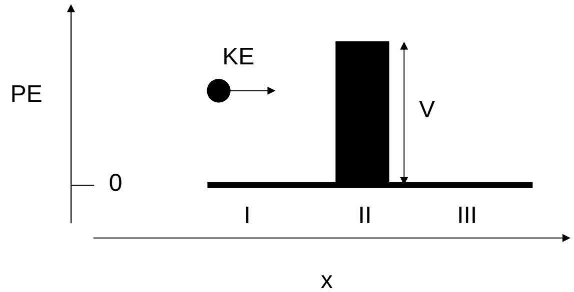
Quantum Mechanical Tunnelling

- A particle is incident on a potential barrier
- Classically if the kinetic energy exceeds the height of the potential barrier the particle will cross
- Conversely if the particle does not have sufficient energy it will bounce back.
- Quantum mechanically things (as you might have guessed) are not so simple.
- The particle may tunnel through the barrier and appear in a ‘classically forbidden’ region of space.
- This is an extremely important effect in chemical kinetics (electron and proton transfer) and spectroscopy (it is the basis of the scanning tunnelling microscopy mentioned earlier).

Setting up the problem

The particle travels from left to right in a region of zero potential (a 1 way free particle).
It encounters a region of thickness L in which the potential energy = *V*.
The particle has a finite probability of transmission through the barrier, where it enters another region of *V* = 0.
What is the transmission probability?
To complete the calculation we need the wavefunction in three regions, I, II, III.



Free Particle Region I

It is useful to look at the free particle solution (exponential form) in more detail.

$$\Psi = c_1 e^{ikx} + c_2 e^{-ikx}$$

Do the two separate terms have separate significance? Let $c_1 = 0$, solve the Schroedinger equation for observable momentum, p_x.

$$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx} \qquad \Psi = c_2 e^{-ikx}$$

$$\frac{\hbar}{i}\frac{d}{dx} c_2 e^{-ikx} = p_x c_2 e^{-ikx}$$

$$p_x = -\hbar k$$

$$\text{using } c_2 = 0 \qquad p_x = \hbar k$$

$c_1 = 0$ corresponds to a particle moving along $-x$, $c_2 = 0$ to a particle in the plus x direction

The wavefunctions

Region I – simply the free particle solution. $\Psi_I = c_1 e^{ik_I x} + c_2 e^{-ik_I x}$

Region II – set up the free particle Schroedinger equation, but with potential V and observable E.

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \Psi_{II}}{\partial x^2} + [V(x) - E]\Psi_{II} = 0$$

The interesting case is when E < V (when classical transmission is forbidden). In this case the solution to the differential equation (see free particle problem) is purely real.

$$\Psi_{II} = c_3 e^{k_{II} x} + c_4 e^{-k_{II} x}$$

The real solution comes from the sign change due to the finite V. The relevant constants are

$$k_I = \left(\frac{2mE}{\hbar^2}\right)^{1/2} \text{ and } \quad k_{II} = \left(\frac{2m(V-E)}{\hbar^2}\right)^{1/2}$$

The wavefunctions

Region III – mathematically, simply the free particle solution again, and $k_{I} = k_{III}$ (same mass). However, we know the particle must travel in the positive x direction, so $c_6 = 0$.

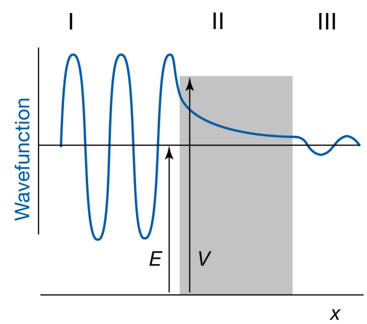
$$\Psi_{III} = c_5 e^{ik_I x} + c_6 e^{-ik_I x}$$

becomes

$$\Psi_{III} = c_5 e^{ik_I x}$$

This is not true in region I. Particles not transmitted are reflected, so $c_2 \neq 0$

In summary we have complex oscillating wavefunctions in regions I and III, and an exponentially decaying real wavefunction in II



Boundary Conditions

The wavefunction must be continuous. ‘No steps’ requires $\Psi_{I}(x = 0) = \Psi_{II}(x = 0)$ and $\Psi_{II}(x = L) = \Psi_{III}(x = L)$, which yields

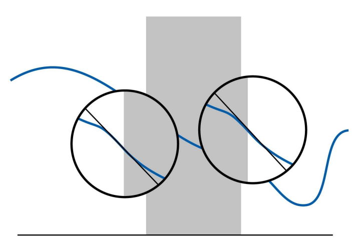
$c_1 + c_2 = c_3 + c_4$ at x = 0 and, at x = L, $c_3\exp(ik_{II}L) + c_4\exp(-ik_{II}L) = c_5\exp(ik_{I}L)$

‘No kinks’ requires that the first derivative of the wavefunction is continuous at the boundaries.

$ik_{I}c_1 – ik_{I}c_2 = k_{II}c_3 – k_{II}c_4$ at x = 0 and, at x = L ,

$c_3k_{ii}\exp(k_{ii}L) – c_4k_{ii}\exp(-k_{ii}L) = -c_5ik_{I}\exp(-ik_{I}L)$

This calculations gives us the proper form of the wavefunction, but also allows us to solve for the transmission, for a given L and k_{II}



The Transmission

The probability of a particle travelling towards the barrier is given by $(\Psi_I)^2$ with $c_2 = 0$, which is proportional to c_1^2.

The probability of a particle moving away from the barrier is given by $(\Psi_{III})^2$ which is proportional to c_5^2.

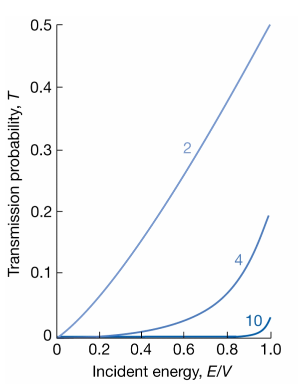
The probability of transmission is given by the ratio of these two. This can be obtained from the relations between them arising from the boundary conditions.

$$T = \frac{|c_1|^2}{|c_5|^2} \quad \text{after a lot of algebra}$$

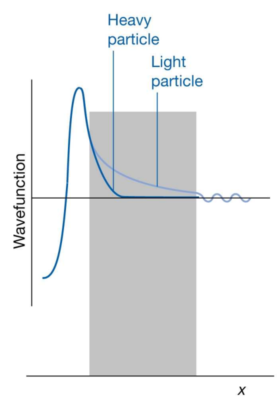
$$T = \left\{1 + \frac{\left(e^{k_{II}L} - e^{-k_{II}L}\right)^2}{16(E/V)[1-(E/V)]}\right\}^{-1}$$

Transmission

The probability of transmission is a strong function of the thickness of the barrier



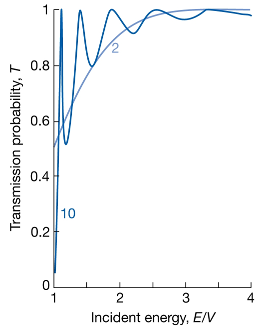
The probability of transmission is a strong function of the mass of the particle (electrons >>>> protons)



Transmission – The case E > V

Classically if a particle has the energy to surmount the barrier it does so.

Quantum mechanically this is not true (the wavefunction for the free particle changes for V ≠ 0). Thus reflection may occur for E > V!



The transmission probability is oscillatory for E > V because Ψ_{II} is complex again.

Calculate the transmission probability of an electron.

Let the barrier height be 1.6×10^{-19} J and the electron energy such that *E*/*V* = 0.9. We will require the electron mass (9.11×10^{-31} kg) and the value of $\hbar$ (1.05×10^{-34}Js) and assume a barrier length of 0.1 nm.

$$k_{II} = \left(\frac{2m(V-E)}{\hbar^2}\right)^{1/2} = \left(\frac{2 \bullet 9.11 \cdot 10^{-31} \bullet \left(0.16 \cdot 10^{-19}\right)^2}{\left(1.05 \cdot 10^{-34}\right)}\right)^{1/2} = 1.63 \cdot 10^{9}\,\mathrm{m}^{-1}$$

Using L = 10^{-10}m

$$T = \left\{1 + \frac{\left(e^{k_{II}L} - e^{-k_{II}L}\right)^2}{16(E/V)[1-(E/V)]}\right\}^{-1} = \left\{1 + \frac{\left[e^{0.163} - e^{-0.163}\right]^2}{16 \bullet 0.9 \bullet 0.1}\right\}^{-1}$$

$$= 0.93$$

i.e. a rather high probability of transmission.

…and for a proton?

The proton mass is 1.67×10^{-27} kg

Scanning Tunnelling Microscopy

It is easy to show that for $k_{II}L$ >>1 the tunnelling probability reduces to

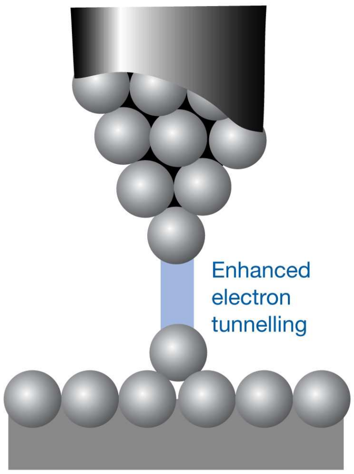
$$T = 16(E/V)[1-(E/V)]\exp(-2k_{II}L)$$

There is thus an exponential dependence on the barrier thickness

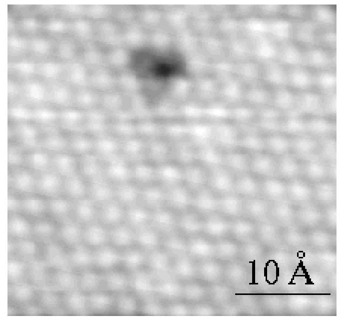
Imagine a metal shard tapering to atomic dimensions, placed as close as possible to a metal surface. Electrons will tunnel between surface and tip, and the 'tunnelling current' can be measured. Because of the exponential dependence on *L* (see above) the resolution of the in the *x* and *y* plane will be on the scale of atomic size, and better than that in the *z* direction.

Measuring the tunnelling current for a tip held a very small very precise distance above the surface as it moves in the *xy* plane yields an atomic scale picture of the surface.

Pictorially



STM image of Pt(111) crystal surface. The dark spot is a C atom impurity.



Vibrational Motion: The Quantum Simple Harmonic Oscillator

- Vibrational motion was described in 1C24 as simple harmonic motion.
- The model worked well in explaining relations between observed frequencies in IR spectroscopy and bond strength.
- It does not tell us why the observed vibrational lines are so narrow (in energy terms).
- The classical SHO cannot explain the existence of bands at twice the frequency, or, in molecules, bands at the sum of two frequencies, etc.
- A much more complete understanding of vibrational spectra is available from the quantum SHO and (better still) the quantum anharmonic oscillator.

The Schroedinger equation for the SHO

As we displace a pendulum from rest we increase its potential energy. When we release it the PE converts to KE

The KE is maximum as the pendulum goes through zero displacement, and reaches zero at the turning point.

Recalling that for harmonic motion the restoring force is proportional to displacement

$F = -\kappa x$ where κ is the force constant

And the force is given by $F = -dV/dx$

We have the potential energy $V = (1/2)\kappa x^2$

And the classical Hamiltonian $H = (1/2)mv^2 + (1/2)\kappa x^2$

The Schroedinger equation for the SHO

Expressing KE in terms of momentum, then momentum and position in operator forms yields

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\Psi + \frac{1}{2}\kappa x^2\Psi = E\Psi$$

using the table method of calculus

$$\Psi = N_v H_v(y)\exp\left(-y^2/2\right)$$

where $y = x/\alpha$ *and* $\alpha = \dfrac{\hbar^2}{m\kappa}$

and H_v are 'Hermite Polynomials'

$v = 0 \quad H_1 = 1$

$v = 1 \quad H_2 = 2y$

$v = 2 \quad H_2 = 4y^2 - 2$

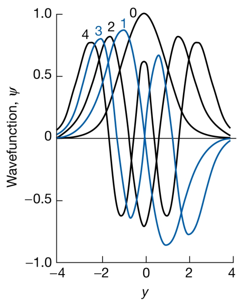
and N_v is a normalisation constant

The SHO wavefunctions

These are more complicated than we have dealt with before. The Normalisation constant depends on *v*. For *v* = 0 we find

$$N^2 \int_{-\infty}^{\infty} \Psi^* \Psi d\tau = 1 \qquad so \qquad N_0^2 \int_{-\infty}^{\infty} \exp\left(\frac{-x^2}{\alpha^2}\right) = 1$$

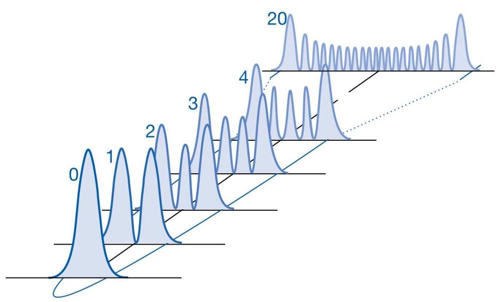
$$N_0 = \left(\frac{1}{\alpha(\pi)^{1/2}}\right)^{1/2} \qquad \text{in general} \qquad N_v = \left(\frac{1}{\alpha(\pi)^{1/2} 2^v v!}\right)^{1/2}$$



Note for *v* = 0 the wavefunction is a Gaussian (bell shape) while for the others there are *v* nodes.

The SHO wavefunctions

For insight into the properties of the SHO the probability distributions are informative. They are calculated from the square of the wavefunction (The SHO wavefunctions being real)



It is apparent that as v increases the particle spends more time at the turning points. This is similar to the classical particle (and very similar for v > 20). However for v = 1 the particle is never at the resting point (x = 0 is a node).

Energy Levels of the SHO

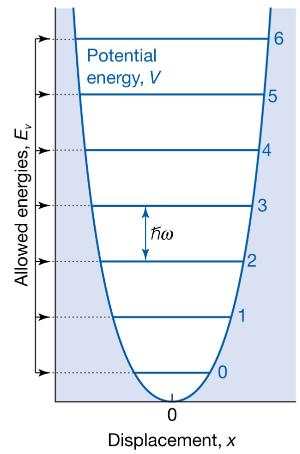
By substituting the results for the wavefunction for v = 0 back in to the Schrödinger equation, completing the double differentiation and cancelling the result with the potential part we recover

$$E_0 = \frac{\hbar\omega}{2} \text{ or in general } E_v = \left(v + \frac{1}{2}\right)\hbar\omega$$

Notice that each successive energy level is equally spaced (by $\hbar\omega$).

That the lowest allowable state (v = 0) has a finite energy. The particle is never at rest. This is a consequence of the uncertainty principle.

Evaluating Ψ_0 at the classical turning point shows also that the particle tunnels into classically forbidden regions (negative KE!)



SHO Summary

- The quantum SHO does a good job of describing simple vibrations in diatomic molecules.
- Force constants can again be calculated, using $\omega = (\kappa/m)^{1/2}$.
- Extensions of the theory account for the appearance of bands in molecules at the sum of 2 vibrational frequencies (combination bands).
- The theory is inadequate for describing the stretching of chemical bonds at large extension (large x).
- In such cases the motion is anharmonic. This requires a further Schroedinger calculation using the 'Morse Potential Energy Surface'