PHY293 Lecture #17

December 4, 2017

1. Solving the Time Dependent Schrodinger Equation

   - Usually use the technique of separation of variables to solve this partial differential equation
   - Assume that $\Psi(x,t) = \psi(x)\phi(t)$ and plug this in to the time dependent Schrodinger equation:

   $$-\frac{\hbar^2}{2m}\frac{\partial^2[\psi(x)\phi(t)]}{\partial x^2} + U(x)\psi(x)\phi(t) = i\hbar\frac{\partial[\psi(x)\phi(t)]}{\partial t} \Rightarrow -\frac{\hbar^2}{2m}\phi(t)\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x)\phi(t) = i\hbar\psi(x)\frac{d\phi(t)}{dt}$$

   - Now divide the whole equation through by $\psi(x)\phi(t)$ to get:

   $$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + U(x) = i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}$$

   - But the LHS of this equation depends only on x (the potential is not time-dependent – that is a complication for a more advanced course in QM) and the RHS depends only on t
   - Satisfy this equality only if each side is equal to constant – this is call the separation constant:

   $$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + U(x) = C \qquad i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = C$$

   - We now have two separate **total** differential equations (ie. equations in only one variable)
   - The "right" one is easiest to solve: $\frac{d\phi(t)}{\phi(t)} = -i\frac{C}{\hbar}dt$ gives $\ln\phi(t) = -i\frac{C}{\hbar}t$ or $\phi(t) = exp(-i\frac{C}{\hbar}t)$
   - Can double check by just substituting this back into the RHS differential equation.
   - This is a sinusoidal oscillation (either $\cos$ or $i\sin$) with frequency $\omega = C/\hbar$
   - The separation constant turns out to be just what we've been calling the particle's energy
   - The energy for these solutions is well-defined ($E = \hbar\omega$) so we can write the full solution as: $\Psi(x,t) = \psi(x)exp(-i\frac{E}{\hbar}t)$
   - Note that this already gives us something 'simpler' for the particle's probability density

   $$\Psi^*\Psi = \psi^*(x)e^{iE/\hbar t}\psi(x) = \psi(x)^*\psi(x)$$

   - Note that this is **independent of time**. These are known as stationary states
   - The probable locations of the particle in space, do not change with time
   - For an electron orbiting a nucleus the spatial probability (and associated charge density $e\psi^*\psi$) does not change this time. As contrasted with the classical electron orbit that would change radius, losing energy and eventually collapse.

2. Spatial part of the wavefunction

   - For the spatial part we have

   $$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + U(x) = E$$

   - Where we have identified the separation constant as the Energy of the system E
   - This is the **Time Independent Schrodinger Equation**. No longer has an imaginary terms
   - Can only proceed further with a solution given a particular potential $U(x)$
   - Full Schrodinger solution usually just amounts to tacking time dependence: $e^{-iE/\hbar t}$ on to spatial part: $\psi(x)$
   - Often just refer to $\psi(x)$ as "the wavefunction"
   - General properties of the wavefunction solutions include
     (a) Must be normalised to give until probability to find one particle 'somewhere'
       - So we want:

   $$\int_{-\infty}^{+\infty}\psi^*(x)\psi(x)dx = 1$$

    - $\psi(x)$ can extend over all of space as long as it falls to zero faster than $1/\sqrt{x}$

  (b) We require the wavefunction to be "smooth"
    - This means it must be continuous and differentiable (ie. the 1st derivative has to be continuous)
    - These conditions will lead to a finite second derivative
    - Kinetic energy of the particle is proportional to the second derivative is $d^2\psi/dx^2$
    - A discontinuity in the wavefunction, or in the first derivative would lead to a particle of infinite kinetic energy
    - A discontinuity, or kink, in the wavefunction would lead to the inclusion of a frequency/wavelength in the solution that is infinitely short (wavelength) which in turn is an infinitely high energy

- Exception to Smoothness rule
  - The one exception (that we will actually discuss here) is when the potential goes to ∞
  - In that case the wavefunction must still be continuous
  - But the restriction on the continuity of the first derivative is lifted
    - The Schrodinger equation is basically just summing the kinetic and potential energy to give E
    - If the potential jumps to ∞ at some point, the kinetic energy can be **anything**
    - In particular it can be be ∞ too so $d^2\psi/dx^2$ doesn't have to be finite and $d\psi/dx$ can be discontinuous
  - In "Particle in a Box" example, $U(x) \rightarrow \infty$ at $x = 0, L$
  - The wavefunction is continuous (wave inside, flat outside)
  - But first derivative is discontinuous (goes from sinusoid to 0 at $X = 0, L$)
  - In PHY294 you will also see box-potential with finite change in energy level
  - Both wavefunction and first derivative will be continuous → interesting physics (ie. $\psi(x)$ and $P(x) = |\psi(x)|^2$)

3. Solving the Infinite Square Well

- Outside the box $U(x) \rightarrow \infty$ and so $\psi(x) \rightarrow 0$ – there is no probability to find the particle there
- It would have to have infinite kinetic energy to overcome the potential and not even a relativistic particle has infinite energy...
- Take the potential to be 0 inside the well and so need to solve:

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \qquad \text{for} \quad 0 < x < L$$

- Rearrange this to give:

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x) \qquad \text{with} \quad k^2 = \frac{2mE}{\hbar^2}$$

- Our solutions must satisfy this equation and the boundary conditions that $\psi(0) = 0$ and $\psi(L) = 0$
- The general solution is of the form $\psi(x) = A\sin kx + B\cos kx$ or $\psi(x) = Ae^{ikx}$
- Apply the boundary conditions to find A and B
- The boundary at 0 implies: $\psi(0) = 0$. This doesn't work for $\cos kx$ so $B = 0$ is the only way out
- Boundary condition at $x = L$ on $\psi(x) = A\sin k_n x$ at $x = L$ gives $\sin kL = 0$ or $k_n = n\pi/L$
- So the solution is $\psi_n(x) = A\sin(\frac{n\pi}{L}x)$ and $k_nL = n\pi \Rightarrow \sqrt{\frac{2mE}{\hbar^2}}L = n\pi$ which finally gives: $E = \frac{n^2\pi^2\hbar^2}{2mL^2}$
- The particle in a box is restricted to a discrete set of energy levels (kind reminiscent of what we saw for the Hydrogen atom)
- But now we've found the solutions in a deterministic way – solving the Schrodinger equation
- Energy levels are quantised for $n = 1, 2, 3...$ because the potential jumps to ∞ there are actually an infinite number of levels
- In contrast to the H-atom, the steps between the levels grow with n^2 rather than falling like $1/n^2$ in the H-atom
- To complete this problem normalise the wavefunctions (find A) using the condition:

$$\int_{-\infty}^{+\infty}\psi^*(x)\psi(x)dx = 1 \Rightarrow \int_0^L A^2\sin^2(\frac{n\pi}{L}x)dx = 1$$

- Recall that $\psi(x) = 0$ for $x < 0$ and $x > L$ so those parts don't contribute to this integral
- This integral (over some integral number of wavelengths, which we have in this case) is just $L/2$ so $A^2L/2 = 1 \rightarrow A = \sqrt{\frac{2}{L}}$

- This is true for all values of n – this is numerical accident for the sinusoidal wave functions. In general the normalisation can be different for each different energy level
- The full solution gives us an infinite (but discrete) set of normalised, continuous wavefunctions, that represent the allowed states of a particle that finds itself in an infinite, square well potential, along with the corresponding energy levels.
- Could have argued for this solution in the same way Bohr described the H-atom
  - Standing waves between $0 < x < L$ (this the square-well analog of 'one complete orbit' around an H-atom)
  - Otherwise linear combinations of states can interfere with each other leading to a vanishing probability to find the particle anywhere in box.
  - The condition that all states are represented by waves that go to 0 at $X = 0, L$ ensures that there will be some positive interference between different wavefunctions so there can't be complete destructive interference.
  - If $p = \hbar k_n = \hbar\pi n/L$ conclude $E = p^2/2m = (\hbar k_n)^2/2m = \frac{\hbar^2\pi^2 n^2}{2mL^2}$ just as we got from the full solution
- What probability density does this give?
  - By construction $|\psi(0, L)|^2 = 0$ (also true everywhere outside the well) so there is no probability to find the particle at the edges of the well, or anywhere outside (good because it would need infinite energy to get outside the well)
  - Inside the well there are $n - 1$ nodes (where $\sin^2(n\pi x/L)$ drops to 0)
  - This is an interesting feature. How does the particle get from one node to another?
  - Answer: ψ predicts where we might find it, if we make a measurement ... not how it moves around in the well. It could end up in any of the lobes (or, with lower probability, the edges of the lobes) if/when you make a measurement. That is all we can predict.
- The state with $n = 1$ is called the **ground state** – it has the lowest energy
- This is the minimum energy a particle confined inside a box can have...
- If it were really stationary then it would violate the uncertainty principle because we'd have some general idea where it is (finite $\Delta x \approx L$) ... ie. inside the box and very precise knowledge of its momentum ($p = 0 \rightarrow \Delta p = 0$)
- Apparently it also has more probability to be found nearer the middle of the box than near the edges. This is a consequence of the infinite potential jump and the continuity of the wavefunction that is necessary from the form of the Schrodinger equation

4. The Quantum Mechanical Correspondence Principle

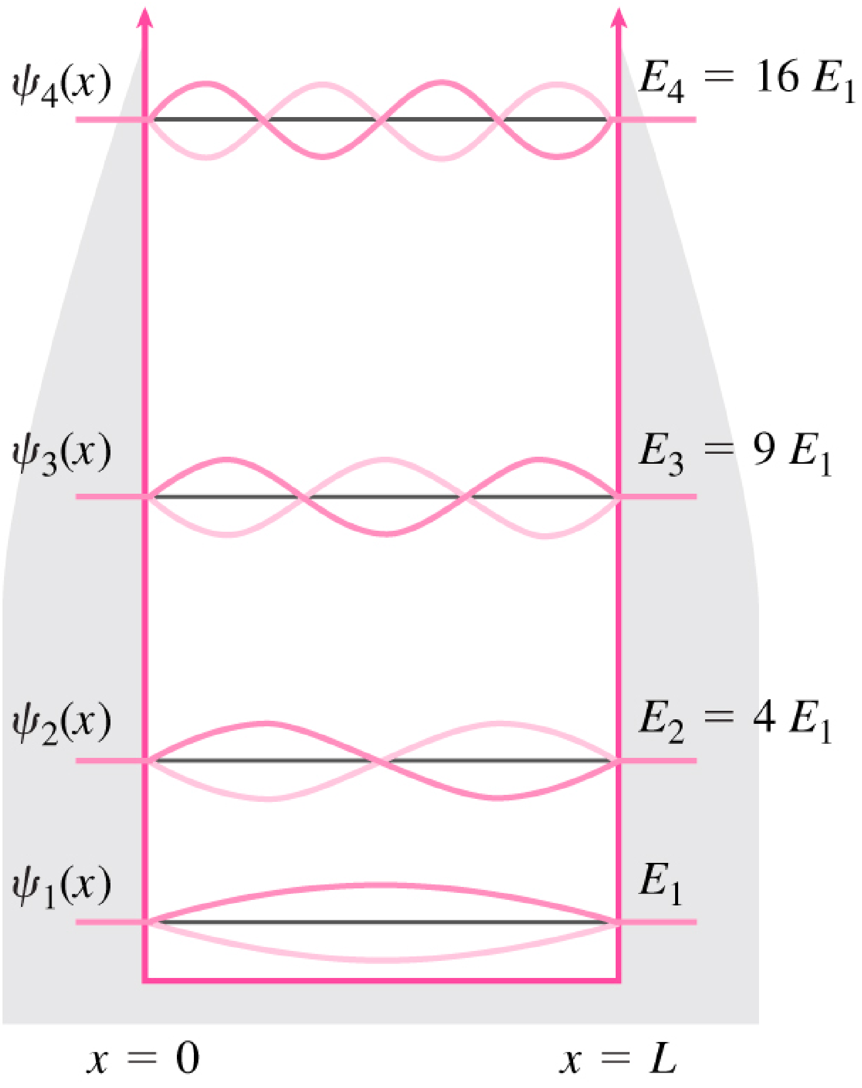
- Just as there is a smooth transition from special relativity to normal mechanics as $v \rightarrow 0$
- So too there is a smooth transition from the quantum predictions to normal mechanics as the size of a system grows from the atomic scale to macroscopic/human scale (or larger)
- To achieve this the solutions to the paritcle in the box must become a better and better approximation to the classical solutions for higher energies (larger n)
  - In this case the probability density becomes more and more uniform as we go up in energy levels
  - But, despite the fact that the steps grow like n^2, if you step back and look from the perspective of the infinite potential step – become almost continuously spaced
  - So a macroscopic particle that has p and x measured in kgm/s or m, can be found anywhere in the box and has an 'almost continuous' set of possible energies.

5. Typical Example Problem (Textbook Example 5.1)

- Given electron confined in infinite well has a ground state energy of 0.1 eV
- What is L? $E = \hbar^2\pi^2/2mL^2$ or $L^2 = \hbar^2\pi^2/2mE = (1.05\times10^{-34})^2 3.14^2/[2\cdot(9.1\times10^{-31})\cdot(0.1\times1.6\times10^{-19})] = 1.9$ nm
- What is the probability that the electron is in the left 1/3 of the well? $\int_0^{L/3}\frac{2}{L}\sin^2(\frac{\pi}{L}x)dx = \frac{2}{L}\frac{L}{\pi}\int_0^{\pi/3}\sin^2(y)dy = \frac{2}{\pi}[y/2 - \sin(2y)/4]\Big|_0^{\pi/3} = \frac{2}{\pi}[\pi/6 - \sin(2\pi/3)/2\pi] = 19.6\%$
- I got this calculation wrong when I tried to do it on my flight home over the weekend and only checked it after class. I even told one of the classes I thought it was going to be even smaller than the 26% I gave in class... and it is... Sorry
- What would the next energy level be? $E_n = E_0 n^2$ so $E_1 = 0.1$ eV and $E_2 = 4E_0 = 0.4$ eV.
- If L were increased to 1 mm with no change in electron energy, what would the probability be to find the electron in the first 1/3 of the well: This is a million times larger, and so just an application of the correspondence principle. It should be 1/3 probable to be in the first 1/3 of the well. Up from 20% in the quantum limit.

Smoothness of Wavefunction

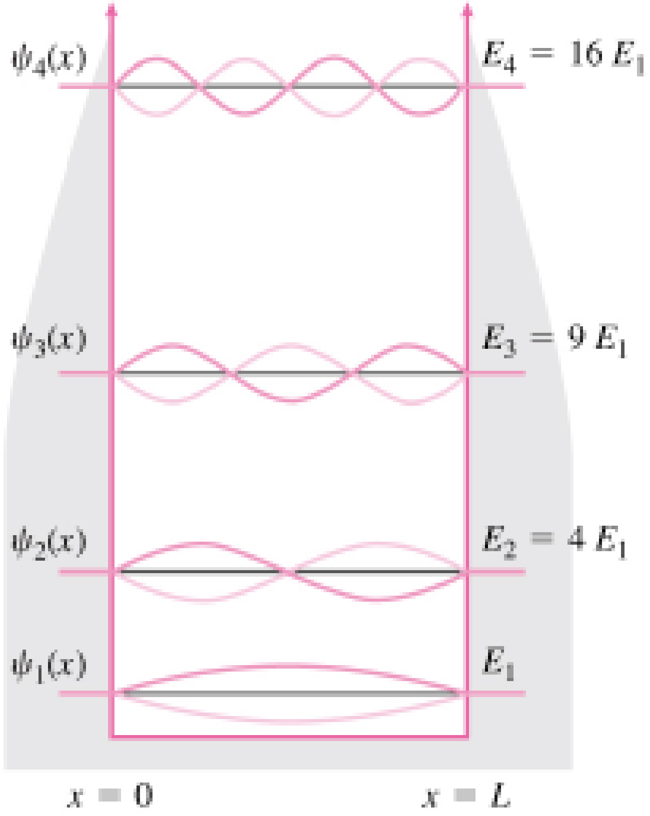
ψ in regions were $U \rightarrow \infty$



Full Solution to Particle in a Box

$$\psi_n(x) = \left\{ \begin{array}{cc} \sqrt{\frac{2}{L}}\sin\frac{n\pi}{L}x & 0 < x < L \\ 0 & x < 0, x > L \end{array} \right\}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$



Position Probailities for Particle in a Box