Quantum Mechanics in 3D: The Hydrogen Atom

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To study quantum mechanics in 3 dimensions, the canonical example is the hydrogen atom. First, we solve the Schrodinger equation in spherical coordinates. We have

$$i\hbar = \frac{\partial \psi}{\partial t} = H\psi$$

The Hamiltonian is just

$$\frac{1}{2}mv^2 + V = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V$$

where the 3D momentum operator is given by[1]

$$p = -i\hbar\nabla$$

Then

$$i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi$$

where we have used the Laplacian,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In spherical coordinates, that's

$$\nabla^2 f = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial f}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}$$

Using spherical coordinates is convenient when the potential is a function of only distance from the origin. The time-independent Schrodinger equation then reads

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial \psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 \psi}{\partial\phi^2}\right] + V\psi = E\psi$$

We begin by looking for solutions that are seperable into products:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

[1] A heuristic argument for why the momentum operator is proportional to a spatial derivative in one dimension is as follows. Start with de Broglie's relation $p = \hbar k$ with $k = 2\pi/\lambda$. Take a plane wave $\psi(x) = e^{ikx}$ and differentiate both sides. Then $(d/dx)\psi(x) = ike^{ikx} = ik\psi(x)$. If you multiply both sides by $-i\hbar$, we get $p\psi(x) = -i\hbar\frac{d\psi}{dx}$. For a more intuitive argument, imagine you're standing still watching a wave pass by. You don't know its momentum directly. But if you measure how rapidly its peaks pass you (its spatial frequency), you can deduce how much momentum it carries.

Plugging in to our Schrodinger equation and performing the separation, we obtain

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]=\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}.$$

As with the last lecture, since each side is dependent on a different variable, and we demand that equality hold for all values of each variable, we then require that each side be equal to a constant. In our case, we will write our "separation constant" in the form $l(l+1)$ (it will make sense later, I promise)

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]=\ell(\ell+1)$$

$$\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}=-\ell(\ell+1)$$

For the angular equation ($Y(\theta,\phi)$) we perform separation again by $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$. Once we plug this back into our angular equation separate again, we obtain (this time calling our separation constant m^2)

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-m^2.$$

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right]+\ell(\ell+1)\sin^2\theta=m^2$$

The first equation is easy, it's $e^{im\phi}$[2] . When ϕ advances by 2π we return to the same point in space, so we require that $\Phi(\phi+2\pi)=\Phi(\phi)$ meaning that $e^{im(\phi+2\pi)}=e^{im\phi}$, which leads to the requirement that m be an integer. The theta equation is less trivial; the solution is actually a family of functions:

$$\Theta(\theta)=AP_l^m(\cos\theta)$$

where P_l^m is a special function called the associated Legendre function, defined by

$$P_l^m(x)=(1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|}P_l(x)$$

where P_l is a special polynomial called the Legendre polynomial, which can be generated by the Rodrigues formula

$$P_l(x)=\frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l(x^2-1)^l$$

If you know your ODE's, you might be asking why I have only presented a single solution for Θ, since the seperated equation is of the second order. Such solutions exist but are physically inadmissible because their values reach infinity near $\theta=0,\pi$ and the wavefunction cannot then be normalized. Speaking

[2]Technically there are two solutions, $e^{\pm im\phi}$, but we can ignore the negative solution because we allow m to be negative anyway

of normalization, if we revert to our separation $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$, the normalization condition in spherical coordinates, using the volume element

$$d^3r = r^2 \sin\theta dr d\theta d\phi$$

becomes

$$\int |\psi|^2 r^2 \sin\theta dr d\theta d\phi = \int |R|^2 r^2 dr \int |Y|^2 \sin\theta d\theta d\phi = 1$$

It is convenient to normalize R and Y individually by requiring that both integrals equal 1. In this case, the normalized angular part of the wavefunctions are called the spherical harmonics, another family of functions given by

$$Y_l^m(\theta,\phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\cos\theta)$$

As for the radial equation, let $u(r) = rR(r)$; then the radial equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right] u = Eu$$

This is identical in form to the 1D Schrodinger equation, but we have an effective potential

$$V_{eff} = V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$$

where the second term is the so-called "centrifugal" term. For Coulomb's law in the Hydrogen atom, the real potential energy is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

For bound states ($E < 0$), the radial motion is confined between turning points r_1 and r_2 satisfying $E = V_{\text{eff}}(r)$.

In the Bohr–Sommerfeld (old quantum) approach, one imposes

$$\int_{r_1}^{r_2} p_r \, dr = \left(n_r + \frac{1}{2}\right) h,$$

where

$$p_r = \sqrt{2m\big[E - V_{\text{eff}}(r)\big]}.$$

For the Coulomb problem, one finds (after standard integration in closed form)

$$\int_{r_1}^{r_2} \sqrt{2m\Big[E + \tfrac{Ze^2}{4\pi\varepsilon_0 r} - \tfrac{\hbar^2\, l(l+1)}{2m\, r^2}\Big]}\, dr = \big(n_r + \tfrac{1}{2}\big)\, h.$$

Introduce the principal quantum number

$$n = n_r + l + 1,$$

and solve for E. The integral evaluation yields

$$E_n = -\frac{mZ^2e^4}{2(4\pi\varepsilon_0)^2\hbar^2\, n^2}, \qquad n = 1, 2, 3, \ldots$$

which is the celebrated *Bohr energy formula*.