PHYS 3313 – Section 001
Lecture #22

Monday, April 15, 2019
Dr. Jaehoon Yu

- Schrodinger Equations on Hydrogen Atom
- Hydrogen Atom Wave Functions
- Solution for Radial Equations
- Solution for Angular and Azimuthal Equations
- Angular Momentum Quantum Numbers
- Magnetic Quantum Numbers
- Zeeman Effects

Announcements

- Bring out HW#5
- Reading assignments
  - CH7.2, CH7.6 and the entire CH8
- Presentations next Monday and Wednesday
- Research presentation deadline is 8pm, Sunday, April 21
- Research paper deadline is Wednesday, 4/24
- You guys have done a marvelous job at the workshop last week! Everyone complimented how good you all were! Let's hit this week's workshop out of the ballpark!

Reminder: Special Project #7

- Show that the Schrodinger wave equation becomes Newton's second law in the classical limit. (15 points)
- Deadline this Wednesday, Apr. 17
- You MUST have your own answers!

Application of the Schrödinger Equation to the Hydrogen Atom

- The approximation of the potential energy of the electron-proton system is the Coulomb potential:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

- To solve this problem, we use the three-dimensional time-independent Schrödinger Wave Equation.

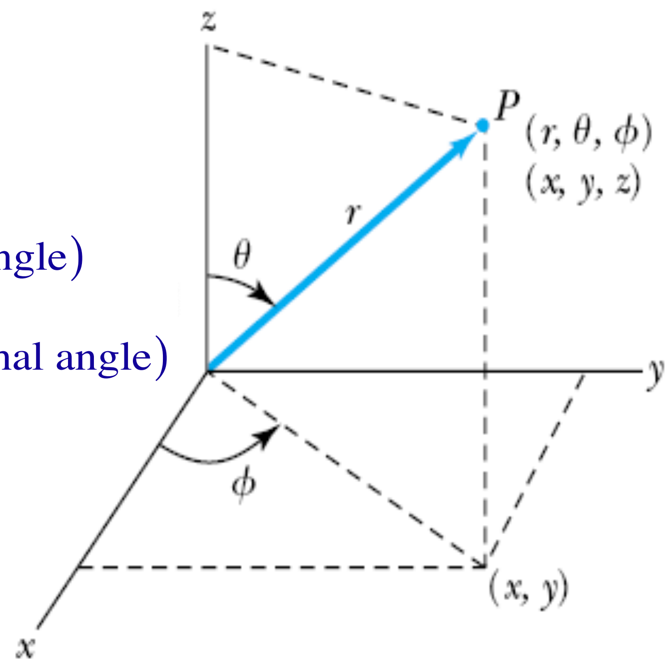
$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x,y,z)}\left(\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right) = E - V(r)$$

- For Hydrogen-like atoms with one electron (He^+ or Li^{++})
  - Replace e^2 with Ze^2 (Z is the atomic number)
- Use the appropriate reduced mass μ $\left(\mu = \frac{m_1 m_2}{m_1 + m_2}\right)$

Application of the Schrödinger Equation

- The potential (central force) *V*(*r*) depends on the distance *r* between the proton and electron.

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$
$$r = \sqrt{x^2 + y^2 + z^2}$$
$$\theta = \cos^{-1}\frac{z}{r}\text{(polar angle)}$$
$$\phi = \tan^{-1}\frac{y}{x}\text{(azimuthal angle)}$$



- Transform to spherical polar coordinates to exploit the radial symmetry.
- Insert the Coulomb potential into the transformed Schrödinger equation.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}(E - V)\psi = 0$$

Application of the Schrödinger Equation

- The wave function ψ is a function of r, θ and φ .

→ The equation is separable into three equations of independent variables

→ The solution may be a product of three functions.

$$\rightarrow \quad \psi(r,\theta,\phi) = R(r) f(\theta) g(\phi)$$

- We can separate the Schrodinger equation in polar coordinate into three separate differential equations, each depending only on one coordinate: r, θ, or φ .

Solution of the Schrödinger Equation for Hydrogen

- Substitute ψ into the polar Schrodinger equation and separate the resulting equation into three equations: *R*(*r*), *f*(*θ*), and *g*(φ).

Separation of Variables

- The derivatives in Schrodinger eq. can be written as

$$\frac{\partial \psi}{\partial r} = fg\frac{\partial R}{\partial r} \qquad \frac{\partial \psi}{\partial \theta} = Rg\frac{\partial f}{\partial \theta} \qquad \frac{\partial^2 \psi}{\partial \phi^2} = Rf\frac{\partial^2 g}{\partial \phi^2}$$

- Substituting them into the polar coord. Schrodinger Eq.

$$\frac{fg}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{Rg}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) + \frac{Rf}{r^2\sin^2\theta}\frac{\partial^2 g}{\partial \phi^2} + \frac{2\mu}{\hbar^2}(E-V)Rgf = 0$$

- Multiply both sides by $r^2 \sin^2 \theta / Rfg$

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{\sin\theta}{f}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) + \frac{1}{g}\frac{\partial^2 g}{\partial \phi^2} + \frac{2\mu}{\hbar^2}r^2\sin^2\theta(E-V) = 0$$

Reorganize

$$-\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta(E-V) - \frac{\sin\theta}{f}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) = \frac{1}{g}\frac{\partial^2 g}{\partial \phi^2}$$

Solution of the Schrödinger Equation

- Only r and θ appear on the left-hand side and only φ appears on the right-hand side of the equation
- The left-hand side of the equation cannot change as φ changes.
- The right-hand side cannot change with either r or θ.
- Each side needs to be equal to a constant for the equation to be true in all cases. Set the constant $-m_\ell^2$ equal to the right-hand side of the reorganized equation

$$\frac{d^2 g}{d\phi^2} = -m_l^2 g$$ -------- **azimuthal equation**

  – The sign in this equation must be negative for a valid solution
- It is convenient to choose a solution to be $e^{im_l\phi}$.

Solution of the Schrödinger Equation

- $e^{im_l\phi}$ satisfies the previous equation for any value of m_ℓ.
- The solution must be single valued in order to have a valid solution for any φ, which requires $g(\phi) = g(\phi + 2\pi)$

$$g(\phi = 0) = g(\phi = 2\pi) \Rightarrow e^0 = e^{2\pi i m_l}$$

- m_ℓ must be zero or an integer (positive or negative) for this to work
- Now, set the remaining equation equal to $-m_\ell^2$ and divide either side with $\sin^2\theta$ and rearrange them as

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2\mu r^2}{\hbar^2}(E - V) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)$$

- Everything depends on r on the left side and θ on the right side of the equation.

Solution of the Schrödinger Equation

- Set each side of the equation equal to constant ℓ(ℓ + 1).
  - The Radial Equation

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)=l(l+1)\Rightarrow\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V-\frac{\hbar^2}{2\mu}l(l+1)\right]R=0$$

  - The Angular Equation

$$\frac{m_l^2}{\sin^2\theta}-\frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)=l(l+1)\Rightarrow\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df}{d\theta}\right)+\left[l(l+1)-\frac{m_l^2}{\sin^2\theta}\right]f=0$$

- Schrödinger equation has been separated into three ordinary second-order differential equations, each containing only one variable.

Solution of the Radial Equation

- The radial equation is called the **associated Laguerre equation,** and the *solutions R* that satisfies the appropriate boundary conditions are called *associated Laguerre functions*.
- Assume the ground state has ℓ = 0, and this requires $m_\ell = 0$. We obtain

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V\right]R=0$$

- The derivative of $r^2\frac{dR}{dr}$ yields two terms, and we obtain

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R=0$$

Solution of the Radial Equation

- Let's try a solution $R = Ae^{-r/a_0}$ where *A* is a normalization constant, and a_0 is a constant with the dimension of length.
- Take derivatives of *R*, we obtain.

$$\left(\frac{1}{a_0^2} + \frac{2\mu}{\hbar^2}E\right) + \left(\frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2} - \frac{2}{a_0}\right)\frac{1}{r} = 0$$

- To satisfy this equation for any *r*, each of the two expressions in parentheses must be **zero**.
- Set the second parentheses equal to zero and solve for a_0.

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

Bohr's radius

- Set the first parentheses equal to zero and solve for *E*.

$$E = -\frac{\hbar^2}{2\mu a_0^2} = -E_0 = -13.6eV$$

Ground state energy of the hydrogen atom

- Both equal to the Bohr's results

Principal Quantum Number *n*

- The principal quantum number, n, results from the solution of $R(r)$ in the separate Schrodinger Eq. since $R(r)$ includes the potential energy $V(r)$.

  The result for this quantized energy is

$$E_n = -\frac{\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2\frac{1}{n^2} = -\frac{E_0}{n^2}$$

- The negative sign of the energy *E* indicates that the electron and proton are bound together.

Quantum Numbers

- The full solution of the radial equation requires an introduction of a quantum number, n, which is a non-zero positive integer.
- The three quantum numbers:
  - n Principal quantum number
  - ℓ Orbital angular momentum quantum number
  - m_ℓ Magnetic quantum number
- The boundary conditions put restrictions on these
  - $n = 1, 2, 3, 4, \ldots$ (n>0) Integer
  - $\ell = 0, 1, 2, 3, \ldots, n - 1$ ($0 =< \ell < n$) Integer
  - $m_\ell = -\ell, -\ell + 1, \ldots, 0, 1, \ldots, \ell - 1, \ell$ ($|m_\ell| \le \ell$) Integer
- The predicted energy level is

$$E_n = -\frac{E_0}{n^2}$$

Ex 7.3: Quantum Numbers & Degeneracy

What are the possible quantum numbers for the state n=4 in atomic hydrogen? How many degenerate states are there?

n	ℓ	m_ℓ
4	0	0
4	1	-1, 0, +1
4	2	-2, -1, 0, +1, +2
4	3	-3, -2, -1, 0, +1, +2, +3

The energy of an atomic hydrogen state is determined only by the primary quantum number, thus, all these quantum states, 1+3+5+7 = 16, are in the same energy state.
Thus, there are 16 degenerate states for the state n=4.