4.4 particle in a 1-D box

consider a particle trapped in a 1-D box by an infinite potential well at $x = 0$ and $x = L$. so $U(x) = \infty$ $x < 0$ and $x > L$ and $U(x) = 0$ for $0 \le x \le L$.

$\psi(x)$ must be zero where the potential is infinite - there is no probability to find a particle here!

in the region with $U(x) = 0$ then we are back to the free particle equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

when we looked at the solution of this for a particle travelling from left to right we had $\psi(x) = e^{ikx}$ but this is not zero for $x < 0$ (our wave went over all space)

but a wave travelling from right to left is also a solution to the free particle Schroedinger equation $\psi(x) = e^{-ikx}$. And so a more general solution is the combination of the two:

$\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$. And physically this is what we actually expect from REFLECTION OF A WAVE FROM A BOUNDAY! (see linked animation!)

so then we have

$$\psi(x) = A_1(\cos kx + i\sin kx) + A_2(\cos -kx + i\sin -kx)$$

$$= A_1(\cos kx + i\sin kx) + A_2(\cos(kx - i\sin kx) = (A_1 + A_2)\cos kx + i(A_1 - A_2)\sin kx$$

we need $\psi(0) = 0$ so this means $A_1 + A_2 = 0$ i.e. $A_2 = -A_1$ which is what we expect for complete reflection. so then

$\psi(x) = 2iA_1 \sin kx = C\sin kx$ where we simplify by setting $C = 2iA_1$.

but we also need $\psi(L) = 0$ so this means that $0 = C\sin kL$ which is satisfied for $kL = n\pi$ or $k = n\pi/L = 2\pi/\lambda$ so $\lambda = 2L/n$ for $n = 1, 2, 3\ldots$

4.4.1 Energy levels

we know $E_n = \hbar^2 k^2/(2m) = n^2\pi^2/(2mL^2)$

each energy level E_n has its own quantum number n and corresponding wavefunction $\psi_n(x) = C\sin n\pi x/L$. The energy levels $E_n \propto n^2$, unlike the Bohr atom where $E_n \propto 1/n^2$ but thats not really surprising as we used a square potential rather than a $1/r^2$ potential and we are in 1D rather than 3D. we'll need to work up to a real atom, but in the meantime we are going to build intuition using simpler potentials.

A particle cannot have zero energy - n=0 does not make sense! the allowed states are all mixtures of $p = \hbar k$ and $p = -\hbar k$ - there is an equal mix of +ve and -ve momentum so the uncertainty on momentum is $\Delta p = \hbar k = \hbar n\pi/L$. But there is an uncertainty in position - the particle is in the box s0 $\Delta x = L/2$. Hence $\Delta p \Delta x = \hbar n\pi/L \times L/2 = \hbar n\pi \geq \hbar/2$ so in fact a particle in a box does not reach the minimum possible uncertainty.

4.4.2 Examples

a) what is the lowest energy of an electron trapped in a 1D infinite potential well box of width 5×10^{-10} m

$E_n = n^2\pi^2\hbar^2/(2mL^2) = 1^2\pi^2(1.06 \times 10^{-34})^2/(2 \times 9.1 \times 10^{-31} \times (5 \times 10^{-10})^2 = 2.44 \times 10^{-19}$ J=1.5eV as $1eV = 1.6 \times 10^{-19}$ J

b) What is the nth energy level in terms of this ground state?

$E_n = n^2 E_2$ for $n > 1$ so $E_n = 1.5n^2$ eV

c) What is the excitation energy to raise the electron from its ground state to the third excited state.

ground is n=1. third excited state is $n = 4$.

$E_4 - E_1 = 1.5(16) - 1.5 = 22.5$ eV

4.4.3 Normalisation

the probability to find the electron if we look over all space must be unity (its somewhere!)

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = \int_{-\infty}^{0} |\psi(x)|^2 dx + \int_{0}^{L} |\psi(x)|^2 dx + \int_{L}^{+\infty} |\psi(x)|^2 dx$$

$$= \int_{0}^{L} |\psi(x)|^2 dx = C^2 \int_{0}^{L} \sin^2 n\pi x/L dx$$

$\sin^2\theta = 1/2[1 - \cos(2\theta)]$ so we can evaluate - set $y = 2n\pi x/L$ so $dy = 2n\pi dx/L$

$$= C^2 \int_{0}^{L} 1/2[1 - \cos 2n\pi x/L]dx = C^2 \int_{0}^{L} 1/2 dx - C^2 \int_{0}^{2n\pi} \cos y(L/(2n\pi)dy$$

$$= C^2 L/2 - C^2(L/(2n\pi)[\sin y]_0^{2n\pi} = C^2 L/2$$

hence $C^2 = L/2 = C^*C$. We can choose $C = \sqrt{L/2}$ for simplicity.

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad n = 1, 2, 3 \ldots$$

4.4.4 Examples

a) sketch the wavefunctions for $n = 1$, $n = 2$ and $n = 3$. sketch the probability distribution for each one. (see linked figure on web page)

the wavefunction is continuous everywhere. and its derivative is continuous everywhere EXCEPT at $x = 0, L$. this is because $d^2\psi/dx^2 = 2m/\hbar(V - E)\psi$ so it changes by an infinite amount at $x = 0, L$ so the gradient has a step. This is artificial, as it comes from this infinite potential approximation. for any finite potential then it won't happen! we'll do this next lecture

b) what is the probability to find the electron within dx of $L/2$ Prob $= \psi^*\psi dx = 2/L \sin^2 n\pi(L/2)/L dx = 2dx/L \sin^2 n\pi/2$ which $\rightarrow 2dx/L$ for n odd or $\rightarrow 0$ for n even. (see linked figure on web page)

so how does a particle get from left to right for an even state as the probability is zero at $L/2$?? this is not the right way to think about it - remember, we don't ever know a complete trajectory, we only get a probability for where the particle would be detected if we put an instrument in to measure it!

c) what is the probability to find the electron within $0 \leq x \leq L/4$ in the $n = 1$ state? compare this to the classically expected probability?

$$2/L \int_0^{L/4} \sin^2(\pi x/L) dx = 2/L \int_0^{L/4} \frac{1}{2}[1 - \cos(2\pi x/L)] dx$$

$$= 1/L \int_0^{L/4} dx - 2/L \int_0^{L/4} \cos(2\pi x/L) dx$$

let $y = 2\pi x/L$ so $dy = 2\pi dx/L$ (remember to change the limits on the integral)

$$(1/L)(L/4) - 2/L 1/2 \int_0^{2\pi L/(4L)} \cos y L dy/(2\pi) = 1/4 - 1/L(L/2\pi)[\sin y]_0^{\pi/2}$$

$$= 1/4 - 1/(2\pi) = 0.0908$$

classically we expect a uniform distribution so $0 - L/4$ probability is 0.25.

4.4.5 Finite well

We are really trying to understand atoms - they have a 3D potential well with shape $\propto -1/r^2$. So far we have just done an infinite 1D potential... so lets try to get closer to the physical system we want, but keeping something very simple. So instead of an infinite potential, lets do a finite potential.

$U(x) = U_0$ for $x < 0$ and $x > L$ and $U(x) = 0$ for $0 < x < L$.

the electron is bound if its in the well with $E < U_0$ - classically there is no way over the barrier. but this is quantum mechanics so lets solve it!

Inside the well we have the same conditions as before so we know the solution is

$$\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx} = (A_1 + A_2)\cos(kx) + i(A_1 - A_2)\sin(kx)$$

where $E = \hbar^2 k^2/(2m)$ i.e. $k = \sqrt{2mE}/\hbar$ but now the boundary conditions are different since its not an infinite potential then it does not have to go to zero at $x = 0, L$! lets find out what it is...

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U_0\psi = E\psi$$

$$\frac{d^2\psi}{dx^2} = \frac{2m(U_0 - E)}{\hbar^2}\psi$$

since $U_0 > E$ for the bound particle states we are trying to determine, then $2m(U_0 - E)/\hbar^2$ is a +ve quantity. lets call it κ^2 so

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi$$

if this were -ve we'd have our standard sine/cosine simple harmonic oscillator. $d^2\psi/dx^2 = -k^2\psi$.but its NOT, its +ve, so instead its solution is a sum of exponentials $\psi = Ce^{\kappa x} + De^{-\kappa x}$.

ψ must be finite as ψ^2 is a probability distribution function! so

$x < 0$

the term $De^{-\kappa x} \to \infty$ as $x \to -\infty$ which is unphysical! hence $D = 0$

$x > L$

the term $Ce^{\kappa x} \to \infty$ as $x \to \infty$ which is unphysical! hence $C = 0$

so there is an exponential tail of ψ which extends into the classically forbidden region! solving this in full generality is nasty, here we are just trying to build physical intuition. we can get some more contraints from continuity:

Continuity of ψ at $x = 0$

$\psi(0) = Ce^{\kappa 0} = C = A\cos k0 + B\sin k0 = A$ so $C = A$

Continuity of ψ at $x = L$ - a bit more tricky

$\psi(L) = De^{-\kappa L} = A\cos kL + B\sin kL$

for odd n then symmetry means that this is the SAME as $x = 0$ so $A = De^{-\kappa L}$ and $D = Ae^{\kappa L}$ so $\psi(x) = Ae^{\kappa L}e^{-\kappa x} = Ae^{-\kappa(x-L)}$ which makes a lot of sense.

for even n its anti-symmetry so its $\psi(x) = -Ae^{-\kappa(x-L)}$

Continuity of $d\psi/dx$ at $x = 0$

this must also be continuous which gives a relation between κ and k which sets the allowed energy levels. But its actually mathematically really nasty and not a simple analytic formula like the infinite potential well!

comparison of infinite and finite square well potentials

its clear that we have something like the infinite well, but with exponential tails which can extend into the classically forbidden regime which has $U > E$. The fact that the wavefunction extends outside of the well means that λ is bigger for any given n, so the energy shifts down compared to the infinite well.

The finite well depth also means that there are only a finite number of bound states, instead of the infinite number in the infinite well. this becomes very obvious when U_0 is only a few times larger than the ground state of the infinite square well $E_{1,\infty} = \pi^2\hbar^2/(2mL^2)$

e.g. if $U_0 = 10.13E_{1,infty}$ then $E_1 = 0.69E_{1,\infty}$ and there are 4 bound states.

e.g. if instead $U_0 = 2.52E_{1,\infty}$ then $E_1 = 0.5E_{1,\infty}$ and there are only 2 bound states.

e.g. in the limit where $U_0 \ll E_{1,\infty}$ then there is only one single bound state with $E_1 = 0.68U_0$

(see the linked animation)