

## 5.1 infinite potential well - 3D

$V = 0$  for  $0 < x < L_x$  and  $0 < y < L_y$  and  $0 < z < L_z$  and  $\infty$  elsewhere. Inside the well then we have

$$\begin{aligned}\frac{-\hbar^2}{2m} \frac{d^2 X(x)}{dx^2} &= E_x X(x) \\ \frac{-\hbar^2}{2m} \frac{d^2 Y(y)}{dy^2} &= E_y Y(y) \\ \frac{-\hbar^2}{2m} \frac{d^2 Z(z)}{dz^2} &= E_z Z(z)\end{aligned}$$

each one of these is just the same as the 1D case. so we can write down the solution as

$$\begin{aligned}X(x) &= \sqrt{\frac{2}{L_x}} \sin n_x \pi x / L_x & E_x &= \frac{n_x^2 \pi^2 \hbar^2}{2m L_x^2} \\ Y(y) &= \sqrt{\frac{2}{L_y}} \sin n_y \pi y / L_y & E_y &= \frac{n_y^2 \pi^2 \hbar^2}{2m L_y^2} \\ Z(z) &= \sqrt{\frac{2}{L_z}} \sin n_z \pi z / L_z & E_z &= \frac{n_z^2 \pi^2 \hbar^2}{2m L_z^2}\end{aligned}$$

where the box extends from  $0 - L_x$  on the x axis,  $0 - L_y$  on the y axis and  $0 - L_z$  on the z axis, so have volume  $V = L_x L_y L_z$ . hence the full wavefunction is

$$\psi(x, y, z) = X(x)Y(y)Z(z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin(n_x \pi x / L_x) \sin(n_y \pi y / L_y) \sin(n_z \pi z / L_z)$$

we can check that this is normalised

$$\begin{aligned}\int_{x=-\infty}^{+\infty} \int_{y=-\infty}^{+\infty} \int_{z=-\infty}^{+\infty} \psi(x, y, z) dx dy dz \\ \int_{x=-\infty}^{+\infty} X(x) dx \int_{y=-\infty}^{+\infty} Y(y) dy \int_{z=-\infty}^{+\infty} Z(z) dz = 1\end{aligned}$$

so if the individual 1D wavefunctions are normalised we can just multiply them together and our 3D wavefunction is automatically normalised.

The allowed energy levels are

$$E = E_x + E_y + E_z = \frac{n_x^2 \pi^2 \hbar^2}{2mL_x^2} + \frac{n_y^2 \pi^2 \hbar^2}{2mL_y^2} + \frac{n_z^2 \pi^2 \hbar^2}{2mL_z^2}$$

$$= \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

but we could of course have made our lives a lot easier by simply choosing a cube! so then

$$\psi_{\underline{n}}(x, y, z) = \sqrt{\frac{8}{V}} \sin(n_x \pi x / L) \sin(n_y \pi y / L) \sin(n_z \pi z / L)$$

with energy

$$E_{\underline{n}} = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$$

The ground state has  $n_x = n_y = n_z = 1$  so  $n^2 = 3$  and there is only one wavefunction with this energy  $E(1, 1, 1) = 3\hbar^2 \pi^2 / (2mL^2)$

but the first excited state we can have in 3 different ways - we can put  $n_x = 2$  and have  $n_y = n_z = 1$  (2,1,1). or  $n_x = 1$  and have  $n_y = 2$  and  $n_z = 1$  (1,2,1). or  $n_x = n_y = 1$  and have  $n_z = 2$ . These 3 are DIFFERENT wavefunctions. but they all have the same energy of  $(4 + 1 + 1) = 6E(1, 1, 1)$

## 5.2 degeneracy

**different sets of quantum numbers can give the same energy. these have DIFFERENT wavefunctions so are different states, but have they can have the same energy**

we get degeneracies because of the *symmetry* of the potential. Each dimension has its own quantization condition. If the potential is the same in each dimension then rotating the wave around gives the same energy as before.

if we had DIFFERENT potentials along the 3 axes then this would not have happened. eg if there are different lengths  $L_x \neq L_y \neq L_z$  (they need to be non-comensurate as well!) over which the potential is zero, then each set of quantum numbers  $n_x, n_y, n_z$  would give a UNIQUE energy level

### 5.3 The 3D harmonic oscillator

$$E_x = (n_x + 1/2)\hbar\omega_x \text{ where } \omega_x = \sqrt{k'_x/m}$$

$$E_y = (n_y + 1/2)\hbar\omega_y \text{ where } \omega_y = \sqrt{k'_y/m}$$

$$E_z = (n_z + 1/2)\hbar\omega_z \text{ where } \omega_z = \sqrt{k'_z/m}$$

if its isotropic so  $k'_x = k'_y = k'_z = k'$  then we get  $E = (n_x + n_y + n_z + 3/2)\hbar\omega$

ground state  $n_x = n_y = n_z = 0$   $E(0,0,0) = 3/2\hbar\omega$  only one way to get this energy - degeneracy 1 (or non-degenerate)

1st excited state  $n_x = 1, n_y = n_z = 0$  (1,0,0). SAME ENERGY as  $n_x = 0, n_y = 1, n_z = 0$  (0,1,0). SAME ENERGY as  $n_x = 0, n_y = 0, n_z = 1$  (0,0,1).

$E = (1 + 3/2)\hbar\omega = 5/2\hbar\omega$  Three ways to get this energy - degeneracy 3

2nd excited state  $n_x = 2, n_y = n_z = 0$  (2,0,0). SAME ENERGY as  $n_x = 0, n_y = 2, n_z = 0$  (0,2,0). SAME ENERGY as  $n_x = 0, n_y = 0, n_z = 2$  (0,0,2). SAME ENERGY as  $n_x = 1, n_y = 1, n_z = 0$  (1,1,0). SAME ENERGY as  $n_x = 1, n_y = 0, n_z = 1$  (1,0,1). SAME ENERGY as  $n_x = 0, n_y = 1, n_z = 1$  (0,1,1).  $E = (2 + 3/2)\hbar\omega = 7/2\hbar\omega$ . six ways to get this energy - degeneracy 6.

### 5.4 Hydrogen as 3D infinite box

We could model H as a 3D infinite potential box. first we could find L which gives the same volume as a sphere of the Bohr radius  $a = 5.3 \times 10^{-11}$  m.

$$4/3\pi a^3 = L^3 \text{ so } L = (4\pi/3)^{1/3}a = 1.61a = 8.5 \times 10^{-11} \text{ m}$$

then ask what is the transition energy between the ground and first excited state?

$$\Delta E = (6 - 3)\pi^2\hbar^2/(2mL^2) = 3\pi^2\hbar^2/(2mL^2) = 2.5 \times 10^{-17} \text{ J} = 1.55 \text{ eV}$$

Compare this to the Bohr model where the energy levels are  $E_n = -13.6/n^2$  eV

$\Delta E = 13.6(1 - 1/4) = 10.2$  eV - so a particle in a box is not a good approximation to the hydrogen atom! and this doesn't surprise us as the energy levels are observed to be like the Bohr model, with  $E_n = -13.6/n^2$  not  $E_n \propto (n_x^2 + n_y^2 + n_z^2)$ . more fundamentally, the potential in Hydrogen is  $\propto 1/R$  so it is not like an infinite wall but has a shape.

## 6 Schroedinger in 3D - spherical polar coordinates

so we really need to put the proper potential in. but  $1/R = 1/(x^2 + y^2 + z^2)^{1/2}$  which is NOT separable as  $V(x) + v(y) + V(z)$ . we cannot use cartesian coordinates - and in fact we would expect to be using spherical polars as they follow the symmetry of the potential.

In spherical polars we have  $r = \sqrt{x^2 + y^2 + z^2}$ ,  $\cos \theta = z/r$  and  $\tan \phi = y/x$ . and then our potential  $U(r, \theta, \phi) = U(r)$ . Then the wavefunction can be separated into  $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$  similarly to the cartesian problem above where we had  $\psi(x, y, z) = X(x)Y(y)Z(z)$ . After a LOT of maths (that you will tangle with in 2nd year) we get three differential equations:

$$\begin{aligned} \frac{-\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left( \frac{\hbar^2 l(l+1)}{2\mu r^2} + U(r) \right) R(r) &= ER(r) \\ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left( l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right) \Theta(\theta) &= 0 \\ \frac{d^2 \Phi}{d\phi^2} + m_l^2 \Phi(\phi) &= 0 \end{aligned}$$

where  $n, l, m_l$  are quantized constants and we are calling mass  $\mu$  to distinguish it from  $m_l$ . Essentially the boundary conditions produce 3 integer quantum numbers (one for each direction!) which are  $n, l$ , and  $m_l$ . Solve these equations (horrible maths) and you get that the energy  $E_{n,l,m_l}$  is actually only a function of  $n$

$$E_n = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = -\frac{13.6}{n^2} \text{ eV}$$

so it reproduces what we see in Hydrogen!! which is what the Bohr atom did for us but this time we're getting here via a wave equation.

**$n$  is called the principle quantum number. Ground state is  $n = 1$**

The radial wavefunction  $R(r)$  is set by BOTH  $n, l$  so better to write it as  $R_{nl}(r)$

**$l$  is called the orbital quantum number and runs from  $0, 1 \dots n - 1$**

The angular wavefunctions are  $\Theta(\theta)$  which depends on  $l, m_l$  and  $\Phi(\phi)$  which depends only on  $m_l$ .