



Aquilanti from Italy



*At the
Centre of
the Universe,
Bithoor, Jan. '90*

Land of Ψ !

Potential energy curves, surfaces, curve crossing,
avoided crossing and conical intersections in
molecular systems

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Outline of the tutorial

- Potential Energy
- Enter Quantum Mechanics (1926)
- Hydrogen atom, many electron atoms
- Molecular system, Born-Oppenheimer approximation
- Representing potential energy curves and surfaces
- Dynamics: Classical and Quantum Mechanical
- Trajectories and wave packets
- Observing the transition state
- Non-crossing rule (Jahn-Teller effect)
- Conical intersections
- Non-adiabatic coupling and the nuances

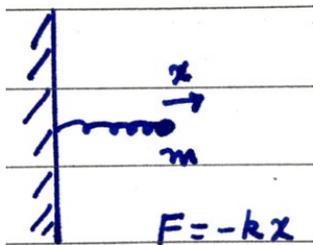
Recipe for chemical dynamics

- Solve the time-independent Schrödinger equation for electronic motion for a given set of nuclear coordinates
- By including the internuclear repulsion, construct the potential energy surface
- Solve the time-(in)dependent Schrödinger equation for nuclear motion
- Obtain the bound (v,j) states for nuclear motion
- Or solve the scattering problem
- When the electronic states are close to each other, go beyond Born-Oppenheimer approximation
- Determine non-adiabatic coupling terms
- Solve the multi-electronic state problem
- Essential for femtosecond and attosecond chemistry
- Remember uncertainty principle for time and energy!

Potential Energy, relative by definition

- $V = mgh,$
- $g = GM_{\oplus}/r_{\oplus}^2,$
- $V = -Gm_1m_2/r.$

- $V = (1/2) k x^2,$ for a mass m held by a spring to an infinite mass



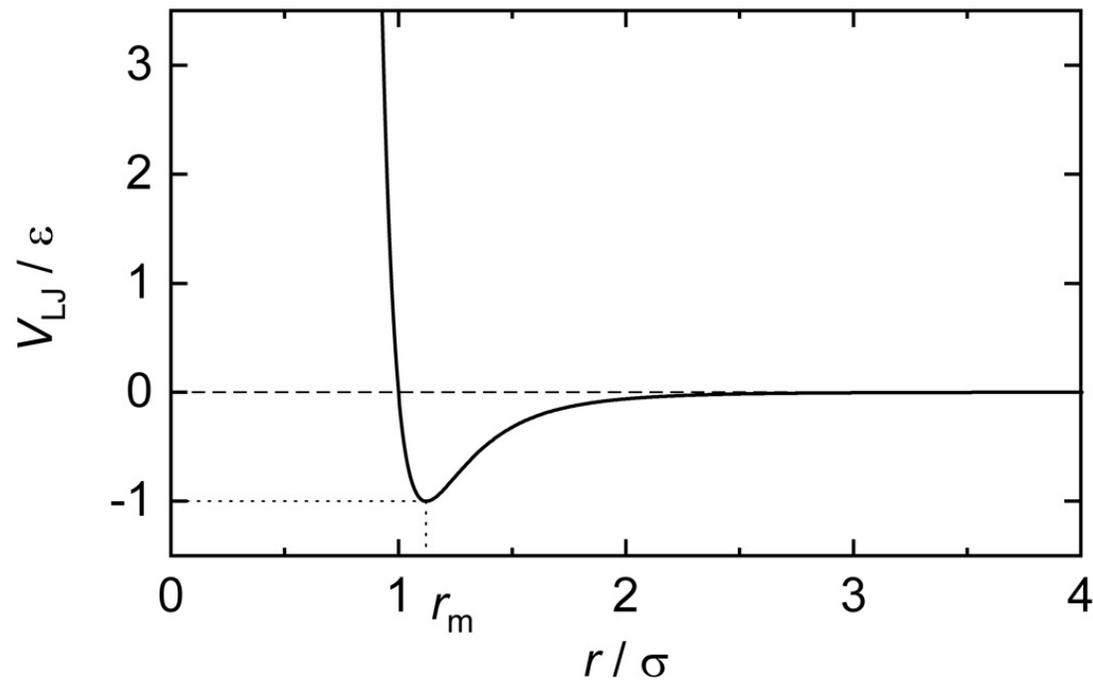
- Coulomb's Law:
- $V = q_1q_2/r$

- Earliest indication of intermolecular interaction in van der Waals equation (1873):
- $\left(P + \frac{n^2a}{V^2}\right) (V - nb) = nRT$

Lennard-Jones potential (1924):

$$V_{LJ} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

Plot in reduced variables



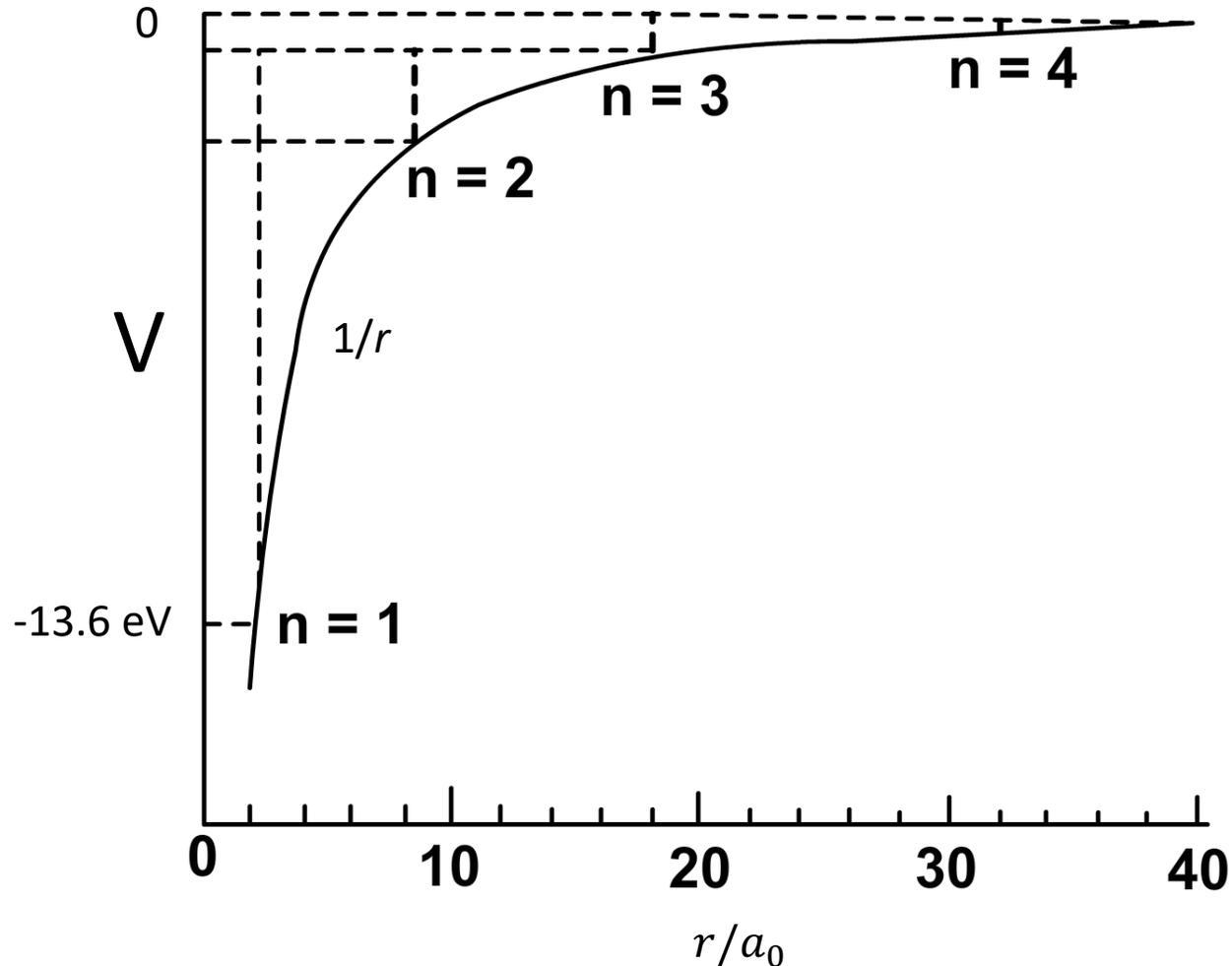
Enter Quantum Mechanics (1926)

- The wave function (Ψ) contains all the information about the system
- It evolves with time
- $-\frac{i\hbar\partial\Psi(t)}{\partial t} = \mathcal{H}\Psi(t)$, \mathcal{H} is the Hamiltonian operator
- First order differential equation in time t
- $\Psi(t) = U(t, t_0) \Psi(t_0)$
- $U(t, t_0) = e^{-i\mathcal{H}t/\hbar}$, evolution operator
- $UU^\dagger = 1$; U is unitary

Time-independent approach

- $H\Psi = E\Psi$
- $H\psi_n = E_n\psi_n$
- $H = T + V$
- $T = p^2/(2m)$
- $V = V(x)$
- $[T, V] \neq 0$
- For hydrogen atom,
- $H_{el} = -\frac{\hbar^2}{2m}\nabla^2(KE) - \frac{e^2}{r}(PE),$
- $m = \frac{m_p m_e}{m_p + m_e} \approx m_e,$
- $H\psi_n(r, \theta, \phi) = E_n\psi_n(r, \theta, \phi),$
- $E_n = -\left(\frac{1}{2}\right) \text{Hartree}$
 $= -\frac{13.6}{n^2} \text{eV}.$

The hydrogen atom potential



The Coulombic potential V goes to $-\infty$ as $r \rightarrow 0$.
Quantum mechanics puts a lower bound: -13.6 eV
Ionization potential: 13.6 eV
Bound states: $n = 1, 2, 3, \dots$

For a many electron atom

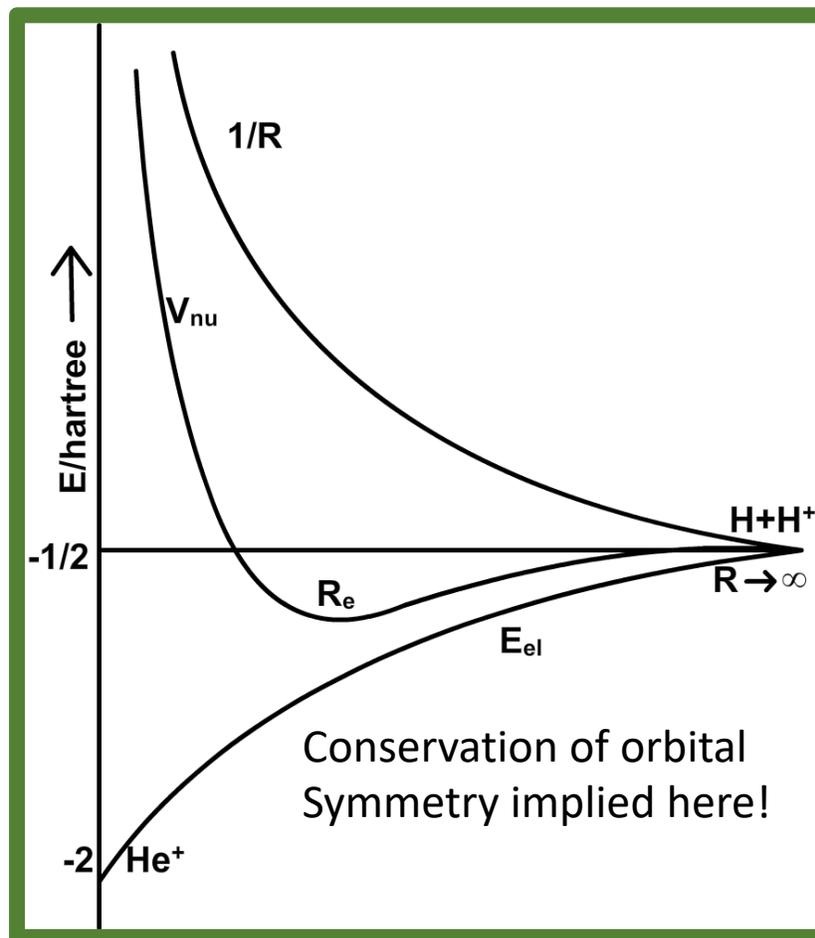
$$\begin{aligned} \bullet H_{el} &= -\frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \frac{Ze^2}{r_i} + \sum_{j>i}^n \sum_{i=1}^n \frac{e^2}{r_{ij}}, \\ &= \text{K.E.} + \text{P.E.} \end{aligned}$$

- P.E. = Potential energy for electronic motion
- No analytic solution

For a molecular system

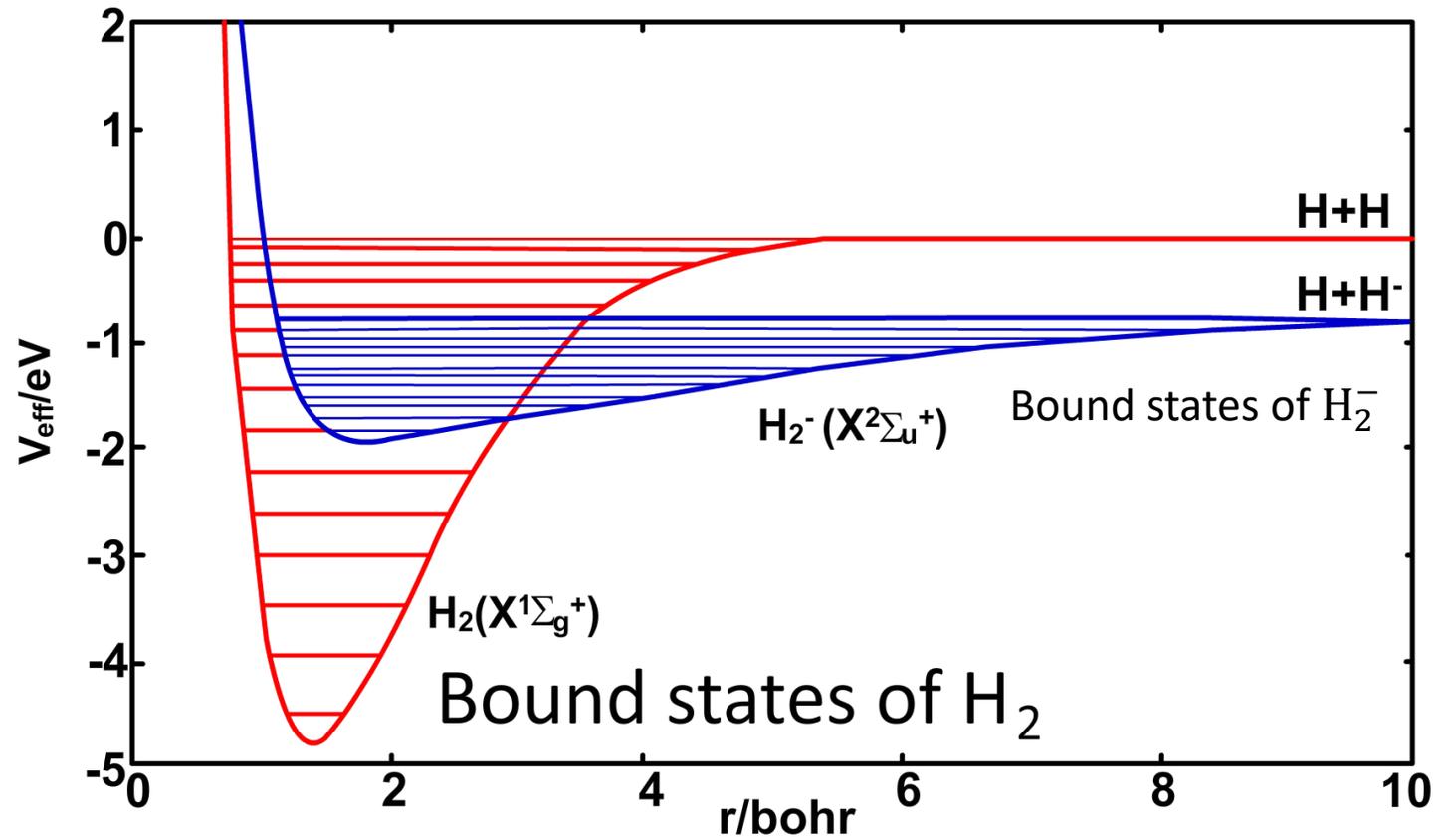
- $\Psi = \Psi (R, r)$, r electron coordinates and R nuclear coordinates
- $\Psi = \chi(R)\Psi (r; R)$.
- Born-Oppenheimer approximation: electronic motion and nuclear motion are separable
- Forms the basis for defining the potential energy for nuclear motion
- For a diatomic molecule AB ,
- $$H = -\frac{\hbar^2}{2\mu} \nabla_A^2 - \frac{\hbar^2}{2\mu} \nabla_B^2 + H_{\text{el}} + \frac{Z_A Z_B e^2}{R_{AB}}.$$
- Kinetic energy + potential energy for the nuclear motion

$$\text{H}_2^+ : V_{\text{nu}} = E_{\text{el}} + \left(\frac{1}{R}\right)$$



For a diatomic system,

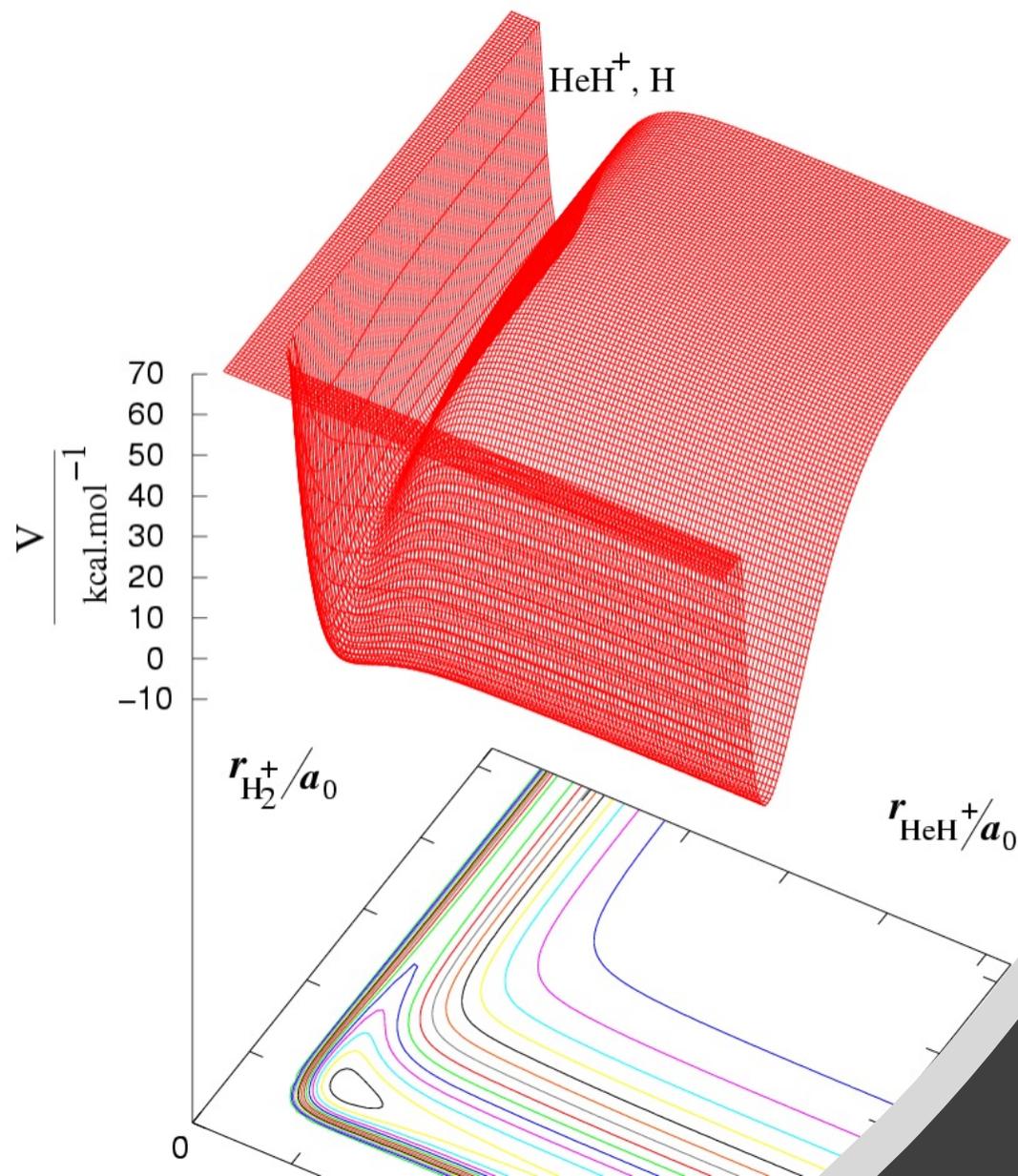
$$H_{\text{nu}}\chi_n(R) = \left[-\frac{\hbar^2}{2\mu} \nabla_R^2 + V(R) \right] \chi(R) = E_n \chi_n(R)$$



Bound states: quantum mechanical signature

Potential energy curves represented by

- $V = D_e [1 - e^{-\beta(R-R_e)}]^2$, Morse function
- $V(R) = \sum \lambda_i x^i$, $x = R - R_e$
- $V(x) = \left(\frac{k}{2}\right)x^2$, Harmonic oscillator
- $E_n = \left(n + \left(\frac{1}{2}\right)\right) h\nu$,
- **Chemical bonds are represented by a "—" but are DYNAMIC!**
- Minimum energy = ZPE $\neq 0$

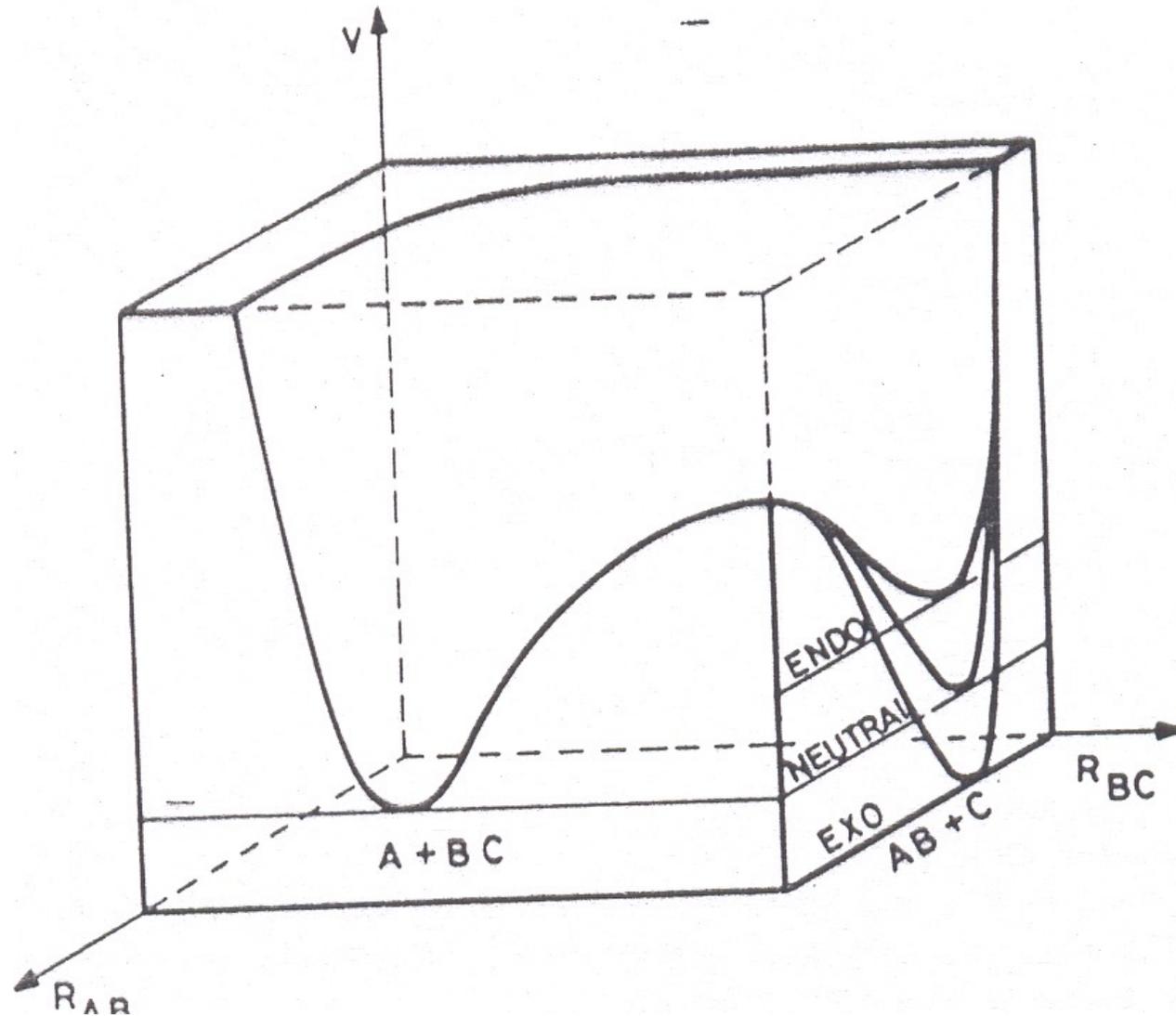


Potential
energy surface
for HeH_2^+

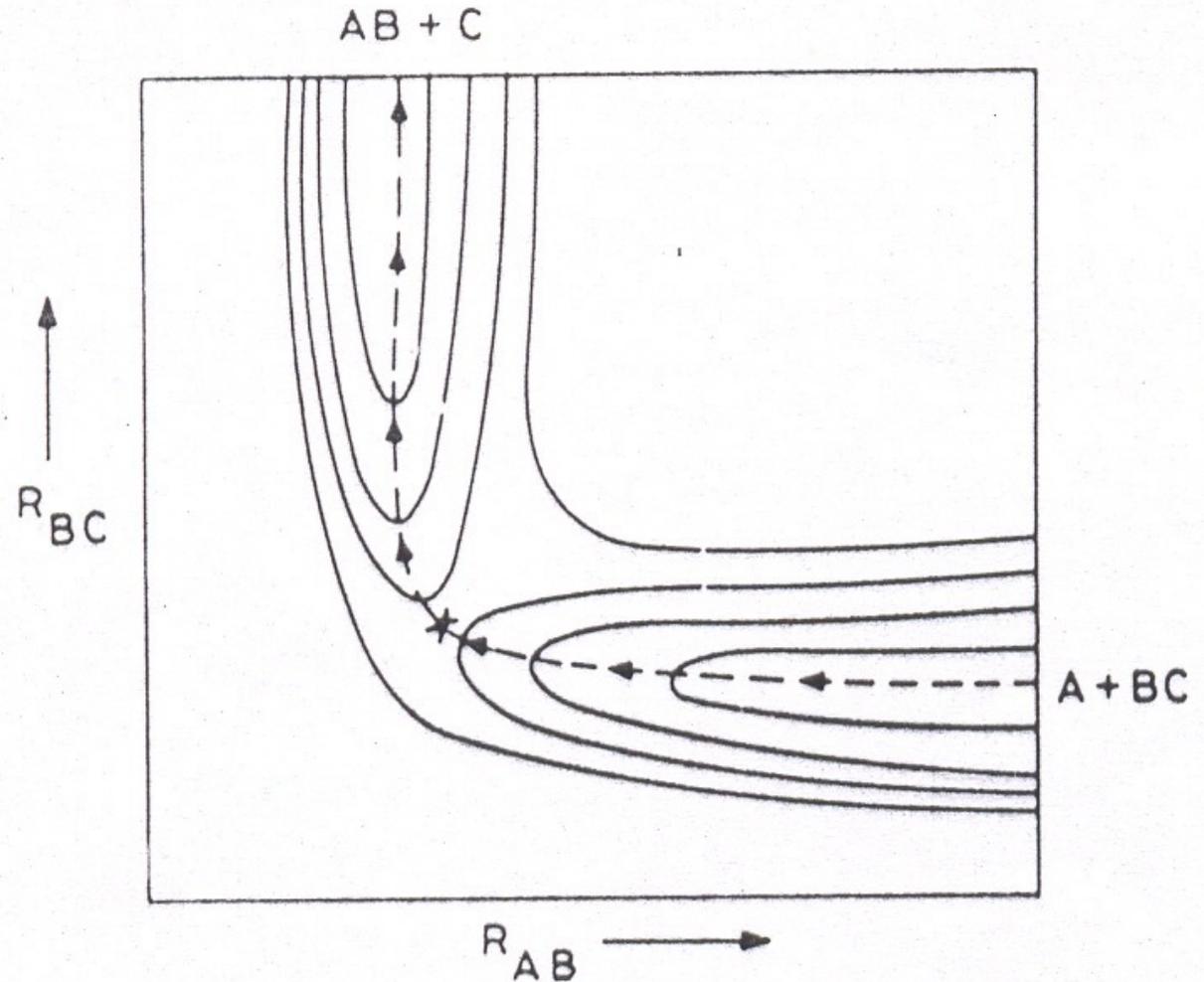
Dynamics of a chemical reaction

- $\text{H} + p\text{-H}_2 (\uparrow\downarrow) (j = 0) \rightarrow o\text{-H}_2 (\uparrow\uparrow) (j = 1) + \text{H}$
- Please note that the **nuclear** (not electron) **spins** are shown
- Farkas (1930), $E_a = 0.24 \text{ eV}$, cf. $D_e(\text{H}_2) = 4.74 \text{ eV}$
- **Puzzle:** The exchange reaction has to take place for the *o-/p-* conversion because the transformation without breaking the bond is symmetry forbidden. Yet, the activation energy is far less than the bond dissociation energy.
- Need to look into the dynamics
- First requirement: potential energy surface

Schematic
diagram of a PES
for an $A + BC \rightarrow$
 $AB + C$ exchange
reaction



Contour
diagram for a
typical
thermoneutral
reaction



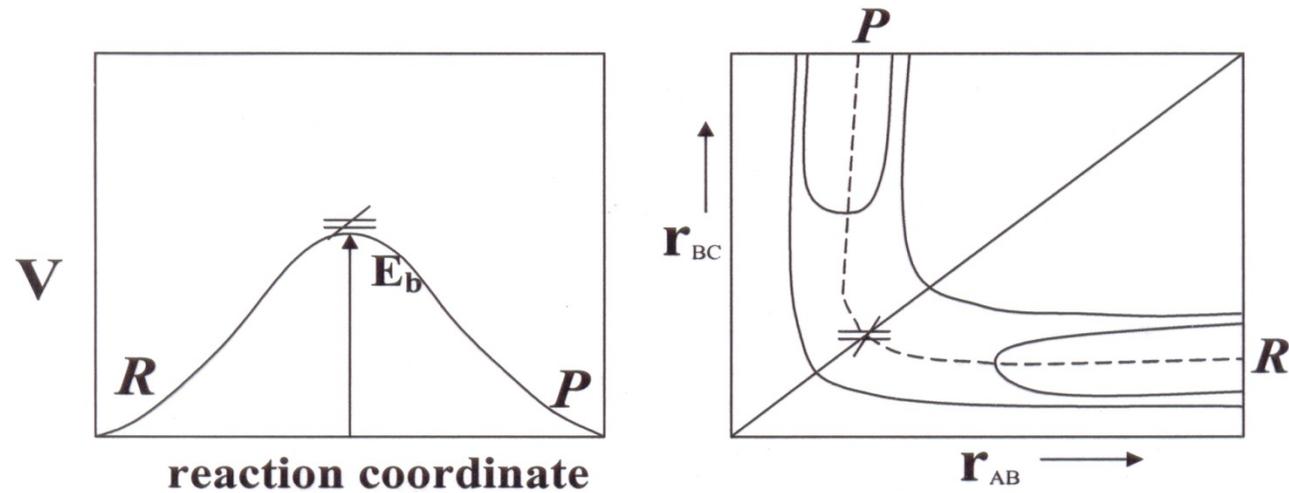
What distinguishes the R from the P ?

“Obviously” the hill that separates the two

Where do you draw the line?

Through the hill-top.

The hill-top is identified as the Transition State \neq



The dashed line is an idealized path

Top of the hill is a potential maximum along the reaction path. Referred to as a saddle

Saddle of a horse and the mountain in Scotland with the same name



Source: wikipedia

Saddle in Siachen Glaciers



Maximum in one direction, minimum in the mutually orthogonal direction

PES for $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$

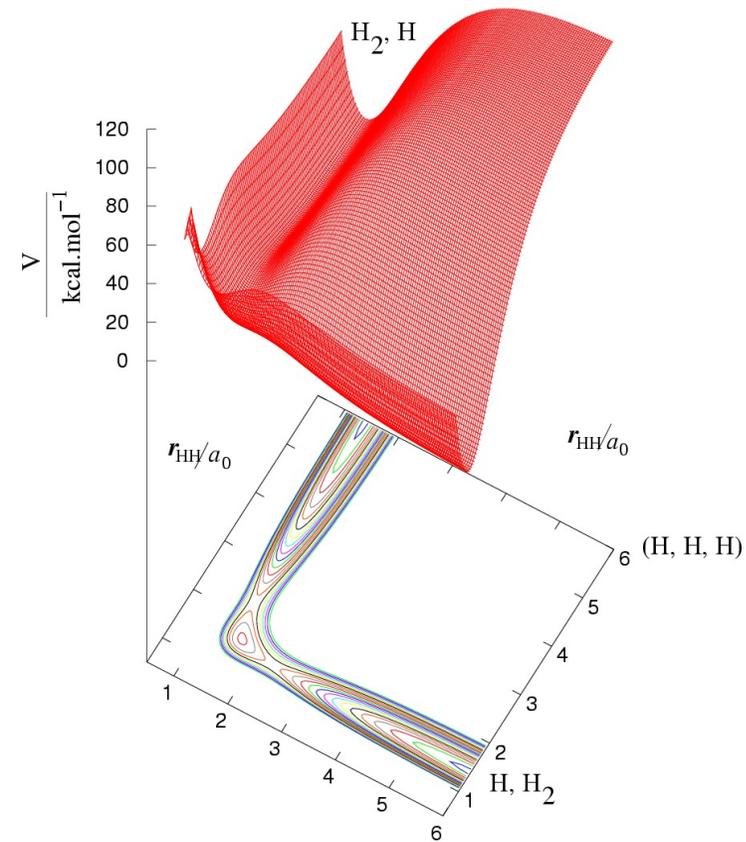
- London equation (1928):

- $$V = \sum_{i=1}^3 Q_i \pm \sqrt{(J_1 - J_2)^2 + (J_2 - J_3)^2 + (J_3 - J_1)^2}$$

- Based on Heitler-London equation (1927) for $V(R) = \frac{Q \pm J}{1 \pm S}$

- London-Eyring-Polanyi equation (1931), setting $Q/E = 0.14$

London- Eyring- Polanyi PES



Eyring lake, in the old literature



Michael Polanyi
(1891–1976)

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Resonance

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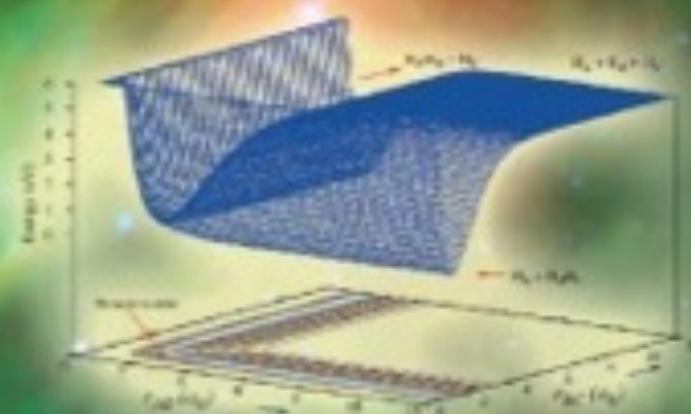
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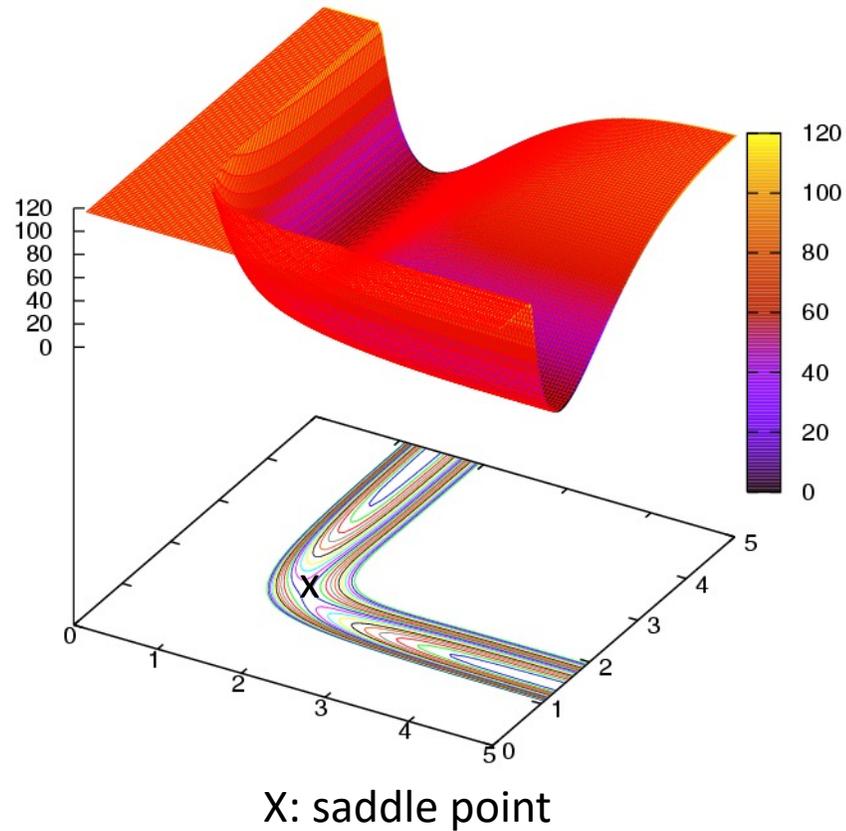
- Michael Polanyi's Philosophy of Science ♦
- Chemistry at the Nanoscale ♦
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- Small Open Reading Frames ♦
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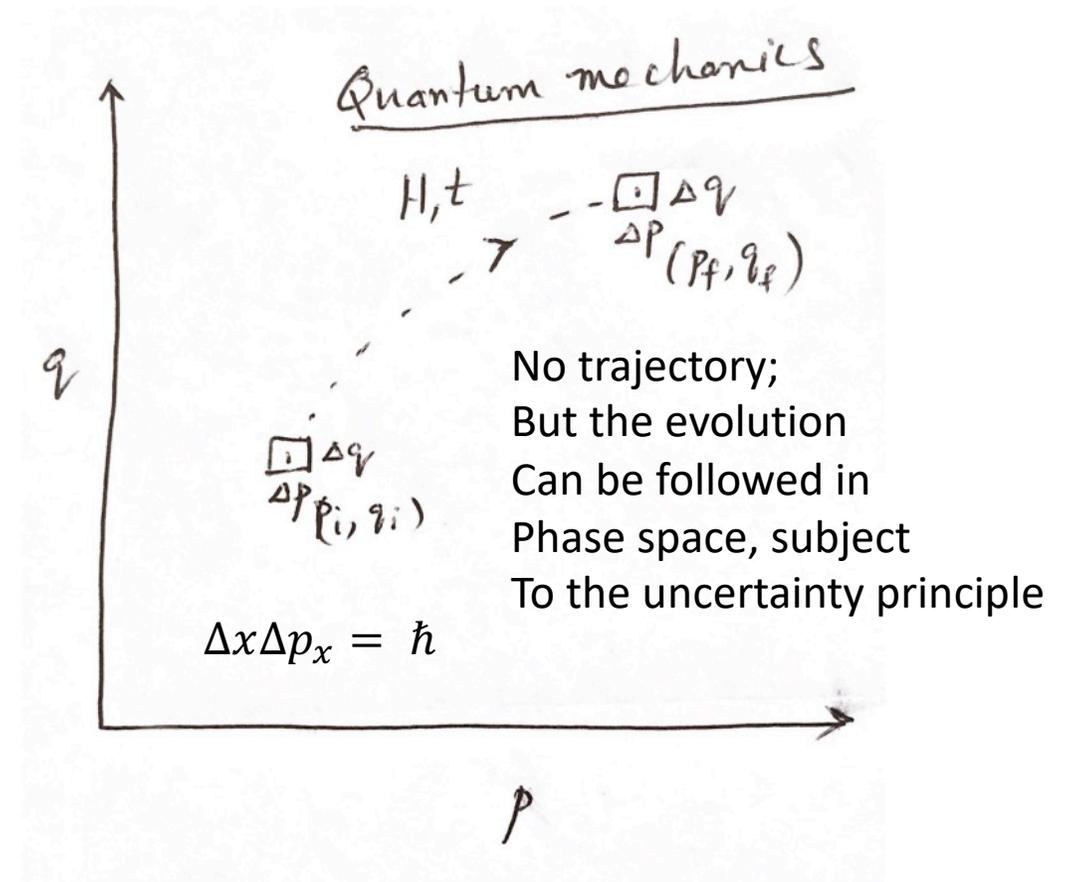
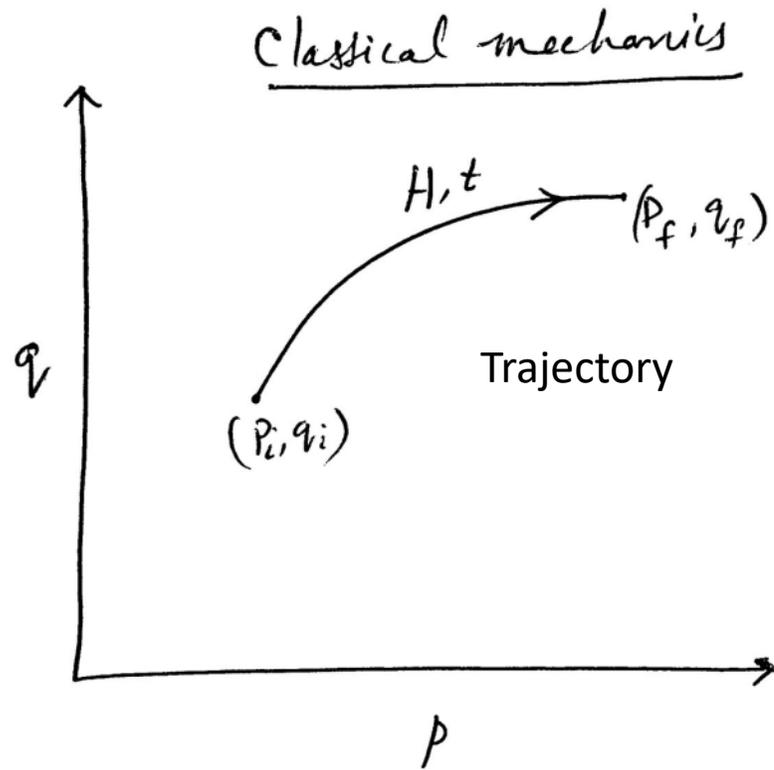


Springer

Ab initio PES (Siegbahn and Liu at IBM (1973))



Dynamics



PES in scaled
and skewed
coordinates:
three particle
motion
converted into
the motion of
a fictitious
single particle

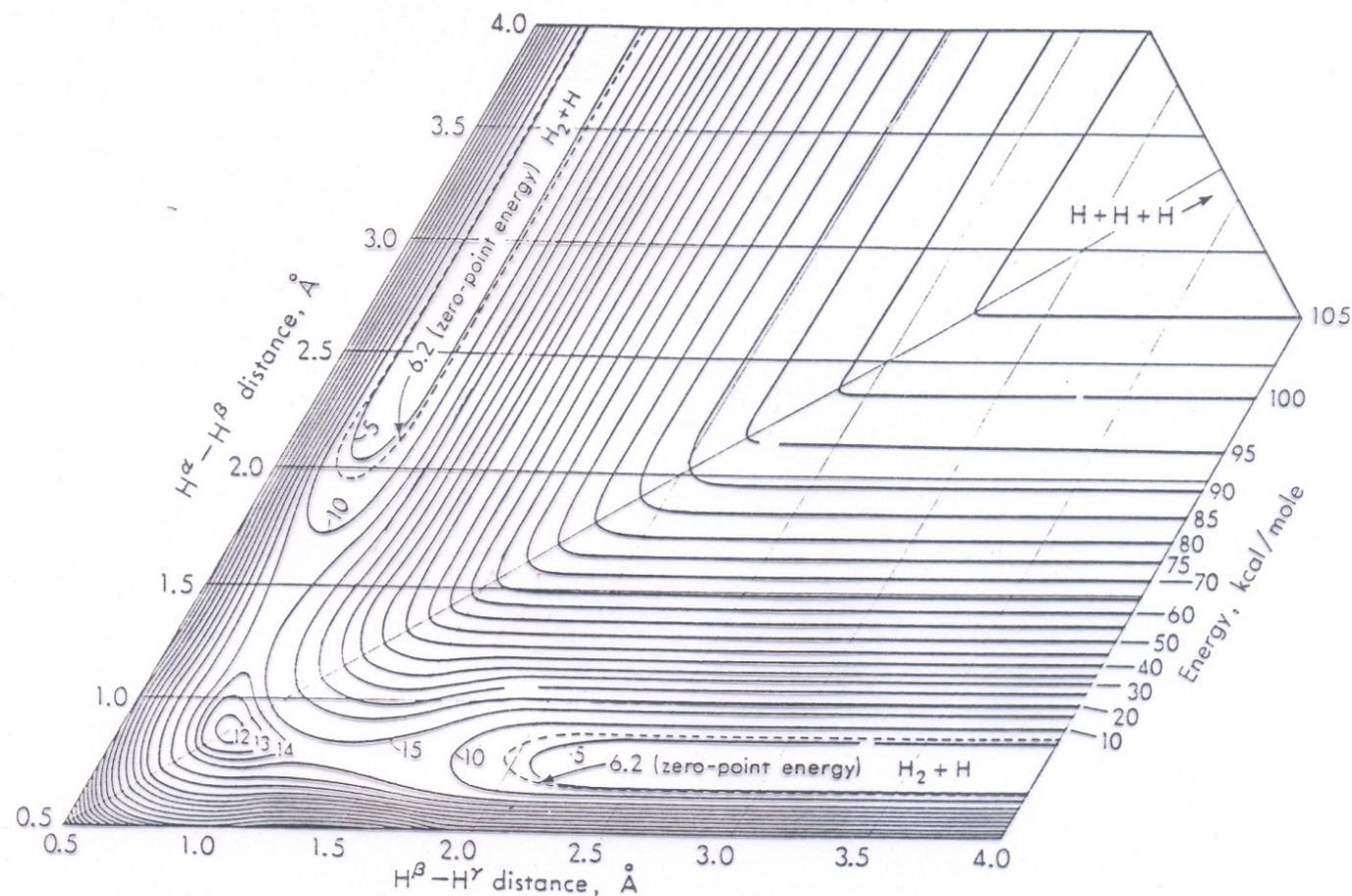
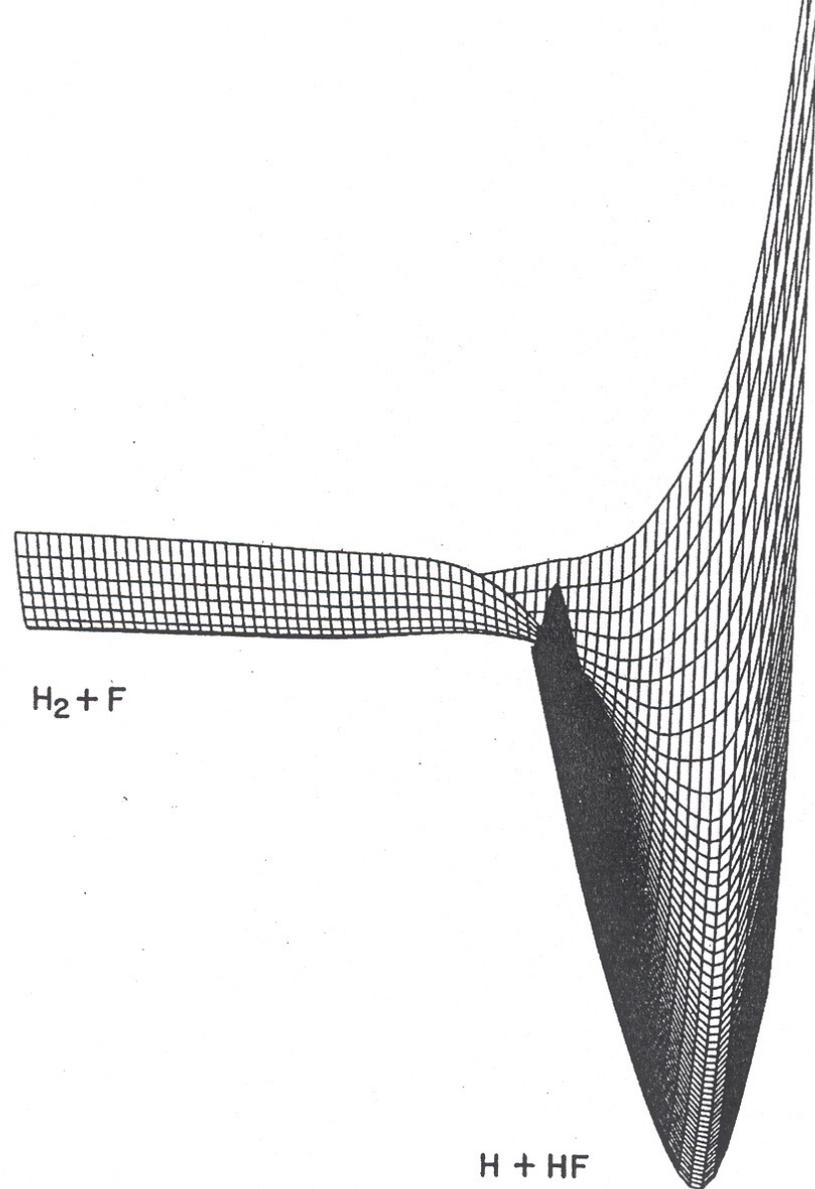


Fig. 13 Potential-energy surface for the $\text{H} + \text{H}_2$ reaction, calculated by Eyring, Gershinowitz, and Sun using the semiempirical LEP method with the coulombic energy taken to be 14 percent of the total energy. The axes are skewed because dynamical calculations (cf. Chap. 7) were made on the basis of this surface.

They could not do the trajectory calculations at that time.

PES for an
exothermic
reaction: early
barrier
(transition state
resembles the
reactants)



(son) Polanyi rules:

+I: early barrier,
translation helps

+II: late barrier,
vibration helps

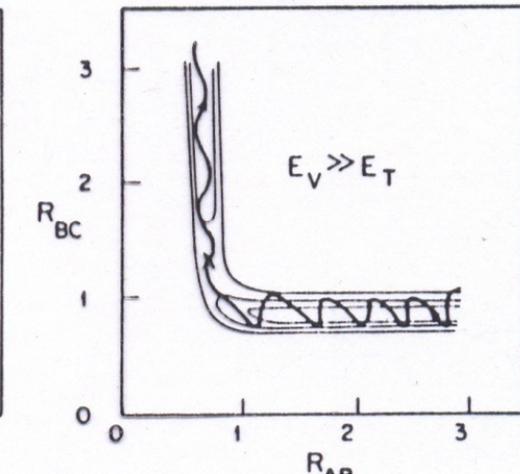
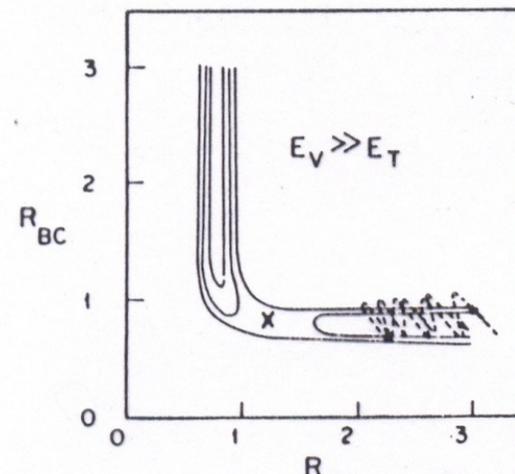
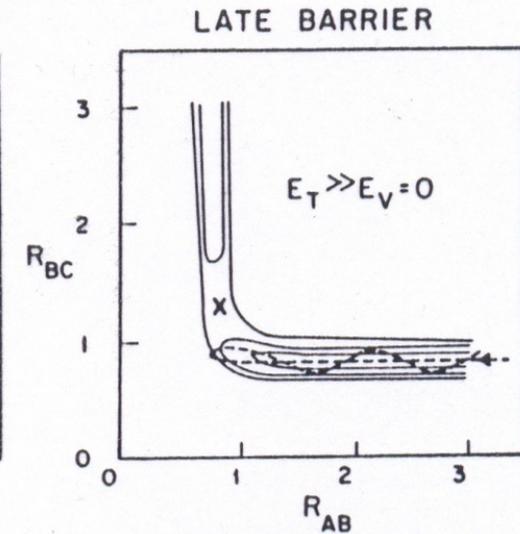
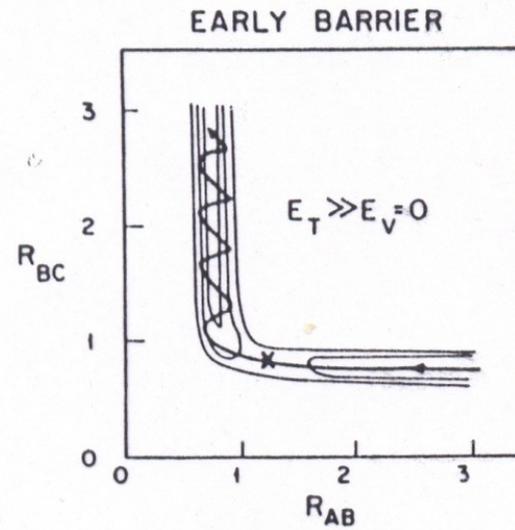
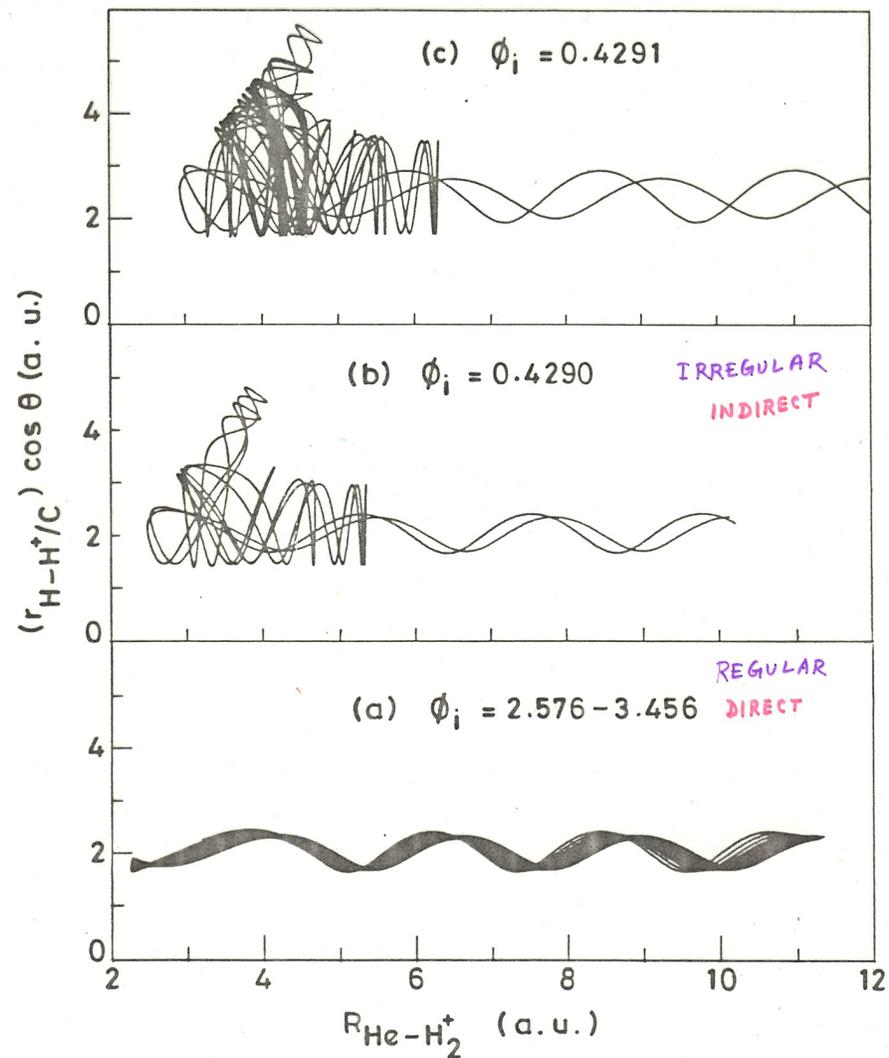


Illustration of trajectories for the He + H₂⁺ collisions; from our lab



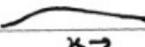
Use of wave packets in quantum mechanics

$$\rightarrow m, \psi, \\ x, p_x$$

$$\vdots m, \{\psi\} \\ \{x_L\}, \{p_{xL}\}$$

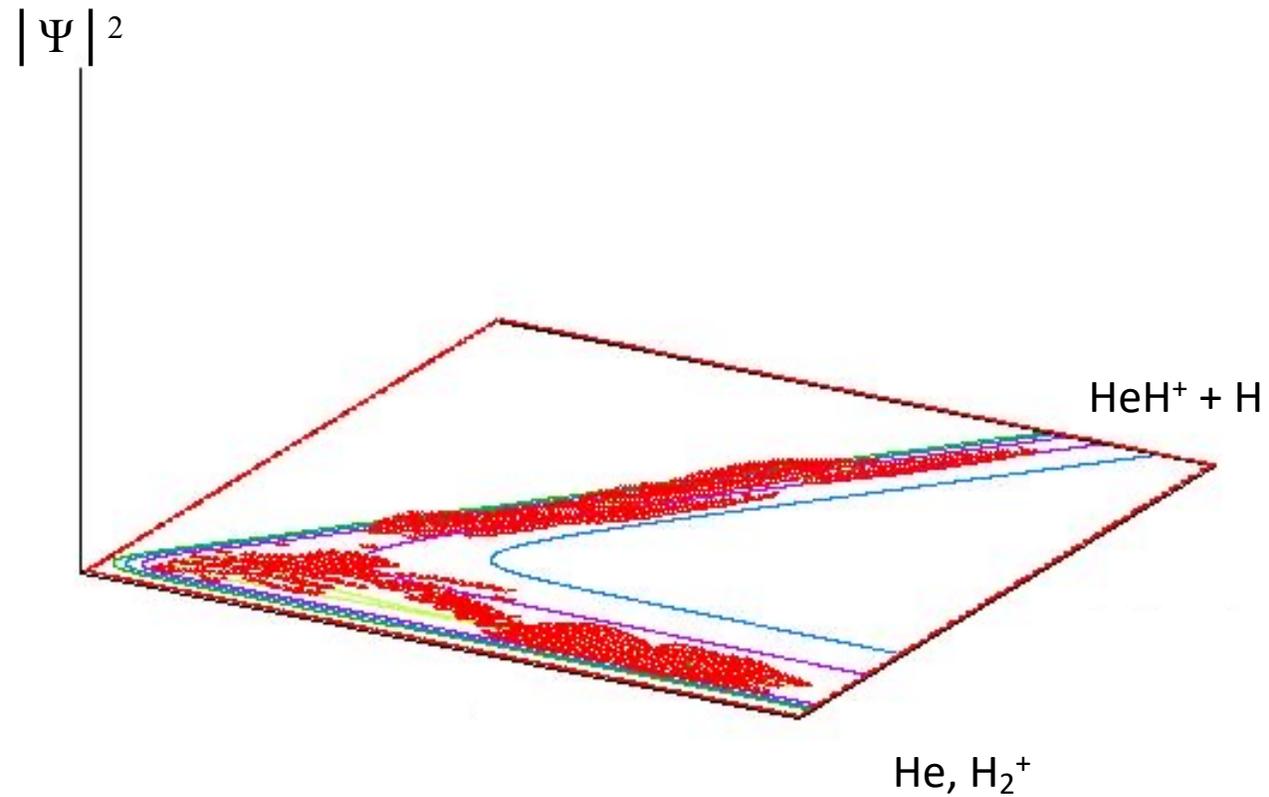
 wave packet = superposition of waves
 $\langle x \rangle, \langle p_x \rangle$: average position & momentum
 $\delta x, \delta p_x$ spread in position & momentum

 $x \rightarrow$ narrow in position \Leftrightarrow wide in momentum

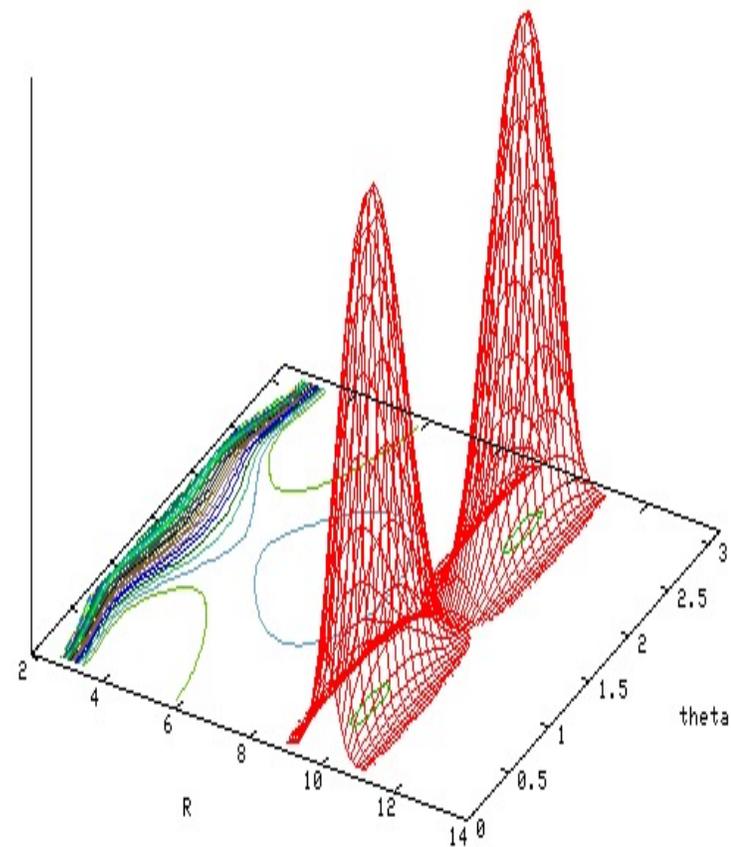
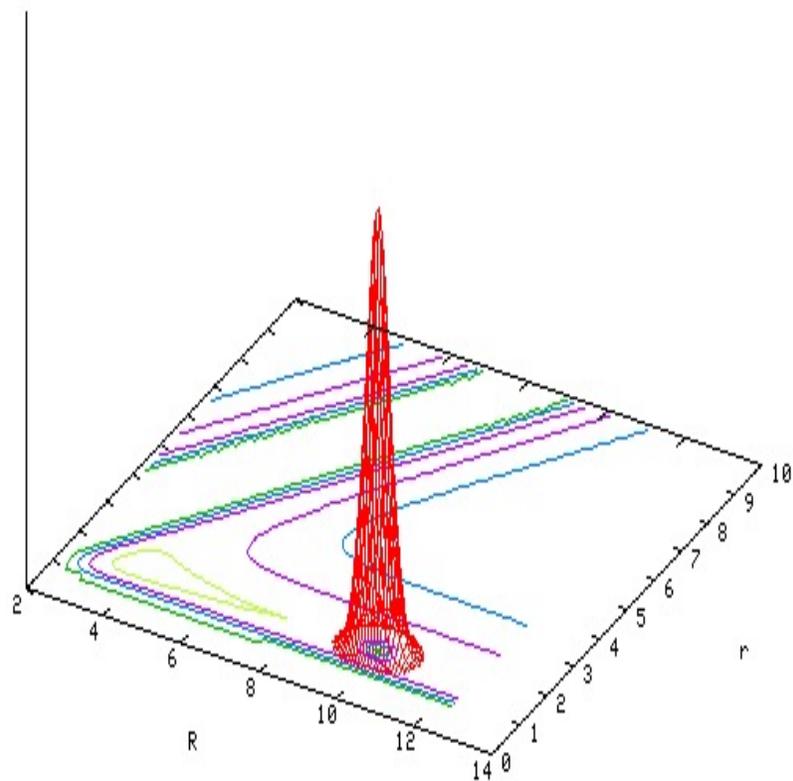
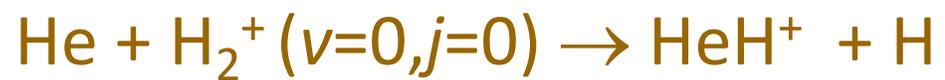
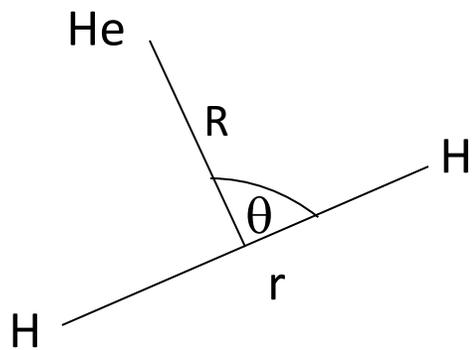
 $x \rightarrow$ wide in position \Leftrightarrow narrow in momentum

 $x \rightarrow$ optimal: Gaussian

Collinear reaction $\text{He} + \text{H}_2^+ (v=0, j=0) \rightarrow \text{HeH}^+ + \text{H}$
Studied quantum mechanically using the wave packet method



Wave packet dynamics



Wave packet dynamics in three dimensions

(Indirect) evidence for the Transition State

- If the location of the barrier influences Specific Energy Disposal (SED) and Selective Energy Consumption (SEC), then the observation of SED and SEC would reveal the nature of the Transition State!
- Can we “OBSERVE” the Transition State directly?
- Yes, we could, if we could record the spectrum of the transition state

“Observing” the transition state

- The story of the wings: $F + Na_2 \rightarrow FNa + Na$
- Observing bond breaking/forming at the molecular level requires time resolution of the order of a few femtoseconds
(1fs = 10^{-15} s)
- Zewail did it! (NL 1999)
- Photodissociation in several fs
- Observing molecules vibrating and rotating in real time and seeing the evidence of tunneling at the molecular level.

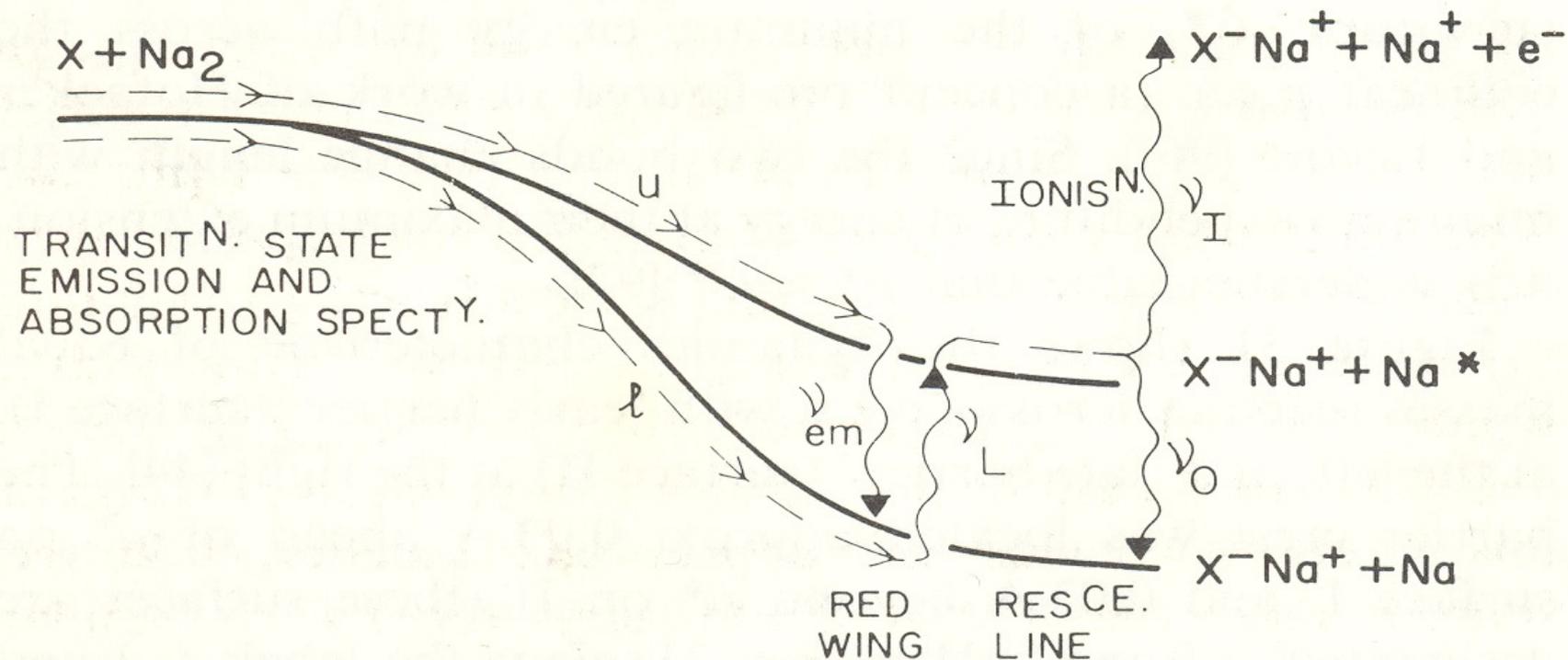
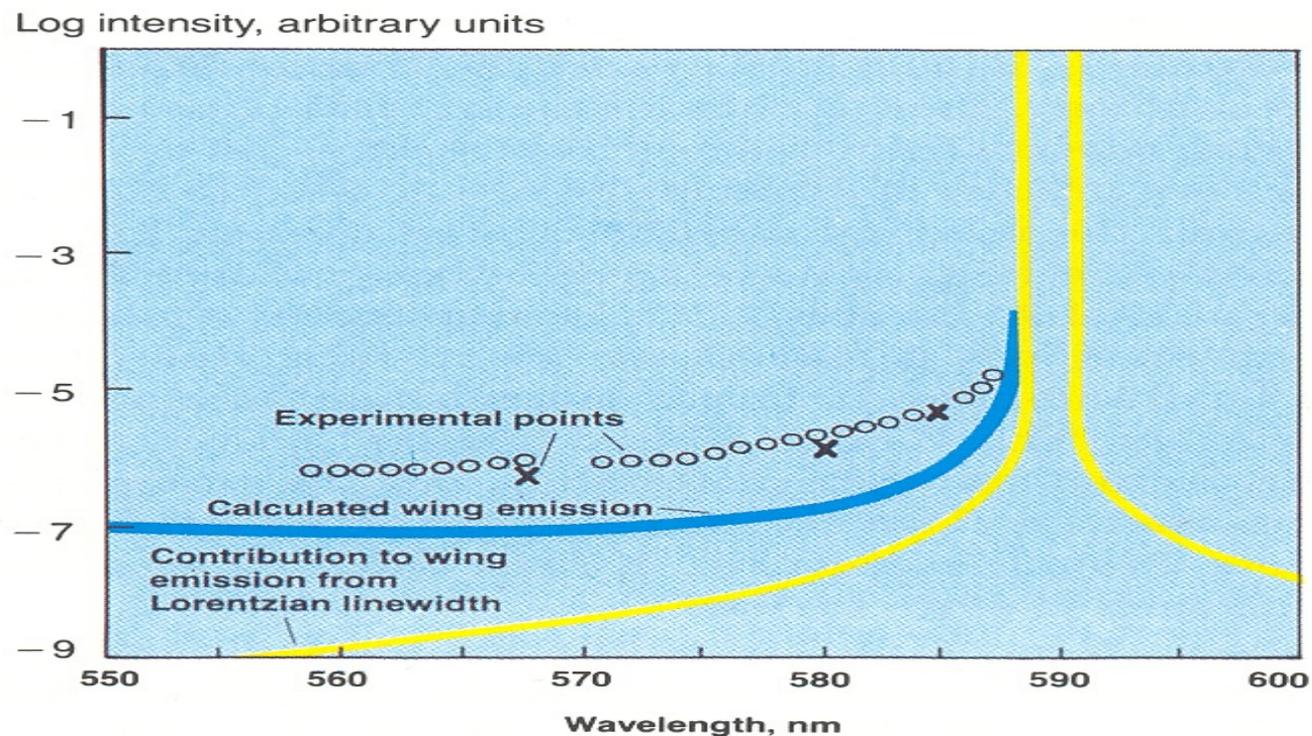


Fig. 33. Illustration of transition state emission and absorption spectroscopy, in analogy to collisional line-broadening. The reaction is $X + Na_2 \rightarrow NaX + Na^{(*)}$ ($X = \text{halogen}$). Reaction on the upper surface, u , leads to emission as the products separate (ν_{em} constitutes a red-shifted 'wing' on the D-line at ν_0). Reaction on the lower surface, l , may be detected by laser absorption as products separate ($\nu_L < \nu_0$ in the illustration); absorption at ν_L may be evidenced by subsequent emission of Na^* at ν_0 , or by laser ionization of Na^* using a second laser tuned to ν_I . (From J. C. Polanyi, *Faraday Disc. Chem. Soc.* **67**, 129 (1979).)

Emission spectroscopy helps characterize transition state



Shown here is the emission spectrum for NaI^* in the process of falling apart. The off-scale peak at 589 nm is the D-line resonance fluorescence of product sodium. The broad spectrum near this peak, called wing emission, comes from several sources, including scattered light and the Lorentzian linewidth of the D-line. The observed

“extra” intensity on the blue side is attributed to fluorescence from the excited state intermediate, NaI^\ddagger , in the process of falling apart. The calculated wing shape is based on a theoretical model and an approximate potential curve for the excited state of NaI. [Adapted from H.-J. Foth, J. C. Polanyi, and H. H. Telle, *J. Phys. Chem.*, **86**, 5027 (1982).]

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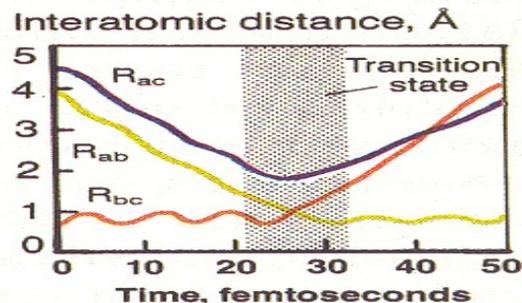
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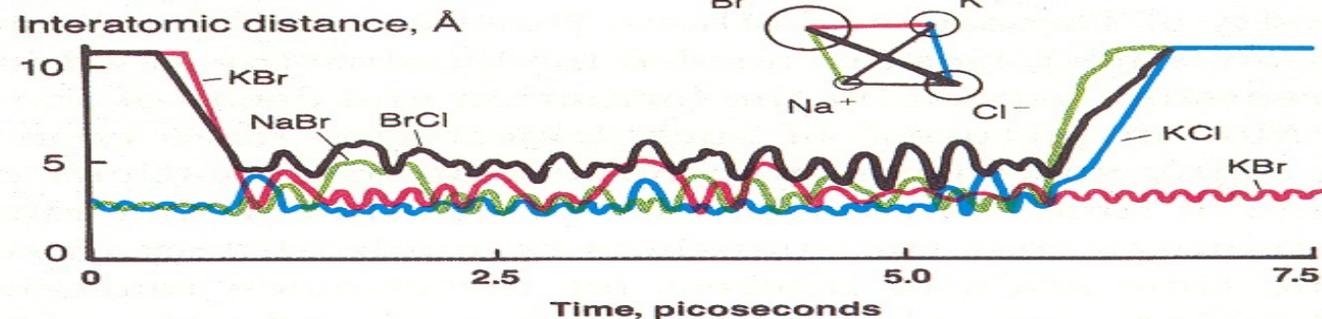
Reviews:
Femtochemistry
(Nobel Lecture by A. H. Zewail) •
Acetylenic Coupling •
Polar Metal-Metal Bonds

Inside:
A EUROPEAN JOURNAL
CHEMPHYSCHEM
OF CHEMICAL PHYSICS AND PHYSICAL CHEMISTRY

Direct-mode reactions take femtoseconds,
complex-mode reactions picoseconds



Computer modelling of
Elementary chemical reactions
Change from reactants to products
In a few fs

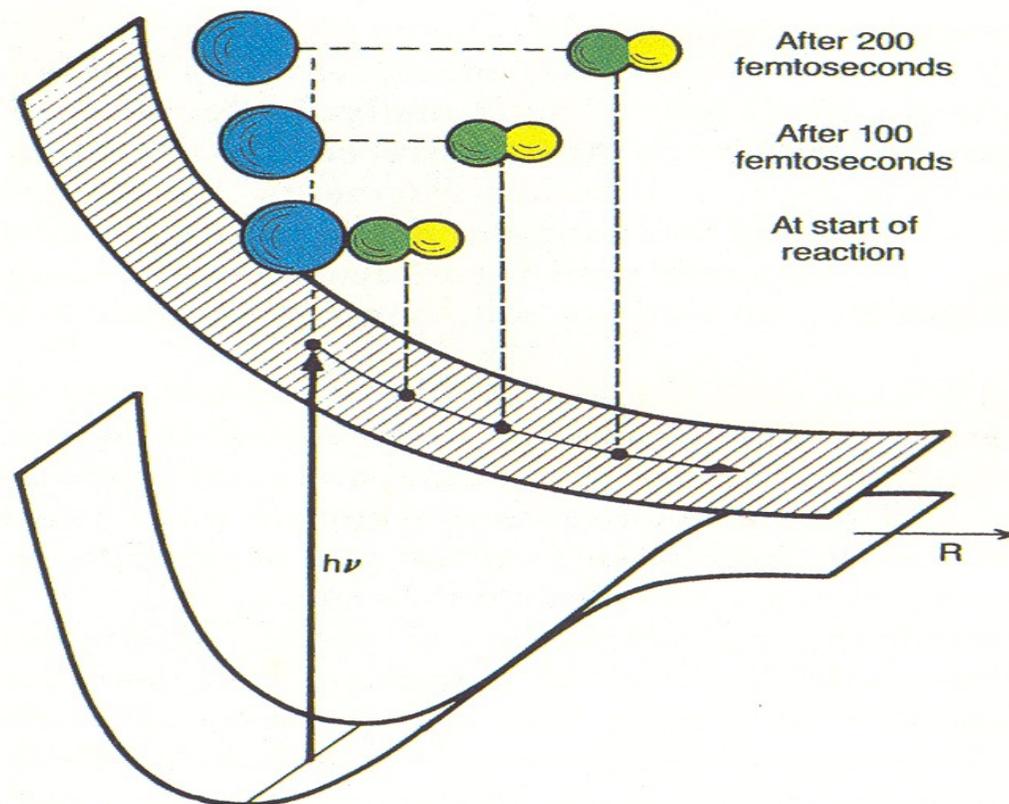


Intermediate ~ 2-3 ps

The lifetimes of transition states in bimolecular collisions can vary from several femtoseconds to many picoseconds. The upper graph shows a single trajectory calculated for the direct-mode exchange reaction $H_a + H_bH_c \rightarrow H_aH_b + H_c$, assuming a collinear configuration. Plotted on the ordinate scale are the interatomic separations R_{ab} , R_{bc} , and R_{ca} as a function of time from an arbitrary starting condition. Note the oscillations in R_{bc} before the encounter, then the exchange taking place, forming the new molecule H_aH_b , whose oscillation is seen in R_{ab} . There is a time interval of about 10 femtoseconds during which the system is in a tran-

sition state—a collinear, triatomic $H_aH_bH_c$. The lower graph is a similar portrayal of a single trajectory calculated for the complex-mode, gas-phase metathesis reaction $KCl + NaBr \rightarrow$ tetrahedral complex (structure shown) $\rightarrow KBr + NaCl$. The “snarled trajectories” are evidence for a long-lived (here about 5 picosecond) collision complex that eventually falls apart to yield products. [Upper graph adapted from M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, **43**, 3258 (1965), lower from P. Brumer and M. Karplus, *Far. Disc. Chem. Soc.*, **55**, 80 (1973) and P. Brumer, Ph.D. thesis (1972).]

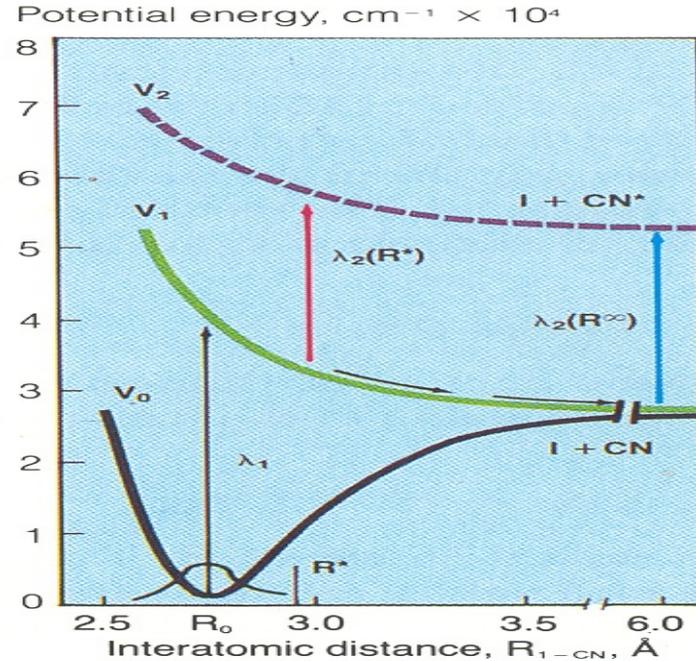
Photofragmentation of a triatomic molecule occurs in femtoseconds



Photofragmentation of a triatomic molecule such as ICN is shown schematically here. The lower surface represents a strip of the ground state potential energy surface as a function only of R , the separation between the atom and the diatomic fragment. The absorption of a photon (energy $h\nu$) excites the triatomic molecule from its ground state to its upper, repulsive potential energy surface at the start

femtoseconds, the photofragments are essentially free of one another. Experiments can measure the real-time progress of the reaction as the triatomic reactant makes the transition to its diatomic and atomic products. Since the recoil velocity of fragments is typically 1 km per second, in 100 fs the distance spanned is 1 Å. [Adapted from M. Rosker, M. Dantus, and A. H. Zewail, *Science*, **241**, 1200 (1988).]

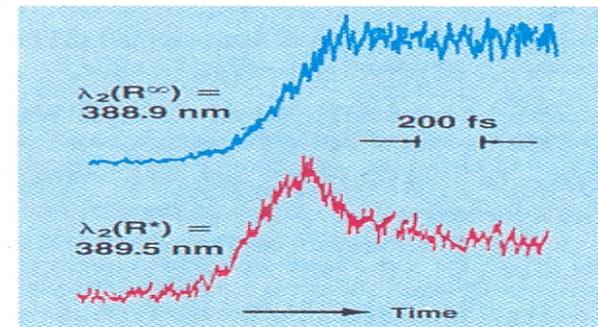
Real-time femtochemistry experiment catches excited ICN molecule in act of falling apart



Above: The drawing shows the three relevant potential energy curves of ICN simplified to describe a femtochemistry study of its photodissociation. The lowest curve, V_0 , refers to the ground state molecule, the middle one, V_1 , to the lowest-lying repulsive excited state. The pump laser photon (λ_1) excites the ICN from V_0 to V_1 at R_0 . Here, R_0 is the equilibrium bond length I—CN. The probe laser pulse, whose wavelength is set for the free CN resonance, $\lambda_2(R^\infty)$, is delayed by variable time intervals with respect to the pump pulse. The laser-induced fluorescence intensity remains zero until the CN has separated to about 6 Å from the I atom. The probe laser pulse, now de-

tuned to the red to $\lambda_2(R^*)$, and delayed by a time interval measured in femtoseconds, excites the ICN at $V_1(R^*)$, as the molecule is in the process of falling apart (when the separation between I and CN has reached the distance R^*), to a higher electronic state, V_2 , which fluoresces. Thus the intensity of the fluorescence increases with time to a peak and then quickly falls as the distance between the I and CN fragments increases and the probe laser wavelength is no longer in resonance.

Below: Pump-probe transients are observed by laser-induced fluorescence of the CN photofragment. Upper: When the probe laser is tuned to the wavelength ($\lambda_2(R^\infty)$) corresponding to free CN, the signal is delayed until the I and CN have "fully" separated. Lower: The probe laser is detuned to the red to detect the perturbed CN in the process of separation from the I atom. The clocking of this reaction from $t = 0$ to complete separation of I and CN yields a 205 ± 30 fs delay time. [Adapted from M. Dantus, M. Rosker and A. H. Zewail, *J. Chem. Phys.*, **87**, 2395 (1987) and M. Rosker, M. Dantus, and A. H. Zewail, *Science*, **241**, 1200 (1988).]



What happens when two electronic states come close together (become degenerate)?

Non-crossing rule

- If $|\psi_A\rangle$ is a solution of the Schrödinger equation for a system and if $|\psi_B\rangle$ is also a solution with the **same energy**, then the linear combination $|\psi_A\rangle \pm |\psi_B\rangle$ is also a solution
- The two states of the same symmetry would avoid each other:

Jahn-Teller effect

Illustration of an avoided crossing in one dimension

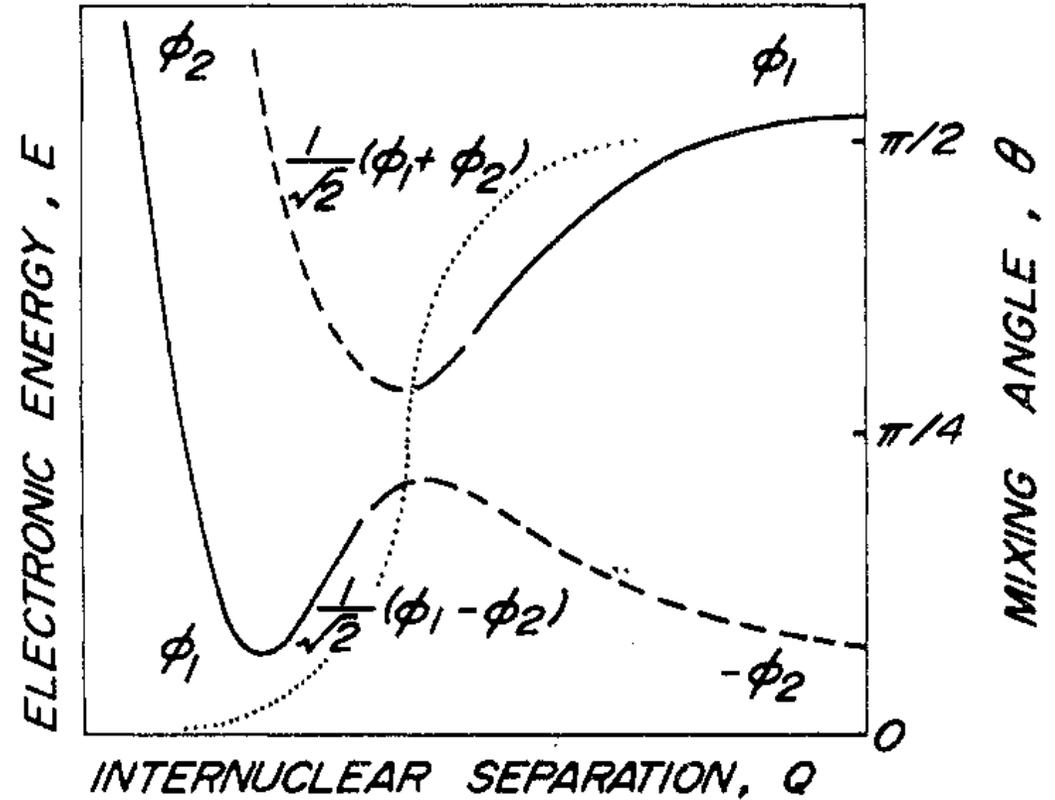
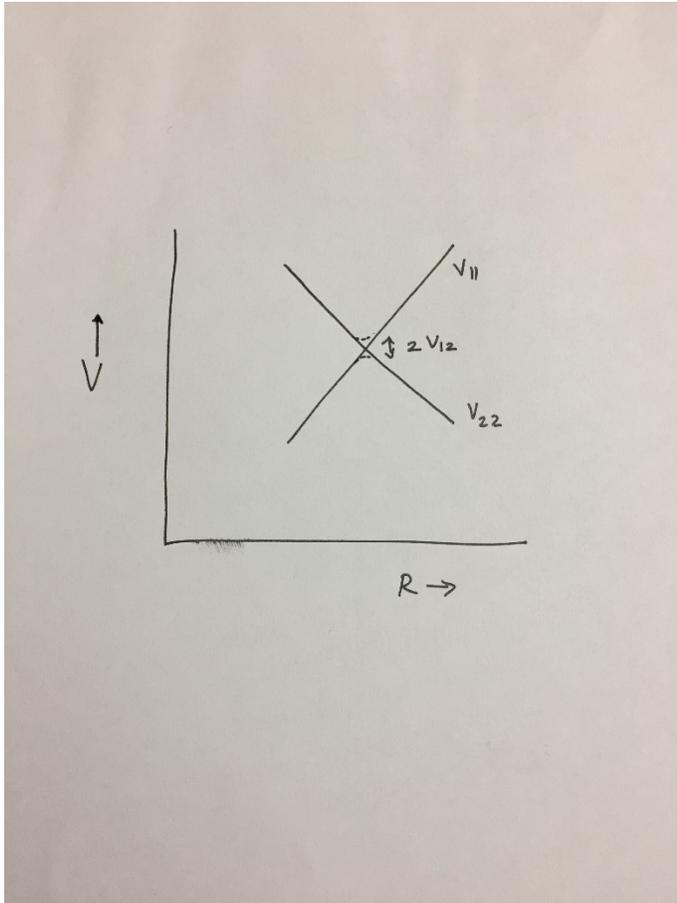


Figure 1. Two adiabatic potential curves with an avoided intersection. The adiabatic states are the indicated linear combinations of the crossing states ϕ_1 , ϕ_2 each of which has a definite orbital occupancy. The dotted line represents the mixing angle, eq 2 and 4.

Potential energy curves of the same symmetry do not cross each other in one dimension!



$$|V - E| = \begin{vmatrix} V_{11} - E & V_{12} \\ V_{21} & V_{22} - E \end{vmatrix} = 0$$

$$(V_{11} - E)(V_{22} - E) - V_{12}^2 = 0, (V_{12} = V_{21})$$

$$E^2 - (V_{11} + V_{22})E + (V_{11}V_{22} - V_{12}^2) = 0$$

$$E = (V_{11} + V_{22})/2$$

$$\pm \sqrt{\{(V_{11} - V_{22})^2 + 4V_{12}^2\}}/2$$

If $V_{11} = V_{22}$ (degenerate),

$$E_{\pm} = (V_{11} + V_{22})/2 \pm V_{12}$$

Degeneracy is lifted by the coupling term

$$V_{12} = \langle \Psi_1 | V | \Psi_2 \rangle = 0, \text{ if } \langle \Psi_1 | \Psi_2 \rangle = 0$$

(states of different symmetry can cross!)

$$V_{12} \neq 0, \text{ if } \langle \Psi_1 | \Psi_2 \rangle \neq 0$$

States of the same symmetry do not cross.

$\text{Na}(\uparrow) + \text{I}(\downarrow) \rightarrow \text{NaI}(\uparrow\downarrow)$ covalent, diabatic

$\text{Na}^+ + \text{I}^- \rightarrow \text{Na}^+\text{I}^-$ ionic, diabatic

Both are of same symmetry and multiplicity ($^1\Sigma$)
The two curves do not cross; they avoid each other

Femtochemistry reveals fragment trapping in alkali halide photodissociation

Zewail's classic experiment:
Photo-excitation of NaI

NaI in the ground electronic state goes asymptotically to the ionic state as $R \rightarrow \infty$
And the upper electronic state goes asymptotically to the covalent state as $R \rightarrow \infty$
Both states have the same symmetry: $^1\Sigma$
They avoid each other at the crossing point

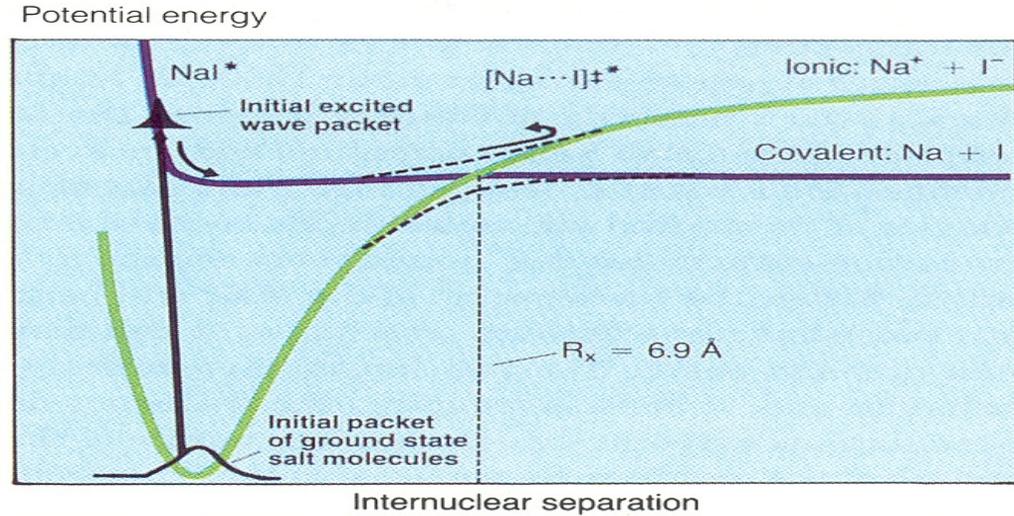
The lowest energy curve over the entire R range is called an adiabatic curve (---)
Similarly, the next higher energy curve is also an adiabat (---)

Adiabat: slow changing

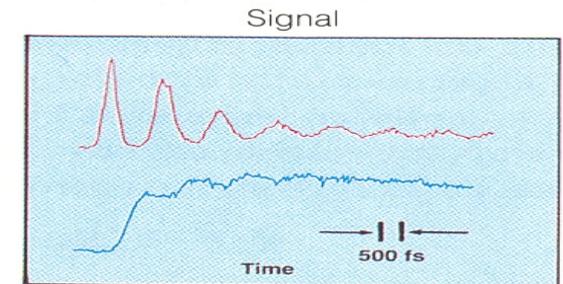
The solid line is called a diabatic

Landau-Zener transition probability

$$P = \exp\left(-\frac{4\pi^2\varepsilon_{12}^2}{h\nu|s_1-s_2|}\right)$$



Wave packet description of the photofragmentation of sodium iodide with two electronic degrees of freedom is shown schematically above. Light excites a packet of ground state NaI molecules into an initial excited state wave packet, shown as the upper bell-shaped curve in the diagram. From here the molecules may follow the purple diabatic potential curve and dissociate covalently, or they may attempt to cross to the ionic curve at an internuclear distance of 6.9 Å. Molecules that attempt this crossing become trapped and oscillate back and forth in the upper potential energy well. Such trapping can be seen experimentally on the femtosecond timescale, at right. The red curve shows the Na—I bond resonating in trapped molecules. The blue curve is that of the sodium



when separating from the iodine along the covalent curve. The curves were observed with different degrees of detuning. [Adapted from M. Rosker, T. S. Rose, and A. H. Zewail, *Chem. Phys. Lett.*, **146**, 175 (1988) and T. S. Rose, M. Rosker, and A. H. Zewail, *J. Chem. Phys.*, **88**, 6672 (1988).]

Non-adiabatic coupling between electronic states

- $\tau_{jk}(R) = \frac{\langle \zeta_j(r|R) | \nabla \hat{H}_e | \zeta_k(r|R) \rangle}{u_k - u_j}$
- When states $|k\rangle$ and $|j\rangle$ become degenerate, there is a singularity.
- The result: **conical intersection in more than one dimension!**

Studies of the Jahn–Teller effect

II. The dynamical problem

BY H. C. LONGUET-HIGGINS,* U. ÖPIK,† M. H. L. PRYCE, F.R.S.‡

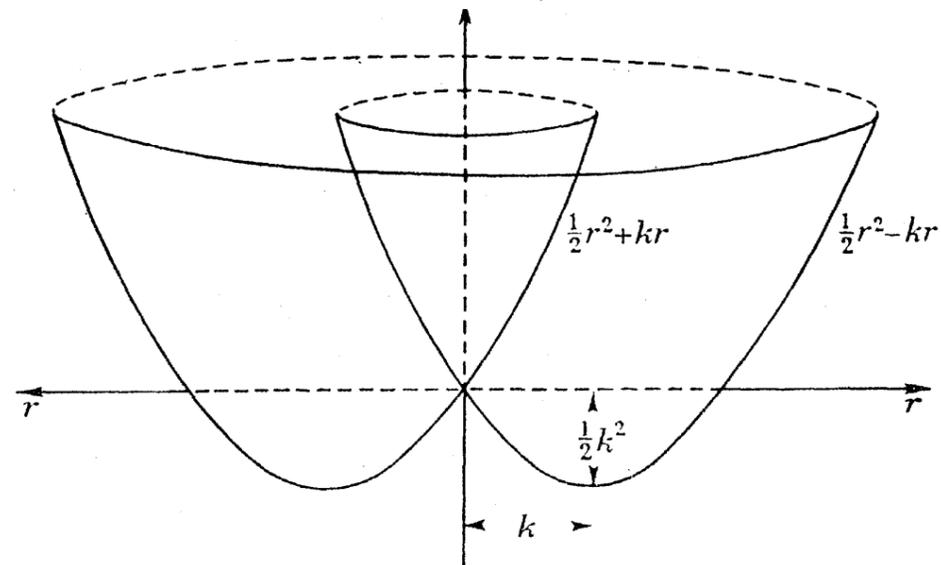


FIGURE 3. Diagram indicating Jahn–Teller splitting of nuclear potential function into two branches, $\frac{1}{2}r^2 \pm kr$.

Conical intersection in two dimensions

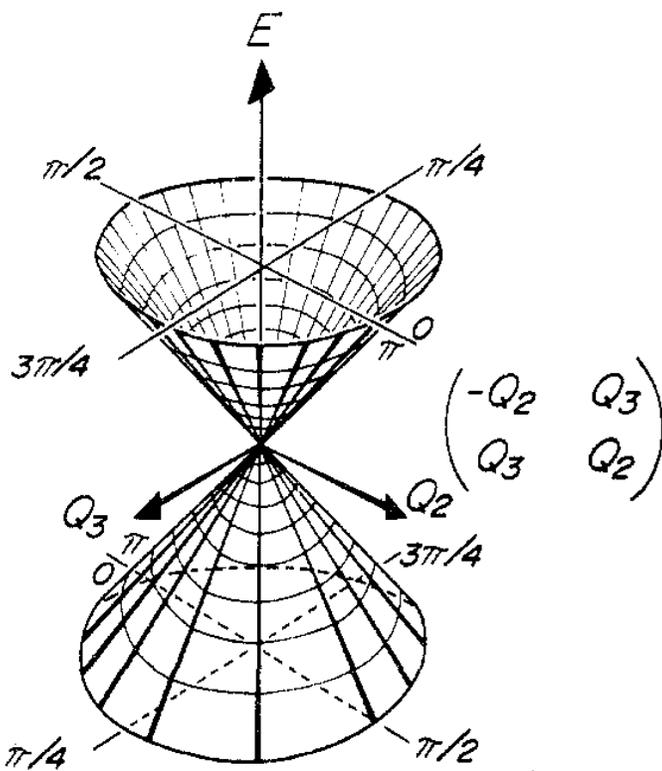
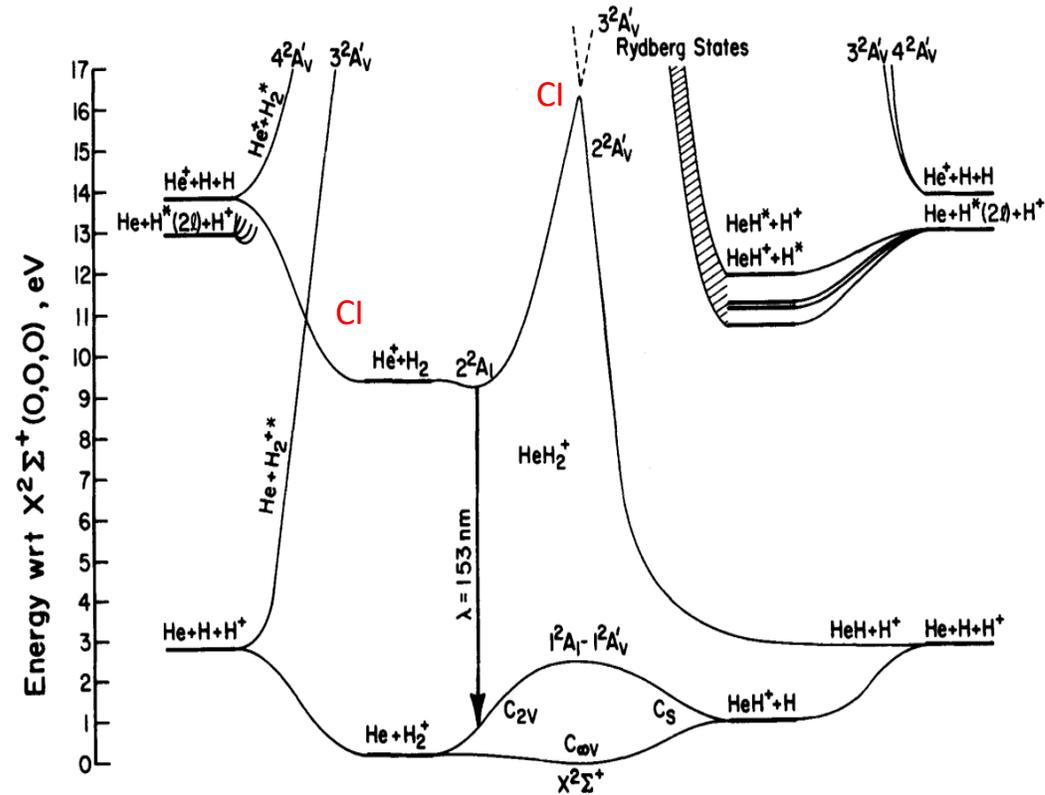
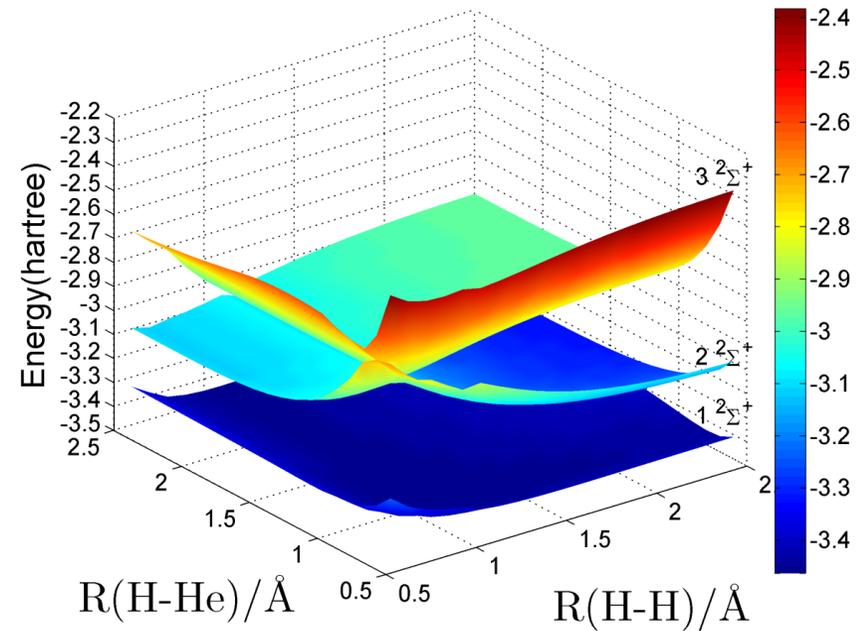


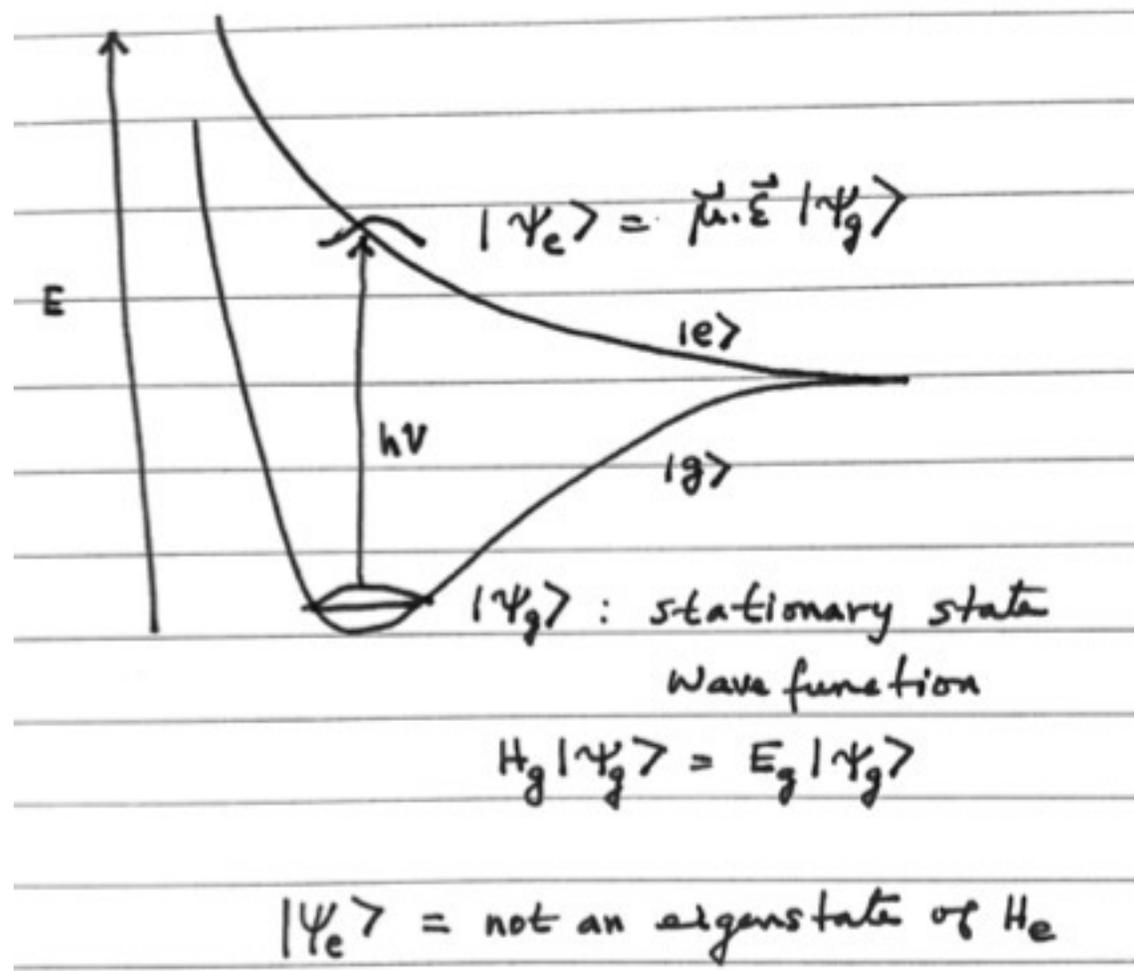
Figure 2. A conical intersection of A_1 and B_2 states in C_{2v} . The mixing of the basis states on the two sheets of the cone is indicated by the mixing angle θ . The Hamiltonian matrix is indicated schematically, showing only the first-order dependence on normal mode displacements. The cone is not in general circular. See eq 11.

Adiabatic state correlation diagram for HeH_2^+ reproduced from D. G. Hopper, J. Chem. Phys. 73, 3289 (1980)



Potential energy surfaces for the lowest three electronic states of linear HeHH⁺

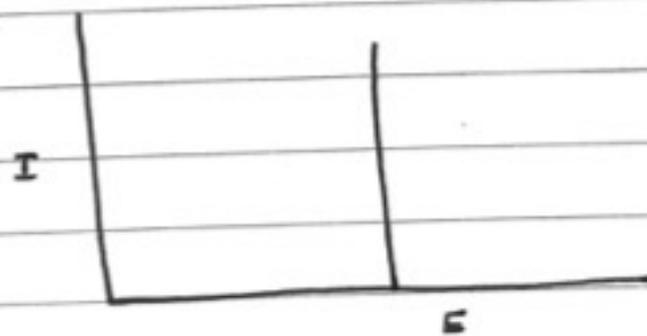
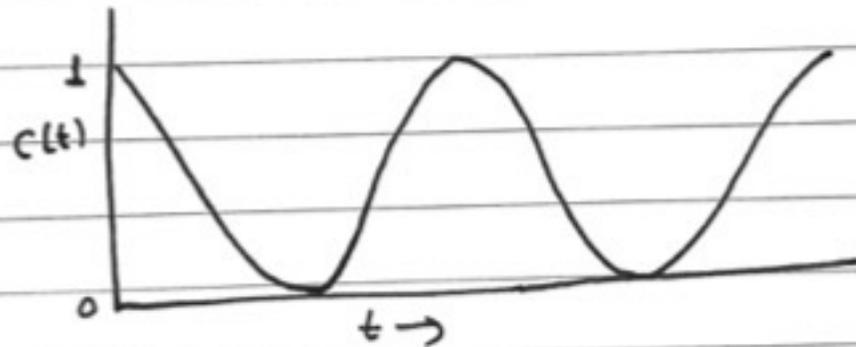




$$C(t) = \langle \psi(0) | \psi(t) \rangle : \text{autocorrelation fn.}$$

↓ FT

$I(\epsilon)$: power spectrum.



for an eigenstate

Thank you