9/16/2024

- Hydrogenic Atoms
  - Schrodinger equation
  - Steps to solving the equation
  - Radial probability density
- Angular Momentum Operators
  - Review of angular momentum operators
  - Commutators
  - Shift operators
- Spin
  - Types of angular momentum
  - Eigenfunctions and eigenvalues
  - Matrix form

- Plan for Wednesday: Practice Midterm, shortened by 15 minutes to go over answers

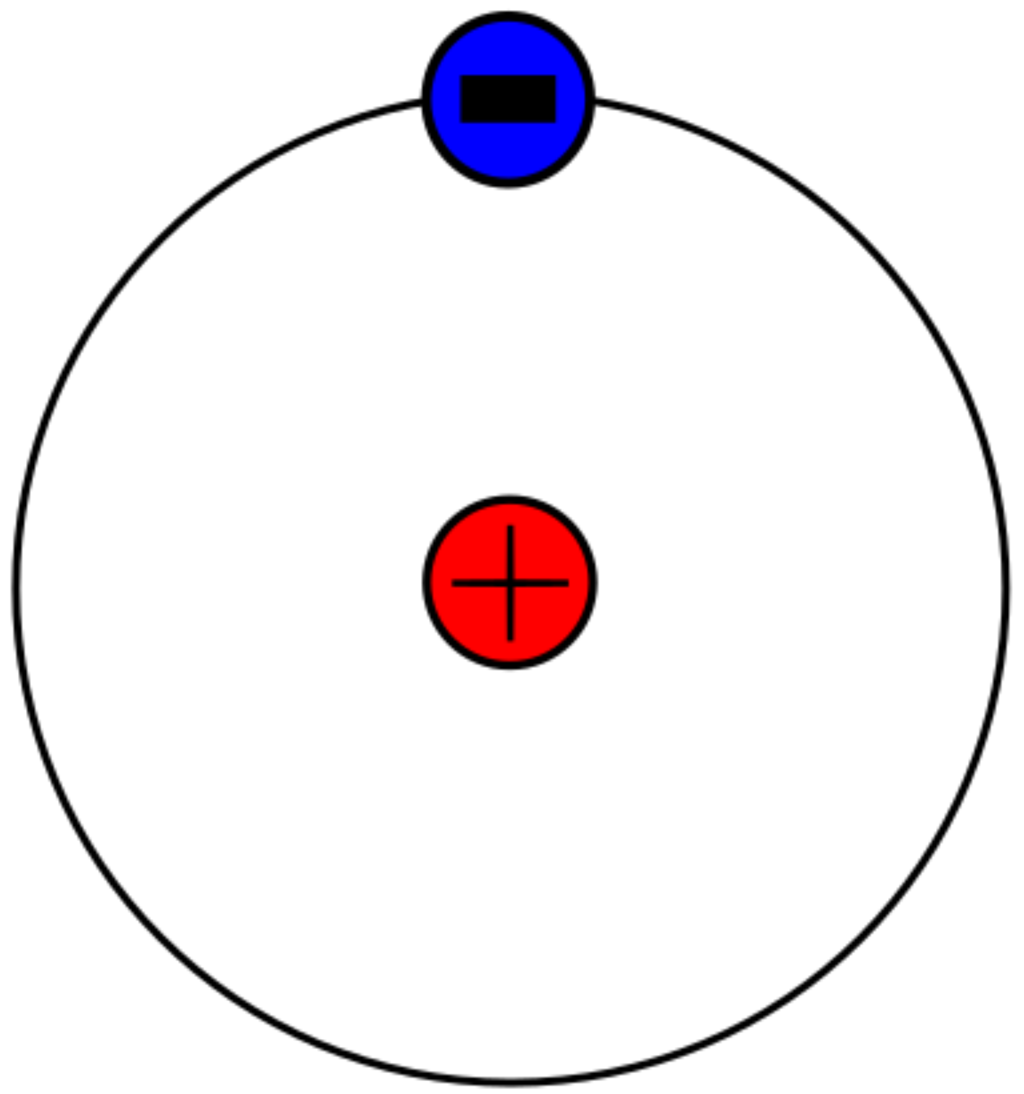
- This lecture is designed to help you achieve the following learning objectives
  - Obtain and interpret solutions of the Schrodinger equation for tractable systems including the particle in a box, harmonic oscillator, rigid rotor, and hydrogen atom

Hydrogenic Atoms

- Hydrogen consists of a proton and an electron
- Potential energy based on Coulomb potential,

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2m_e}\hat{\nabla}_e^2 - \frac{\hbar^2}{2m_N}\hat{\nabla}_{\mathbf{N}}^{\ 2} - \frac{Ze^2}{4\pi\epsilon_o r}$$

- Also describes other *hydrogenic* atoms with one electron and a charged nucleus with arbitrary atomic number
- Can be thought of as a set of concentric spheres

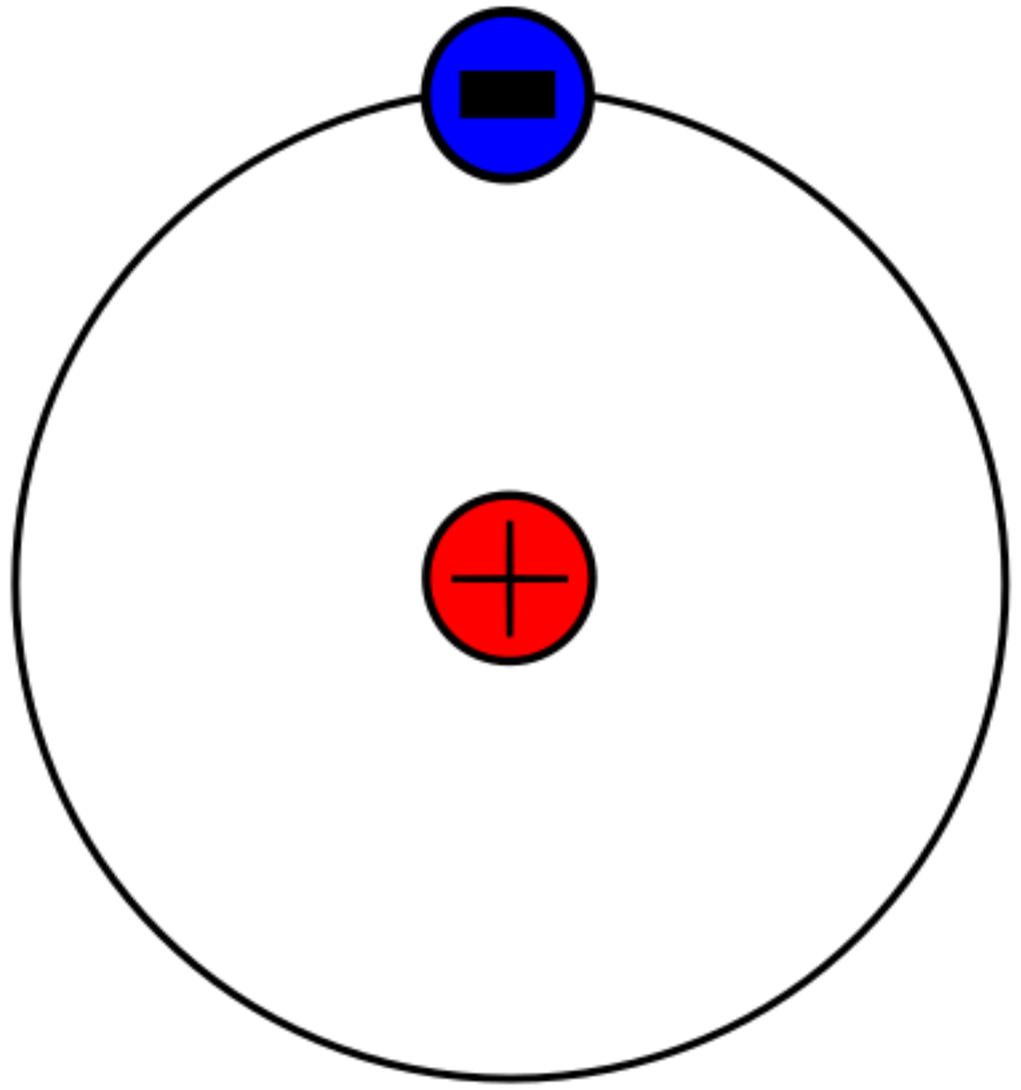


Coordinate Transformation

- Changing the coordinate system,

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2m}\hat{\nabla}^2_{cm} - \frac{\hbar^2}{2\mu}\hat{\nabla}^2 - \frac{Ze^2}{4\pi\epsilon_o r}$$

  - $m = m_e + m_N$
  - $\dfrac{1}{\mu} = \dfrac{1}{m_e} + \dfrac{1}{m_N}$
- Terms 1 & 2 are like rigid rotor
- Term 1 is translation
- Terms 2 & 3 depend on relative positions



Separation of translational and internal variables

- $$\hat{\mathbf{H}}\Psi_{total} = \left[-\frac{\hbar^2}{2m}\hat{\nabla}^2_{cm} - \frac{\hbar^2}{2\mu}\hat{\nabla}^2 - \frac{Ze^2}{4\pi\epsilon_o r}\right]\Psi_{total} = E_{total}\Psi_{total}$$
- $\left[-\frac{\hbar^2}{2m}\hat{\nabla}^2_{cm}\right]\Psi_{cm} = E_{cm}\Psi_{cm}$ for center of mass, will no longer consider
- $\left[-\frac{\hbar^2}{2\mu}\hat{\nabla}^2 - \frac{Ze^2}{4\pi\epsilon_o r}\right]\Psi = E\Psi$ for internal coordinates, will be focus here

Separation of radial and angular variables

- $\left[-\frac{\hbar^2}{2\mu}\hat{\nabla}^2 - \frac{Ze^2}{4\pi\epsilon_o r}\right]\Psi = E\Psi$ is for internal coordinates
- $\frac{1}{r}\frac{\partial^2}{\partial r^2}r\Psi + \frac{1}{r^2}\hat{\mathbf{\Lambda}}^2\Psi + \frac{Ze^2\mu}{2\pi\epsilon_o\hbar^2 r}\Psi = -\left(\frac{2\mu E}{\hbar^2}\right)\Psi$, by applying Laplacian in spherical polar coordinates and rearranging

- Assuming separation of variables, $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$,
  - $\frac{1}{r}\frac{\partial^2}{\partial r^2}rRY + \frac{1}{r^2}\hat{\mathbf{\Lambda}}^2 RY + \frac{Ze^2\mu}{2\pi\epsilon_o\hbar^2 r}RY = -\left(\frac{2\mu E}{\hbar^2}\right)RY$
  - $\frac{1}{r}\frac{d^2}{dr^2}rR + \left(\frac{Ze^2\mu}{2\pi\epsilon_o\hbar^2 r} - \frac{l(l+1)}{r^2}\right)R = -\left(\frac{2\mu E}{\hbar^2}\right)R$, by dividing by Y
  - Thus, $Y(\theta,\phi)$ is independent of R. Solutions are spherical harmonics. What about radial portion?

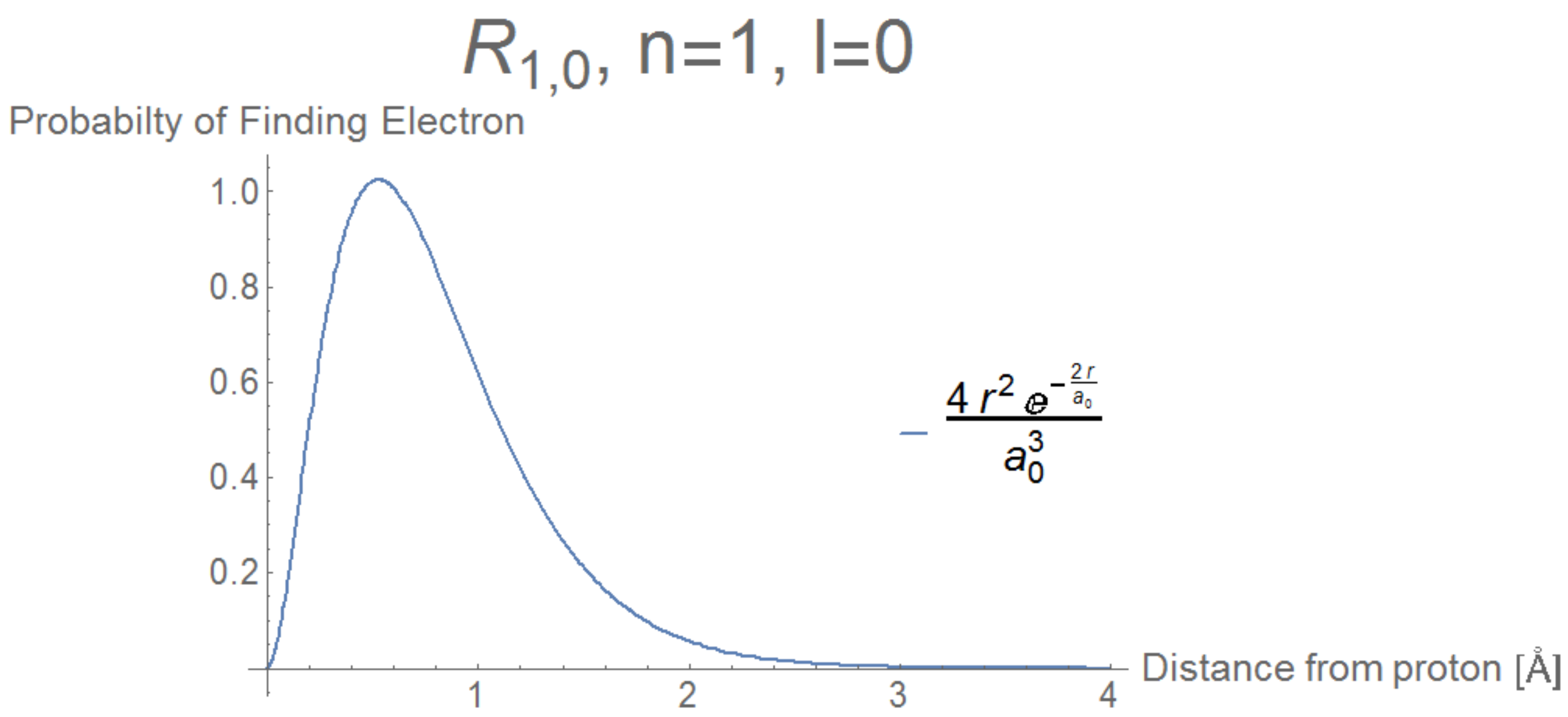
Radial Solution

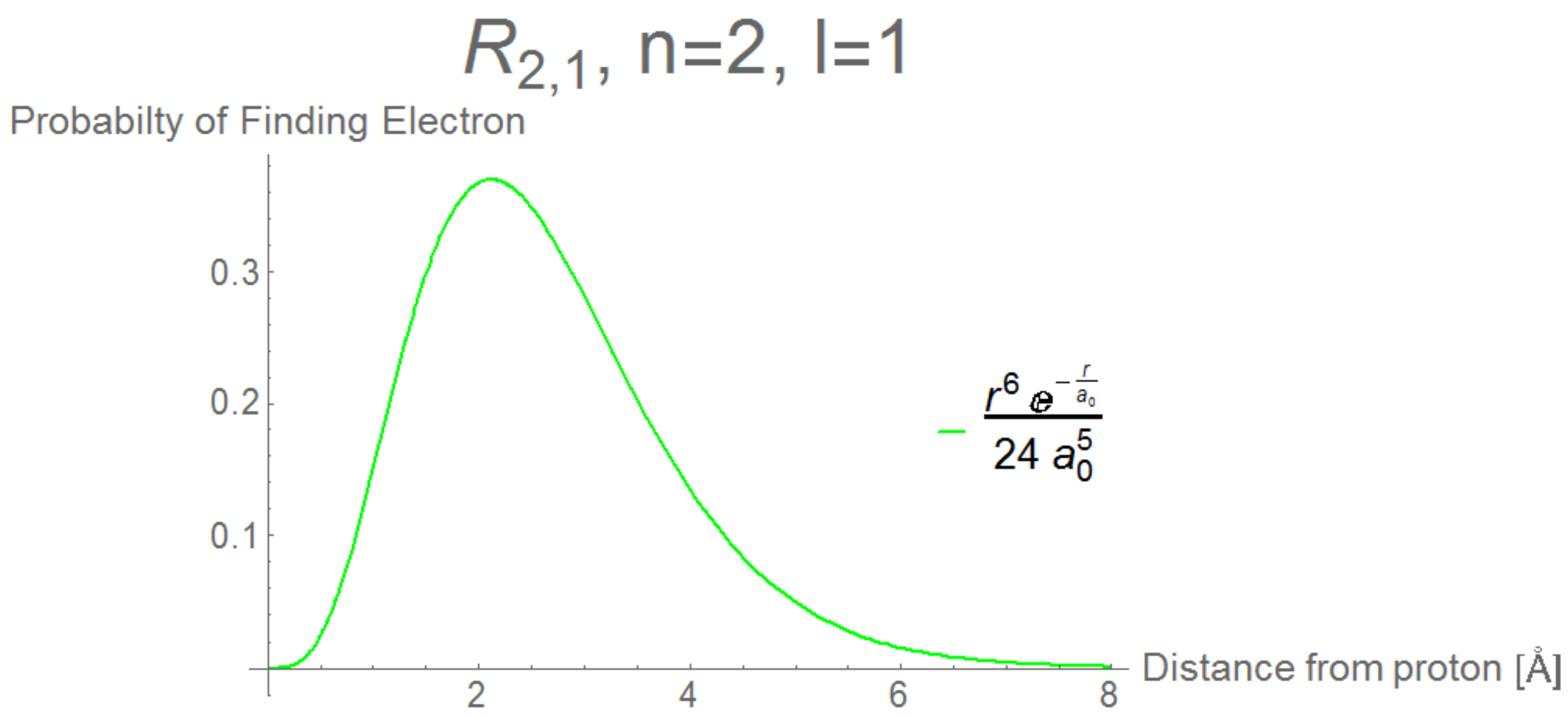
- $$\frac{1}{r}\frac{d^2}{dr^2}rR + \left(\frac{Ze^2\mu}{2\pi\epsilon_o\hbar^2 r} - \frac{l(l+1)}{r^2}\right)R = -\left(\frac{2\mu E}{\hbar^2}\right)R$$
- By setting $u = rR$ and multiplying all by $-\frac{\hbar^2}{2\mu}r$,

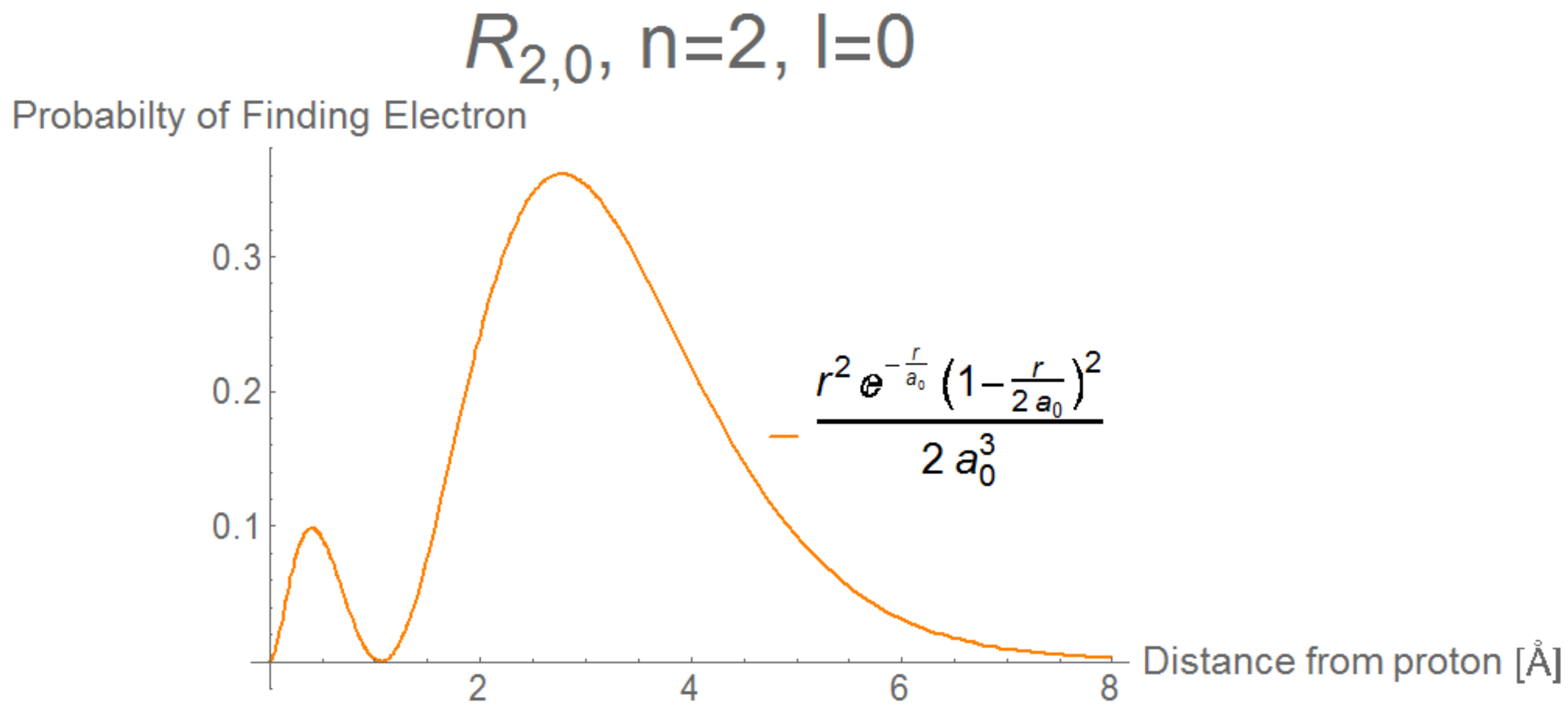
$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}u + \left(-\frac{Ze^2}{4\pi\epsilon_o r} + \frac{l(l+1)\hbar^2}{2\mu r^2}\right)u = Eu$$

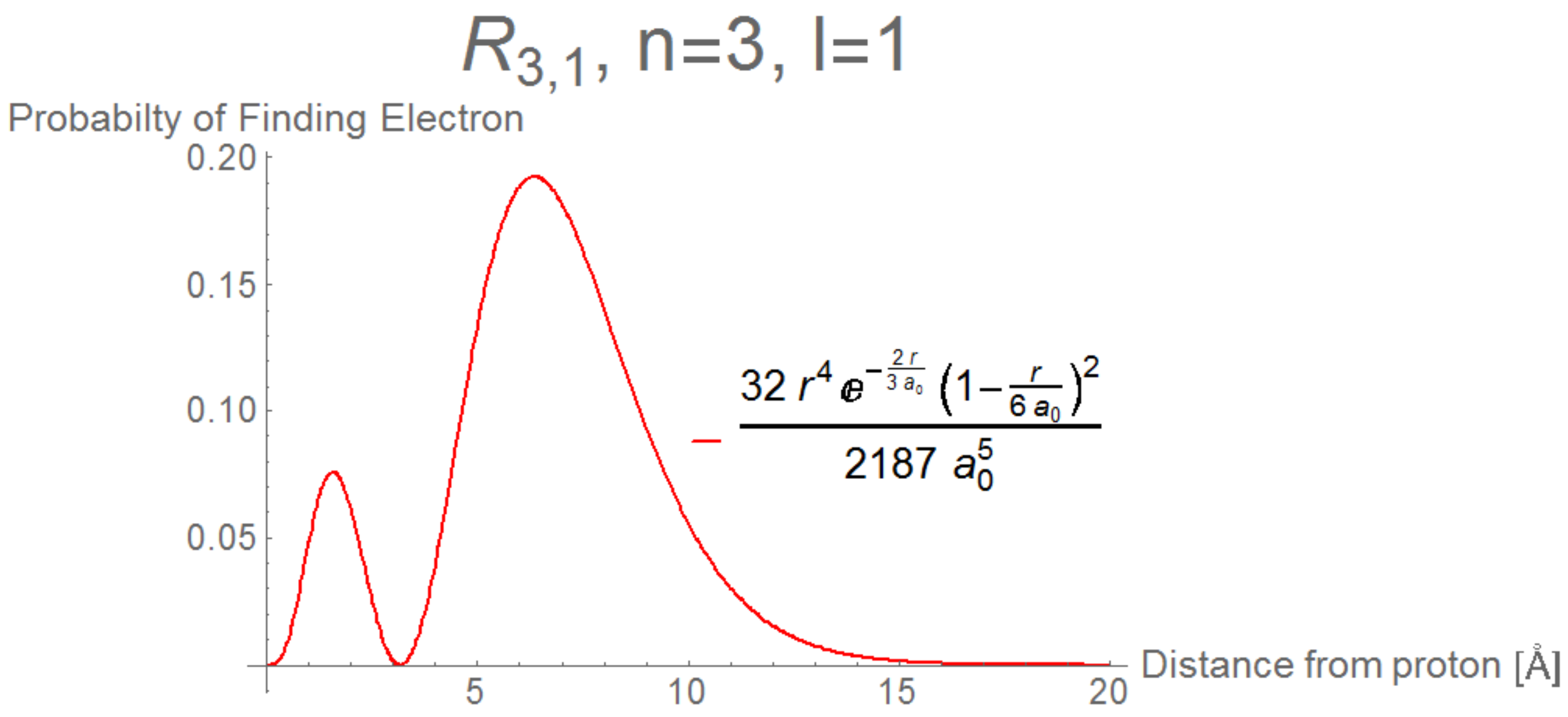
- This is a 1D Schrodinger equation with $V_{eff} = -\frac{Ze^2}{4\pi\epsilon_o r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$, the sum of a Coulomb potential energy and angular momentum term

Radial Probability Densities









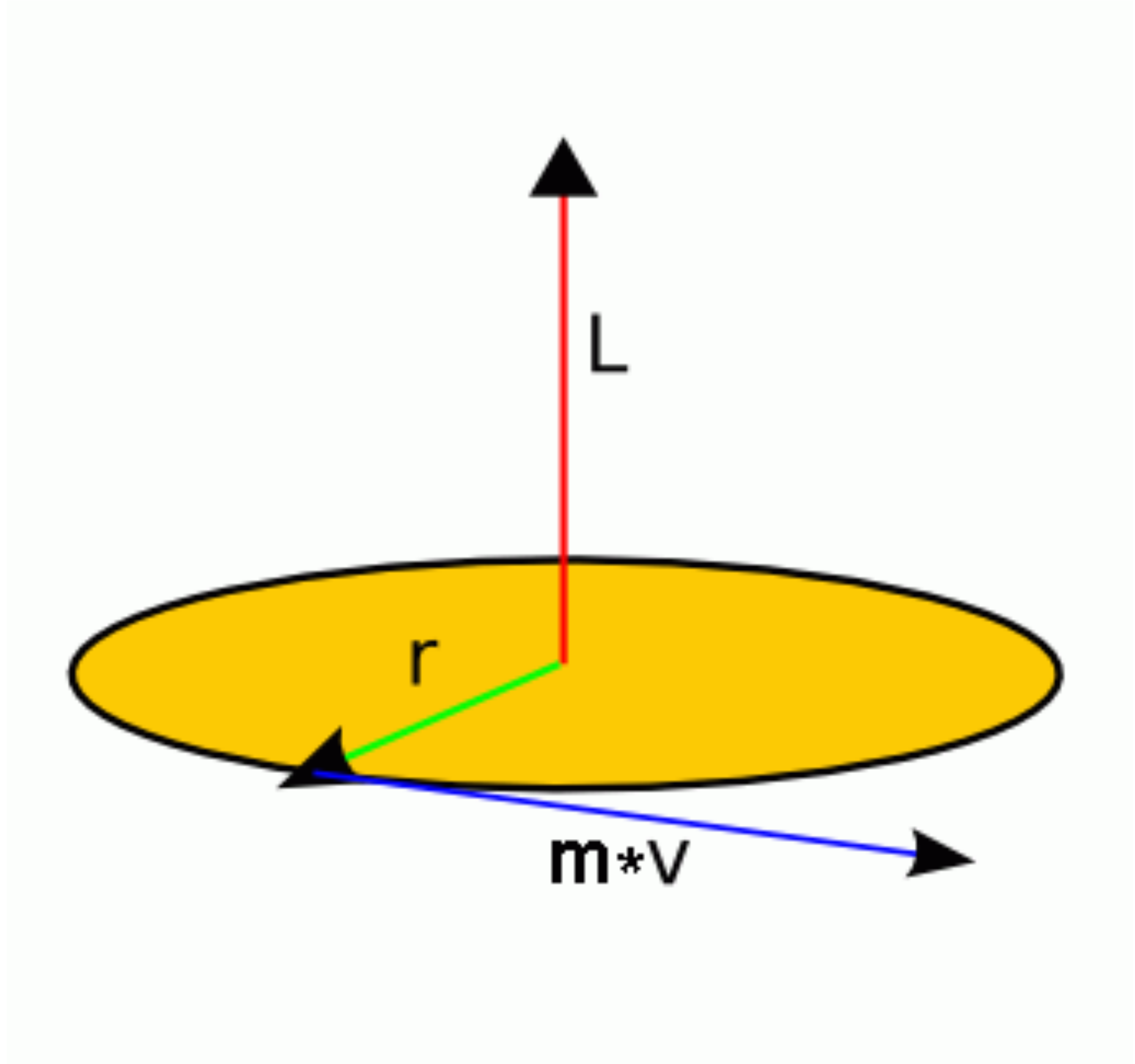
Review of derivation

- Setting up coordinate system
- Separation of variables for center of mass and internal
- Separation of variables for radial and angular
- Solution for radial

General Angular Momentum Operators

Review: Classical Angular Momentum

- $$\mathbf{l} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_z & p_y & p_z \end{vmatrix}$$
- Components are
  - $l_x = yp_z - zp_y$
  - $l_y = zp_x - xp_z$
  - $l_z = xp_y - yp_x$
- $l^2 = l_x^2 + l_y^2 + l_z^2$ is the magnitude of the angular momentum
- $E = l^2/2I$ is the rotational kinetic energy
- Classically, there are *no restrictions* on the magnitude or any of the components, except that none of the components may exceed the magnitude



Review: Angular Momentum Operators

- By substitution of the position and momentum operators into the classical expression, we obtain
  - $\hat{\mathbf{l}}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$
  - $\hat{\mathbf{l}}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$
  - $\hat{\mathbf{l}}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

- Previously we focused on $\hat{\mathbf{l}}_z$
- Notably, as I will show soon, components do not *commute*
- Properties of angular momentum may be derived
  - *without a representation.*
  - *Results more general*

Angular Momentum Commutators

- $\left[\hat{\mathbf{l}}_x, \hat{\mathbf{l}}_y\right] = \left[yp_z - zp_y, zp_x - xp_z\right]$
- $= \left[yp_z, zp_x\right] - \left[yp_z, xp_z\right] - \left[zp_y, zp_x\right] + \left[zp_y, xp_z\right]$
- Note that the middle terms are zero. Position and momenta for different directions commute.
- $= \left(yp_z zp_x - zp_x yp_z\right) + \left(zp_y xp_z - xp_z zp_y\right)$, by expanding commutators
- $= y\left[p_z, z\right]p_x + xp_y\left[z, p_z\right]$
- $= i\hbar\left(-yp_x + xp_y\right) = i\hbar l_z$
- Similarly, $\left[\hat{\mathbf{l}}_x, \hat{\mathbf{l}}_y\right] = i\hbar\hat{\mathbf{l}}_z$, $\left[\hat{\mathbf{l}}_y, \hat{\mathbf{l}}_z\right] = i\hbar\hat{\mathbf{l}}_x$, $\left[\hat{\mathbf{l}}_z, \hat{\mathbf{l}}_x\right] = i\hbar\hat{\mathbf{l}}_y$, $\left[\hat{\mathbf{l}}^2, \hat{\mathbf{l}}_q\right] = 0$
- An observable is an angular momentum if its operators have these commutators

Shift Operators

- The shift operators are defined as,
  - $\hat{\mathbf{I}}_+ = \hat{\mathbf{I}}_x + i\hat{\mathbf{I}}_y$
  - $\hat{\mathbf{I}}_- = \hat{\mathbf{I}}_x - i\hat{\mathbf{I}}_y$
- The corresponding inverse operators are,
  - $\hat{\mathbf{I}}_x = \dfrac{\hat{\mathbf{I}}_+ + \hat{\mathbf{I}}_-}{2}$
  - $\hat{\mathbf{I}}_y = \dfrac{\hat{\mathbf{I}}_+ - \hat{\mathbf{I}}_-}{2i}$
- Several commutators are,
  - $\left[\hat{\mathbf{I}}_z, \hat{\mathbf{I}}_+\right] = \left[\hat{\mathbf{I}}_z, \hat{\mathbf{I}}_x + i\hat{\mathbf{I}}_y\right] = \left[\hat{\mathbf{I}}_z, \hat{\mathbf{I}}_x\right] + \left[\hat{\mathbf{I}}_z, i\hat{\mathbf{I}}_y\right] = i\hbar\hat{\mathbf{I}}_y - i^2\hbar\hat{\mathbf{I}}_x = \hbar\left(i\hat{\mathbf{I}}_y + \hat{\mathbf{I}}_x\right) = \hbar\hat{\mathbf{I}}_+$
  - $\left[\hat{\mathbf{I}}_z, \hat{\mathbf{I}}_-\right] = \hbar\hat{\mathbf{I}}_-$
  - $\left[\hat{\mathbf{I}}_+, \hat{\mathbf{I}}_-\right] = \left[\hat{\mathbf{I}}_x + i\hat{\mathbf{I}}_y, \hat{\mathbf{I}}_x - i\hat{\mathbf{I}}_y\right] = -i[\hat{\mathbf{I}}_x, \hat{\mathbf{I}}_y] + i[\hat{\mathbf{I}}_y, \hat{\mathbf{I}}_x] = -i(i\hbar\hat{\mathbf{I}}_z) + i(-i\hbar\hat{\mathbf{I}}_z) = 2\hbar\hat{\mathbf{I}}_z$
  - $\left[\hat{\mathbf{I}}^2, \hat{\mathbf{I}}_+\right] = \left[\hat{\mathbf{I}}^2, \hat{\mathbf{I}}_-\right] = 0$

Eigenvalues of Angular Momentum Operators

- Consider a more general solution than the spherical harmonics. Suppose that $\left|\lambda, m_l\right\rangle$ is an eigenfunction of both $\hat{\mathbf{l}}_z$ and $\hat{\mathbf{l}}^2$ with quantum numbers λ and m_l.
- $\hat{\mathbf{l}}_z \left|\lambda, m_l\right\rangle = m_l\hbar \left|\lambda, m_l\right\rangle$, where m_l is any *real* number. $\hbar$ has the dimensionality of angular momentum.
- $\hat{\mathbf{l}}^2 \left|\lambda, m_l\right\rangle = f(\lambda, m_l)\hbar^2 \left|\lambda, m_l\right\rangle$, where $f(\lambda, m_l)$ is a function that we do not know yet. $\hbar^2$ has the dimensionality of squared angular momentum.
- What do we know about $f(\lambda, m_l)$? Is it real or complex? Is it negative or nonnegative? How do we know?

Effect of Shift Operators

- From the definition $\hat{\mathbf{l}}^2 = \hat{\mathbf{l}}_x^2 + \hat{\mathbf{l}}_y^2 + \hat{\mathbf{l}}_z^2$,
  $\left(\hat{\mathbf{l}}^2 - \hat{\mathbf{l}}_z^2\right) \left|\lambda, m_l\right\rangle = \left(\hat{\mathbf{l}}_x^2 + \hat{\mathbf{l}}_y^2\right) \left|\lambda, m_l\right\rangle \geq 0$
- From the eigenvalues,
  $\left(\hat{\mathbf{l}}^2 - \hat{\mathbf{l}}_z^2\right) \left|\lambda, m_l\right\rangle = \left(f(\lambda, m_l)\hbar^2 - m_l^2\hbar^2\right) \left|\lambda, m_l\right\rangle \geq 0$thus $f(\lambda, m_l) \geq m_l^2$.
- This establishes that m_l has a minimum and maximum

Effect of Shift Operators

- Does $\hat{\mathbf{l}}_+$ affect $f(\lambda, m_l)$?
  - $\hat{\mathbf{l}}^2\hat{\mathbf{l}}_+ \left|\lambda, m_l\right\rangle = \hat{\mathbf{l}}_+\hat{\mathbf{l}}^2 \left|\lambda, m_l\right\rangle = \hat{\mathbf{l}}_+ f(\lambda, m_l)\hbar^2 \left|\lambda, m_l\right\rangle$
  - No, it does not.
- Does $\hat{\mathbf{l}}_+$ affect the eigenvalue of l_z?
  - $\hat{\mathbf{l}}_z\hat{\mathbf{l}}_+ \left|\lambda, m_l\right\rangle = \left(\hat{\mathbf{l}}_+\hat{\mathbf{l}}_z + \left[\hat{\mathbf{l}}_z, \hat{\mathbf{l}}_+\right]\right) \left|\lambda, m_l\right\rangle$
  - $= \left(\hat{\mathbf{l}}_+ m_l\hbar + \hbar\hat{\mathbf{l}}_+\right) \left|\lambda, m_l\right\rangle$
  - $= \left(m_l + 1\right) \hbar\hat{\mathbf{l}}_+ \left|\lambda, m_l\right\rangle$
- We also know that $\hat{\mathbf{l}}_+ \left|\lambda, m_l + 1\right\rangle = (m_l + 1)\hbar \left|\lambda, m_l + 1\right\rangle$
- Therefore $\hat{\mathbf{l}}_+ \left|\lambda, m_l\right\rangle = c_+(\lambda, m_l)\hbar \left|\lambda, m_l + 1\right\rangle$ where $c_+(\lambda, m_l)$ is a numerical coefficient.
- Similarly, we can show that $l\_$ lowers m_l by one.

Eigenvalues of the angular momentum

- We know that there is a maximum value for m_l. Let us call that l.
  - For this state, $\hat{\mathbf{l}}_+ \left|\lambda, l\right\rangle = 0$ because there is no eigenstate with larger m_l
  - $\hat{\mathbf{l}}_-\hat{\mathbf{l}}_+ \left|\lambda, l\right\rangle = 0$ because acting on nothing gives nothing
- We also know that
  - $\hat{\mathbf{l}}_-\hat{\mathbf{l}}_+ = \left(\hat{\mathbf{l}}_x - i\hat{\mathbf{l}}_y\right)\left(\hat{\mathbf{l}}_x + i\hat{\mathbf{l}}_y\right) = \hat{\mathbf{l}}_x^2 + \hat{\mathbf{l}}_y^2 + i\hat{\mathbf{l}}_x\hat{\mathbf{l}}_y - i\hat{\mathbf{l}}_y\hat{\mathbf{l}}_x = \hat{\mathbf{l}}_x^2 + \hat{\mathbf{l}}_y^2 + i\left[\hat{\mathbf{l}}_x, \hat{\mathbf{l}}_y\right]$
  - $= \hat{\mathbf{l}}^2 - \hat{\mathbf{l}}_z^2 - \hbar l_z$
- Therefore, $\left(\hat{\mathbf{l}}^2 - \hat{\mathbf{l}}_z^2 - \hbar l_z\right)\left|\lambda, l\right\rangle = 0$. This means that,
  - $f(\lambda, l)\hbar^2 - l^2\hbar^2 - l\hbar^2 = 0$
  - $f(\lambda, l) = l^2 + l = l(l+1)$
- Because $\hat{\mathbf{l}}_-$ does not affect the eigenvalue of $\hat{\mathbf{l}}^2$, $f(\lambda, m_l) = l(l+1)$ is the same for all m_l.

Eigenvalues of the angular momentum

- Similarly, we know that there is a minimum value for m_l. Let us call that k.
  - For this state, $\hat{\mathbf{l}}_- \left|\lambda, k\right\rangle = 0$
  - $\hat{\mathbf{l}}_+\hat{\mathbf{l}}_- \left|\lambda, k\right\rangle = 0$
- By analogous logic as the previous slide, we can show that $f(\lambda, k) = k(k-1)$, and therefore $l(l+1) = k(k-1)$
  - Solutions are $k = -l$ or $k = l + 1$
  - Only $k = -l$ makes sense, because the lower bound must be less than the upper bound.
- Because m_l can go in integer steps, $f(\lambda, m_l) = l(l+1)$ for $m_l = -l, -l+1, ..., l$.
- What are allowed values of l? Any real number? Any integer? Any integer or half integer? Show series of numbers that satisfy or violate the conditions.
- So far we have shown that $l = 0, \frac{1}{2}, 1, ...$ and $m_l = -l, -l+1, ..., l$. This differs from the previous treatment because we see half integral values of l are permitted.

Spin

Forms of the Angular Momentum

- $$\mathbf{l} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_z & p_y & p_z \end{vmatrix}$$
- Several types:
  - Orbital - $\left| l, m_l \right\rangle$ based on spherical harmonics. l is an integer.
  - Spin - $\left| s, m_s \right\rangle$ has no spatial wave function.
    - Often depicted as a particle literally spinning around an axis
    - Spin is an *intrinsic property* of a particle, unrelated to any sort of motion in space
    - s is an integer or half integer1
- Generally,
  - $\left| j, m_j \right\rangle$ is an eigenfunction of the angular momentum operators with eigenvalues,
    - $\hat{\mathbf{J}}^2 \left| j, m_j \right\rangle = j(j+1)\hbar^2 \left| j, m_j \right\rangle$
    - $\hat{\mathbf{J}}_z \left| j, m_j \right\rangle = m_j\hbar \left| j, m_j \right\rangle$.
  - All types of angular momentum have the same commutators

Spin Angular Momentum

- Inferred from experiments, such as the Stern-Gerlach experiment
- Particles observed to have angular momentum that cannot be accounted for by orbital angular momentum alone.
- For an electron, the quantum numbers are $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$.
- The two kets are, $\alpha = \left|\frac{1}{2}, \frac{1}{2}\right\rangle$ and $\beta = \left|\frac{1}{2}, -\frac{1}{2}\right\rangle$.
- The effects of operators on these kets are
  - $\hat{\mathbf{s}}_z\alpha = \frac{1}{2}\hbar\alpha$
  - $\hat{\mathbf{s}}^2\alpha = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\alpha = \frac{3}{4}\hbar^2\alpha$
  - $\hat{\mathbf{s}}_z\beta = -\frac{1}{2}\hbar\beta$
  - $\hat{\mathbf{s}}^2\beta = \frac{3}{4}\hbar^2\beta$
  - $\hat{\mathbf{s}}_+\alpha = 0, \hat{\mathbf{s}}_+\beta = \hbar\alpha, \hat{\mathbf{s}}\_\alpha = \hbar\beta, \hat{\mathbf{s}}\_\beta = 0$

Matrix form of spin

- As a reminder $\left\langle a \,|\, \hat{\mathbf{\Omega}} \,|\, b \right\rangle \equiv \int \Psi_a^* \hat{\mathbf{\Omega}} \Psi_b d\tau \equiv \Omega_{a,b}$. In the context of electron spin, the first row and column correspond to α. Second row and column are β.
- For example, $\hat{\mathbf{s}}_z = \begin{pmatrix} \frac{1}{2}\hbar & 0 \\ 0 & -\frac{1}{2}\hbar \end{pmatrix} = = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{1}{2}\hbar\boldsymbol{\sigma}_z$, where $\boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
- Exercise: Write the matrices corresponding to the shift operators for electron spin
- Exercise: Use the inverse shift operators $\hat{\mathbf{s}}_x = \dfrac{\hat{\mathbf{s}}_+ + \hat{\mathbf{s}}_-}{2}$ and $\hat{\mathbf{s}}_y = \dfrac{\hat{\mathbf{s}}_+ - \hat{\mathbf{s}}_-}{2i}$ to write the matrix elements for $\hat{\mathbf{s}}_x$ and $\hat{\mathbf{s}}_y$.

Review Questions

- Besides hydrogen, what is a system that the solution of the hydrogenic atom is applicable to?
- Are angular and radial solutions of the hydrogenic atom independent?
- How are the eigenvalues of the angular momentum operators more general than those of spherical harmonics?
- What is the effect of a raising and lowering operator?
- What are the eigenfunctions of the spin operator for an electron?