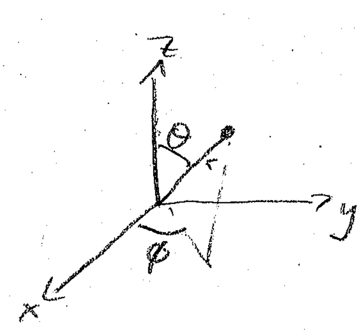
Quantum Mechanics

3D Schrödinger Equation + Separation of Variables

- We remember that the Schrödinger equation is like the definition of energy:
  - Classically, $E = \vec{P}^2/2m + V(\vec{x})$
  - The time-independent Schr. eqn is $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x}) + V(\vec{x})\psi(\vec{x}) = E\psi(\vec{x})$
- Cartesian Coordinates
  - The Laplacian is $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$
  - Suppose that $V(\vec{x})$ has a rectangular symmetry
    - For example, $V(\vec{x}) = 0$ for $0 \le x \le l_x$, $0 \le y \le l_y$, $0 \le z \le l_z$ and infinite elsewhere. This is a 3D rectangular box.
    - Let's try a solution that factors $\psi(\vec{x}) = X(x)\,Y(y)\,Z(z)$
    - Then we can re-write
      $$-\frac{\hbar^2}{2m}\left[\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2}\right] = E$$
    - Each term on LHS must be constant. So write $-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_x X$, etc. You've seen the solution before: $X = A_x \sin(n_x\pi x/l_x)$, $E_x = \frac{\hbar^2 n_x^2\pi^2}{2m l_x^2}$
    - Any eigenfunction is of the form
      $$\psi(\vec{x}) = X_{n_x}(x)\,Y_{n_y}(y)\,Z_{n_z}(z) \text{ with } E = E_x + E_y + E_z = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right)$$
  - Strategy is to separate the dependence on each variable. A time-dependent solution is a sum of terms of this form, but eigenfunctions in symmetric situations separate
- Spherical Coordinates
  - Remember spherical polar coordinates
    - $r = \sqrt{x^2+y^2+z^2}$, $\cos\theta = z/r$, $\tan\phi = y/x$
    - $z = r\cos\theta$, $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$



- Let's re-write the classical energy.
  + First, split $\vec{p}$ into radial p_r and transverse $\vec{p}_\perp$ components.
    Then $\vec{p}^{\,2} = p_r^2 + \vec{p}_\perp^{\,2}$
  + The angular momentum is $\vec{L} = \vec{r} \times \vec{p} = \vec{r} \times \vec{p}_\perp$, so $\vec{L}^2 = r^2 \vec{p}_\perp^{\,2}$.
  + This means
$$E = p_r^2/2m + L^2/2mr^2 + V(\vec{x})$$
- In quantum mechanics, the corresponding statement is
  + $$\nabla^2 \psi = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}$$
  + or $$-\frac{\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{2mr^2}\vec{L}^2\cdot\psi + V(\vec{x})\psi = E\psi$$
- If $V(\vec{x}) = V(r)$ is spherically symmetric, we separate variables using $\psi(\vec{x}) = R(r)\,Y(\theta,\phi)$.
  + We'll discuss the solution for $R(r)$ shortly
  + The angular solution for $Y(\theta,\phi)$ will come a little later.
  + The key point is that $\frac{1}{Y}\vec{L}^2\cdot Y$ depends only on θ,ϕ and must be constant, so Y is an eigenfunction. It turns out
    $$(1/Y)\,\vec{L}^2\cdot Y = \hbar^2 l(l+1) \text{ where } l = 0, 1, 2, \ldots$$
  + The function Y also depends on another integer $m = -l, -l+1, \ldots, +l$.

- Brief review of hydrogen atom

— The time-independent Schrödinger equation is

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

- This is separable. We can write $\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$

+ Then we get

$$\frac{-\hbar^2}{2mr}\frac{\partial^2}{\partial r^2}(rR)+(V(r)-E)R=\frac{-\hbar^2}{2m}\frac{l(l+1)}{r^2}R$$

+ The $l(l+1)$ is the eigenvalue of the angular equation. $l=0,1,2,\dots$ is a non-negative integer (more later)

- If we re-write in terms of $u(r)=rR(r)$,

$$\frac{-\hbar^2}{2m}\frac{d^2u}{dr^2}+V_{eff}(r)\,u=Eu$$

+ Effective Potential $V_{eff}(r)=V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$ ← centrifugal term

+ For hydrogen $V(r)=\frac{-1}{4\pi\epsilon_0}\frac{e^2}{r}$: Coulomb potential

— The Solution for hydrogen

- Look at the asymptotic behavior $(r\to\infty)$

$$\frac{d^2u}{dr^2}\approx\frac{-2mE}{\hbar^2}u \Rightarrow u\approx Ae^{-r/b}+Be^{+r/b}$$

We keep only the dying exponential for normalizability

- We use a power series (Frobenius) method for the full solution

+ $u(r)\equiv v(r)\exp\left[-\sqrt{-2mE}\,r/\hbar\right]$

+ Then

$$\frac{d^2v}{dr^2}-\frac{2}{\hbar}\sqrt{-2mE}\frac{dv}{dr}+\frac{e^2}{4\pi\epsilon_0}\frac{2m}{\hbar^2}\frac{v}{r}-\frac{l(l+1)}{r^2}v=0$$

(can work out)

+ A guess $v(r) = \sum_{p=0}^{\infty} A_p r^p$ gives

$$\sum_p \left[p(p-1) A_p r^{p-2} - \frac{2}{\hbar}\sqrt{-2mE}\, p A_p r^{p-1} + \frac{e^2}{4\pi\epsilon_0}\left(\frac{2m}{\hbar^2}\right) A_p r^{p-1} - l(l+1) A_p r^{p-2} \right] = 0$$

- How do we find the series?
  + Each power of r must vanish separately for solution at all r

    So $\quad -l(l+1) A_0 r^{-2} = 0 \implies A_0 = 0$

    $$\left[\left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{2m}{\hbar^2}\right) A_0 - l(l+1) A_1\right] r^{-1} = 0 \implies l = 0 \text{ or } A_1 = 0$$

    $$\left[\big(p(p+1) - l(l+1)\big) A_{p+1} + \left(\left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{2m}{\hbar^2}\right) - \frac{2}{\hbar}\sqrt{-2mE}\, p\right) A_p\right] r^{p-1} = 0, \quad p \geq 1.$$

  + The last equation means $A_{p=l} = 0$. Then every $A_{p<l} = 0$ also.
  + Furthermore, $v(r)$ must have a finite # of terms to avoid messing up the asymptotic behavior $\implies$ there must be some integer n such that $A_{p>n} = 0$. That requires

    $$\frac{2}{\hbar}\sqrt{-2mE}\, n = \left(\frac{e^2}{4\pi\epsilon_0}\right)\left(\frac{2m}{\hbar^2}\right) \implies E = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2}\frac{1}{n^2}$$

  + Therefore

    $$v(r) = A_{l+1} r^{l+1} + \cdots + A_n r^n$$

- The overall wavefunction takes the form

$$\psi_{nlm}(\vec{x}) = \frac{v(r)}{r} e^{-r/na_0} Y_l^m(\theta, \phi)$$

$$a_0 = \left(\frac{4\pi\epsilon_0}{e^2}\right)\frac{\hbar^2}{m} = \text{Bohr radius} = \text{"size" of hydrogen}$$

$$E = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2}\frac{1}{n^2} = -\frac{(13.6\,\text{eV})}{n^2}$$

$n = 1, 2, 3, \ldots$ = principal quantum #

$l = 0, 1, \ldots, n-1$

$m = -l, -l+1, \ldots, l-1, l$

See specific wavefunctions in the text