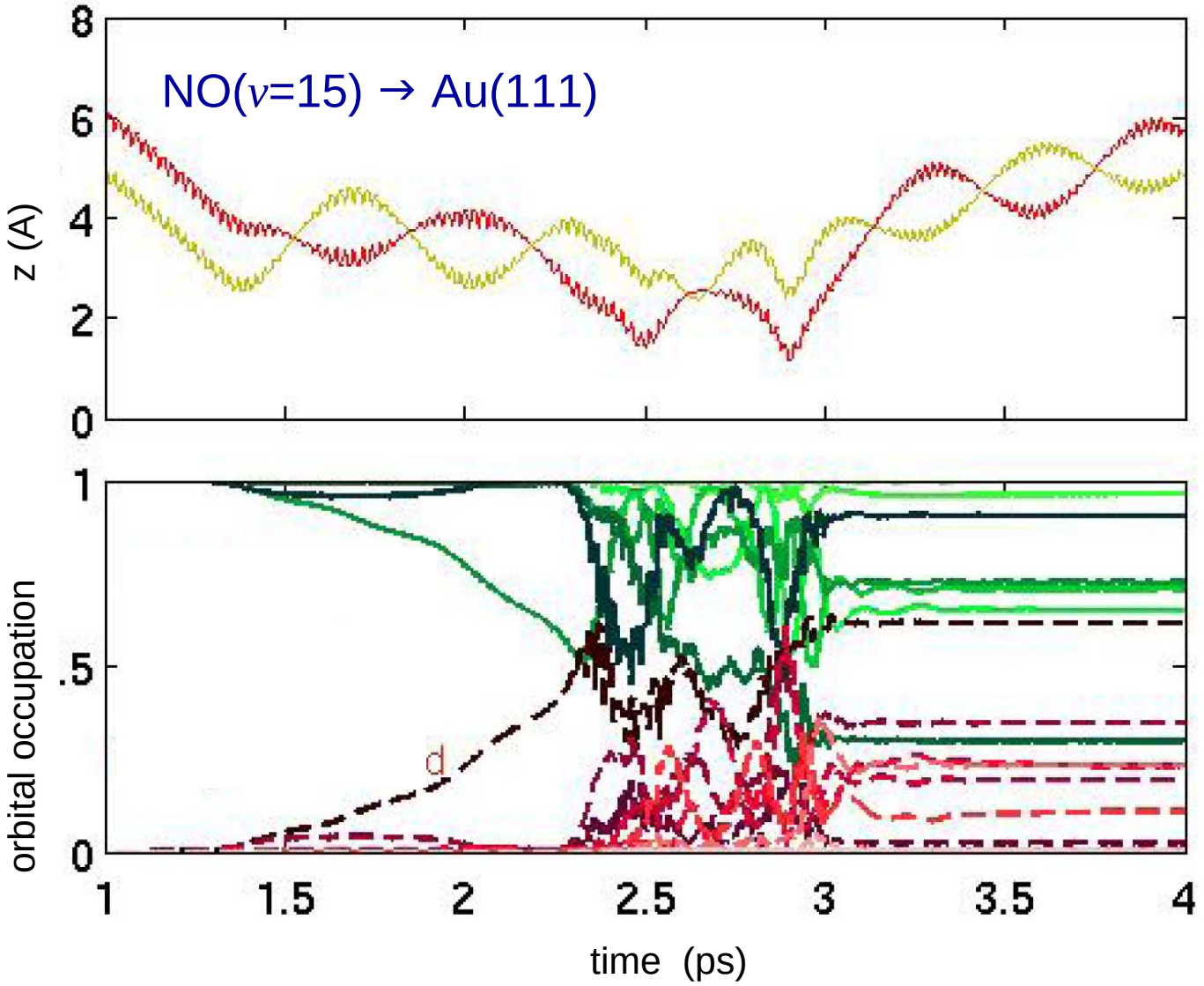
continuous discrete

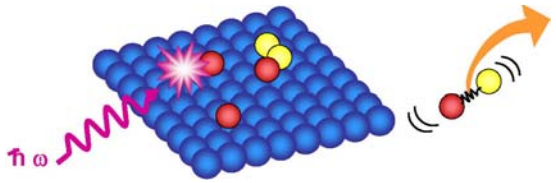
Optimally (non-equally) spaced discrete levels

"Efficient discretization of the continuum through contour integration",
N. Shenvi, J. R. Schmidt, S. Edwards and JCT, *Phys. Rev*. A **78**, 022502 (2008)

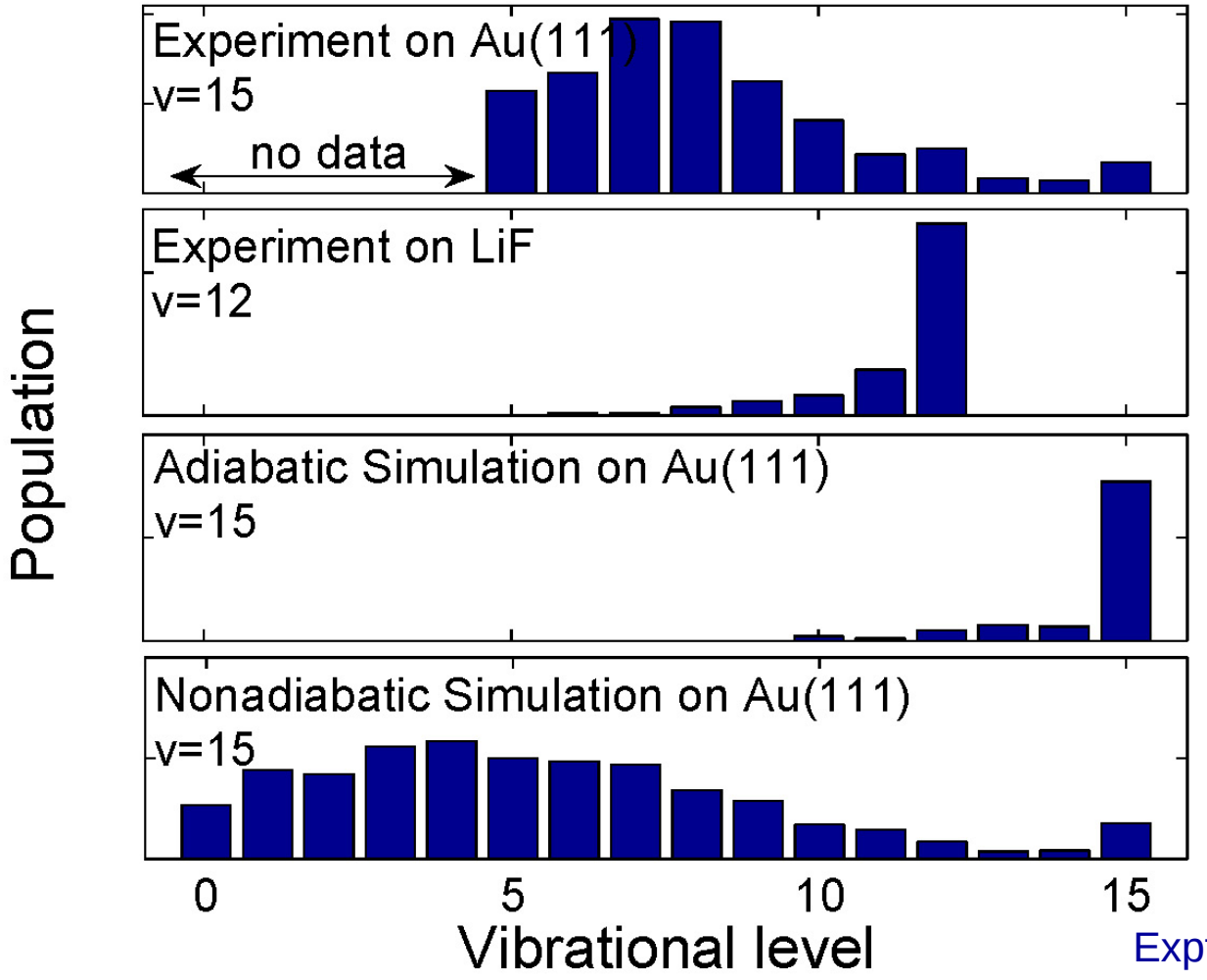


XI. Dynamics at Metal Surfaces

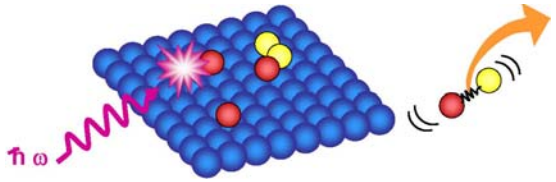




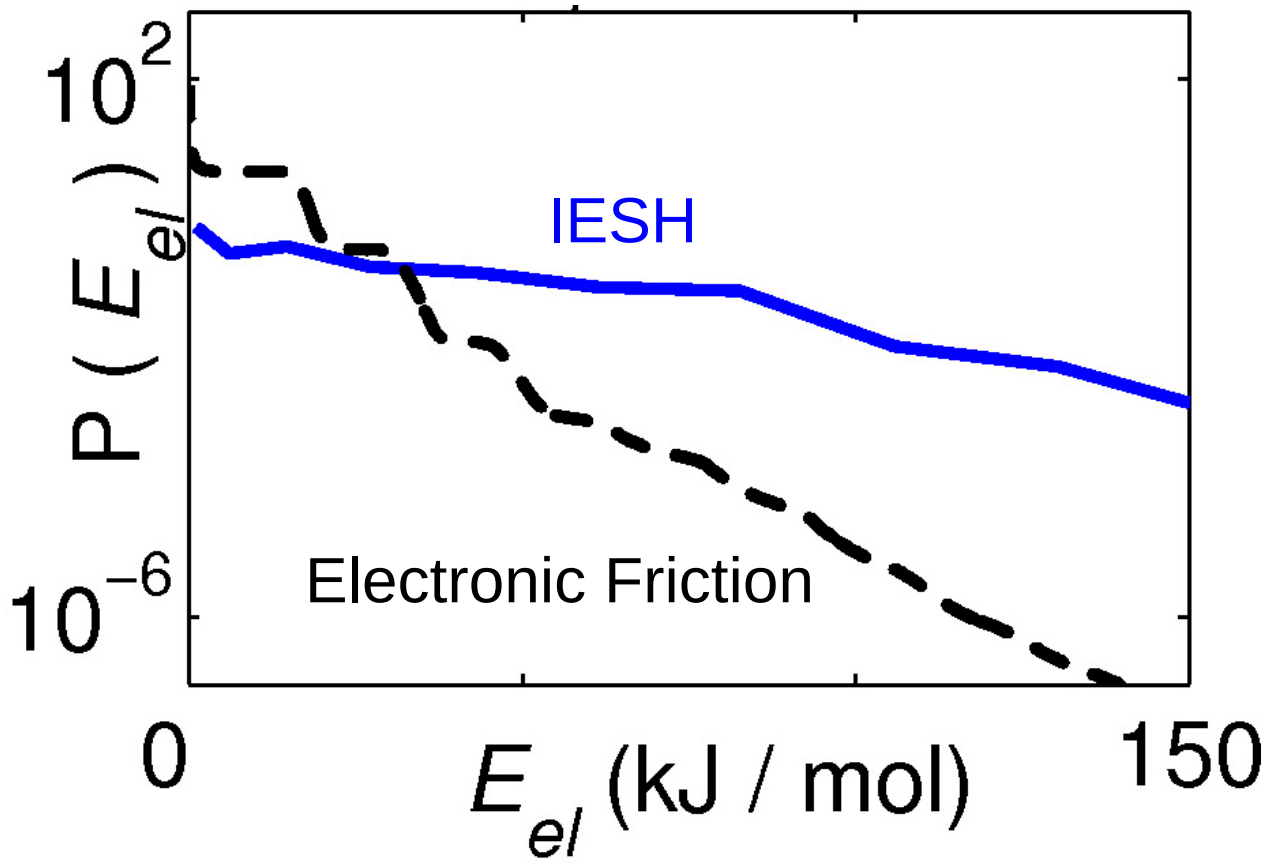
XI. Dynamics at Metal Surfaces

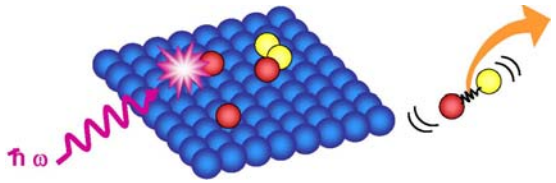


Expts: Huang, Rettner, Auerbach, Wodtke, *Science* **2000**, *290*, 111.



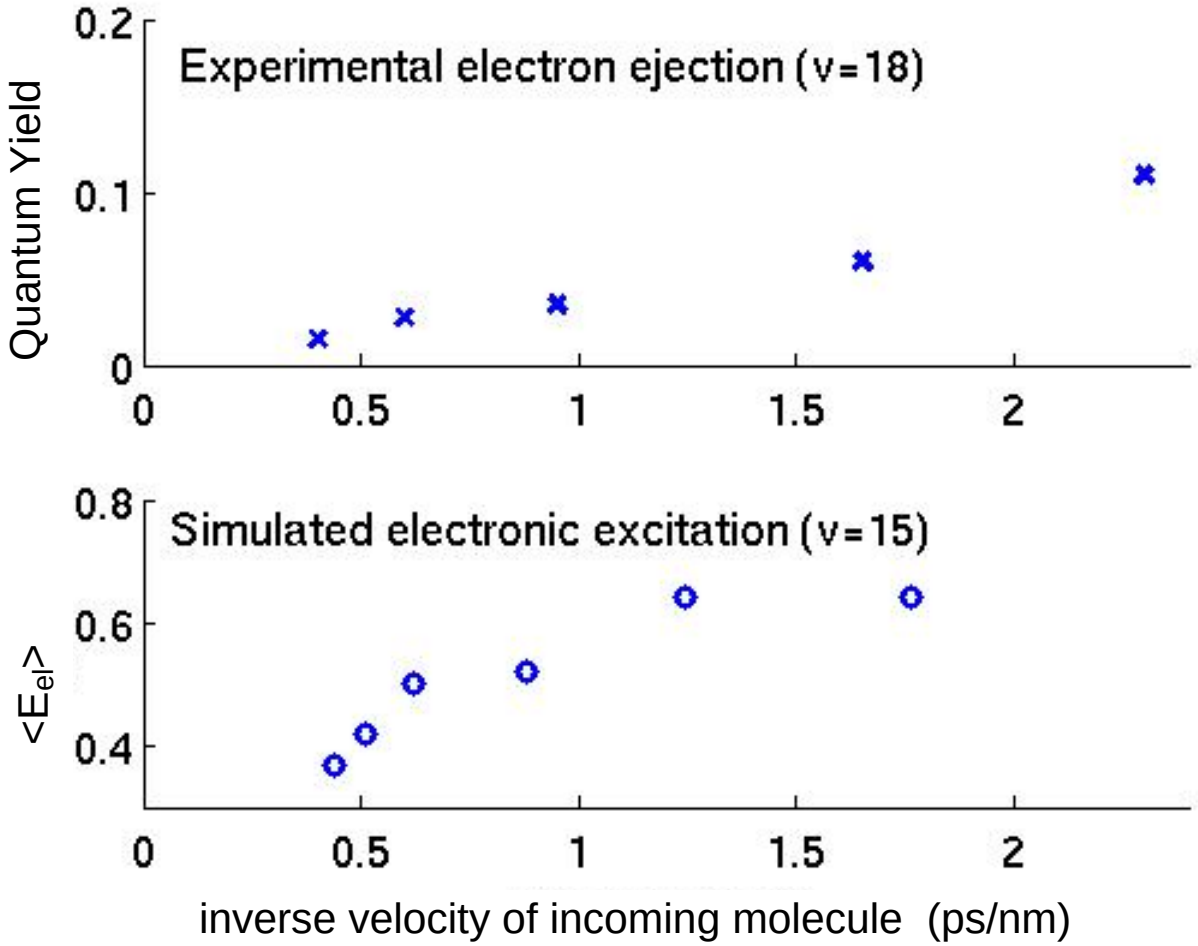
XI. Dynamics at Metal Surfaces

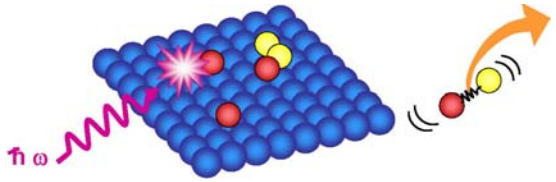




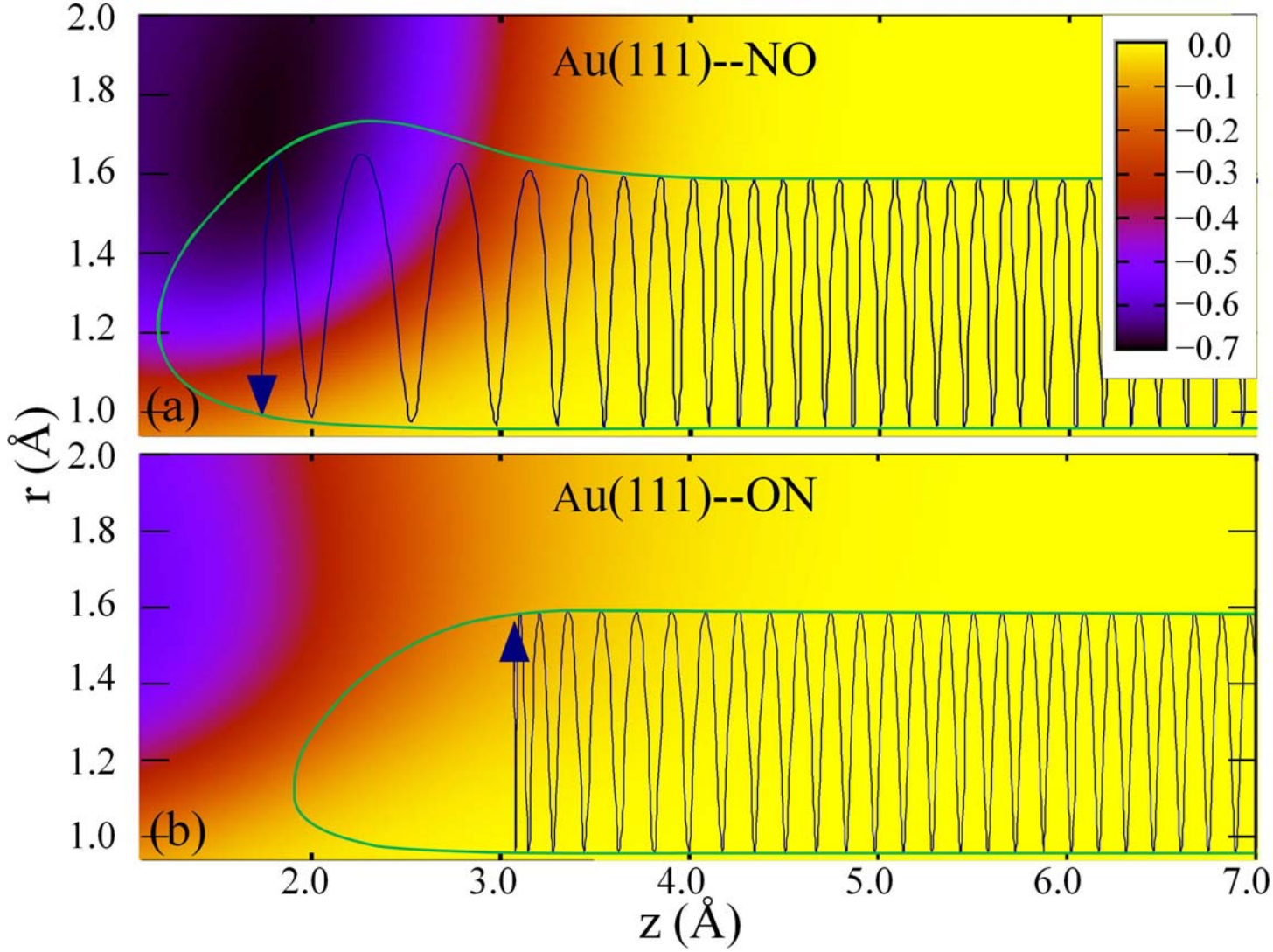
XI. Dynamics at Metal Surfaces

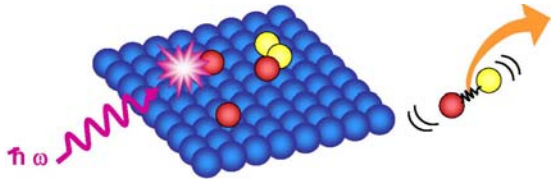
"Inverse Velocity Dependence of Vibrationally Promoted Electron Emission from a Metal Surface", Nahler, White, LaRue, Auerbach, Wodtke, *Science* **321**, 1191 (2008)





XI. Dynamics at Metal Surfaces





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

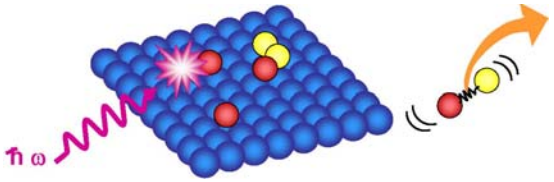
VIII. Beyond Born Oppenheimer

IX. Ehrenfest Dynamics

X. Surface Hopping

XI. Dynamics at Metal Surfaces

XII. Mixed Quantum-Classical Nuclear Dynamics

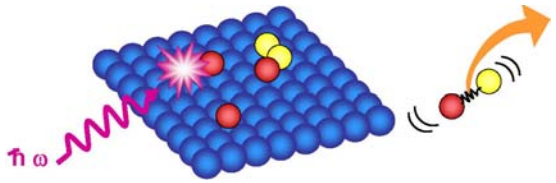


XII. Mixed Quantum-Classical Nuclear Motion

Tenets of Conventional Molecular Dynamics

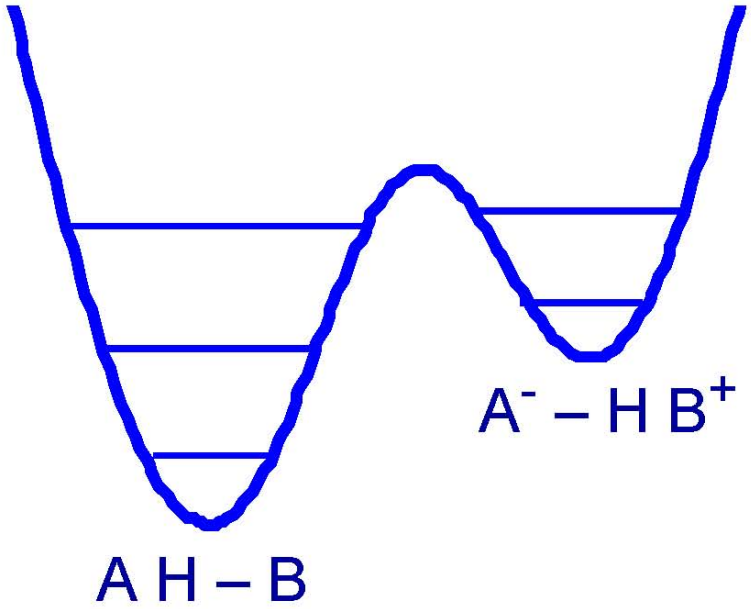
1. The Born-Oppenheimer Approximation — Multiple Electronic States, Metals, …

2. Classical Mechanical Nuclear Motion — Zero Point Motion, Quantized Energy Levels, Tunneling



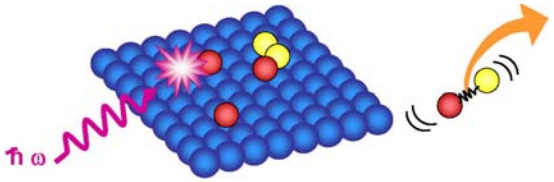
XII. Mixed Quantum-Classical Nuclear Motion

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



Quantum Effects:

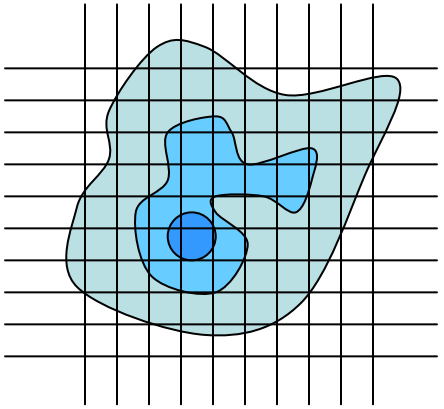
- Zero-Point Energy
- Quantized Energy Levels
- Tunneling



XII. Mixed Quantum-Classical Nuclear Motion

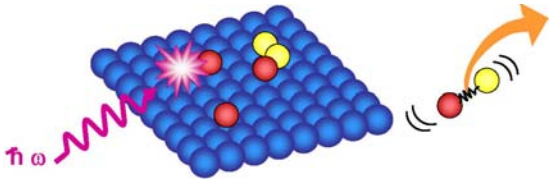
Ultimate Solution:

Treat All Electrons and Nuclei
by Quantum Mechanics



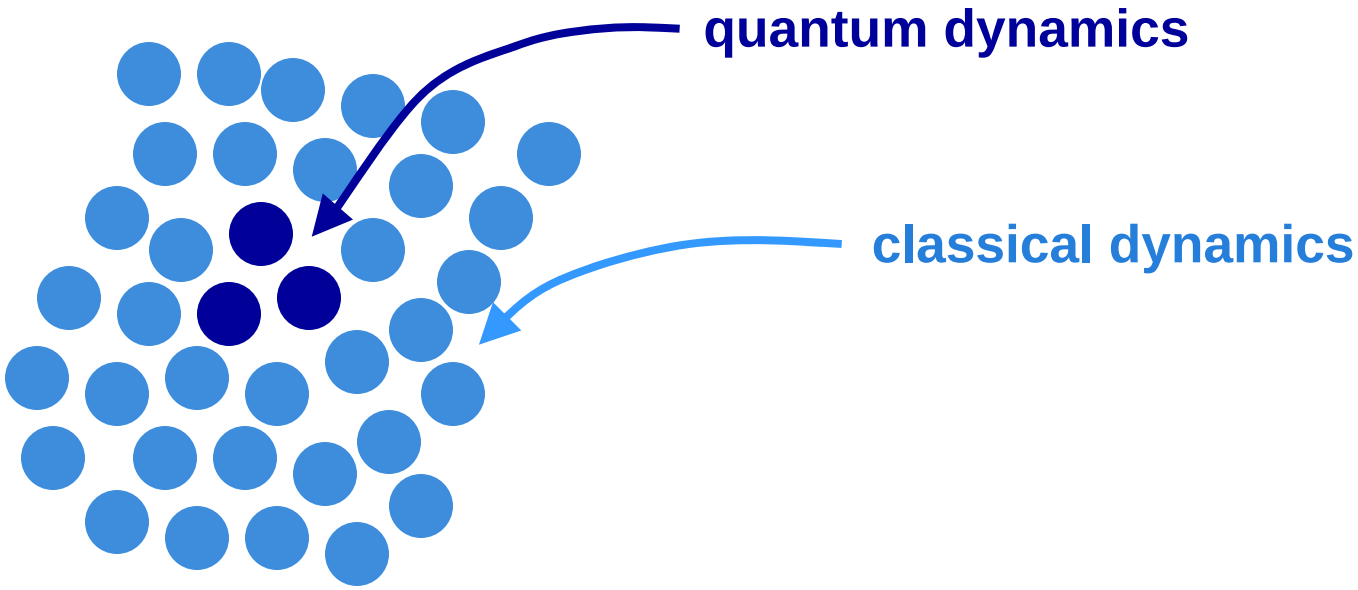
Problem:

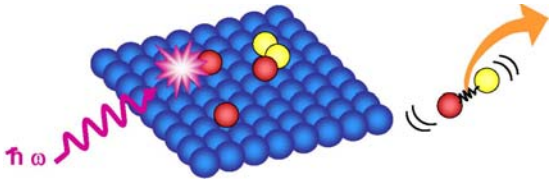
Scaling with Size is Prohibitive



XII. Mixed Quantum-Classical Nuclear Motion

AN ALTERNATIVE STRATEGY:
MIXED QUANTUM–CLASSICAL DYNAMICS





XII. Mixed Quantum-Classical Nuclear Motion

AN ALTERNATIVE STRATEGY: MIXED QUANTUM–CLASSICAL DYNAMICS

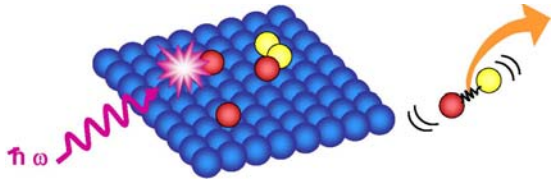
Treat crucial electronic or nuclear degrees of freedom by quantum mechanics, and the remaining nuclei by classical mechanics.

self-consistency

quantum "back-reaction" on classical particles

Ehrenfest vs. Surface Hopping

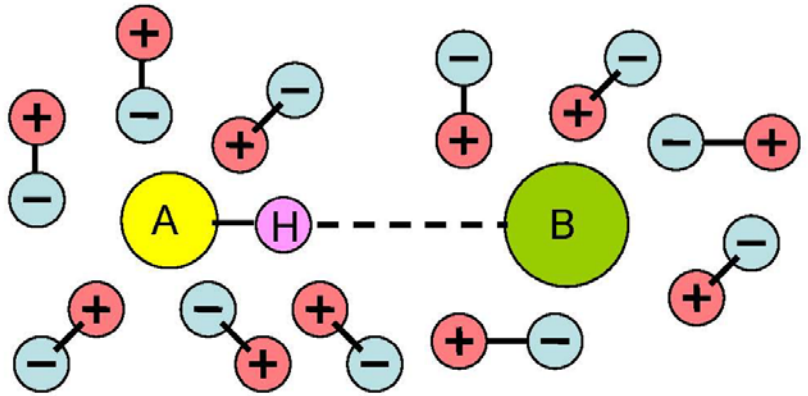
Sharon Hammes-Schiffer



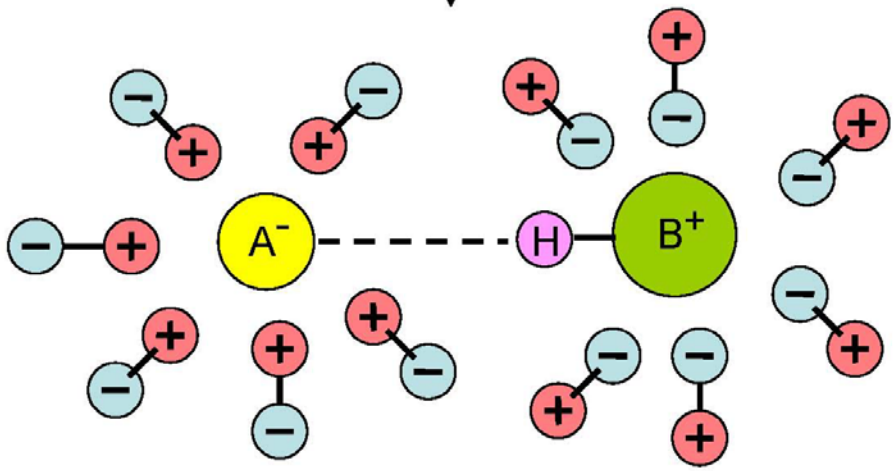
XII. Mixed Quantum-Classical Nuclear Motion

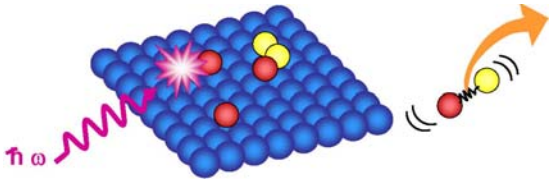
PROTON TRANSFER IN SOLUTION

covalent reactant:



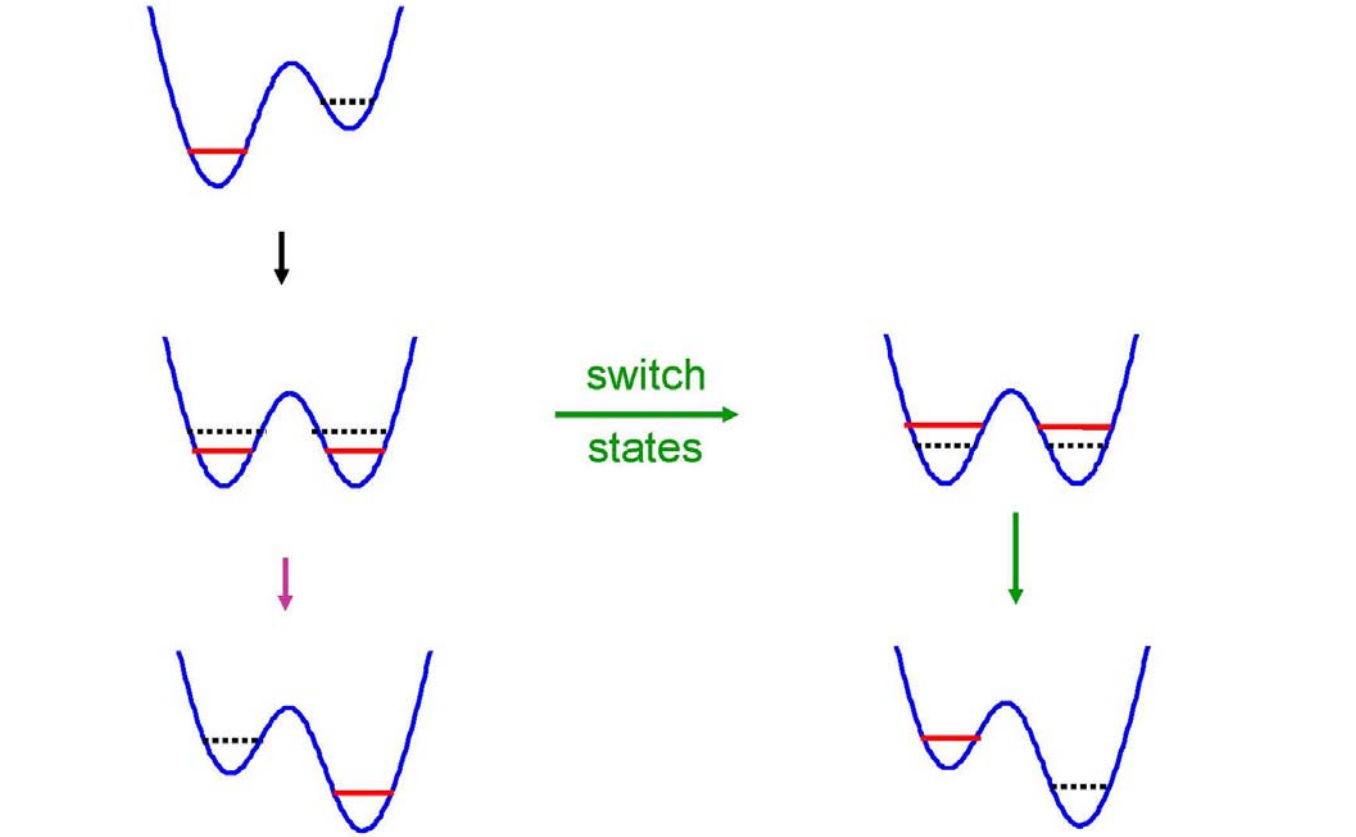
ionic product:

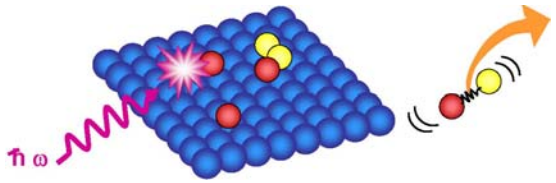




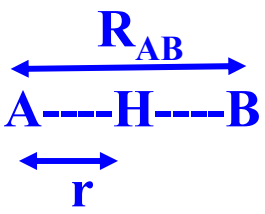
XII. Mixed Quantum-Classical Nuclear Motion

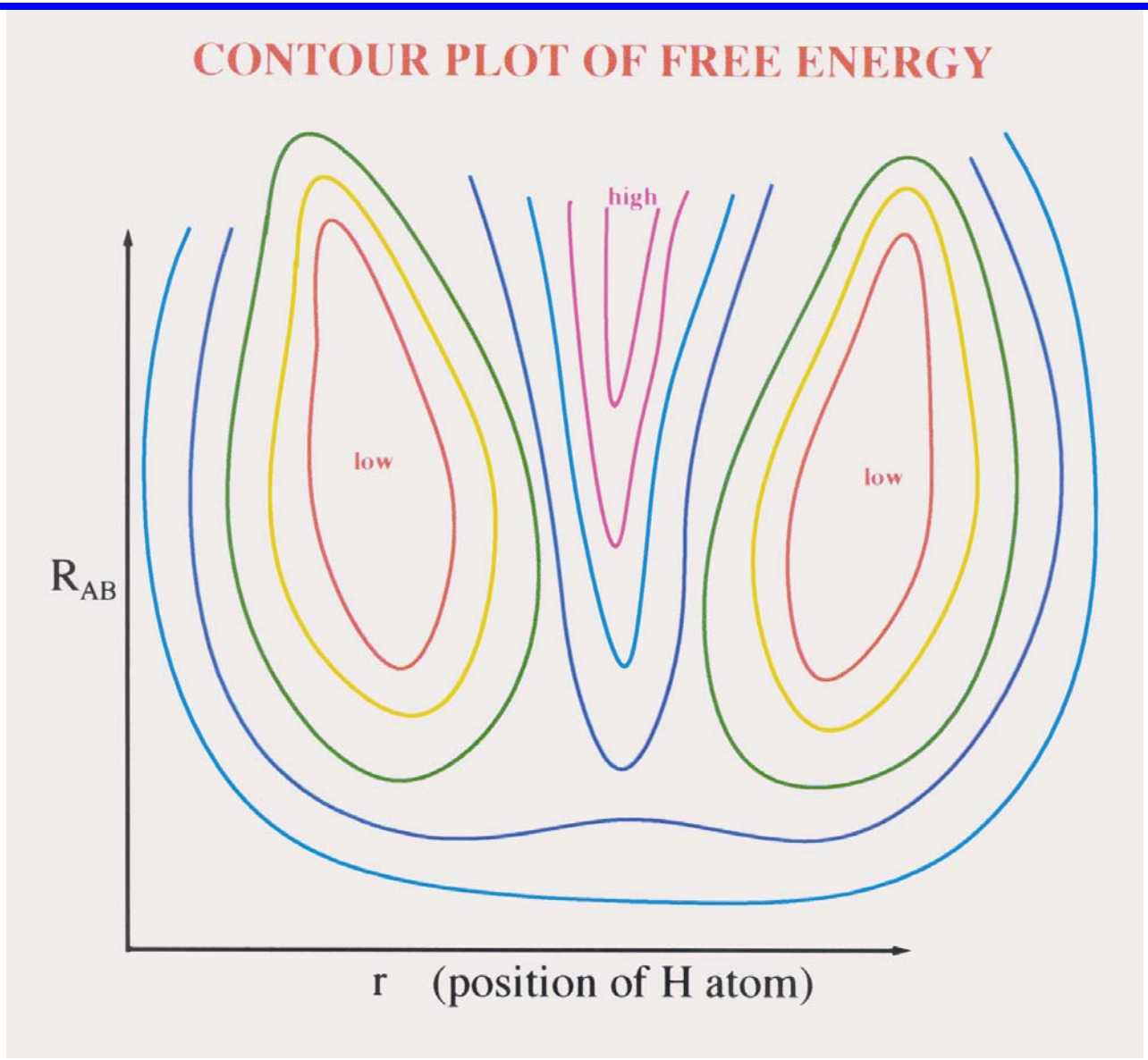
ADIABATIC vs. NON-ADIABATIC

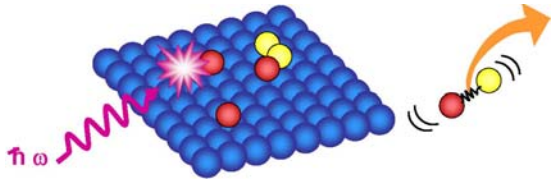




XII. Mixed Quantum-Classical Nuclear Motion





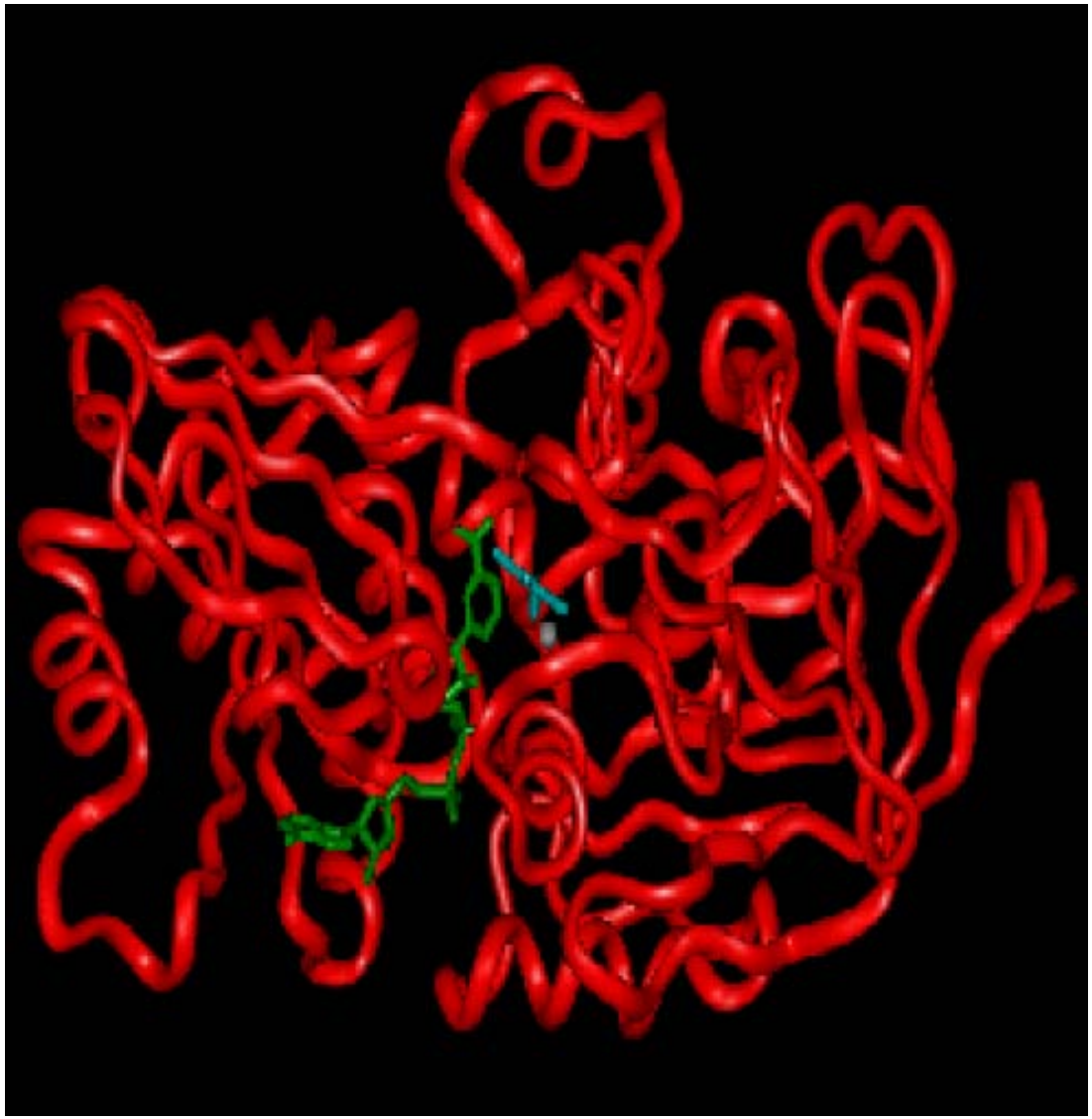


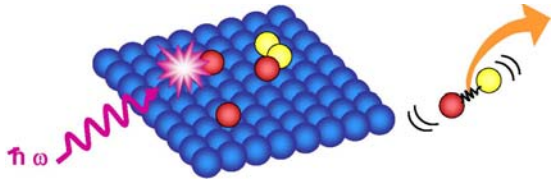
XII. Mixed Quantum-Classical Nuclear Motion

Proton and Hydride Transfer in Enzymes:

Sharon Hammes-Schiffer
Penn State University

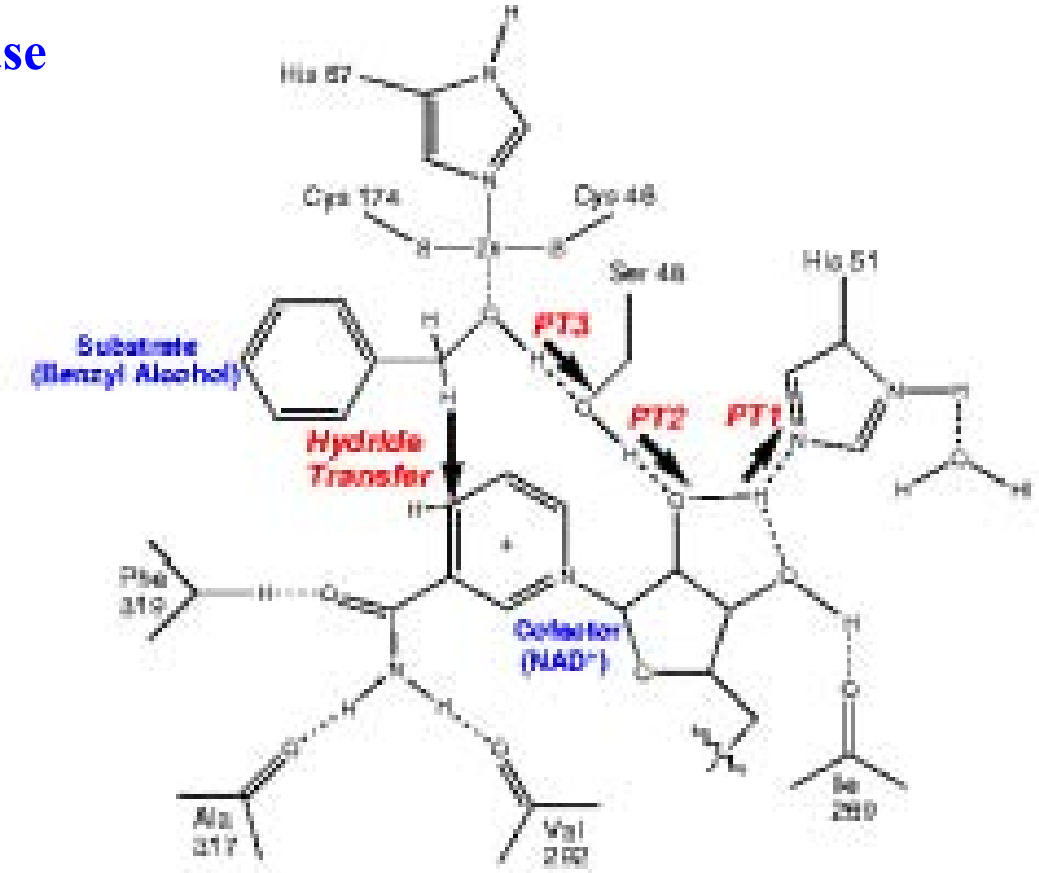
liver alcohol dehydrogenase (LADH)





XII. Mixed Quantum-Classical Nuclear Motion

liver alcohol dehydrogenase



Sharon Hammes-Schiffer