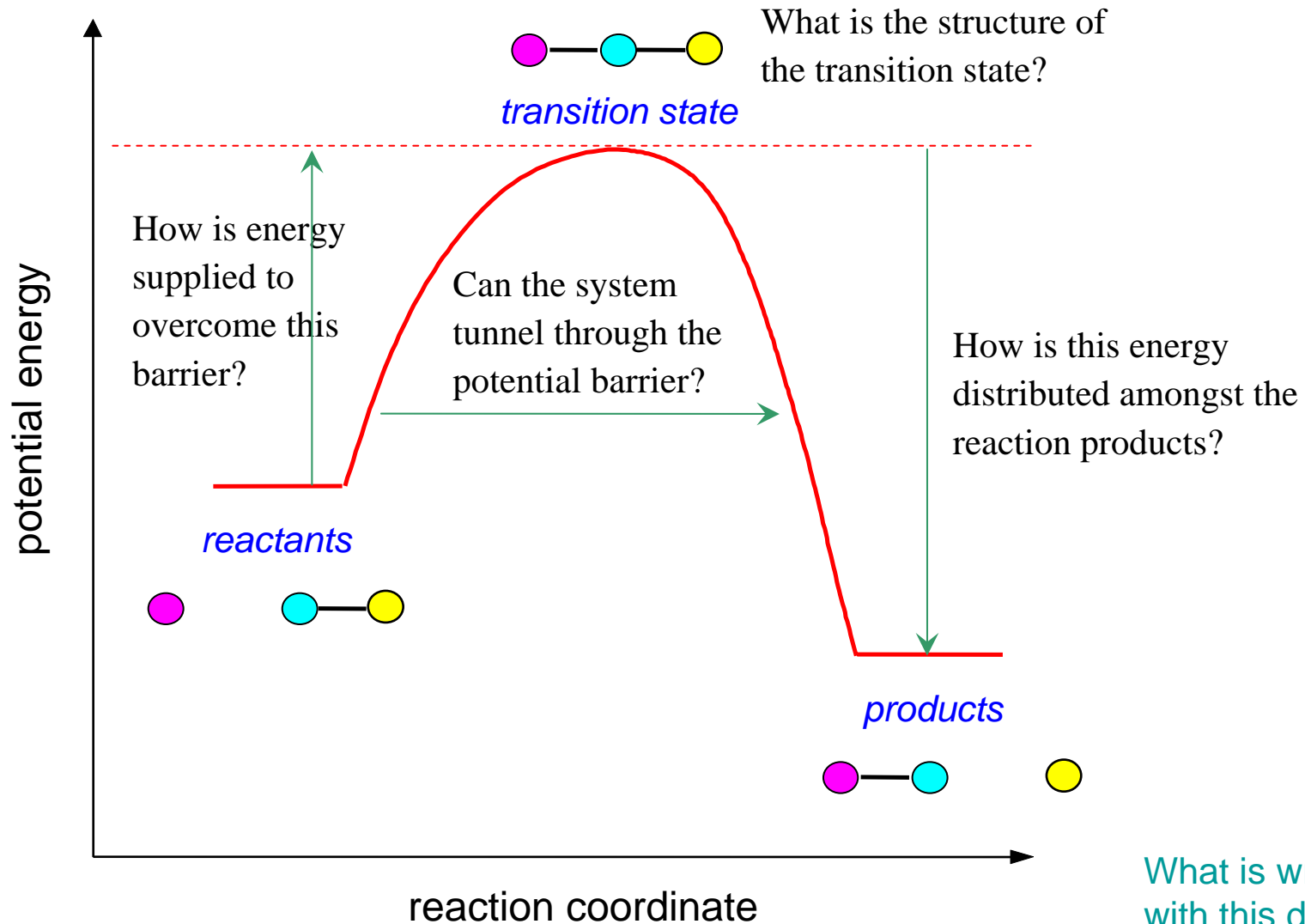


Reaction Dynamics

What is the probability that the system will move from reactants to products?



1-D Reaction Coordinate

The **potential energy** V is the internal energy U from thermodynamics.

In the **Born-Oppenheimer Approximation** the nuclear and electronic parameters are separable: **product of wavefunctions, sum of energies.**

The potential energy surface then corresponds to a plot of the energy of the system as a function of nuclear coordinates.

The simplest reaction "surface" has 1 dimension, such as the interatomic distance in the dissociation of a diatomic. **e.g.** $AB \rightarrow A + B$

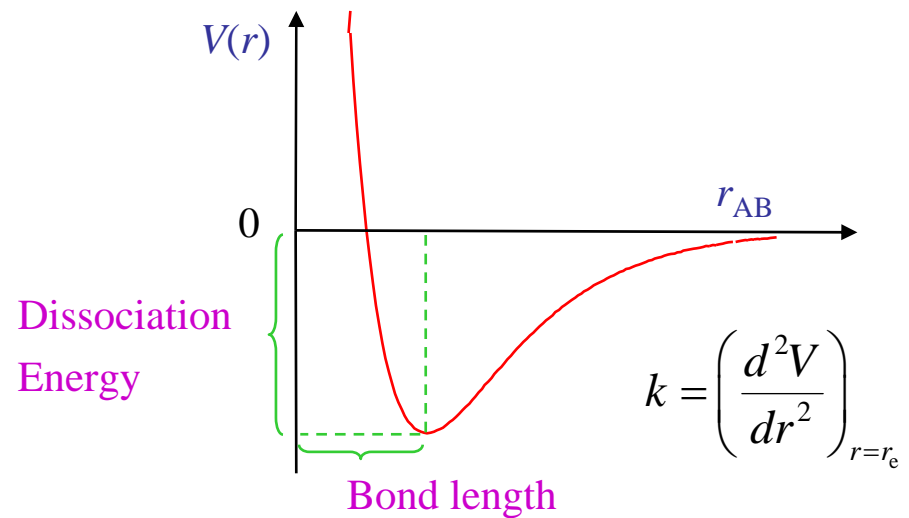
For $r \approx r_e$ the potential can be modelled by the simple harmonic oscillator.

$$V(r) = V(r_e) + \frac{1}{2}k(r - r_e)^2$$

But extreme anharmonicity is needed to model dissociation:

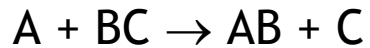
The Morse Potential

$$V(r) = D_e \left[1 - e^{-\alpha(r-r_e)} \right]^2 - D_e$$

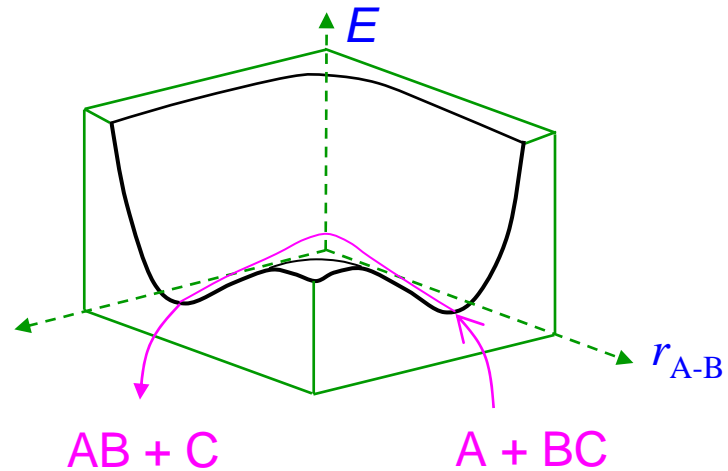


2-D Potential Energy Surface

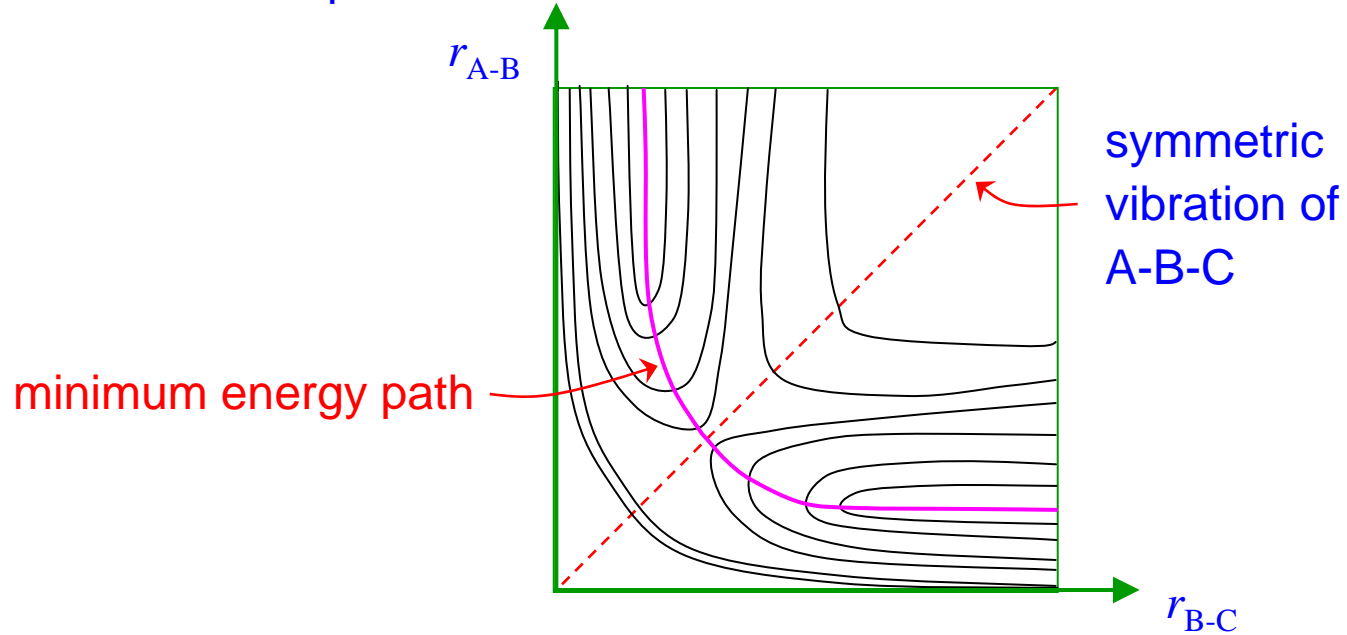
A collinear triatomic
reaction such as



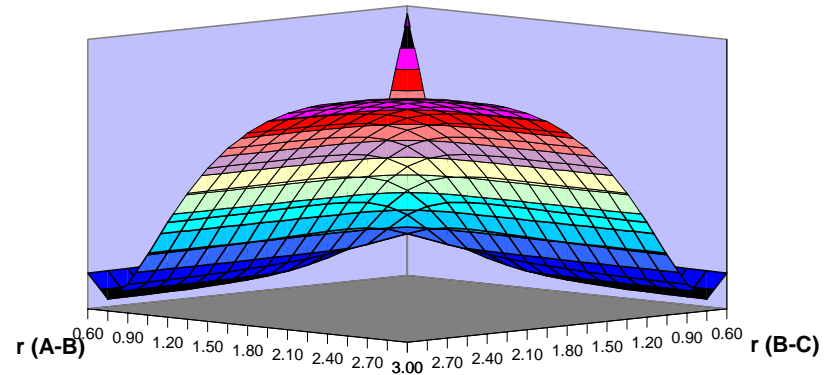
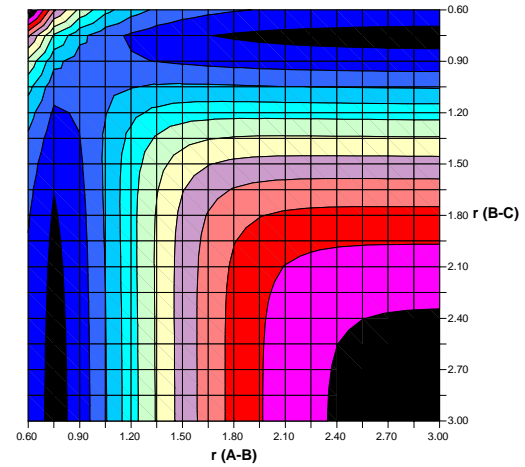
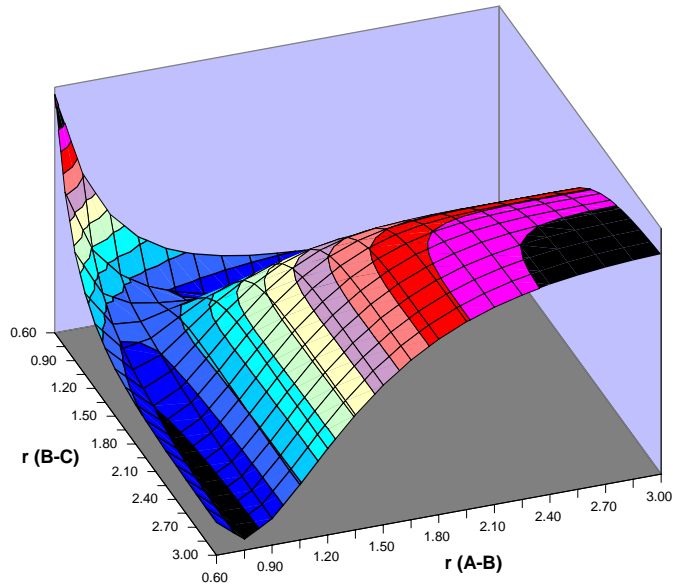
needs a 3-D plot:



or a contour plot:



Views of a Potential Energy Surface



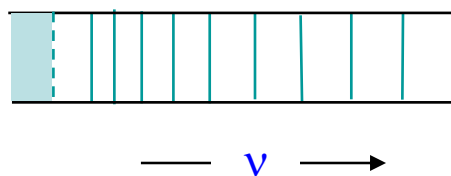
Determination of PE Surfaces

A reaction PE surface can be built up from a grid of individual points calculated for different atomic positions (geometry optimized for other dimensions).

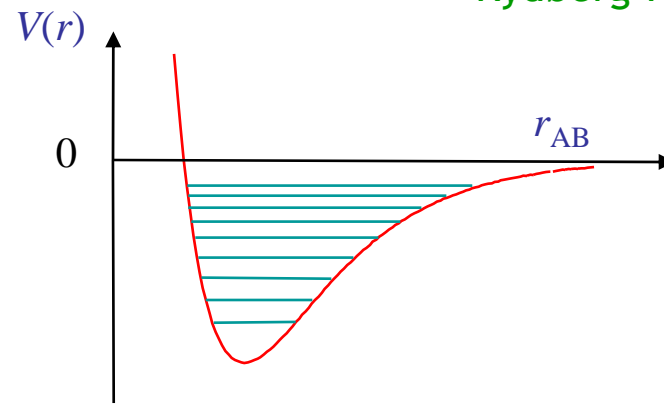
Standard semi-empirical (MNDO, AM1, PM3,...) and *ab initio* packages can be used (Gaussian, Gamess, ...) but parameters and basis sets are usually optimized for structures close to equilibrium. Spin correlation effects can be very important when bonds are broken/formed, so density functional methods are preferred over Hartree-Fock.

PE surfaces can also be derived from experimental spectroscopic data.

e.g. The RKR method is based on extrapolation of a vibrational series to the dissociation limit.



⇒



Rydberg-Klein-Rees

The LEPS Surface

An analytic function is often more practical than a table of points – it is continuous and can have adjustable parameters.

London-Eyring-Polanyi-Sato (LEPS) surface

$$V(r_{ab}, r_{bc}, r_{ac}) = \frac{Q_{ab}}{1+S_{ab}} + \frac{Q_{bc}}{1+S_{bc}} + \frac{Q_{ac}}{1+S_{ac}} - \frac{1}{\sqrt{2}} \left[\left(\frac{J_{ab}}{1+S_{ab}} - \frac{J_{bc}}{1+S_{bc}} \right)^2 + \left(\frac{J_{bc}}{1+S_{bc}} - \frac{J_{ac}}{1+S_{ac}} \right)^2 + \left(\frac{J_{ac}}{1+S_{ac}} - \frac{J_{ab}}{1+S_{ab}} \right)^2 \right]^{1/2}$$

$$Q(r) = \frac{1}{2} \left[M(r)(1+S^2) + AM(r)(1-S^2) \right]$$

$$J(r) = \frac{1}{2} \left[M(r)(1+S^2) - AM(r)(1-S^2) \right]$$

$$M(r) = D_e \left[e^{-2\alpha(r-r_e)} - 2e^{-\alpha(r-r_e)} \right]$$

$$AM(r) = \frac{1}{2} D_e \left[e^{-2\alpha(r-r_e)} + 2e^{-\alpha(r-r_e)} \right]$$

Morse function

anti-Morse function

Q , J and S are derived from the Coulomb, exchange and overlap integrals of the Heitler-London valence-bond theory

The BEBO Method

BEBO = Bond-Energy-Bond-Order

Johnston and Parr

It is completely empirical and mostly used for 1-D reaction paths (estimation of activation energies).

For $A + BC \rightarrow AB + C$

$$r = r_s - 0.26 \ln n \text{ \AA}$$

Pauling

$$D = D_s n^p$$

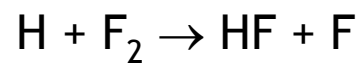
single-bond length and energy

$$n_{ab} + n_{bc} = 1$$

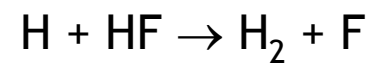
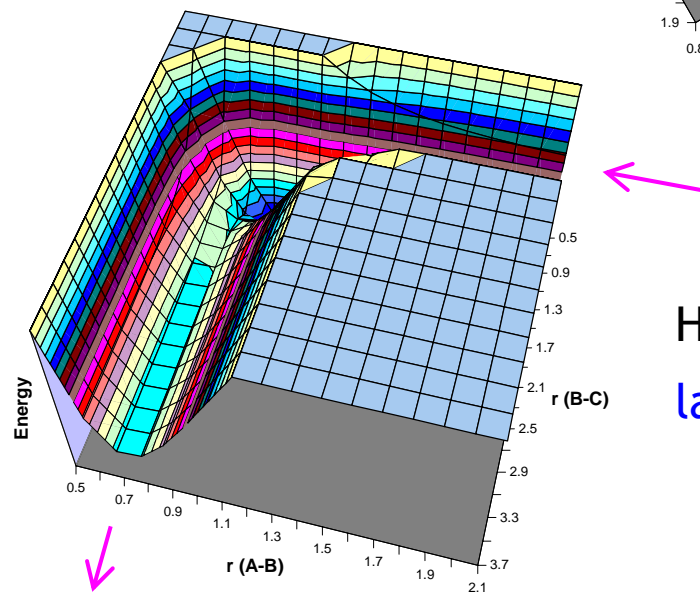
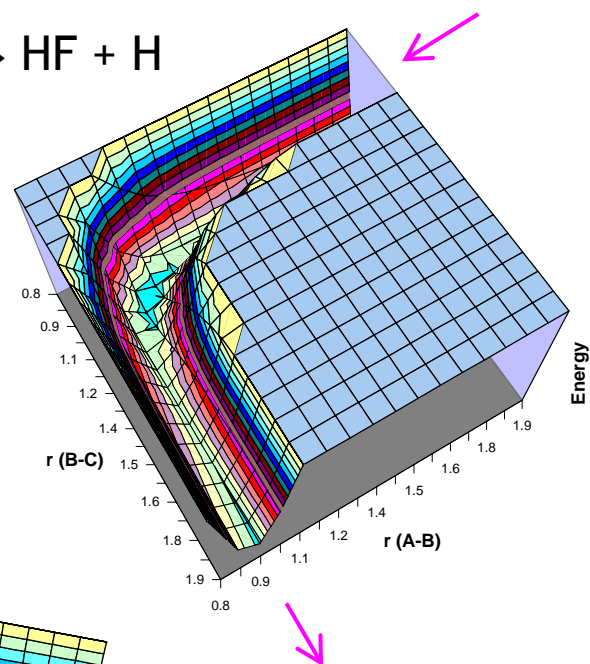
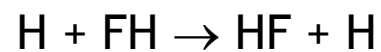
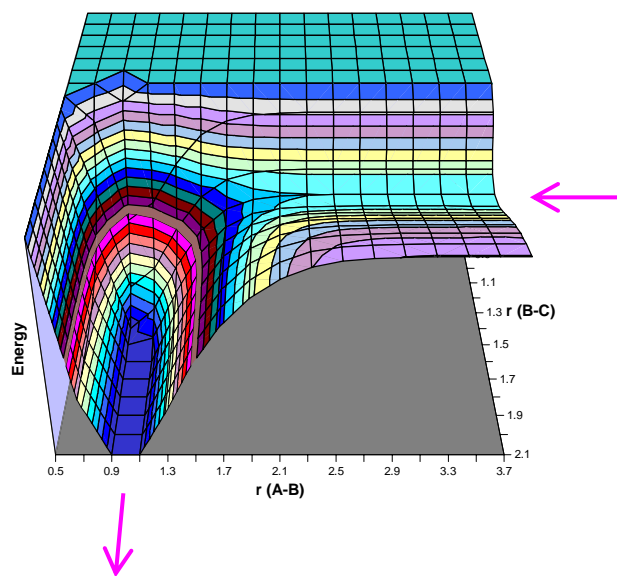
the bond-order is conserved

$$V = D_{bc} - D_{bc} n_{bc}^{p_{bc}} - D_{ab} n_{ab}^{p_{ab}} + AM(r_{ac})$$

Miscellaneous Reaction Surfaces



early barrier

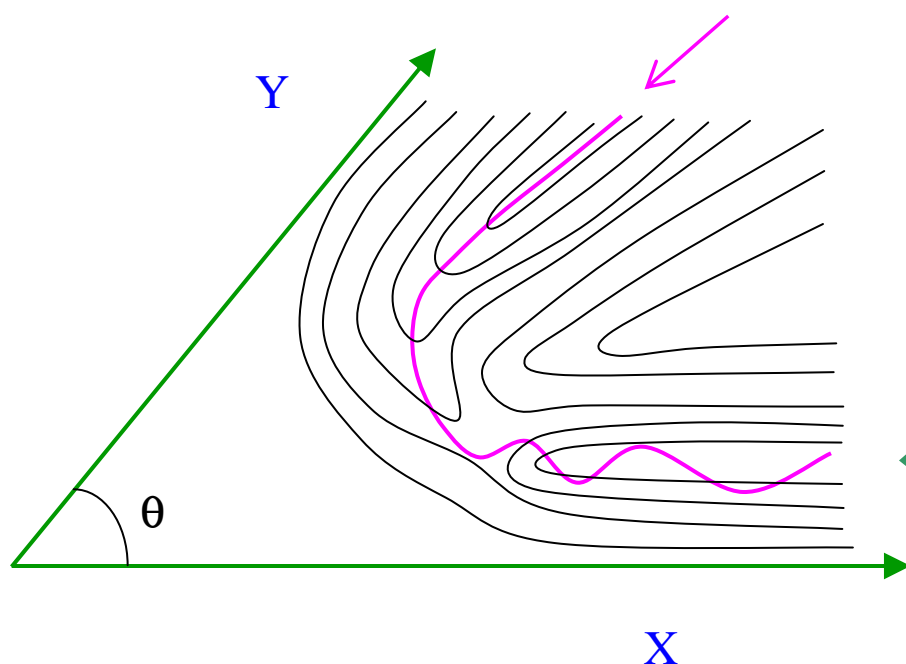


late barrier

Skewed Coordinate System

PE surfaces can be used for classical trajectory calculations as long as the effective mass of the reacting system (modelled by rolling ball) is constant.

A mass-weighted coordinate system diagonalizes the kinetic energy of the system.



$$X = \alpha r_{ab} + \beta r_{bc} \cos \theta$$

$$Y = \beta r_{bc} \sin \theta$$

$$\alpha = \left[\frac{m_a (m_b + m_c)}{M} \right]^{\frac{1}{2}}$$

$$\beta = \left[\frac{m_c (m_b + m_a)}{M} \right]^{\frac{1}{2}}$$

$$M = m_a + m_b + m_c$$

$$\cos^2 \theta = \frac{m_a m_c}{(m_a + m_b)(m_b + m_c)}$$

vibrational
excitation
of product

Tunnelling

Consider a particle of energy E striking a potential barrier of height V .

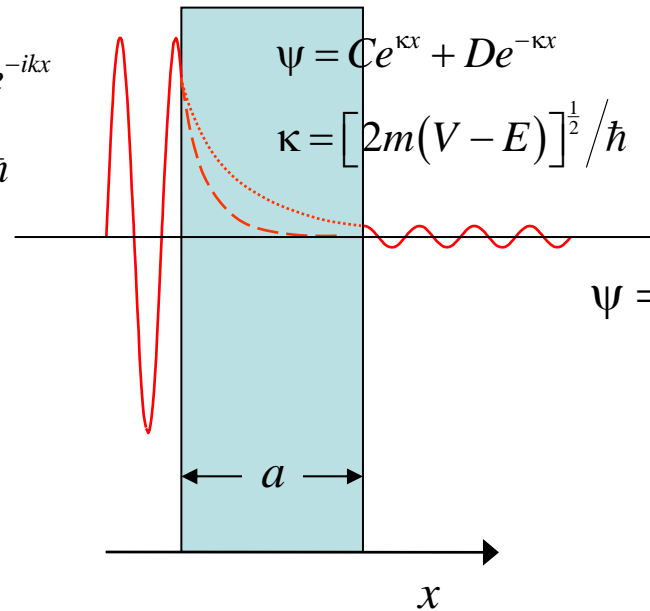
$$\psi = Ae^{ikx} + Be^{-ikx}$$

$$k = (2mE)^{1/2} / \hbar$$

$$\psi = Ce^{\kappa x} + De^{-\kappa x}$$

$$\kappa = [2m(V - E)]^{1/2} / \hbar$$

$$\psi = A'e^{ikx} + B'e^{-ikx}$$

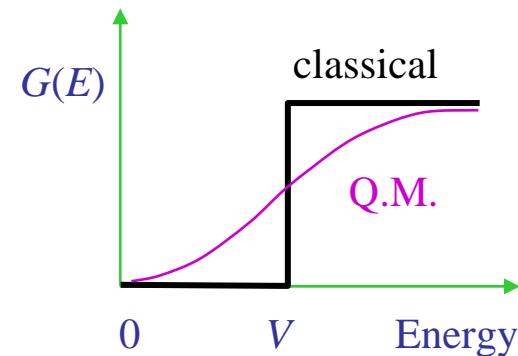


Application of boundary conditions gives the transmission probability:

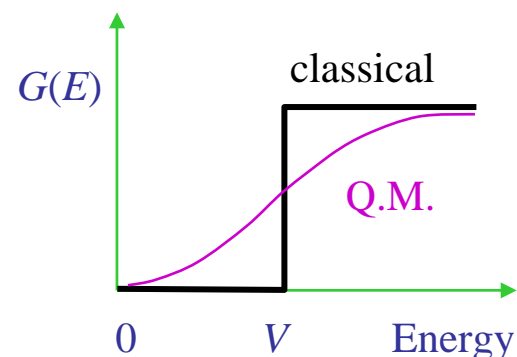
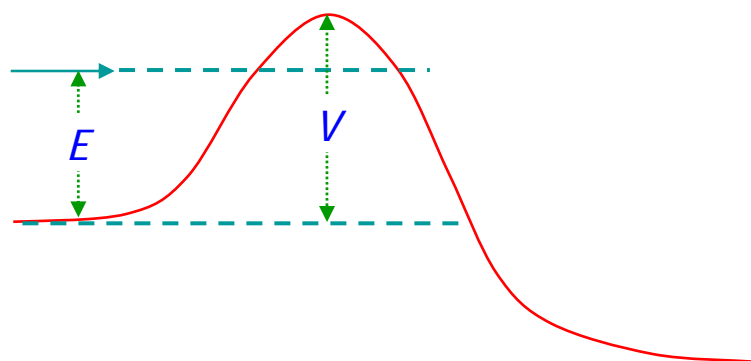
$$G = \frac{A'^2}{A^2} = \left\{ 1 + \frac{(e^{\kappa a} - e^{-\kappa a})^2}{16 \frac{E}{V} (1 - \frac{E}{V})} \right\}^{-1}$$

Tunnelling depends on:

- the mass of the particle
- its energy (compared to the barrier)
- the width of the barrier



Tunnelling in Chemical Reactions



The transmission probability G or permeability depends on energy.

The transmission coefficient κ is the correction factor

$$\kappa(T) = \frac{\int_0^\infty k_{\text{quant}}(T) dE}{\int_0^\infty k_{\text{class}}(T) dE} = \frac{\int_0^\infty G_{\text{quant}} e^{-E/RT} dE}{\int_0^\infty G_{\text{class}} e^{-E/RT} dE} = \frac{\int_0^\infty G_{\text{quant}} e^{-E/k_B T} dE}{\int_V^\infty e^{-E/k_B T} dE} = \frac{e^{V/k_B T}}{k_B T} \int_0^\infty G_{\text{quant}} e^{-E/k_B T} dE$$

$k_{\text{quantum}}(T) = \kappa(T) k_{\text{classical}}(T)$

The PE curve is often approximated by a standard function to get an analytic solution.

e.g the Eckart barrier gives

$$\kappa(T) = 1 + \frac{1}{24} \left(\frac{h\nu^\ddagger}{k_B T} \right)^2 + \dots$$

imaginary frequency
of reaction coordinate