Hydrogen Atom

- Returning now to the hydrogen atom we have the radial equation left to solve

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

$$\text{where } V(r)=-\frac{Ze^2}{4\pi\varepsilon_0 r} \text{ and note } m\rightarrow\mu$$

- The solution to the radial equation is complicated and we must be content with the result

$$R_{nl}(r)=Ne^{-\frac{Zr}{na_0}}\left(\frac{2Zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

Hydrogen Atom

Comments

L_{n+l}^{2l+1} are the associated Laguerre polynomials

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} = 0.529\dot{A} \text{ is the familiar Bohr radius}$$

- The radial wave functions are listed and shown on the following slides
- The solution near r=0 is

$$R_{nl}(r) \rightarrow r^l$$

  - This means the larger the l the smaller the probability of finding the electron close to the nucleus

- The asymptotic solution is

$$R_{nl}(r) \rightarrow e^{-\frac{Zr}{na_0}}$$

Hydrogen Atom

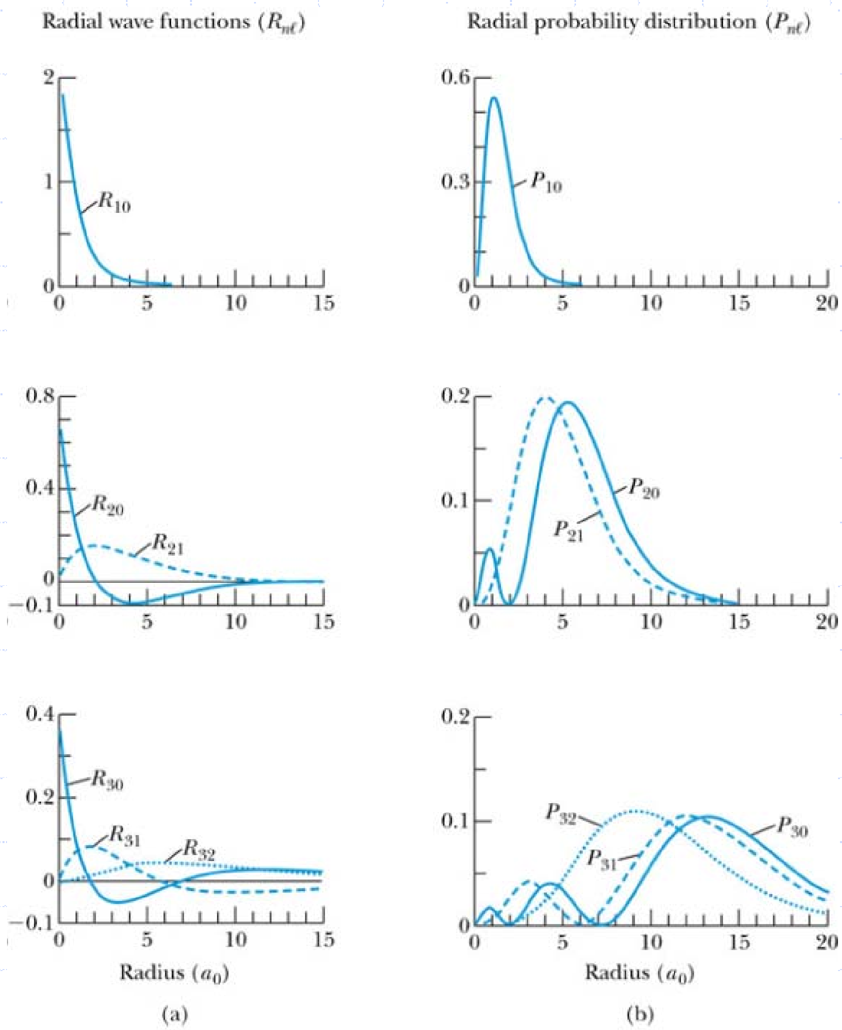
- Radial wave functions

Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$

Hydrogen Atom

- Radial wave function and probability distribution



Hydrogen Atom

➢ Comments

The full hydrogen wave function is

$$\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta,\varphi)$$

The angular probability density is $|\mathrm{Y}_{\mathrm{lm}}|^2$

The radial probability density is $\mathrm{r}^2|\mathrm{R}_{\mathrm{nl}}|^2$

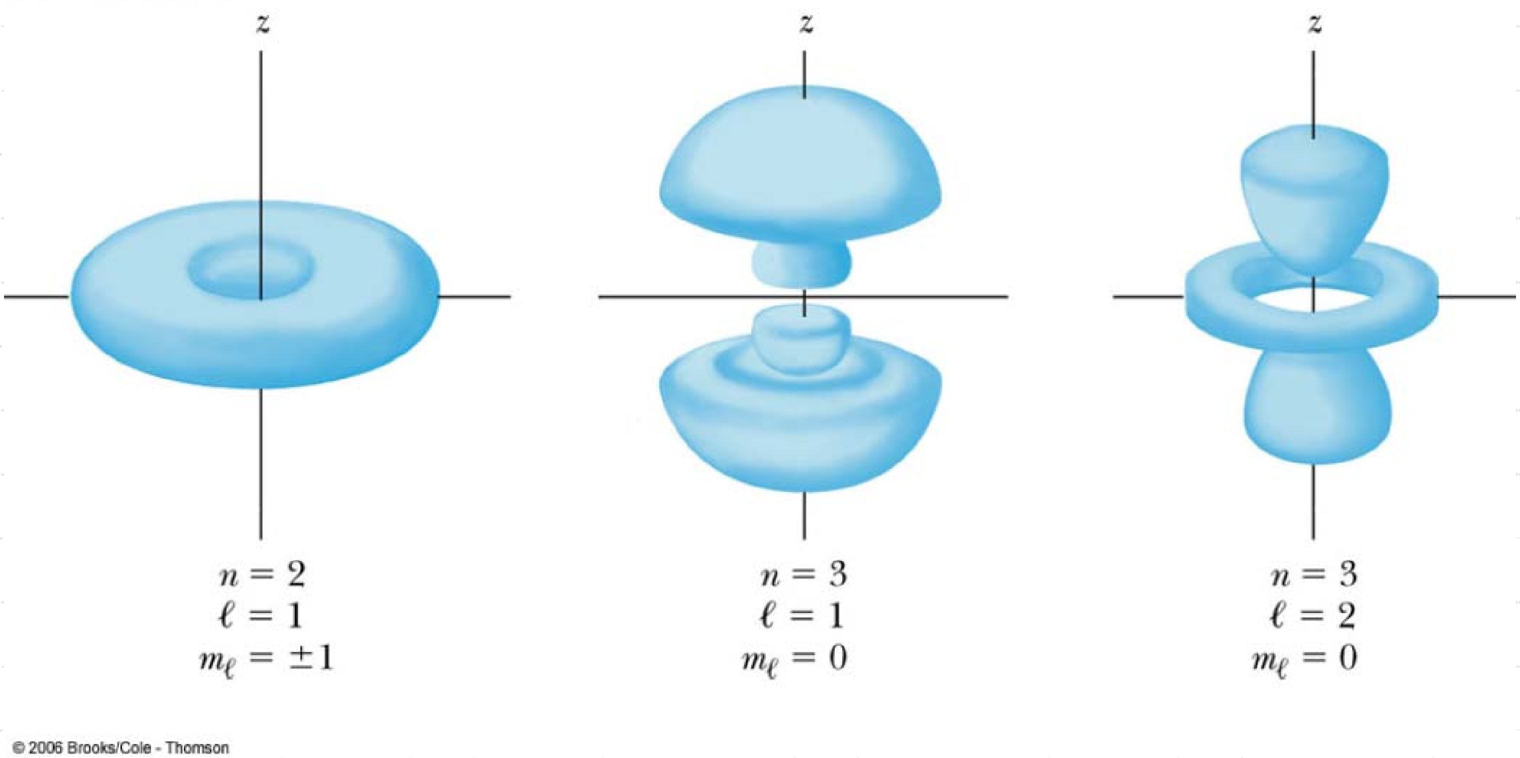
The total probability density is $|\psi_{nlm}|^2$

$|\psi_{nlm}|^2 d^3r$ is the probability of finding the particle

in volume element $d^3r = r^2 dr d\Omega = r^2 dr \sin\theta d\theta d\varphi$

Hydrogen Atom

- Probability density function $|\psi_{nlm}|^2$



Hydrogen Atom

- Problems
  - What is the expectation value for r for the 1s state?
  - What is the most probable value for r for the 1s state?

Hydrogen Atom

Comments

- The quantum numbers associated with the radial wave function are n and l
- The quantum numbers associated with the angular wave function are l and m
- Boundary conditions on the solutions lead to

n is the principle quantum number

The allowed values of n are $1, 2, 3, \ldots$

The allowed values of l are $0 \le l < n$

Sometimes we use letter names for l instead $s, p, d, f, g, \ldots$

The allowed values of m are $0, \pm 1, \ldots, \pm l$

Hydrogen quantum states are specified by n, l, m

Hydrogen Atom

Comments

- The energy eigenvalues for bound states are also found from the requirement that the radial wave function remain finite

$$E_n = -\frac{\mu Z^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} = -\frac{Z^2 13.6eV}{n^2}$$

- This is identical to the prediction of the Bohr model and in good agreement with data
- Note the eigenfunction degeneracy
  - For each n, there are n possible values of l
  - For each l, there are 2l+1 possible values of m
  - For each n, there are n^2 degenerate eigenfunctions

Hydrogen Atom

- The hydrogen wave functions can be used to calculate transition probabilities for the electron to change from one state to another
- Selection rules governing allowed transitions are found to be

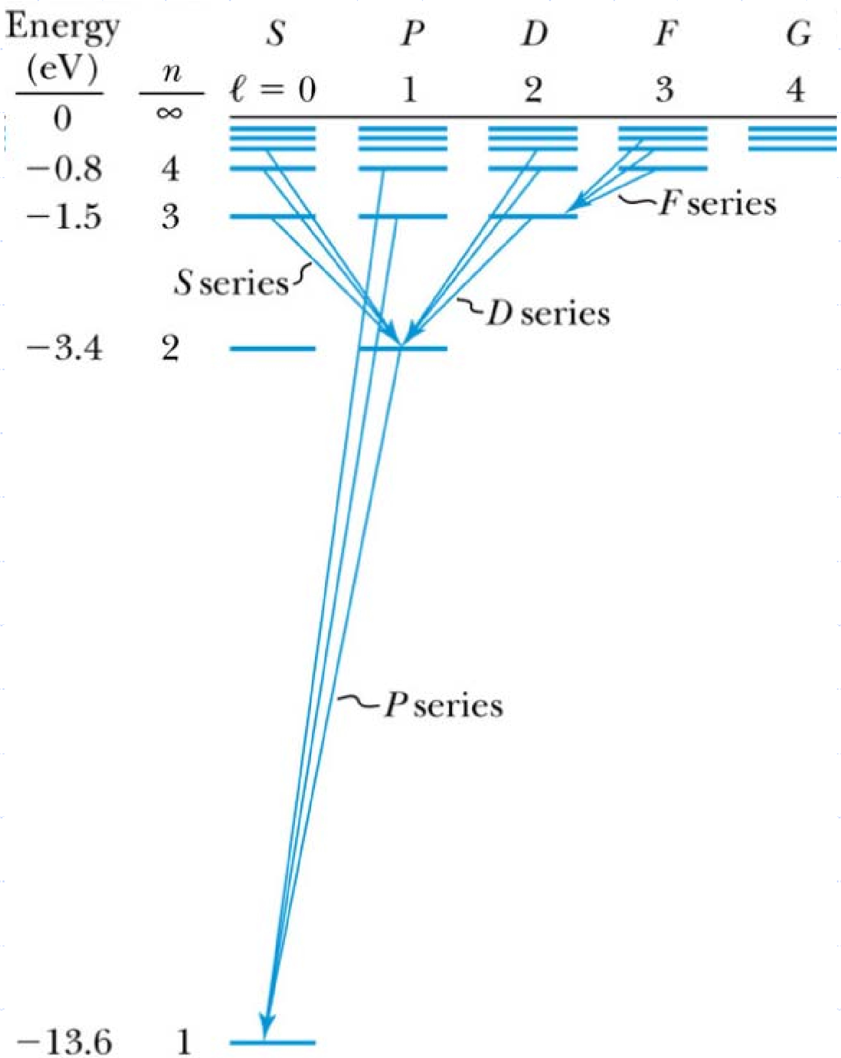
$$\Delta n = \text{anything}$$

$$\Delta \mathrm{l} = \pm 1$$

$$\Delta \mathrm{m} = 0, \pm 1$$

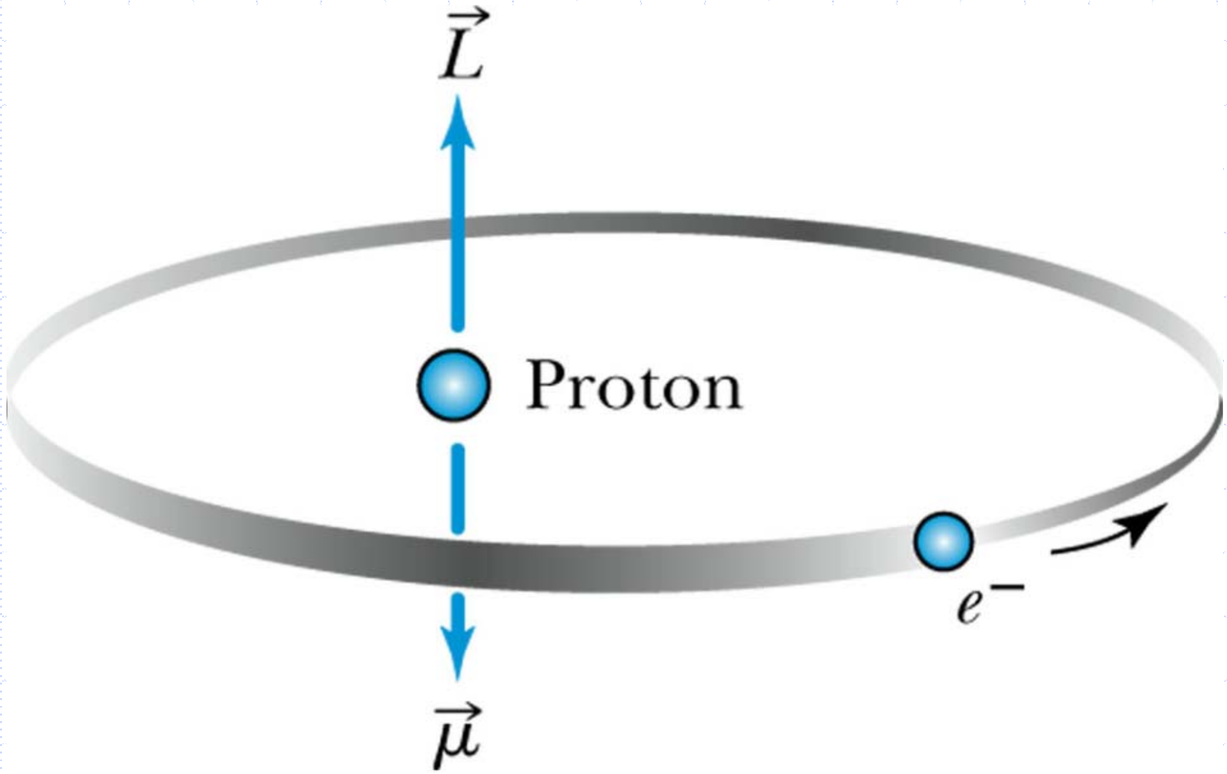
Hydrogen Atom

- Hydrogen energy levels



Atoms in Magnetic Fields

- Return to the Bohr atom



Atoms in Magnetic Fields

Recall a circulating charge produces

an orbital magnetic dipole moment μ_l

$$\mu_l = iA$$

$$i = \frac{e}{T} = \frac{ev}{2\pi r} \text{ so } \mu_l = \frac{evr}{2}$$

$$L = m_e vr \text{ so } \frac{\mu_l}{L} = \frac{e}{2m_e}$$

Usually we write $\frac{\mu_l}{L} = \frac{g_l \mu_b}{\hbar}$

where $\mu_{\mathrm{B}} = \frac{e\hbar}{2m_e}$ is called the Bohr magneton and $g_l = 1$

Thus $\vec{\mu}_l = -\frac{g_l \mu_B}{\hbar} \vec{L}$

Atoms in Magnetic Fields

- This relation holds true in quantum mechanics as well thus

$$\vec{\mu}_l = -\frac{g_l \mu_b}{\hbar}\vec{L}$$

$$\mu_l = g_l \mu_b \sqrt{l(l+1)}$$

$$\mu_{l_z} = -g_l \mu_b m_l$$

Atoms in Magnetic Fields

- Recall from E+M that when a magnetic dipole is placed in a magnetic field

$$\vec{\tau} = \vec{\mu}_l \times \vec{B}$$

$$\Delta E = -\vec{\mu}_l \cdot \vec{B}$$

- We expect the operator for this potential energy to look like

$$-\vec{\mu}_l \cdot \vec{B} = \frac{\mu_B \vec{L} \cdot \vec{B}}{\hbar} = \frac{\mu_B L_Z B_Z}{\hbar}$$

Then the full Hamiltonian is

$$\hat{H} = \hat{H}_0 + \frac{\mu_B L_Z B_Z}{\hbar} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{\mu_B L_Z B_Z}{\hbar}$$

Atoms in Magnetic Fields

- Now we have shown that the ψ_{nlm} are simultaneous eigenfunctions of E, L^2, and L_Z
- Thus the additional term in the Hamiltonian only changes the energy

$$E = E_0 + m\mu_B B_Z \text{ where } -l \leq m \leq l$$

- The m degeneracy of the hydrogen energy levels is lifted
  - In an external magnetic field there will be m=2l+1 states with distinct energies
  - This is why m is called the magnetic quantum number

Hydrogen Atom

- Normal Zeeman effect