CHAPTER 7
The Hydrogen Atom

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> *The atom of modern physics can be symbolized only through a partial differential equation in an abstract space of many dimensions. All its qualities are inferential; no material properties can be directly attributed to it. An understanding of the atomic world in that primary sensuous fashion…is impossible.*
>
> \- Werner Heisenberg

7.1: Application of the Schrödinger Equation to the Hydrogen Atom

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

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

- Rewrite the three-dimensional time-independent Schrödinger Equation.

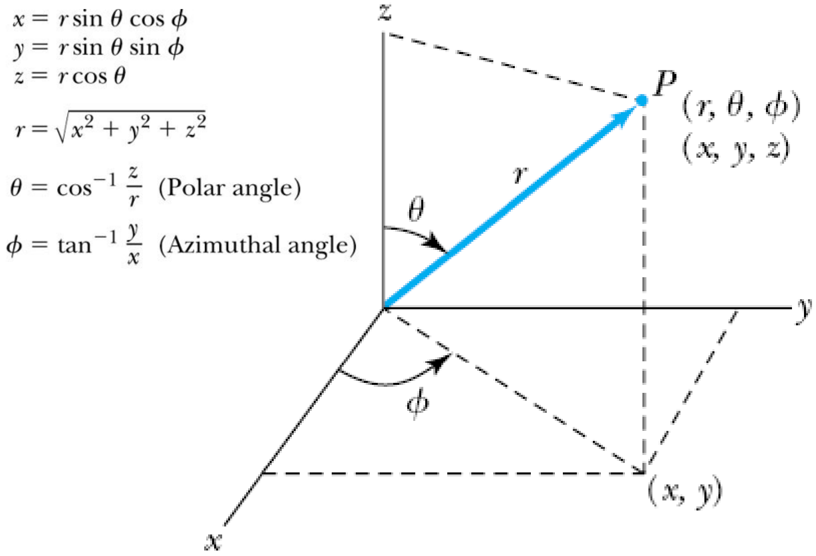
$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x,y,z)}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right] = E - V(r)$$

For Hydrogen-like atoms (He^+ or Li^{++})

- Replace e^2 with Ze^2 (Z is the atomic number).
- Use appropriate reduced mass μ.

Application of the Schrödinger Equation

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



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

Transform to spherical polar coordinates because of 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, ϕ

$\longrightarrow$ Equation is separable.

$\longrightarrow$ Solution may be a product of three functions.

$\longrightarrow$ $\psi(r,\theta,\phi) = R(r)f(\theta)g(\phi)$ Equation 7.3

- We can separate Equation 7.3 into three separate differential equations, each depending on one coordinate: r, θ, or ϕ.

7.2: Solution of the Schrödinger Equation for Hydrogen

- Substitute Eq (7.4) into Eq (7.3) and separate the resulting equation into three equations: $R(r)$, $f(\theta)$, and $g(\phi)$.

Separation of Variables

- The derivatives from Eq (7.4)

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

- Substitute them into Eq (7.3)

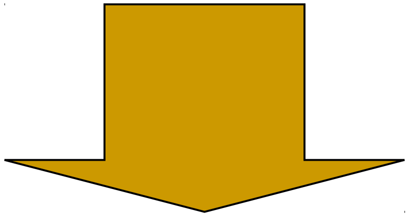
$$\frac{fg}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{Rg}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial f}{\partial \theta}\right) + \frac{Rf}{r^2\sin^2\theta}\frac{\partial^2 g}{\partial \phi^2} + \frac{2\mu}{\hbar^2}(E-V)Rfg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

- Multiply both sides of Eq (7.6) by $r^2 \sin^2\theta / Rfg$

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

Solution of the Schrödinger Equation

- Only r and θ appear on the left side and only ϕ appears on the right side of Eq (7.7)
- The left side of the equation cannot change as ϕ changes.
- The right side cannot change with either r or θ.



- Each side needs to be equal to a constant for the equation to be true.

  Set the constant $-m_\ell^2$ equal to the right side of Eq (7.7)

$$\frac{d^2 g}{d\phi^2} = -m_\ell^{\,2} g$$ -------- **azimuthal equation**

- It is convenient to choose a solution to be $e^{im_\ell\phi}$.

Solution of the Schrödinger Equation

- $e^{im_\ell\phi}$ satisfies Eq (7.8) for any value of m_ℓ.
- The solution be single valued in order to have a valid solution for any ϕ, which is $g(\phi) = g(\phi + 2\pi)$

  $$g(\phi = 0) = g(\phi = 2\pi) \longrightarrow e^0 = e^{2\pi i m_\ell}$$

- m_ℓ to be zero or an integer (positive or negative) for this to be true.
- If Eq (7.8) were positive, the solution would not be realized.
- Set the left side of Eq (7.7) equal to $-m_\ell^2$ and rearrange it.

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

- 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 Eq (7.9) equal to constant ℓ(ℓ + 1).

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

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df}{d\theta}\right)+\left[\ell(\ell+1)-\frac{m_\ell{}^2}{\sin^2\theta}\right]f=0$$ ----**Angular equation**

- Schrödinger equation has been separated into three ordinary second-order differential equations [Eq (7.8), (7.10), and (7.11)], each containing only one variable.

Solution of the Radial Equation

- The radial equation is called the **associated Laguerre equation** and the *solutions R* that satisfy the appropriate boundary conditions are called *associated Laguerre functions*.

- Assume the ground state has ℓ = 0 and this requires $m_\ell = 0$.

  Eq (7.10) becomes

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

- The derivative of $r^2\frac{dR}{dr}$ yields two terms.

  Write those terms and insert Eq (7.1)

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

Solution of the Radial Equation

- Try a solution $R = Ae^{-r/a_0}$
  A is a normalized constant.
  a_0 is a constant with the dimension of length.
  Take derivatives of *R* and insert them into Eq (7.13).

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

- To satisfy Eq (7.14) for any *r* is for each of the two expressions in parentheses to be zero.
  Set the second parentheses equal to zero and solve for a_0.

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

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

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

Both equal to the Bohr result.

Quantum Numbers

- The appropriate boundary conditions to Eq (7.10) and (7.11) leads to the following restrictions on the quantum numbers ℓ and m_ℓ:
    - $\ell = 0, 1, 2, 3, . . .$
    - $m_\ell = -\ell, -\ell + 1, . . . , -2, -1, 0, 1, 2, . \ell . , \ell - 1, \ell$
    - $|m_\ell| \leq \ell$ and $\ell < 0$.

- The predicted energy level is

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

Hydrogen Atom Radial Wave Functions

- First few radial wave functions $R_{n\ell}$

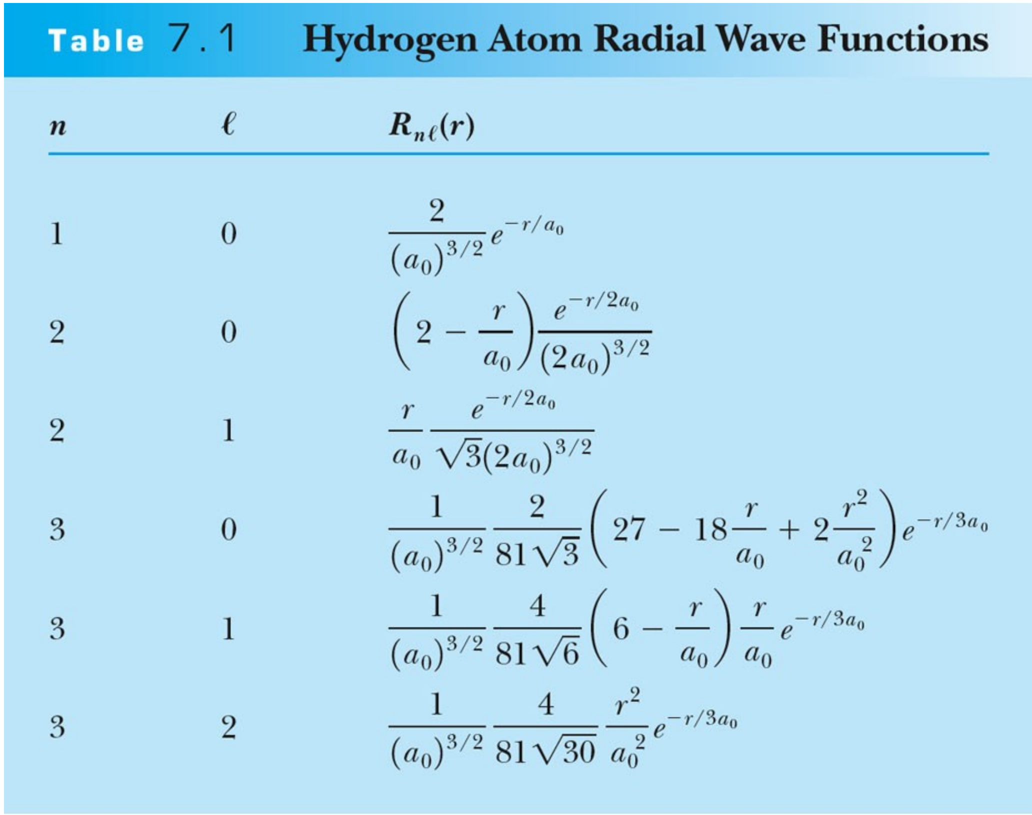


Table 7.1 Hydrogen Atom Radial Wave Functions

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	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0^2}e^{-r/3a_0}$

- Subscripts on *R* specify the values of *n* and ℓ.

Solution of the Angular and Azimuthal Equations

- The solutions for Eq (7.8) are $e^{im_\ell\phi}$ or $e^{-im_\ell\phi}$.
- Solutions to the angular and azimuthal equations are linked because both have m_ℓ.
- Group these solutions together into functions.

$$Y(\theta,\phi) = f(\theta)g(\phi)$$ ---- **spherical harmonics**

Normalized Spherical Harmonics

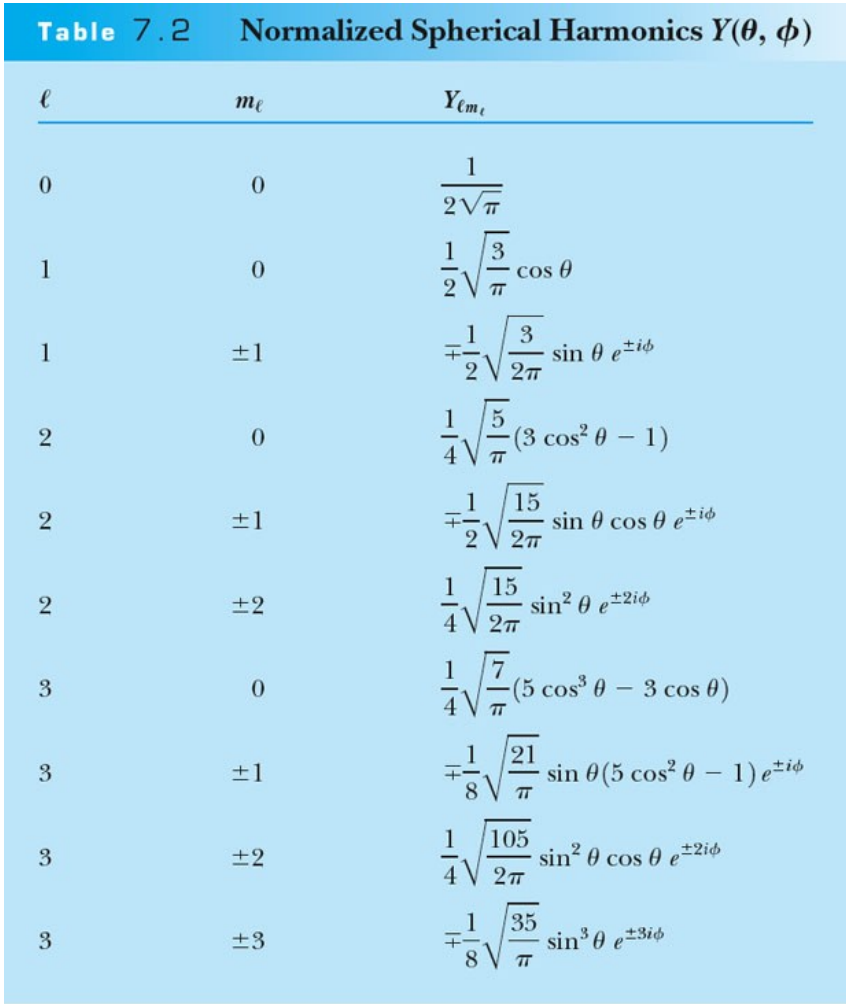


Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

Solution of the Angular and Azimuthal Equations

- The radial wave function *R* and the spherical harmonics *Y* determine the probability density for the various quantum states. The total wave function $\psi(r,\theta,\phi)$ depends on *n*, ℓ, and m_ℓ. The wave function becomes

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m_\ell}(\theta,\phi)$$

7.3: Quantum Numbers

The three quantum numbers:

n	Principal quantum number
ℓ	Orbital angular momentum quantum number
m_ℓ	Magnetic quantum number

The boundary conditions:

$n = 1, 2, 3, 4, \ldots$	Integer
$\ell = 0, 1, 2, 3, \ldots, n - 1$	Integer
$m_\ell = -\ell, -\ell + 1, \ldots, 0, 1, \ldots, \ell - 1, \ell$	Integer

The restrictions for quantum numbers:

- $n > 0$
- $\ell < n$
- $|m_\ell| \leq \ell$

Principal Quantum Number *n*

- It results from the solution of *R*(*r*) in Eq (7.4) because *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 means the energy *E* indicates that the electron and proton are bound together.

Orbital Angular Momentum Quantum Number ℓ

- It is associated with the $R(r)$ and $f(\theta)$ parts of the wave function.

- Classically, the orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$ with $L = mv_{\text{orbital}}r$.

- ℓ is related to L by $L = \sqrt{\ell(\ell+1)}\hbar$.

- In an ℓ = 0 state, $L = \sqrt{0(1)}\hbar = 0$

⇓

It disagrees with Bohr's semiclassical "planetary" model of electrons orbiting a nucleus $L = n\hbar$.

Orbital Angular Momentum Quantum Number ℓ

- A certain energy level is **degenerate** with respect to ℓ when the energy is independent of ℓ.

- Use letter names for the various ℓ values.

ℓ =	0	1	2	3	4	5 . . .
Letter =	*s*	*p*	*d*	*f*	*g*	*h* . . .

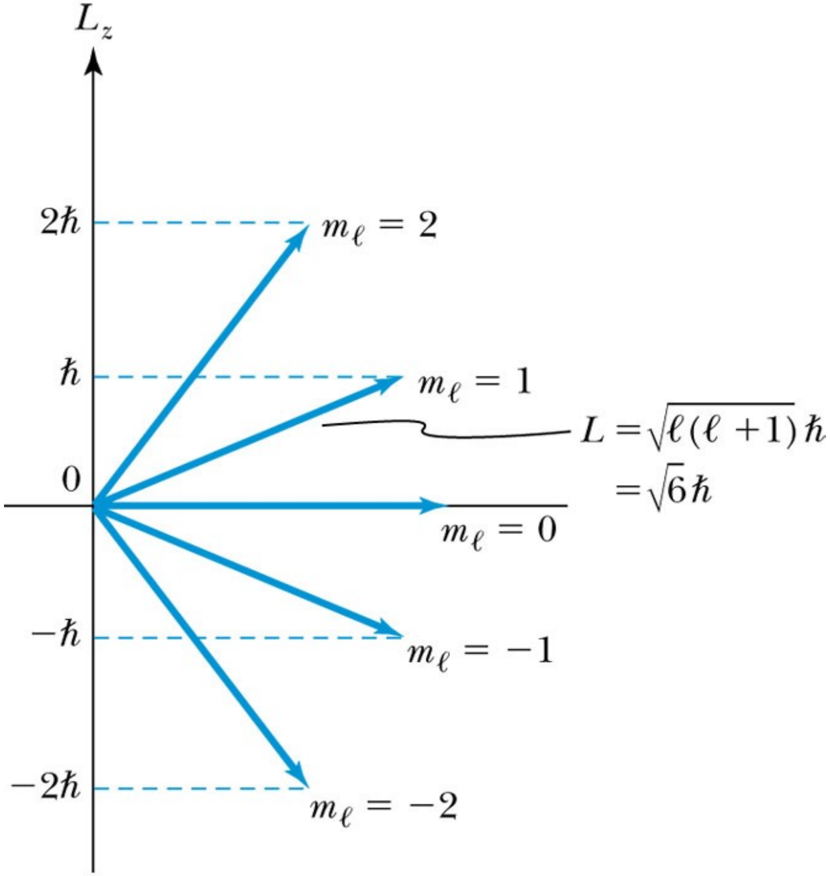
- Atomic states are referred to by their n and ℓ.
- A state with $n = 2$ and $\ell = 1$ is called a 2*p* state.
- The boundary conditions require $n > \ell$.

Magnetic Quantum Number m_ℓ

- The angle ϕ is a measure of the rotation about the z axis.
- The solution for $g(\phi)$ specifies that m_ℓ is an integer and related to the z component of L.

$$L_z = m_\ell \hbar$$

- The relationship of L, L_z, ℓ, and m_ℓ for ℓ = 2.
- $L = \sqrt{\ell(\ell+1)}\hbar = \sqrt{6}\hbar$ is fixed because L_z is quantized.
- Only certain orientations of $\vec{L}$ are possible and this is called **space quantization**.



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Magnetic Quantum Number m_ℓ

- Quantum mechanics allows $\vec{L}$ to be quantized along only one direction in space. Because of the relation $L^2 = L_x^2 + L_y^2 + L_z^2$ the knowledge of a second component would imply a knowledge of the third component because we know $\vec{L}$.

- We expect the average of the angular momentum components squared to be $\langle L_x{}^2 \rangle = \langle L_y{}^2 \rangle = \langle L_z{}^2 \rangle$.

$$\langle L^2 \rangle = 3\langle L_z{}^2 \rangle = \frac{3}{2\ell+1} \sum_{m_\ell=-\ell}^{\ell} m_\ell{}^2 \hbar^2 = \ell(\ell+1)\hbar^2$$

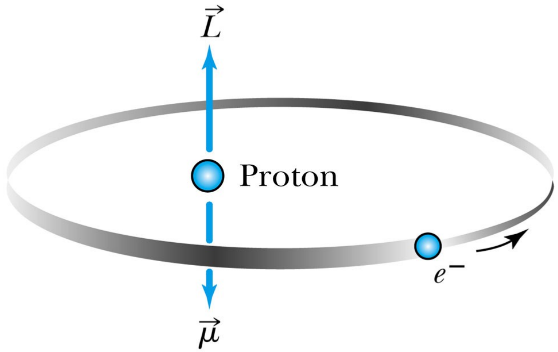
7.4: Magnetic Effects on Atomic Spectra—The Normal Zeeman Effect

- The Dutch physicist Pieter Zeeman showed the spectral lines emitted by atoms in a magnetic field split into multiple energy levels. It is called the **Zeeman effect**.

Anomalous Zeeman effect:

- A spectral line is split into three lines.
- Consider the atom to behave like a small magnet.
- Think of an electron as an orbiting circular current loop of $I = dq / dt$ around the nucleus.
- The current loop has a magnetic moment $\mu = IA$ and the period $T = 2\pi r / v$.
- $\vec{\mu} = -\frac{e}{2m}\vec{L}$ where $L = mvr$ is the magnitude of the orbital angular momentum.

The Normal Zeeman Effect



- Since there is no magnetic field to align them, $\vec{\mu}$ point in random directions. The dipole has a potential energy

$$V_B = -\vec{\mu} \cdot \vec{B}$$

- The angular momentum is aligned with the magnetic moment, and the torque between $\vec{\mu}$ and $\vec{B}$ causes a precession of $\vec{\mu}$.

$$\mu_z = \frac{e\hbar}{2m} m_\ell = -\mu_{\mathrm{B}} m_\ell$$

Where $\mu_B = e\hbar / 2m$ is called a **Bohr magneton**.

- $\vec{\mu}$ cannot align exactly in the z direction and has only certain allowed quantized orientations.

$$\vec{\mu} = -\mu_{\mathrm{B}} \vec{L} / \hbar$$

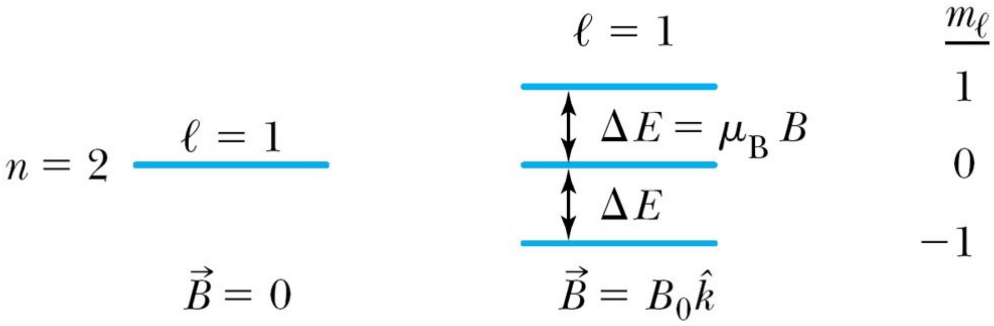
The Normal Zeeman Effect

- The potential energy is quantized due to the magnetic quantum number m_ℓ.

$$V_B = -\mu_z B = +\mu_{\mathrm{B}} m_\ell B$$

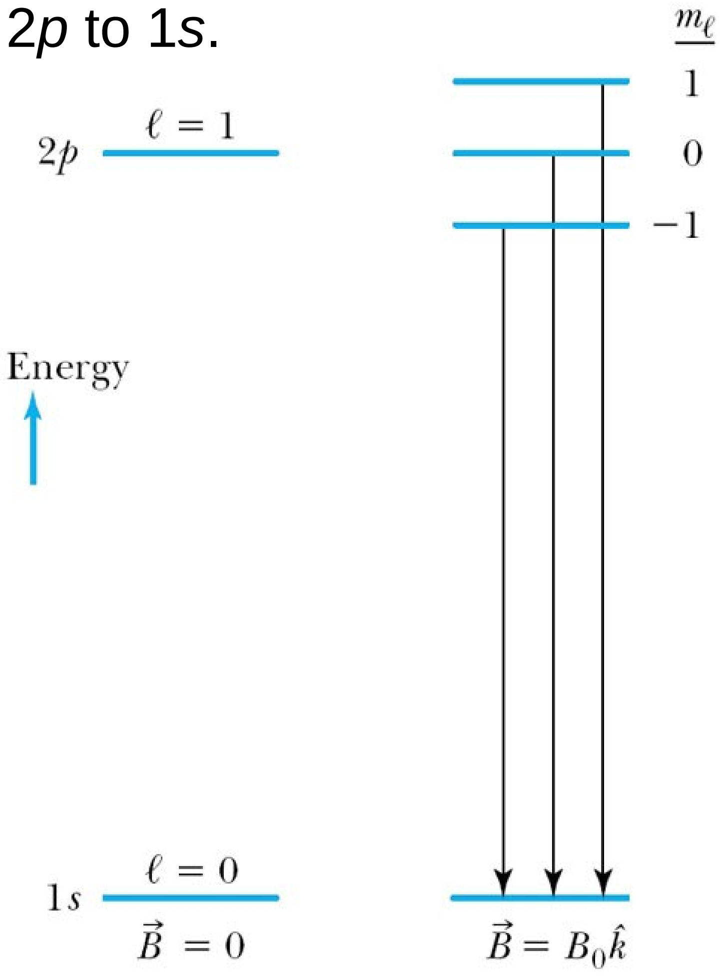
- When a magnetic field is applied, the 2*p* level of atomic hydrogen is split into three different energy states with energy difference of $\Delta E = \mu_{\mathrm{B}} B \, \Delta m_\ell$.

m_ℓ	**Energy**
1	$E_0 + \mu_B B$
0	E_0
−1	$E_0 - \mu_B B$



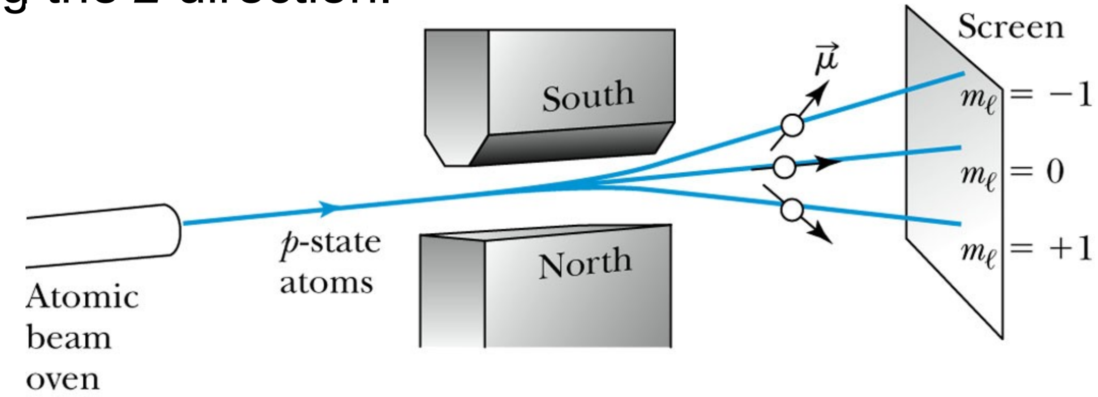
The Normal Zeeman Effect

- A transition from 2*p* to 1*s*.



The Normal Zeeman Effect

- An atomic beam of particles in the ℓ = 1 state pass through a magnetic field along the *z* direction.



- $V_B = -\mu_z B$
- $F_z = -(dV_B / dz) = \mu_z (dB / dz)$
- The $m_\ell = +1$ state will be deflected down, the $m_\ell = -1$ state up, and the $m_\ell = 0$ state will be undeflected.
- If the space quantization were due to the magnetic quantum number m_ℓ, m_ℓ states is always odd (2ℓ + 1) and should have produced an odd number of lines.

7.5: Intrinsic Spin

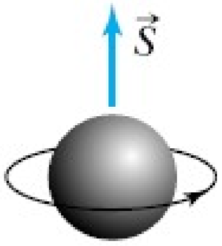
- Samuel Goudsmit and George Uhlenbeck in Holland proposed that *the electron must have an intrinsic angular momentum* and therefore a magnetic moment.

- Paul Ehrenfest showed that the surface of the spinning electron should be moving faster than the speed of light!

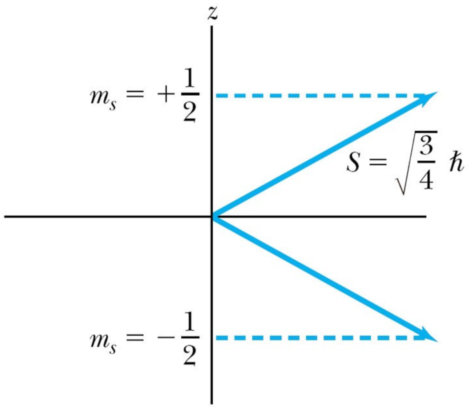
- In order to explain experimental data, Goudsmit and Uhlenbeck proposed that the electron must have an **intrinsic spin quantum number** $s = ½$.

Intrinsic Spin

- The spinning electron reacts similarly to the orbiting electron in a magnetic field.
- We should try to find *L*, L_z, ℓ, and m_ℓ.
- The **magnetic spin quantum number** m_s has only two values, $m_s = \pm ½$.



The electron's spin will be either "up" or "down" and can never be spinning with its magnetic moment μ_s exactly along the z axis.



The **intrinsic spin angular momentum** vector $\left|\vec{S}\right| = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$.

Intrinsic Spin

- The magnetic moment is $\vec{\mu}_s = -(e/m)\vec{S}$, or $-2\mu_B \vec{S}/\hbar$.
- The coefficient of $\vec{S}/\hbar$ is $-2\mu_B$ as with $\vec{L}$ is a consequence of theory of relativity.

- The **gyromagnetic ratio** (ℓ or *s*).
- $g_\ell = 1$ and $g_s = 2$, then

$$\mu_\ell = -\frac{g_\ell \mu_B \vec{L}}{\hbar} = -\frac{\mu_B \vec{L}}{\hbar} \quad \text{and} \quad \vec{\mu}_s = -\frac{g_s \mu_B \vec{L}}{\hbar} = -2\frac{\mu_B \vec{L}}{\hbar}$$

- The z component of $\vec{S}$ is $S_z = m_s\hbar = \pm\hbar/2$.
- In ℓ = 0 state → no splitting due to $\vec{\mu}_s$.

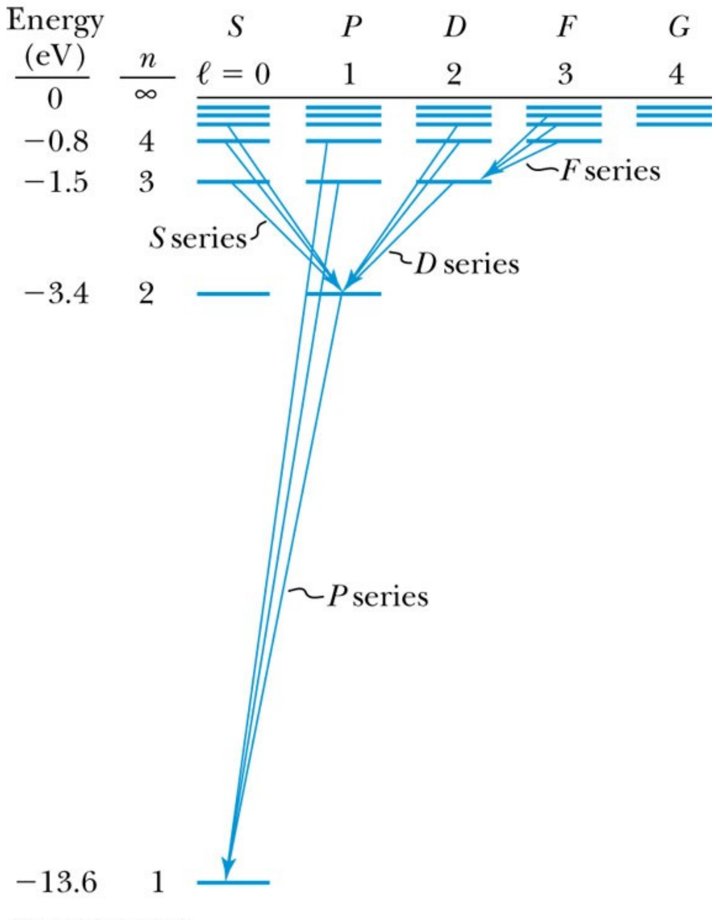
  → there is space quantization due to the intrinsic spin.

- Apply m_ℓ and the potential energy becomes

$$V_B = -\vec{\mu}_s \cdot \vec{B} = +\frac{e}{m}\vec{S}\cdot\vec{B}$$

7.6: Energy Levels and Electron Probabilities

- For hydrogen, the energy level depends on the principle quantum number *n*.



- In ground state an atom cannot emit radiation. It can absorb electromagnetic radiation, or gain energy through inelastic bombardment by particles.

Selection Rules

- We can use the wave functions to calculate transition probabilities for the electron to change from one state to another.

Allowed transitions:

- Electrons absorbing or emitting photons to change states when $\Delta\ell = \pm 1$.

Forbidden transitions:

- Other transitions possible but occur with much smaller probabilities when $\Delta\ell \neq \pm 1$.

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

$$\Delta\ell = \pm 1$$

$$\Delta m_\ell = 0, \pm 1$$

Probability Distribution Functions

- We must use wave functions to calculate the probability distributions of the electrons.
- The “position” of the electron is spread over space and is not well defined.
- We may use the radial wave function *R*(*r*) to calculate radial probability distributions of the electron.
- The probability of finding the electron in a differential volume element $d\tau$ is $dP = \psi^*(r,\theta,\phi)\ \psi(r,\theta,\phi)\ d\tau$.

Probability Distribution Functions

- The differential volume element in spherical polar coordinates is

$$d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi$$

Therefore,

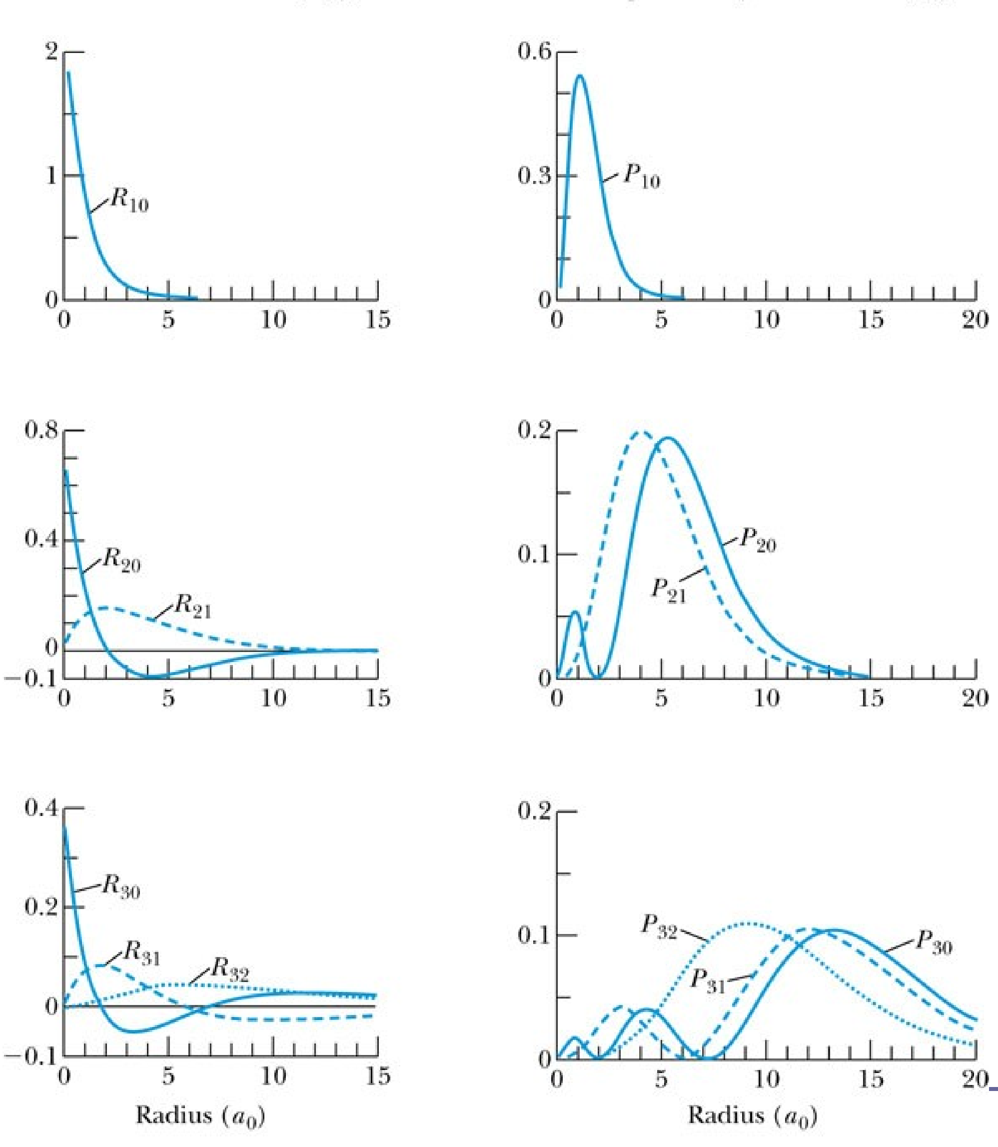
$$P(r)\,dr = r^2 R^*(r)R(r)\,dr \int_0^{\pi} |f(\theta)|^2 \sin\theta \, d\theta \int_0^{2\pi} |g(\phi)|^2 \, d\phi$$

- We are only interested in the radial dependence.

$$P(r)\,dr = r^2 |R(r)|^2 \, dr$$

- The radial probability density is $P(r) = r^2|R(r)|^2$ and it depends only on n and l.

Probability Distribution Functions



(a)   (b)

- *R*(*r*) and *P*(*r*) for the lowest-lying states of the hydrogen atom.

Probability Distribution Functions

- The probability density for the hydrogen atom for three different electron states.