Lecture 37
(Schrödinger Equation)

Physics 2310-01 Spring 2020

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Reduced Mass

- OK, so the Bohr model of the atom gives energy levels:

$$E_n = \frac{-1}{2}\frac{k^2 m_e e^4}{n^2 \hbar^2} \qquad\qquad E_n = \frac{-1}{2}\frac{k^2 m_e e^4}{n^2 \hbar^2}$$

- But, this has one problem – it was developed assuming the acceleration of the electron was given as an object revolving around a fixed point.

- In fact, the proton is also free to move.

- The acceleration of the electron must then take this into account.

- Since we know from Newton's third law that:

$$F_p' = -F_e'$$
$$m_p \vec{a}_p = -m_e \vec{a}_e \Rightarrow$$
$$\vec{a}_p = -\frac{m_e}{m_p}\vec{a}_e$$

- If we want to relate the real acceleration of the electron to the force on the electron, we have to take into account the motion of the proton too.

Reduced Mass

- So, the relative acceleration of the electron to the proton is just:

$$\vec{a}_{e,rel} = \vec{a}_e - \vec{a}_p = \vec{a}_e + \frac{m_e}{m_p}\vec{a}_e$$

$$= \left(1 + \frac{m_e}{m_p}\right)\vec{a}_e = \left(\frac{m_p + m_e}{m_p}\right)\vec{a}_e$$

$$= \left(\frac{m_p + m_e}{m_p m_e}\right)m_e\vec{a}_e = \frac{\vec{F}_e}{m_{red}}$$

- Then, the force relation becomes:

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_n^2} = m_{red}\frac{v_n^2}{r_n}, \quad m_{red} = \left(\frac{m_e m_p}{m_e + m_p}\right)$$

- And the energy levels become:

$$E_n = \frac{-1}{2}\frac{k^2 m_{red} e^4}{n^2 \hbar^2}$$

Reduced Mass

$$m_{\text{red}} = \left(\frac{m_e m_p}{m_e + m_p} \right) = \left(\frac{m_e \left(1836.2 \right) m_e}{m_e + \left(1836.2 \right) m_e} \right) = 0.99946 m_e$$

- The reduced mass is close to the electron mass, but the 0.0054% difference is measurable in hydrogen and important in the energy levels of muonium (a hydrogen atom with a muon instead of an electron) since the muon mass is 200 times heavier than the electron.

$$m_{\text{red}} = \left(\frac{m_\mu m_p}{m_\mu + m_p} \right) = \left(\frac{m_\mu \left(8.880 \right) m_\mu}{m_\mu + \left(8.880 \right) m_\mu} \right) = 0.898 m_\mu$$
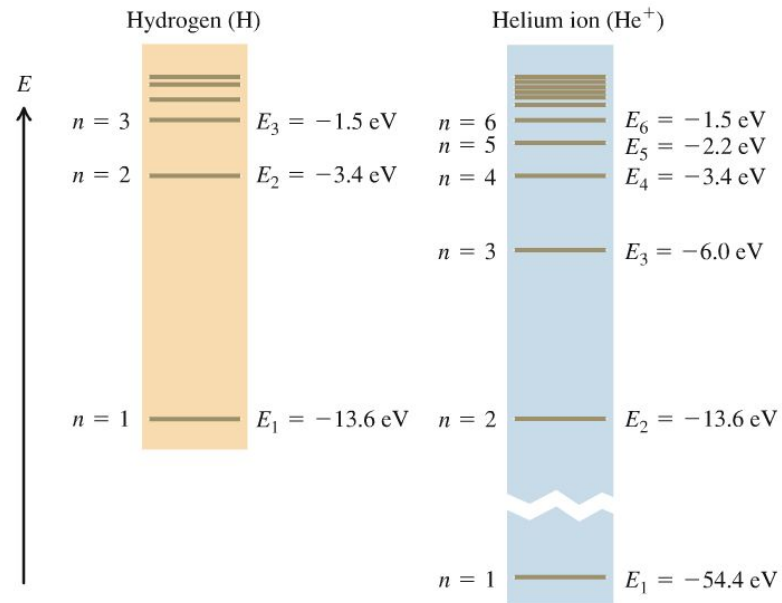
- Or, in general:

$$m_{1,\text{red}} = \left(\frac{m_1 m_2}{m_1 + m_2} \right) = m_1 \left(\frac{m_2}{m_1 + m_2} \right) = m_1 \left(\frac{1}{\dfrac{m_1}{m_2} + 1} \right)$$

Hydrogen-like atoms

- For single electron atoms with more than one proton in the nucleus, we can use the Bohr energy levels with a minor change: $e^4 \rightarrow Z^2 e^4$.

- For instance, for He^+,

$$E_n = \frac{-1}{2} \frac{k^2 m_{red} 4 Z^2 e^4}{n^2 \hbar^2}$$

Uncertainty Revisited

- Let's go back to the wave function for a travelling plane wave: $\Psi(x,t) = A\cos(kx - \omega t)$

- Notice that we derived an uncertainty relationship between k and x that ended being an uncertainty relation between p and x (since p=ℏk): $\Delta x \Delta p_x \geq \dfrac{\hbar}{2}$

Uncertainty Revisited

- Well it turns out that the same relation holds for ω and t, and therefore for E and t: $\Delta E \Delta t \geq \dfrac{\hbar}{2}$

- We see this playing an important role in the lifetime of excited states.

- Each state has a characteristic width in energy, inversely proportional to how long it takes to de-excite.
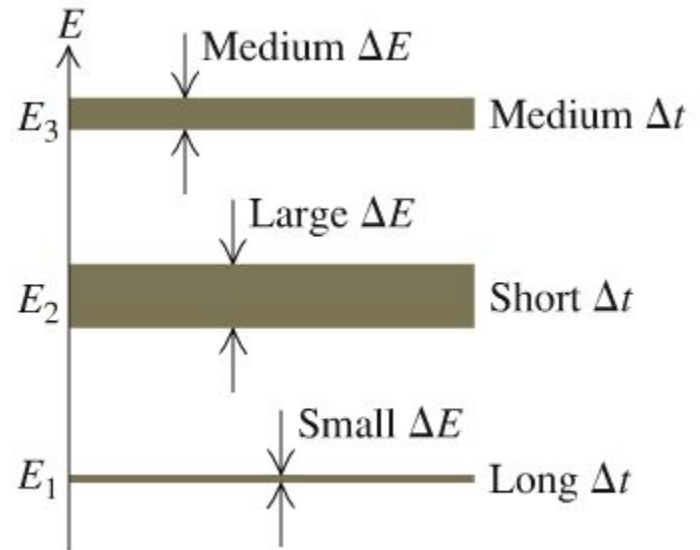
Problems for Bohr Model

- There were many problems with the semi-classical model of Bohr:
    - He quantized orbital angular momentum, and an electron with orbital motion would produce a magnetic dipole moment, BUT *hydrogen in its ground state doesn't have a magnetic dipole moment*.
    - It couldn't be extended to multi-electron atoms.
    - Since the electrons moved in circular orbits (say in the x-y plane at z = 0), then they also had no momentum in z. This didn't obey the uncertainty principle in the z-dimension.
- We need a more comprehensive model of the atom, and for that we need to understand the consequences of matter waves more thoroughly.
- This was the goal of Erwin Schrodinger in 1926.

Schrödinger's Wave Equation

- If particles behave as waves, they must then have an associated wave equation (like light or a guitar string).

- In a paper published in 1923, Erwin Schrödinger developed such an equation using the following reasoning:

  – He started by examining plane waves, whose wave function would be:

$$\Psi\left(x,t\right) = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} = Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$$

Some Mathematics

- If you haven't worked with imaginary numbers before (or maybe even if you have), some of what we are going to cover will seem strange.
- First, we define i, as the square root of -1.
- Then, we have (the Maclaurin series expansion):

$$e^{ix} = 1 + ix + \frac{(ix)^2}{2!} + \frac{(ix)^3}{3!} + \frac{(ix)^4}{4!} + \frac{(ix)^5}{5!} + \frac{(ix)^6}{6!} + \frac{(ix)^7}{7!} + \frac{(ix)^8}{8!} + \cdots$$

$$= 1 + ix - \frac{x^2}{2!} - \frac{ix^3}{3!} + \frac{x^4}{4!} + \frac{ix^5}{5!} - \frac{x^6}{6!} - \frac{ix^7}{7!} + \frac{x^8}{8!} + \cdots$$

$$= \left(1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \frac{x^8}{8!} - \cdots\right) + i\left(x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots\right)$$

$$= \cos x + i \sin x.$$

- So that our free particle wave function is just a combination of cos and sin functions with both a real part and imaginary part.

$$\Psi(x,t) = A e^{i(\mathbf{p} \cdot \mathbf{r} - Et)/\hbar} = \mathrm{Re}(\Psi) + i\,\mathrm{Im}(\Psi)$$

$$\mathrm{Re}(\Psi) = \cos\left((\mathbf{p} \cdot \mathbf{r} - Et)/\hbar\right)$$

$$\mathrm{Im}(\Psi) = \sin\left((\mathbf{p} \cdot \mathbf{r} - Et)/\hbar\right)$$

WHY???

- But why introduce complex numbers???
- Here is a hand waving answer:
  - We want the wave nature of the particle when we are dealing with its wave properties (like interference, etc.).
  - But we don't want the wiggles in the wave function when we want to deal with it's particle nature.
- Let's look again at the free particle wave function, and define the probability distribution of finding it (detection is a particle aspect) within a region dx at time t as the square of its wave function:
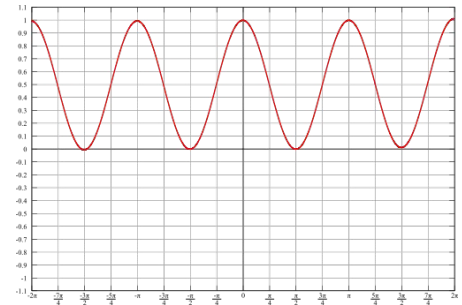
$$\Psi(\mathbf{r},t) = Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$$

$$P(\mathbf{r},t) = |\Psi(\mathbf{r},t)|^2 = \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t) = Ae^{-i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} = A^2$$

- See? No wiggles, and uniformly distributed in space (since it has a definite momentum).
- What would we have gotten without the complex wave function?

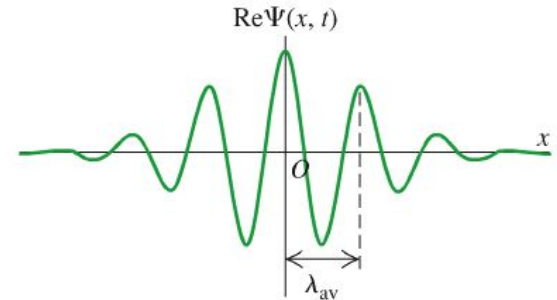$$\Psi(\mathbf{r},t) = A\cos(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar$$

$$P = |\Psi(\mathbf{r},t)|^2 = \Psi^*(\mathbf{r},t)\Psi(\mathbf{r},t) = A^2\cos^2(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar$$
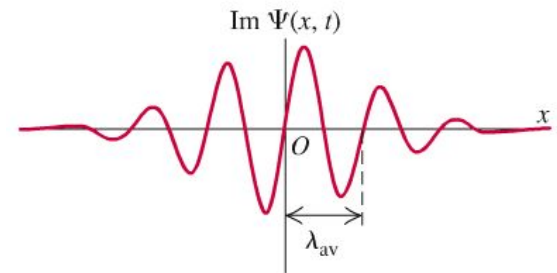
Wave Packets

- The same is true for a wave packet.
- The particle's wave nature is encoded in the wavefunction's real and imaginary parts, but the complex conjugate squared is real, and has the type of probability distribution that we are looking for!

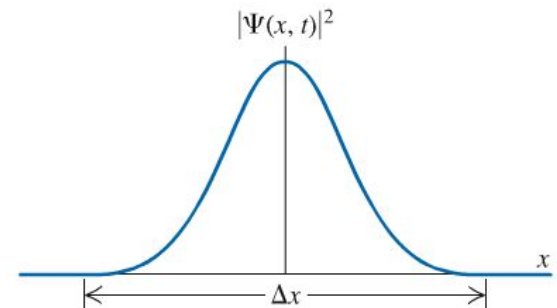(a) Real part of the wave function at time t

$\text{Re}\Psi(x, t)$

λ_{av}

(b) Imaginary part of the wave function at time t

$\text{Im }\Psi(x, t)$

λ_{av}

(c) Probability distribution function at time t

$|\Psi(x, t)|^2$

Δx

Interpretation of the Wave Function

- Here, we need to spend a minute talking about what the wave function is.

- As I said on the previous slide, the probability distribution is given by:

$$P(\mathbf{r},t) = \left|\Psi(\mathbf{r},t)\right|^2$$

- This means if you want to know the probability of finding the particle at a certain point in time and over a certain range in space, you have to integrate the probability distribution over that range:

$$P(a \le |\mathbf{r}| \le b, t) = \int_a^b \left|\Psi(\mathbf{r},t)\right|^2 d^3 r$$

- Then, an additional condition on the wave function is that the total probability of finding the particle over all space must be = 1:

$$P_{\text{Total}} = \int_{\text{All Space}} \left|\Psi(\mathbf{r},t)\right|^2 d^3 r = 1$$

- Note that the free particle wave function is **non-normalizable**! Need to use wave packets.

Schrödinger's Wave Equation

- OK, we start with the free particle (plane wave) wave function

$$\Psi(x,t) = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} = Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$$

- Now, we notice that for the E&M and matter wave equations, there are derivatives with respect to position and time involved.

- Let's take the first spatial derivative of the wave function and see what we have:

$$\nabla\Psi = \frac{i}{\hbar}\mathbf{p}Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} = \frac{i}{\hbar}\mathbf{p}\Psi$$

- OK, now let's define the **momentum operator** such that when it operates on the wave function, it gives us back the momentum times the wave function:

$$\hat{\mathbf{p}}\Psi = -i\hbar\nabla\Psi = \mathbf{p}\Psi \Rightarrow$$

$$\boxed{\hat{\mathbf{p}} \equiv -i\hbar\nabla}$$

Schrödinger's Wave Equation

$$\Psi(x,t) = Ae^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} = Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}$$

- And now we do the same thing only taking the first time derivative of the wave function:

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar}Ae^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} = -\frac{iE}{\hbar}\Psi$$

- And we see that we can define an energy operator in the same way:

$$\hat{E}\Psi = i\hbar\frac{\partial}{\partial t}\Psi = E\Psi \Rightarrow$$

$$\boxed{\hat{E} \equiv i\hbar\frac{\partial}{\partial t}}$$

Schrödinger's Wave Equation

$$\Psi\left(x,t\right) = Ae^{i\left(\mathbf{k}\cdot\mathbf{r}-\omega t\right)} = Ae^{i\left(\mathbf{p}\cdot\mathbf{r}-Et\right)/\hbar}$$

- And now we just state conservation of energy using our new operators and the wave function:

$$E = \frac{\mathbf{p}\cdot\mathbf{p}}{2m} + V \quad \rightarrow \quad \hat{E} = \frac{\hat{\mathbf{p}}\cdot\hat{\mathbf{p}}}{2m} + V$$

with

$$\hat{\mathbf{p}} \equiv -i\hbar\nabla$$

and

$$\hat{E} \equiv i\hbar\frac{\partial}{\partial t},$$

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi \qquad \text{Schrödinger's Wave Equation}$$

$$E_{Total} = KE + PE$$

Schrödinger's Wave Equation in 1D

- If motion is restricted to one-dimension, the del operator can just be replaced by the partial derivative in one dimension:

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi + V(x)\Psi$$

- And then the wave function, of course, is also just a function of one dimension:

$$\Psi = \Psi(x,t) = Ae^{i(p_x x - Et)/\hbar} = Ae^{ip_x x/\hbar}e^{-iEt/\hbar}$$

- Now, this solution works for when V(x) = 0 everywhere (FREE PARTICLE SOLUTION), but fails when not. However, when the solution has a **definite energy**, the general form is:

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

Time Independent Schrödinger's Wave Equation

- Plugging this into the 1D Schrödinger's equation gives:

$$i\hbar\frac{\partial}{\partial t}\left(\psi(x)e^{-iEt/\hbar}\right)=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(\psi(x)e^{-iEt/\hbar}\right)+V(x)\left(\psi(x)e^{-iEt/\hbar}\right)\Rightarrow$$

$$E\psi(x)e^{-iEt/\hbar}=-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}e^{-iEt/\hbar}+V(x)\psi(x)e^{-iEt/\hbar}$$

- And we can divide both sides of the equation by the time dependent part to get:

$$E\psi(x)=-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)$$

- This is called the time-independent (1D) Schrödinger's equation, which we can use to solve for the position dependence of the wave function.
- One must remember though, that the full wave function needs the time dependent part put back in:

$$\Psi(x,t)=\psi(x)e^{-iEt/\hbar}$$

Example

Consider the wave function $\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$, where k is positive. Is this a valid time-independent wave function for a free particle in a stationary state? What is the energy corresponding to this wave function?

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x)$$

Example

Consider the wave function $\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx}$, where k is positive. Is this a valid time-independent wave function for a free particle in a stationary state? What is the energy corresponding to this wave function?

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x)}{\partial x^2} + V(x)^{\!\!\!\!0}\psi(x)$$

$$\frac{\partial^2}{\partial x^2}\left[A_1 e^{ikx} + A_2 e^{-ikx}\right] = \frac{\partial}{\partial x}\left[ikA_1 e^{ikx} - ikA_2 e^{-ikx}\right] = -k^2 A_1 e^{ikx} + k^2 A_2 e^{-ikx} = -k^2 \psi(x) \Rightarrow$$

$$E\psi(x) = \frac{\hbar^2 k^2}{2m}\psi(x) \Rightarrow$$

$$E = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m} = KE$$