

4.7 review of wavefunctions

back on our quest to understand atoms! we have now built up intuition for both bound and free electrons - these have quite different properties.

solve the time independent Schroedinger equation for $E - U_0 > 0$ (allowed) and we get solutions of the form

$$\frac{d^2\psi}{dx^2} = -k^2\psi \quad k = \frac{\sqrt{2m(E - U_0)}}{\hbar} \quad \psi = Ae^{ikx} + B^{-ikx}$$

i.e. the solutions are oscillatory - sines and cosines. and the wavelength $\lambda = 2\pi/k$ increases as $E - U_0$ decreases i.e. as more of the energy goes to PE rather than KE.

solve the time independent Schroedinger equation for $E - U_0 < 0$ (forbidden) and we get solutions of the form

$$\frac{d^2\psi}{dx^2} = \alpha^2\psi \quad \alpha = \frac{\sqrt{2m(U_0 - E)}}{\hbar} \quad \psi = Ae^{\alpha x} + B^{-\alpha x}$$

i.e. the solutions are exponentials!

if the particle is bound, so that the potential changes from allowed to forbidden with the particle inside, then the oscillatory part of the wavefunction (incident e^{ikx} and reflected e^{-ikx}) sets up an interference pattern which sets up solutions which are a series of standing waves. these are the allowed states we are looking for

whereas where a particle is not contained on each side by a potential then we have travelling waves, though we still have reflection and transmission when the potential changes.

4.7.1 Example: harmonic oscillator

The simple harmonic oscillator gives us a simple potential which $\rightarrow \infty$ at $x \rightarrow \infty$ which is smoothly varying.

$U(x) = 1/2k'x^2$ as in a harmonic oscillator (calling it k' so we don't get confused between oscillator constant and wavenumber k).

we can now intuitively sketch the wavefunctions for this - the lowest energy state will have the smallest classical extent, and a single peak in the centre with exponentially decaying tails into the 'forbidden' region

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}k'x^2\psi = E\psi$$

We can sketch the ground state - and in fact (after a lot of maths) we get that its a gaussian! $\psi(x) = Ce^{-a^2x^2/2}$. Lets prove this, and find out what the energy is. so we put it in Schroedinger

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}k'x^2\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} = \frac{2m}{\hbar^2} \left(\frac{1}{2}k'x^2 - E \right) \psi$$

LHS $d\psi/dx = C(du/dx)e^u/du$ where $u = -\frac{1}{2}a^2x^2$ so $du/dx = -\frac{1}{2}a^2 \cdot 2x = -a^2x$ and $d\psi/dx = C(-a^2x)e^{-a^2x^2/2}$

$$\frac{d^2\psi}{dx^2} = C \frac{d}{dx} (-a^2x e^{-a^2x^2/2}) = C e^{-a^2x^2/2} [-a^2 - a^2x(-a^2x)]$$

$$= C(a^4x^2 - a^2)e^{-a^2x^2/2}$$

$$\text{RHS} = C \frac{2m}{\hbar^2} \left(\frac{1}{2}k'x^2 - E \right) e^{-a^2x^2}$$

equate coefficients of $e^{-a^2x^2}$ and we get $a^2 = 2mE/\hbar^2$ so $E = \hbar^2 a^2 / (2m)$
equate coefficients of $x^2 e^{-a^2x^2}$ and we get $\frac{1}{2}k' = a^4 \hbar^2 / 2m$ so $a^2 = \sqrt{k'm}/\hbar$

hence energy $E = a^2 \hbar^2 / (2m) = \sqrt{k'm} \hbar^2 / (2m \hbar) = \frac{1}{2} \hbar \sqrt{k'/m} = \frac{1}{2} \hbar \omega$

where $\omega = \sqrt{k'/m}$ is the classical result for the oscillation.

We saw when we looked at blackbody radiation that it worked if the electrons in the metal walls were excited into SHM by the EM wave and had energies which were quantised $E = nhf = n\hbar\omega$

so we might expect that $E_n = E_{min} + n\hbar\omega$ where $n \geq 1$ (we can do a LOT of maths to show that this is true!)

so we can COMBINE from $n=0$ (ground state) and get

$$E_n = \frac{1}{2} \hbar \omega + n \hbar \omega = \left(n + \frac{1}{2} \right) \hbar \omega$$

and we can sketch the wavefunctions corresponding to each one - see linked animation

The minimum energy of a classical SHM is zero - particle is at rest at the equilibrium position. this is not possible in quantum mechanics because we cannot be EXACTLY at $x = 0$, there is always some uncertainty $\Delta x \Delta p \geq \hbar/2$, and as the particle is not at $x = 0$ it must have some energy.

we can set $KE = PE$ and classically the particle will go between $x = A$ to 0 to $-A$ with energy all as potential at $x = A$ and all as kinetic at $x = 0$.

$$\frac{1}{2}k'A^2 = \frac{1}{2}\hbar\omega = \frac{p^2}{2m}$$

so $A^2 = \hbar\omega/k' = \hbar/\sqrt{k'm}$ and $p^2 = m\hbar\omega = \hbar\sqrt{k'm}$

so let $\Delta x \sim A/\sqrt{2}$ and $\Delta p \sim p/\sqrt{2}$ where the factors of $\sqrt{2}$ come from looking at the rms. then we get

$$\Delta x' \Delta p = \left(\frac{\hbar}{\sqrt{2k'm}} \frac{\hbar\sqrt{k'm}}{2} \right)^{1/2} = \hbar/2$$

and this is the absolute minimum according to the heisenburg uncertainty principle.

5 Schroedinger in 3 dimensions - cartesian coordinates

Atoms are in 3 dimensional space, not 1 dimensional potentials! so we need to extend our treatment. we got to the 1D Schroedinger by saying $E = KE = \hbar^2 k^2 / 2m = p_x^2 / 2m$ for a free particle. now in 3D we could say for a free particle

$$E = p^2 / 2m = p_x^2 / 2m + p_y^2 / 2m + p_z^2 / 2m = \hbar^2 (k_x^2 + k_y^2 + k_z^2) / 2m$$

so then we have the 3D time dependent Schroedinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V(x, y, z, t) \Psi = E \Psi$$

where $\Psi = \Psi(x, y, z, t)$.

and we can use the same separation of variables techniques to show that as long as the potential is NOT dependent on time then the equation is separable in time and space so $\Psi(x, y, z, t) = \psi(x, y, z) e^{-iEt/\hbar}$ where the time independent equation to solve is

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V(x, y, z) \psi = E \psi(x, y, z)$$

This is separable into $\psi(x, y, z) = X(x)Y(y)Z(z)$ if $V(x, y, z) = V_x(x) + V_y(y) + V_z(z)$.

$$\frac{-\hbar^2}{2m} \left(YZ \frac{\partial^2 X}{\partial x^2} + XZ \frac{\partial^2 Y}{\partial y^2} + XY \frac{\partial^2 Z}{\partial z^2} \right) + (V_x + V_y + V_z)XYZ = EXYZ$$

divide by XYZ to get

$$\left(\frac{-\hbar^2}{2mX} \frac{\partial^2 X}{\partial x^2} + V_x \right) + \left(-\frac{\hbar^2}{2mY} \frac{\partial^2 Y}{\partial y^2} + V_y \right) + \left(-\frac{\hbar^2}{2mZ} \frac{\partial^2 Z}{\partial z^2} + V_z \right) = E$$

these three groups are each dependent only on x , y and z respectively so NONE of them can depend on x, y or z - they must be constants which we'll call E_x, E_y, E_z . Then we get the three equations

$$\frac{-\hbar^2}{2m} \frac{d^2 X(x)}{dx^2} + V_x X(x) = E_x X(x)$$

$$\frac{-\hbar^2}{2m} \frac{d^2 Y(y)}{dy^2} + V_y Y(y) = E_y Y(y)$$

$$\frac{-\hbar^2}{2m} \frac{d^2 Z(z)}{dz^2} + V_z Z(z) = E_z Z(z)$$

and $E_x + E_y + E_z = E$

so now we need 3 quantum numbers, one in each direction, rather than the 1 we needed in the 1D case.