

Physics 342 Lecture 28

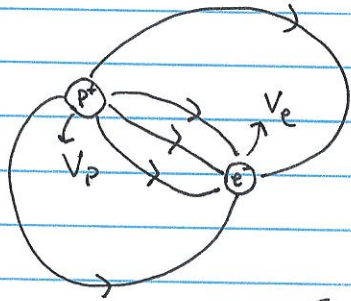
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Hello and welcome back to yet another week of quantum mechanics!

Over the past few weeks we have been studying consequences of rotations and angular momentum in three dimensions, building up to this week's topic: the quantum mechanics of the hydrogen atom. Hydrogen is, of course, the lightest element of the periodic table and consists of a proton and an electron bound through electromagnetism. Our goal for studying this problem is to determine the bound state energy eigenstates, just like we did with the infinite square well and harmonic oscillator. These energy eigenstates will then tell us how the proton and electron are positioned with respect to one another in space, as well as the energy levels and how energy is transferred when the hydrogen atom transforms from one energy level to another. As always, our goal is to diagonalize the Hamiltonian \hat{H} ; that is, determine the states $|\psi\rangle$ and energies E such that:

$$\hat{H}|\psi\rangle = E|\psi\rangle.$$

Our very first step in doing this is to determine what the Hamiltonian is in the first place! To make progress, and to accomplish our goal within the time constraints of an introductory quantum mechanics class, we will make a number of simplifying assumptions. The first and biggest assumption is in regards to how we will treat electromagnetism within the Hamiltonian. Generally, would imagine the proton-electron bound state as some configuration not unlike the orbit of the Earth around the sun:



Where the hydrogen atom is bound by electromagnetism (where I've drawn some field lines) and the proton and electron are continuously moving around.

So, the distribution of electric and magnetic fields and their effect on how the proton and electron are bound continuously changes. Thus, we might expect that to determine how they are bound we would need the full weight of Maxwell's equations, notions like retarded potentials, etc. However, we also know that the information carried by electromagnetic fields (e.g., the force they would exert on a charged particle) ~~and~~ travels at the speed of light, c . So, if the proton and electron have a relative velocity that is much less than c , $v_{pe} \ll c$, then from the perspective of electromagnetism, we can approximate them as at rest.

Further, in addition to this small speed approximation, we will assume that the electromagnetic field is actually completely classical, and has no corresponding Schrödinger equation. That is, we will assume that the electromagnetic field is "large" compared to \hbar , and has no non-trivial uncertainty relations, etc. With these assumptions, the potential that appears in the Hamiltonian is just the potential energy we know and love for two point particles from physics 102:

$$V(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}|}, \text{ where } \vec{r} \text{ is the } \overset{\text{position}}{\text{vector}} \text{ of the electron relative to the proton.}$$

Here, e is the fundamental electric charge which is

$e \approx 1.6 \times 10^{-19}$ C in SI units. The proton carries electric charge $+e$, and the electron carries electric charge $-e$, hence the "-" sign in the potential: the proton and electron are attracted to one another.

The other part of the Hamiltonian is the kinetic energy, \hat{K} , which we can simply express as the sum of kinetic energies of the proton and electron:

$$\hat{K} = \frac{\hat{p}_p^2}{2m_p} + \frac{\hat{p}_e^2}{2m_e}$$

Now, this is all well and good, but as written, this kinetic energy is sensitive to the position/velocity of both the proton and electron so is a total of 6 quantities (two three-dimensional vectors). We can make progress by rephrasing the problem slightly. First, the total momentum of the hydrogen atom (proton + electron) is irrelevant and does not affect the Hamiltonian eigenvalue equation we wish to solve. Only the relative momentum of the proton and electron is important, so we can set

$$\hat{p}_H = \hat{p}_p + \hat{p}_e = 0, \text{ with } \hat{p}_p = -\hat{p}_e \equiv -\hat{p}, \text{ so that the}$$

kinetic energy reduces to:
$$\hat{K} = \frac{\hat{p}^2}{2m_p} + \frac{\hat{p}^2}{2m_e} = \frac{m_e + m_p}{2m_e m_p} \hat{p}^2$$

We call the combination of electron and proton masses the reduced mass μ :

$$\mu = \frac{m_e m_p}{m_e + m_p}$$

as a kind of "center-of-mass" mass for the system.

Now, we can just work with μ in everything we do later,

but it is useful to approximate this reduced mass given the known masses of the proton and electron. It turns out that the proton has a mass that is about 2000 times that of the electron:

$m_p \approx 2000 m_e$, so we can approximate the reduced mass as

$$\mu = \frac{m_e m_p}{m_e + m_p} = \frac{m_e}{1 + \frac{m_e}{m_p}} = m_e \left(1 - \frac{m_e}{m_p} + \dots \right) \approx m_e,$$

where we use the Taylor expansion of $\frac{1}{1 + \frac{m_e}{m_p}}$ in the third equality. Because of this huge difference between the electron and proton masses, we will just take the reduced mass to be the mass of the electron.

With all of these assumptions, the Hamiltonian can be written as:

$$\hat{H} = \frac{\hat{p}^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 \hat{r}}, \text{ where } \hat{r} \text{ is the "radius operator" that measures the distance between the proton and electron.}$$

To go further, we would like to write the square of the momentum operator \hat{p}^2 in a nice way. As we are working in three dimensions, we need to think about a coordinate system in which to express \hat{p}^2 . Cartesian coordinates aren't so nice, because the potential is purely a function of distance r , where $r^2 = x^2 + y^2 + z^2$. Because we assume that the proton is effectively infinitely massive, it is at rest, and this $1/r$ potential is a "central" potential which exhibits a spherical symmetry about it. So, we should use spherical coordinates to express the Hamiltonian as a differential operator that acts on the wave function ψ . This is the tack that

~~The~~ Griffith's and Schroeter takes; here, I want to motivate a nice form of the Hamiltonian from other considerations.

Let's go back to Physics 101 and the description of circular motion. Recall that for a particle of mass m moving with respect to some identified axis, its kinetic energy can be expressed as:

$K = \frac{1}{2} m \dot{r}^2 + \frac{1}{2} I \omega^2$, where r is the distance of the particle to the axis, I is its moment of inertia about that axis, $I = m r^2$, and ω is its angular velocity about the axis. If we identify the radial momentum p_r as

$p_r = m \dot{r}$ and the angular momentum $L = I \omega$, then,

we can express the kinetic energy as:

$$K = \frac{p_r^2}{2m} + \frac{1}{2} I \left(\frac{L}{I} \right)^2 = \frac{p_r^2}{2m} + \frac{L^2}{2I} = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}.$$

Now, with this construction, in quantum mechanics, we just put little hats above every function of phase space to promote it to be an operator on Hilbert space. That is, for this central potential, the kinetic energy operator

is $\hat{K} = \frac{\hat{p}_r^2}{2m} + \frac{\hat{L}^2}{2m\hat{r}^2}$, and so the Hamiltonian is

$$\hat{H} = \frac{\hat{p}_r^2}{2me} + \frac{\hat{L}^2}{2m\hat{r}^2} - \frac{e^2}{4\pi\epsilon_0 \hat{r}}.$$

Further, we know what the square of the angular momentum \hat{L}^2 is from our considerations last week: it is just the quadratic Casimir of rotations in three-dimensions:

$$\hat{L}^2 = \hbar^2 l(l+1), \text{ where } l \text{ is the spin/total angular momentum of the electron.}$$

Thus, the Hamiltonian of the hydrogen atom, with all of our assumptions, is

$$\hat{H} = \frac{\hat{P}_r^2}{2m_e} + \frac{\hbar^2 l(l+1)}{2m_e \hat{r}^2} - \frac{e^2}{4\pi\epsilon_0 \hat{r}}$$

Thus, the eigenvalue equation for the Hamiltonian of the hydrogen atom is:

$$\hat{H}|\psi\rangle = E|\psi\rangle = \left(\frac{\hat{P}_r^2}{2m_e} + \frac{\hbar^2 l(l+1)}{2m_e \hat{r}^2} - \frac{e^2}{4\pi\epsilon_0 \hat{r}} \right) |\psi\rangle,$$

along with the eigenvalue equation for the squared angular momentum operator:

$$\hat{L}^2 |\psi\rangle = \hbar^2 l(l+1) |\psi\rangle.$$

We'll spend time with these eigenvalue problems on Wednesday and Friday; for now, let's calculate the position-space wave function in the energy eigenstate equation. We'll first consider $l=0$, or the state in which the electron carries no angular momentum. In position space, the radial angular momentum p_r is

$$p_r = -i\hbar \frac{\partial}{\partial r}, \text{ and so this } l=0 \text{ Hamiltonian equation reads}$$

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = E\psi.$$

To solve this differential equation we will use the following approach. We note that $r > 0$, so a way to visualize the potential is as:

$$V(r) = \begin{cases} \infty, & r < 0 \\ -\frac{e^2}{4\pi\epsilon_0 r}, & r > 0 \end{cases}$$

As such, $\psi(r)$ must vanish for $r=0$, and, for it to be normalizable, $\psi(r) \rightarrow 0$ for $r \rightarrow \infty$, as well. For $r \rightarrow \infty$, the potential vanishes, so the energy eigenvalue problem reduces to:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \psi = E\psi, \quad r \rightarrow \infty.$$

For this to describe a bound state, $E < 0$ because the potential is negative for all $r > 0$. Thus, we can write

$E = -|E|$ and the solution to this differential equation is

$$\psi(r \rightarrow \infty) = A e^{\frac{\sqrt{2m|E|}}{\hbar} r} + B e^{-\frac{\sqrt{2m|E|}}{\hbar} r}$$

We must require $A=0$ for ψ to be L^2 -normalized. So, with this asymptotic identification, we make the ansatz that the wave function for all r can be written as:

$$\psi(r) = f(r) e^{-\frac{r}{a}}, \quad \text{where } a = \frac{\hbar}{\sqrt{2m|E|}} \quad \text{and } f(r=0) = 0.$$

Then, with this ansatz, our energy eigenvalue equation becomes:

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) f(r) e^{-\frac{r}{a}} = E f(r) e^{-\frac{r}{a}}$$

or that

$$-\frac{\hbar^2}{2m} f''(r) + \frac{\hbar^2}{2ma} f'(r) - \left(\frac{\hbar^2}{2ma^2} + \frac{e^2}{4\pi\epsilon_0 r} \right) f(r) = E f(r)$$

The textbook solves this differential equation by a Taylor expansion of $f(r)$, enforcing that $f(r) = 0$ at $r = 0$. You can see the details there; here, I will just identify the ground state $f(r)$; that is the simplest function that vanishes at $r = 0$. What function is this? Why not just $f(r) = r$? With this, then $f''(r) = 0$, $f'(r) = 1$ and the eigenvalue problem becomes:

$$\frac{\hbar^2}{ma} - \frac{\hbar^2 r}{2ma^2} - \frac{e^2}{4\pi\epsilon_0} = E r. \quad \text{Matching powers of } r \text{ on both sides enforces:}$$

$$\frac{\hbar^2}{ma} = \frac{e^2}{4\pi\epsilon_0}, \text{ or } a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}, \text{ which is called the Bohr radius.}$$

It's often denoted as a_0 . Then, the terms linear in r are:

$$-\frac{\hbar^2}{2ma^2} = E_0 = -\frac{\hbar^2}{2m_e} \frac{m_e^2 e^4}{16\pi^2 \epsilon_0^2 \hbar^2} = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2}$$

The ground state energy of the hydrogen atom is often denoted as E_0 , in analogy with the Bohr radius. If you evaluate a_0 with the values of \hbar , ϵ_0 , m_e , and e that have been established, you find

$$a_0 = 5.3 \times 10^{-11} \text{ m. The ground state energy is}$$

$$E_0 = -13.6 \text{ eV (electron-Volts)}$$

We'll study the other energy eigenstates and properties of the manifestation of angular momentum later.