Physical Chemistry

Quantum tunnelling

Quantum tunnelling uses quantum principles to explain a property of molecules at the quantum level.

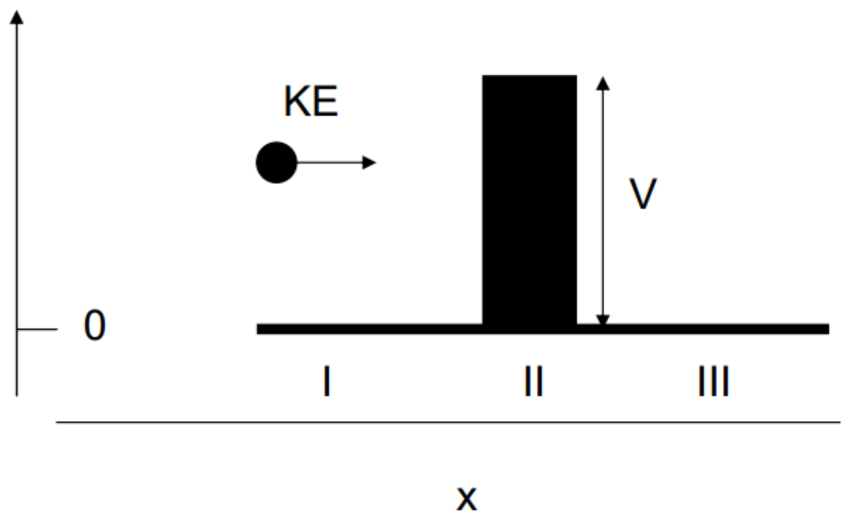
Principles of quantum tunnelling

Quantum tunnelling can be used to explain the act of quantum species travelling from one side of a material to the other. It seems to break classical physics perception. If a molecule has enough energy to pass through or over a barrier in classical physics it will do so with 100% success if it doesn't then it will fail 100% of the time. Both of these assumptions are wrong in quantum mechanics.

The act of quantum tunnelling is an extremely important effect in chemical kinetics and it can be used to explain many different functions and functions of systems.

Understanding tunnelling

A simple tunnelling problem can be explained with 3 regions in one dimension



This shows 3 regions I, II and III. Here the region II is filled with a potential barrier. This has a length L and a potential V. Both I and III have zero potentials.

Schrödinger's equation shows that:

$$\frac{d^2\Psi}{dx^2}\left(\frac{\hbar^2}{2m}\right) = (E - V)\Psi$$

The wavefunction at each point can be represented by the following:

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

So do these separate terms have a significance? This can be looked at by setting one of the terms to equal one. When this is done the following equations are obtained.

$$c_1 = 0$$

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

The momentum of a particle can be found by using the following operator on the wavefunction equation:

$$P_x = \frac{\hbar}{i}\frac{d}{dx}$$

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

$$p_x = -\hbar k$$

$$when\ c_2 = 0 \quad p_x = \hbar k$$

This shows that $c_1 = 0$ the particle is moving in the positive x direction and when $c_2 = 0$ the particle is moving in the negative x direction.

This can be applied to each section of the barrier:

Region I

This means that in region I it is simply the free particle solution to Schrodinger's equation.

$$\frac{d^2\Psi_I}{dx^2}\left(\frac{\hbar^2}{2m}\right) = E\Psi_I$$

The general solution to this equation is:

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

This shows how the particle can move both forwards and backwards through the space, and as there is no potential it can be represented as the wavefunction above.

Region 2

$$\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + (V - E)\Psi_{II} = 0$$

The point to be made here is when classical transition is forbidden. When E<V the solution to the equation is purely real. The absence of i means that there is no oscillation occurring in the wave. This means that a purely exponential decay forms from this point. This is now due to k becoming real due to the finite V that can be given:

$$\Psi_{II} = Ce^{k_{II}x} + De^{-k_{II}x}$$

$$k_1 = \left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}} \quad and \quad k_{II} = \left(\frac{2m(V-E)}{\hbar^2}\right)^{\frac{1}{2}}$$

This shows how the particle can still move in both directions although there is oscillation of the particle.

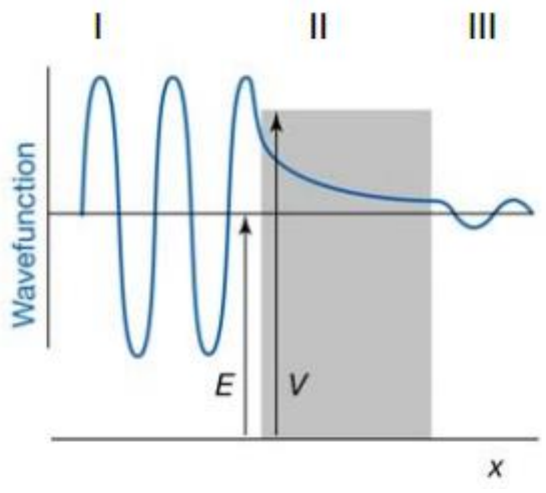
Region 3

Now it has to be assumed that if the particle travels through the barrier it can only be travelling in one direction which means its wavefunction becomes:

$$\Psi_{III} = Ee^{ik_I x}$$

This is not true anywhere else as reflected particles may be present.

This means that the three regions have very different properties compared to the one before it. These can be easily represented in this diagram:



From earlier notes we know that the wavefunction must be continuous. This includes moving from one area of potential to another. This means that no sudden kinks must be present at the boundaries. As the basis of each wavefunction is the same the constants must change. So:

$$ik_I A - ik_I B = k_{II} C - k_{II} D \quad at\ x = L$$

$$Ck_{II}e^{k_{II}L} - Dk_{II}e^{k_{II}L} = Eik_I e^{-ik_I L}$$

This gives us a proper form of the wavefunction and the values of k_{II} this allows the equation to be solved for transmission:

$$T = \frac{A^2}{E^2}$$

This is produced due to the relationships between the movement in the positive x direction and the ability for this to pass through the barrier into the final area. This can form the final equation:

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

$$k_{II} = \left(\frac{2m(V - E)}{\hbar^2}\right)^{\frac{1}{2}}$$