CHAPTER 7
The Hydrogen Atom

- Some mathematics again
- 7.1 Application of the Schrödinger Equation to the Hydrogen Atom
- 7.2 Solution of the Schrödinger Equation for Hydrogen
- 7.3 Quantum Numbers
- **7.6** Energy Levels and Probabilities of finding the electron/orbitals
- 7.4 Magnetic Effects on Atomic Spectra – The so-called ***normal*** Zeeman Effect (which is only observed with crude spectrometers)
- **Stern – Gerlach experiment**
- 7.5 Intrinsic Spin (nothing is spinning !!!)
- 8.2 Total Angular Momentum

> *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

Laplacian $$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad \psi(\mathbf{r}) = \psi(x, y, z) = \psi_1(x)\psi_2(y)\psi_3(z)$$

in spherical coordinates

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \left(\frac{2}{r}\right)\frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{\partial^2}{\partial \theta^2} + \cot\theta\frac{\partial}{\partial \theta} + \csc^2\theta\frac{\partial^2}{\partial \phi^2}\right]$$

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + U(\mathbf{r})\Psi = i\hbar\frac{\partial \Psi}{\partial t}$$

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-i\omega t}$$

For all time independent potential energy functions

3D spherical potential, so we will end up with three different quantum numbers, labels on the wavefunctions

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Very high symmetry of the potential, so lots of degeneracy

Use reduced mass μ of electron instead of m

Key to progress is

$$\psi(\mathbf{r}) = \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \tag{8.11}$$

Separation of variables for the stationary state wavefunction

7.1: Application of the Schrödinger Equation to the Hydrogen Atom

- Potential energy of the electron-proton system is electrostatic (no magnetic effects in the beginning):

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

- Rewrite the three-dimensional time-independent Schrödinger Equation using spherical coordinates.

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

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

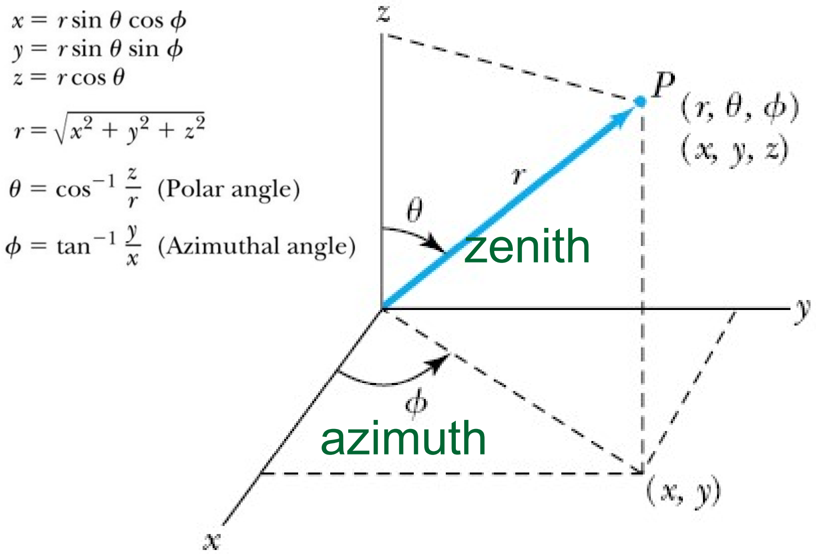
- Replace e^2 with Ze^2 (Z is the atomic number, Z = 1 for hydrogen).
- Use appropriate reduced mass μ.

$$\mu = \frac{mM}{m+M} = \frac{m}{1+m/M}$$

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

Always use the symmetry of the problem

- The potential energy *V*(*r*) of a central force depends only 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.

following Thornton-Rex p. 240-246

Equation 7.3

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

$$\psi(\mathbf{r}) = \psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) \qquad (8.11)$$

Separation of variables for the stationary state wavefunction

Application of the Schrödinger Equation

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

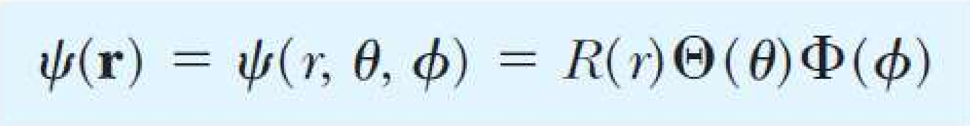
→ Equation is separable.

→ Solution are product of three functions.

→ $\psi(r,\theta,\phi) = R(r)f(\theta)g(\phi)$ Equation 7.4

- We separate Schrödinger equation, eq. 7.3, into three separate differential equations, each depending only on one coordinate: r, θ, or ϕ
- From that we will get three quantum numbers, just as we had for the 3D infinitely deep square well

Other books:



$$\psi(\mathbf{r}) = \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

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*(*θ*), and *g*(*ϕ*).

Separation of Variables

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

- 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. above by **-** $r^2\sin^2\theta / Rfg$, *rearrange*

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

sign error in book

Equation 7.7

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 identity 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-angular equation**

Equation 7.8

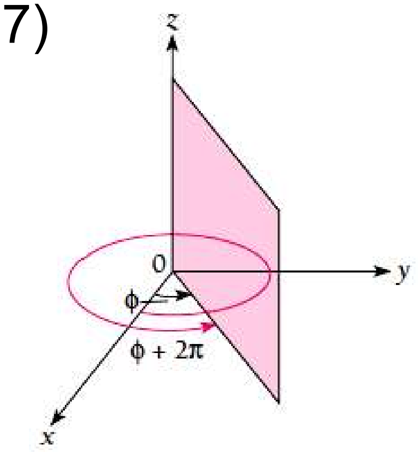


Figure 6.2 The angles ϕ and $\phi + 2\pi$ both indentify the same meridian plane.

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

note the *i* in the exponent

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.

- **Set the left side of Eq (7.7) equal** to $-m_\ell^2$ and rearrange

Equation 7.9

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

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

Solution of the Schrödinger Equation

- Set each side of Eq (7.9) equal to constant ℓ(ℓ + 1) and rearrange

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

----**Radial equation**

Equation 7.10

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

---- **zenithal-angular equation**

Equation 7.11

- **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. Now solutions need to be found for the boundary conditions …**
- No longer need of dealing with partial differentials !!
- Everything falls into place by boundary conditions, that wavefunction amplitudes need to go to zero at infinity, that they need to be single valued, ….

Types of Quantum Numbers

- The appropriate boundary conditions to Eq (7.10) and (7.11) lead to the following restrictions on the quantum numbers ℓ and m_ℓ:
  - $\ell = 0, 1, 2, 3, \ldots \ell < n$, $n >= 0$, positive integer
  - $m_\ell = -\ell, -\ell + 1, \ldots, -2, -1, 0, 1, 2, . \ell . , \ell - 1, \ell$
  - $|m_\ell| \le \ell$.

- The predicted (sharp) energy levels depend only on principle quantum number *n*, lots of degeneracy

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

$E_1 = E_0$ when n = 1, ground state

- **n > 0, integer**, all quantum numbers can become very large for very highly excited states – transition to classical physics

n = 7 max for ground state of all atoms, > approx. 50 to 500 for Rydberg atoms

How many periods are there in the periodic table of chemical elements?

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 polynomials*.

- 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 (product rule).

  Write those terms and insert the spherical electrostatic potential energy

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

Equation 7.13

Solution of the Radial Equation

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

$$\frac{dR}{dr} = -\frac{1}{a_0}R \qquad \frac{d^2R}{dr^2} = \frac{1}{a_0{}^2}R$$

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

Eq (7.14)

- Condition to satisfy Eq (7.14) for any $r > 0$ 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 in ground state*.

Both equal to the Bohr's results !!
Backed up by spectral lines !!

$$E_1 = -\frac{\hbar^2}{2\mu a_0{}^2}$$

Other books often ignore the reduced mass refinement, but we need it to explain differences in spectra of different isotopes of H, and ions of He^{+}, Li^{++}

Hydrogen Atom Radial Wave Functions

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

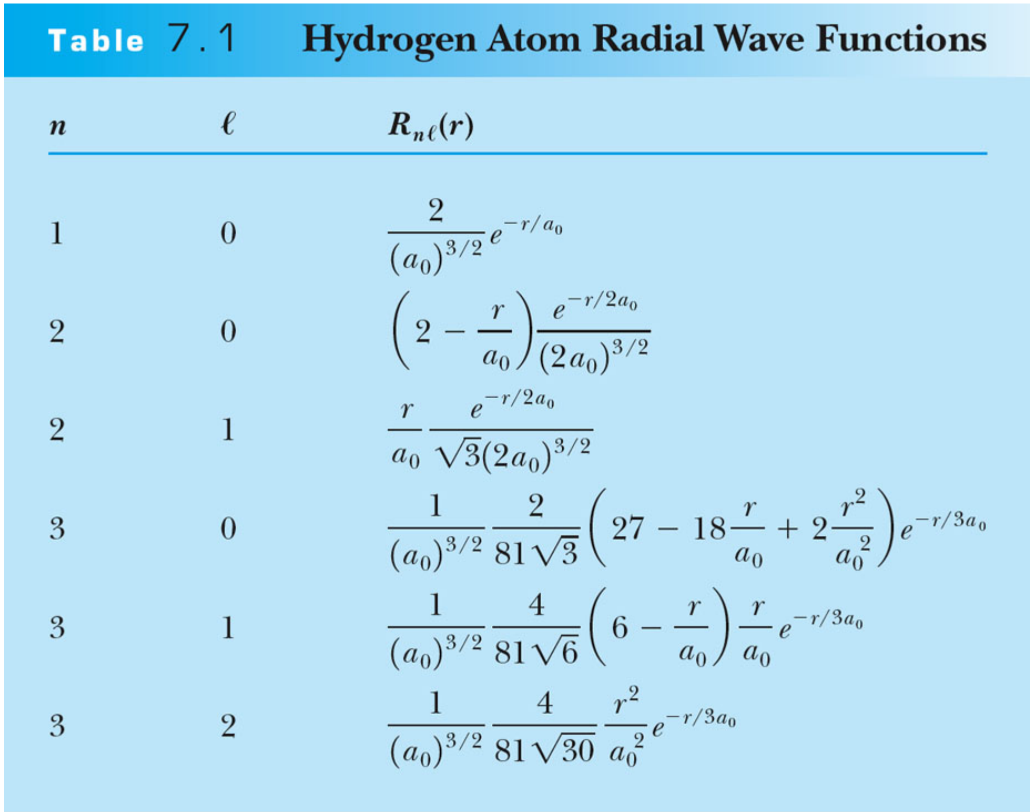


Table 7.1 Hydrogen Atom Radial Wave Functions

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

already normalized

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

associated Laguerre polynomials

Table 8.2 Some Associated Legendre Polynomials $P_\ell^{m_\ell}(\cos\theta)$

All about the zenith angle

$P_0^0 = 1$
$P_1^0 = 2\cos\theta$
$P_1^1 = \sin\theta$
$P_2^0 = 4(3\cos^2\theta - 1)$
$P_2^1 = 4\sin\theta\cos\theta$
$P_2^2 = \sin^2\theta$
$P_3^0 = 24(5\cos^3\theta - 3\cos\theta)$
$P_3^1 = 6\sin\theta(5\cos^2\theta - 1)$
$P_3^2 = 6\sin^2\theta\cos\theta$
$P_3^3 = \sin^3\theta$

Remember: l and m_l

were constants used to separate the Schrödinger equation in spherical coordinates, they were cleverly chosen and became quantum numbers

$$f = f(\theta) = \Theta(\theta)$$

Solutions to the Angular equation

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

To be normalized for usages, so in present form less useful, see full table of normalized wavefunctions below

Products of solution of the "zenith and azimuth angle dependence" Equations are spherical harmonics

- The solutions for Eq (7.8) $\frac{d^2 g}{d\phi^2} = -m_\ell{}^2 g$
- 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

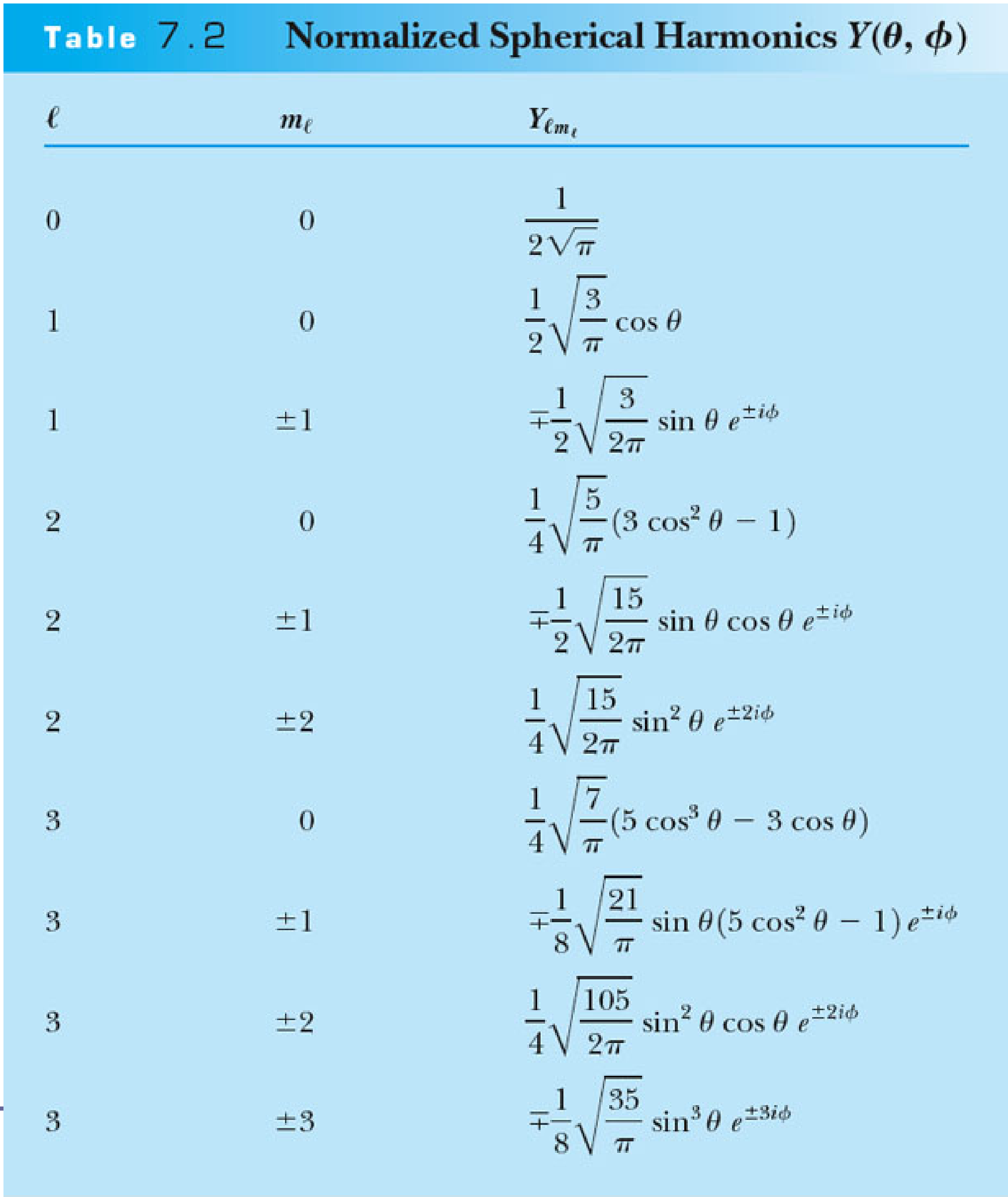


Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

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	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

Already normalized

Note that this gives us insights in 3D, none of this was part of the Bohr model

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

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

Some books prefer product of three wave functions

$$\psi(\mathbf{r}) = \psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Table 6.1 Normalized Wave Functions of the Hydrogen Atom for $n = 1, 2,$ and 3*

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$
2	1	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\, a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\, a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos\theta$
3	1	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin\theta\, e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3\cos^2\theta - 1)$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3\cos^2\theta - 1)$
3	2	±1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin\theta\cos\theta\, e^{\pm i\phi}$
3	2	±2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2\theta\, e^{\pm 2i\phi}$

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.292 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

$$\psi(\mathbf{r}) = \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Summary: Quantum Numbers

The three quantum numbers:

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

The boundary conditions wavefunctions go to zero at r goes to infinity result in :

$n = 1, 2, 3, 4, \ldots$	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:

- $n > 0$
- $0 <= \ell < n$, $\ell_{max} = n-1$
- $|m_\ell| \leq \ell$

Principal Quantum Number *n*

Because E showed up only in radial equation, *R*(*r*) and potential energy function *V*(*r*) depend only on r

The result for this quantized energy is

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

Just as in the Bohr model

- The negative sign means the energy *E* indicates that the electron and proton are bound together. $E_1 = E_0/1$

As energy depends on *n* only, there will be a lot of degeneracy due to the high symmetry of the potential (a 3D sphere has the highest symmetry that is possible in 3D)

Orbital Angular Momentum Quantum Number ℓ and spectroscopic notation

- Use letter names for the various ℓ values. When reference is to an electron

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

- electronic states are referred to by a combination of their *n* and ℓ.
- A state with *n* = 2 and ℓ = 1 is called a 2*p* state.
- The boundary conditions require *n* > ℓ.

- When referred to the H atom *S, P, D,*

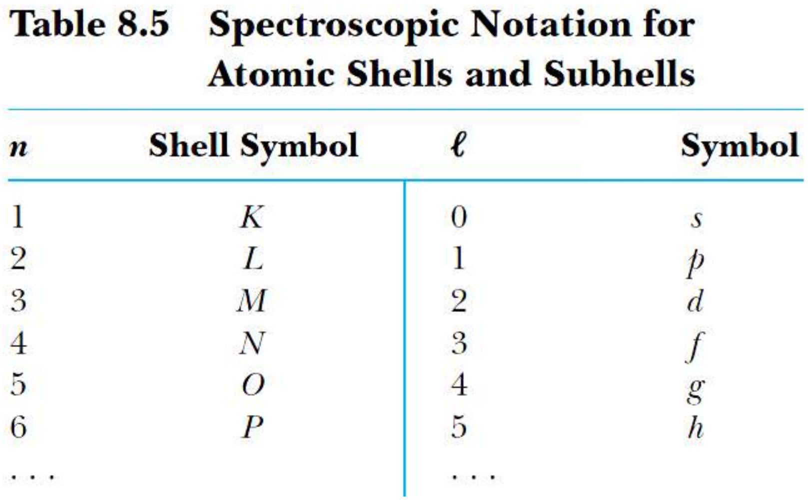


Table 8.5 Spectroscopic Notation for Atomic Shells and Subhells

n	Shell Symbol	ℓ	Symbol
1	*K*	0	*s*
2	*L*	1	*p*
3	*M*	2	*d*
4	*N*	3	*f*
5	*O*	4	*g*
6	*P*	5	*h*
. . .		. . .	

Selection rules and intensity of spectral lines results from oscillating expectation value calculations for 3D position *x in 3D = r*

A property of these wave functions

$$\int_{-\infty}^{+\infty} \psi_n^* x \psi_m \, dx = 0$$

Simplified, but meant for 3D

Oscillating expectation value determines the selection rules for each system

Whereby *n* and *m* stand for combinations of all three quantum numbers

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Each quantum number is connected to a conserved entity

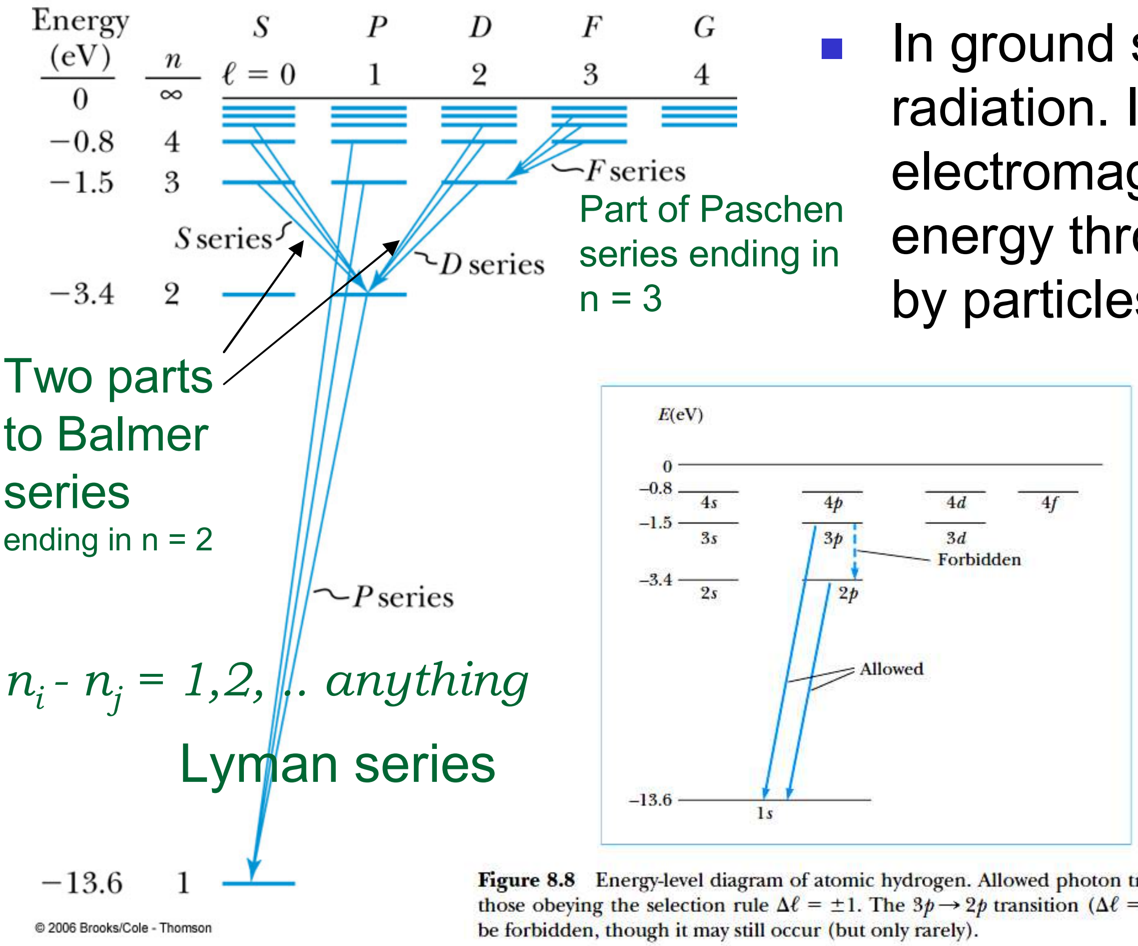
n	Principal quantum number connected with total energy
ℓ	Orbital angular momentum quantum number connected with magnitude of angular momentum
m_ℓ	Magnetic quantum number connected with z-component of angular momentum vector (per convention)

A perturbation is needed to change from one stationary state to another

Selection rules listed

Energy depends only on n, so lot of degeneracy

- For hydrogen (in the absence of a magnetic field), the energy level depends on the principle quantum number *n*.



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Part of Paschen series ending in n = 3

Two parts to Balmer series ending in n = 2

$n_i - n_j = 1, 2, \ldots$ *anything*

Lyman series

Figure 8.8 Energy-level diagram of atomic hydrogen. Allowed photon transitions are those obeying the selection rule $\Delta\ell = \pm 1$. The $3p \rightarrow 2p$ transition ($\Delta\ell = 0$) is said to be forbidden, though it may still occur (but only rarely).

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

Only transitions with

$l_i - l_j$ = +- 1 ,

$m_{li} - m_{lj}$ = +- 1 or 0

Δn arbitrary, all consequences of the forms of the wavefunctions (as discussed earlier for harmonic oscillator)

One unit of h-bar omega is removed by emission of photon, which has spin = 1

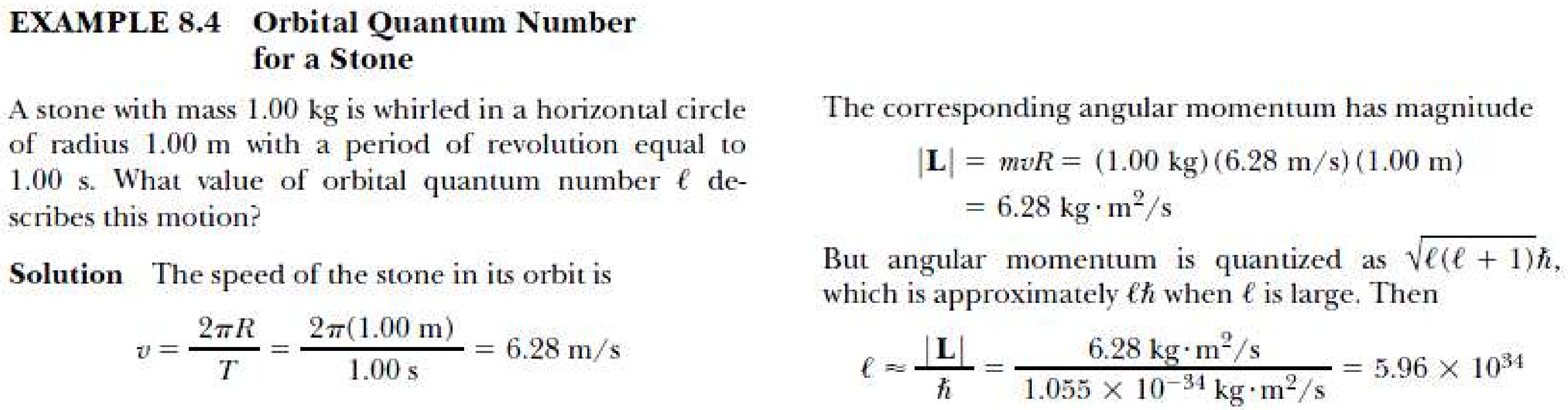
Angular Momentum as function of quantum number ℓ

- Angular momentum is associated with both the $R(r)$ and $f(\theta)$ parts of the full wave function.
- Classically, the orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$ with $L = mv_{\text{orbital}}r$ for circular motion
- ℓ is related to L by $L = \sqrt{\ell(\ell+1)}\hbar$
- In an ℓ = 0 state, $L = \sqrt{0(1)}\hbar = 0$

So no electron goes around the proton or the common center of mass, it does not have angular momentum in this state

New law of nature blatantly **disagrees** with Bohr's semi-classical "planetary" model of electrons orbiting a nucleus $L = n\hbar$, n = 1, 2, 3, … still quantized in units of $\hbar$, just not integer units

For large quantum numbers, we recover the classical results, i.e. the classical angular momentum formula for this case



EXAMPLE 8.4 Orbital Quantum Number for a Stone

A stone with mass 1.00 kg is whirled in a horizontal circle of radius 1.00 m with a period of revolution equal to 1.00 s. What value of orbital quantum number ℓ describes this motion?

Solution The speed of the stone in its orbit is

$$v = \frac{2\pi R}{T} = \frac{2\pi(1.00\ \text{m})}{1.00\ \text{s}} = 6.28\ \text{m/s}$$

The corresponding angular momentum has magnitude

$$|\mathbf{L}| = mvR = (1.00\ \text{kg})(6.28\ \text{m/s})(1.00\ \text{m}) = 6.28\ \text{kg}\cdot\text{m}^2/\text{s}$$

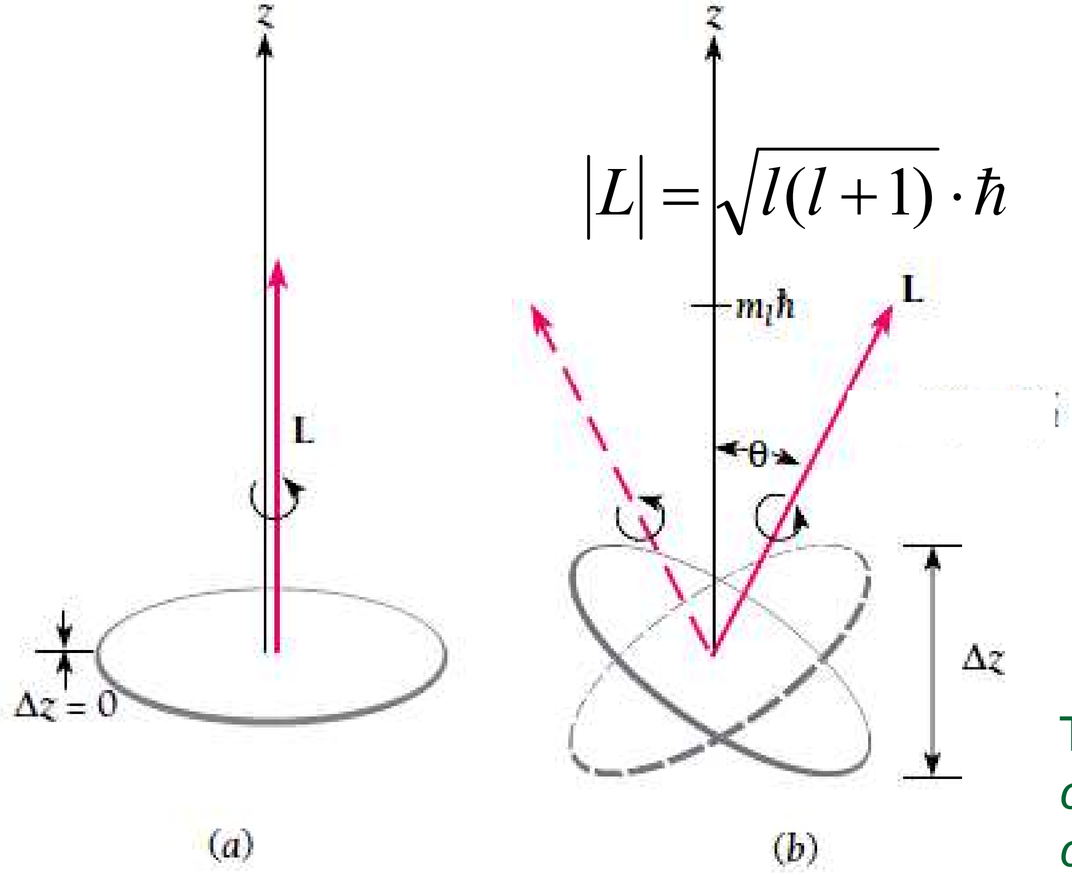
But angular momentum is quantized as $\sqrt{\ell(\ell+1)}\hbar$, which is approximately $\ell\hbar$ when ℓ is large. Then

$$\ell \approx \frac{|\mathbf{L}|}{\hbar} = \frac{6.28\ \text{kg}\cdot\text{m}^2/\text{s}}{1.055 \times 10^{-34}\ \text{kg}\cdot\text{m}^2/\text{s}} = 5.96 \times 10^{34}$$

Bohr’s correspondence principle

Angular momentum is subject to an uncertainty principle, because it is momentum about a certain axis $\Delta L \, \Delta \phi \leq h/2\pi$

Only visualizations of mathematical models



$$|L| = \sqrt{l(l+1)} \cdot \hbar$$

Figure 6.5 The uncertainty principle prohibits the angular momentum vector **L** from having a definite direction in space.

We can just know the magnitude of the angular momentum vector and one of the components of this vector, we choose the z-component by convention, note its connection to m_l

This θ is discrete not *coordinate θ, which is continuous*

(a) Forbidden by the uncertainty principle (b) about any possible z-axis all the time, the projection of L on z-axis is sharp

Space quantization, a consequence of the uncertainty principle and wavical properties

Only classically

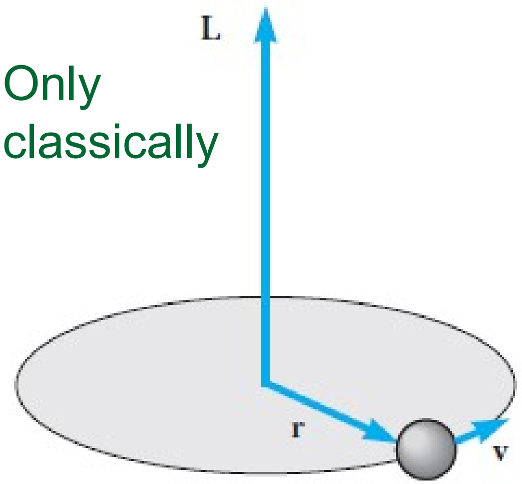


Figure 8.6 The angular momentum **L** of an orbiting particle is perpendicular to the plane of the orbit. If the direction of **L** were known precisely, both the coordinate and momentum in the direction perpendicular to the orbit would be known, in violation of the uncertainty principle.

What is wrong with (a)?

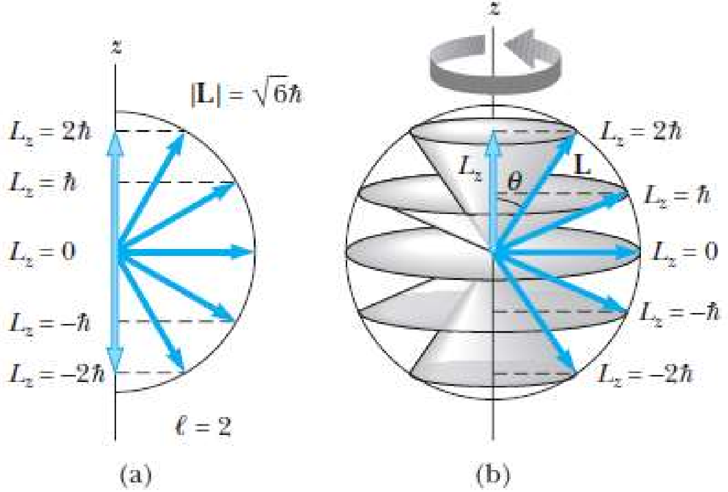


Figure 8.7 (a) The allowed projections of the orbital angular momentum for the case $\ell = 2$. (b) From a three-dimensional perspective, the orbital angular momentum vector **L** lies on the surface of a cone. The fuzzy character of L_x and L_y is depicted by allowing **L** to precess about the z-axis, so that L_x and L_y change continually while L_z maintains the fixed value $m_\ell \hbar$.

Angular momentum is conserved in classical physics, and as a rule of thumb, classically conserved quantities are sharp in quantum mechanics, also there are different expressions of the uncertainty principle

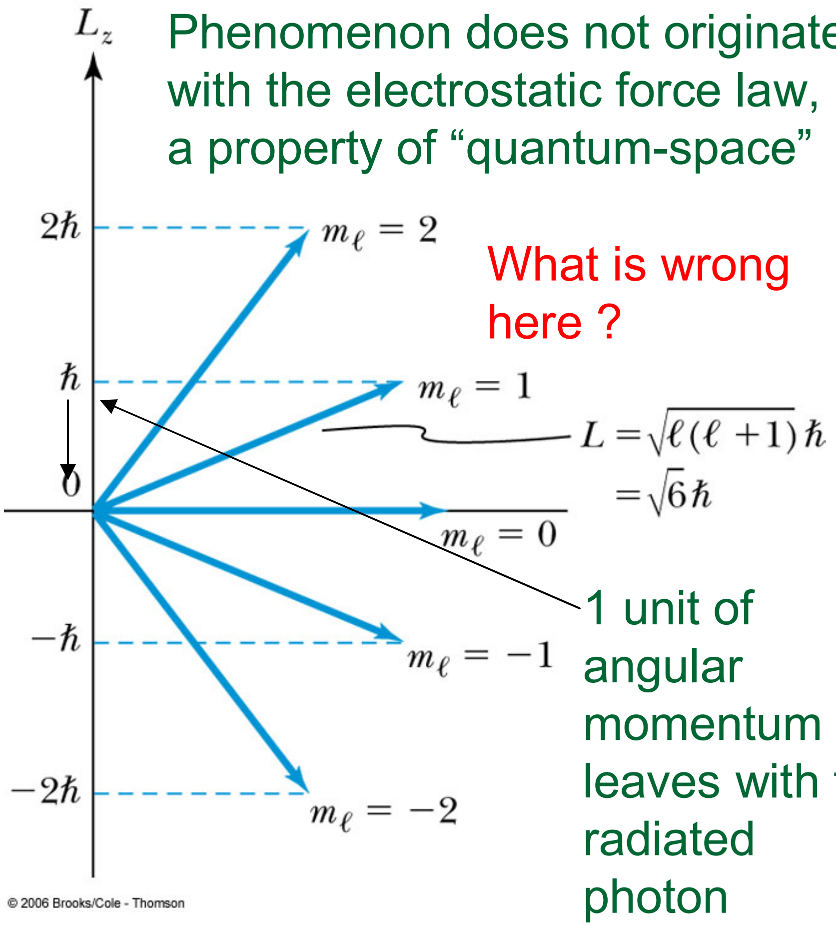
Only the magnitude of angular momentum will have a sharp value and one of its component, we typically choose the z- component

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



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Phenomenon does not originate with the electrostatic force law, is a property of "quantum-space"

What is wrong here ?

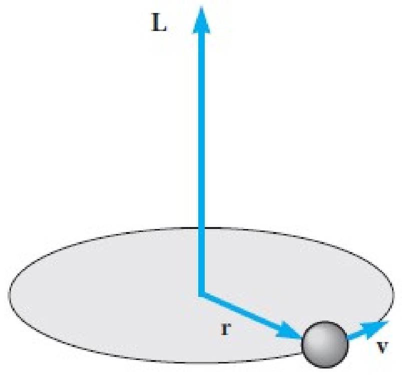
1 unit of angular momentum leaves with the radiated photon

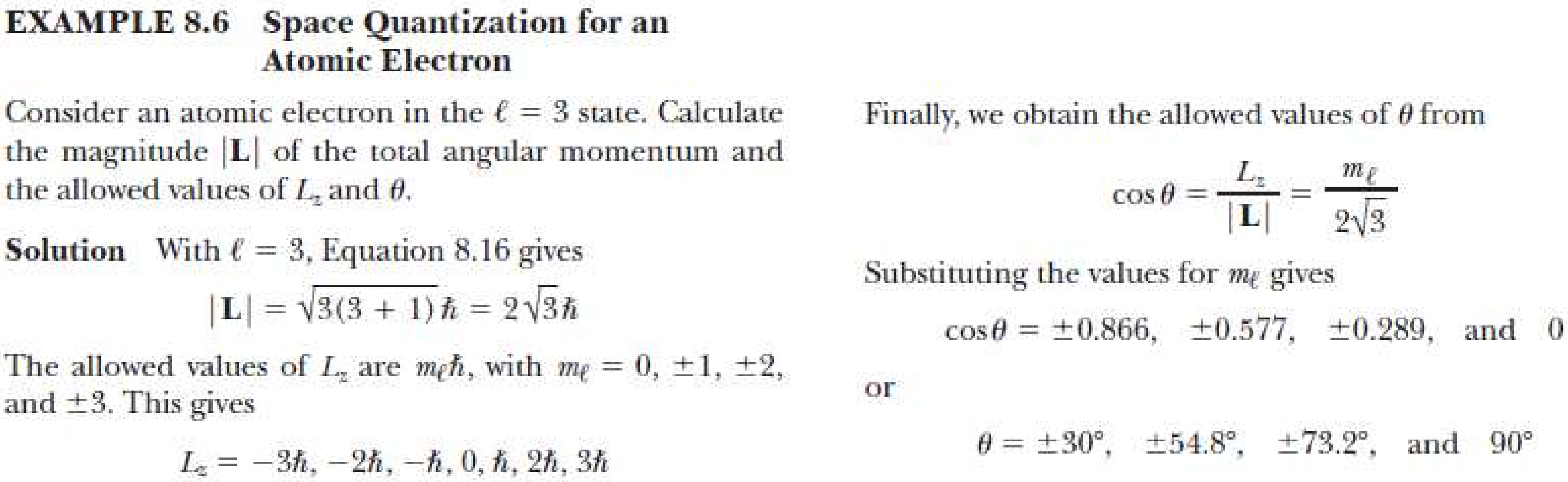
This θ is not coordinate θ!

$$\cos\theta = \frac{L_z}{|\mathbf{L}|} = \frac{m_\ell}{\sqrt{\ell(\ell+1)}}$$

What happens if m_l and l get very large? Bohr's correspondence principle

For classical physics, smallest discrete zenith angle θ becomes essentially zero, looks then like a continuous variable, uncertainty principle is no longer noticeable





EXAMPLE 8.6 Space Quantization for an Atomic Electron

Consider an atomic electron in the $\ell = 3$ state. Calculate the magnitude $|\mathbf{L}|$ of the total angular momentum and the allowed values of L_z and θ.

Solution With $\ell = 3$, Equation 8.16 gives

$$|\mathbf{L}| = \sqrt{3(3+1)}\,\hbar = 2\sqrt{3}\,\hbar$$

The allowed values of L_z are $m_\ell \hbar$, with $m_\ell = 0, \pm 1, \pm 2$, and ± 3. This gives

$$L_z = -3\hbar, -2\hbar, -\hbar, 0, \hbar, 2\hbar, 3\hbar$$

Finally, we obtain the allowed values of θ from

$$\cos\theta = \frac{L_z}{|\mathbf{L}|} = \frac{m_\ell}{2\sqrt{3}}$$

Substituting the values for m_ℓ gives

$$\cos\theta = \pm 0.866, \quad \pm 0.577, \quad \pm 0.289, \quad \text{and} \quad 0$$

or

$$\theta = \pm 30^\circ, \quad \pm 54.8^\circ, \quad \pm 73.2^\circ, \quad \text{and} \quad 90^\circ$$

other angles for other angular momentum quantum numbers, always one unit of angular momentum is accepted or lost in an atomic transition that leads to a spectral line

Probability Distribution Functions

- from wave functions one calculates the probability density distributions of the electron.

- The “position” of the electron is spread over space and not well defined.

- We 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 *dτ* is $dP = \psi^*(r,\theta,\phi)\ \psi(r,\theta,\phi)\ d\tau$.

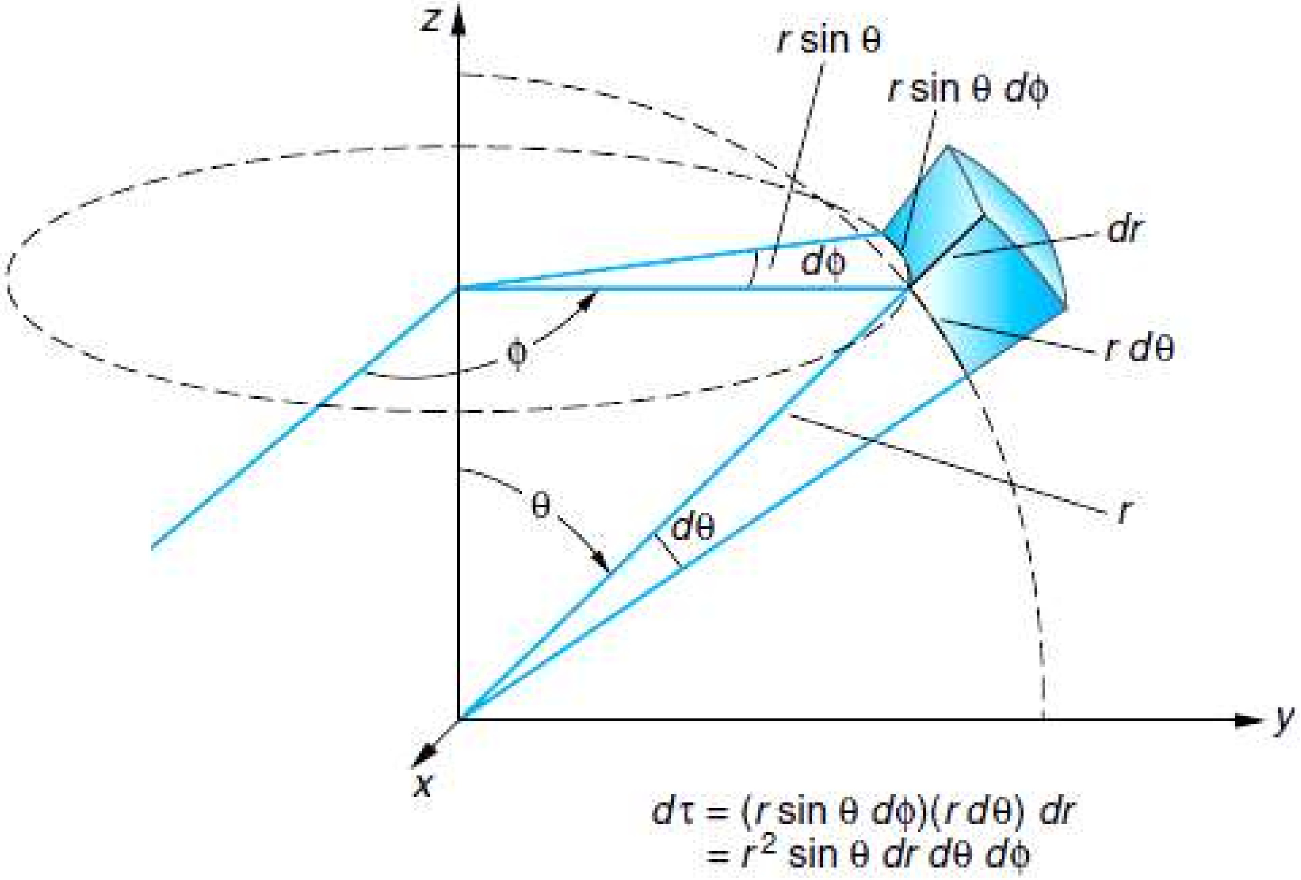


Figure 7-7 Volume element $d\tau$ in spherical coordinates.

$$P = \int \psi^*(r,\theta,\phi) \cdot \psi(r,\theta,\phi) \cdot d\tau$$

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

Radial part of Probability Distribution Functions

- The differential volume element in spherical polar coordinates is

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

Are both 1 due to normalization !!

Therefore,

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

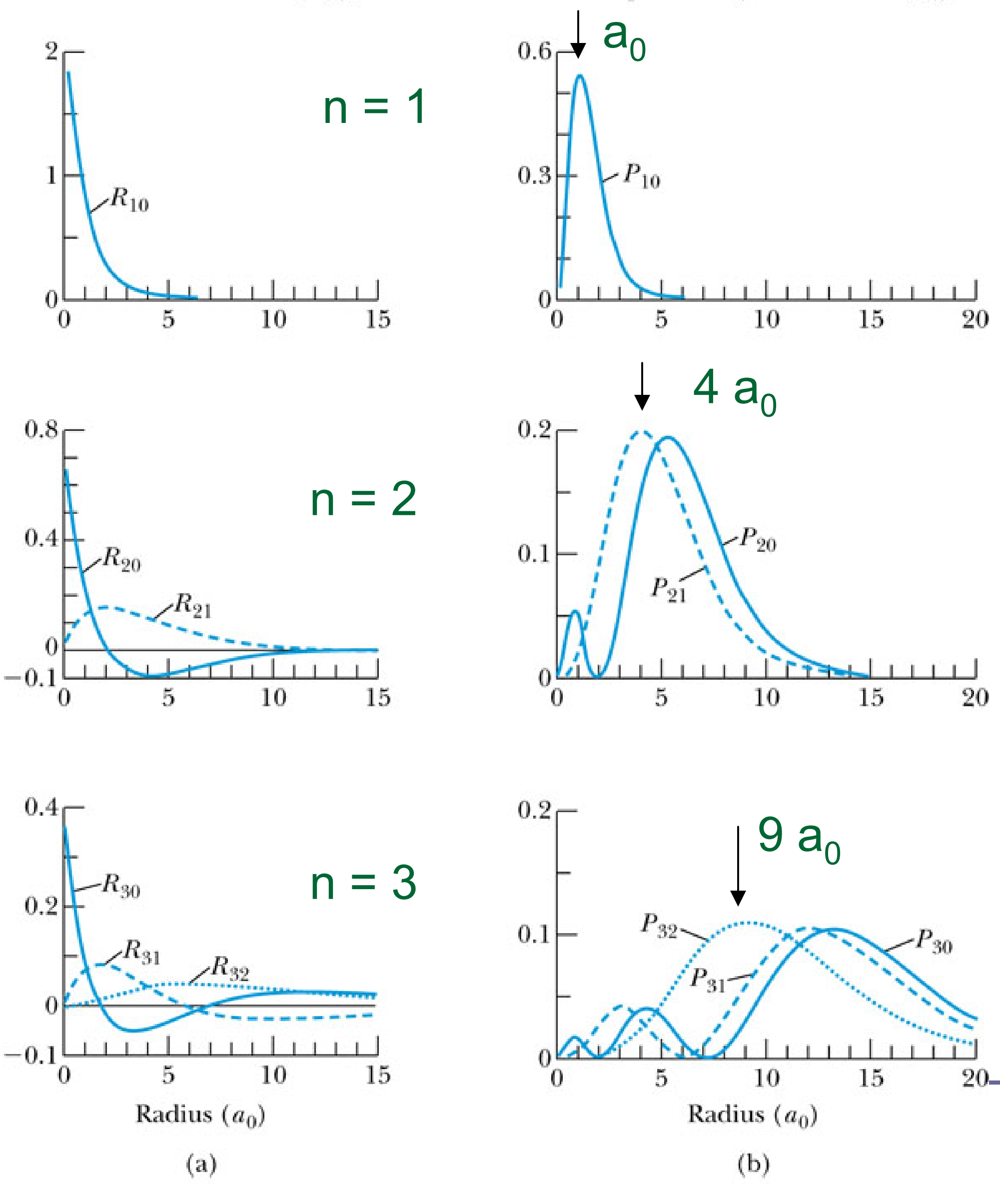
- We are at first interested in the radial dependence.

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

- The radial probability density is $P_{nl}(r) = r^2|R_{nl}(r)|^2$ (and it depends only on n and l.

all R(r) functions are real, stationary states

Probability Distribution Functions



n = 1

a_0

n = 2

4 a_0

n = 3

9 a_0

- $R_{n,l}(r)$ and $P_{n,l}(r)$ for the lowest-lying states of the hydrogen atom.

In units of Bohr radius

It is always the states with the highest l for each n that "correspond" to the Bohr radii predictions.

Actually a_0 is just a length scale as nothing is moving in the ground state – no angular momentum

Why the extra r^2 factor?, see also slide 31

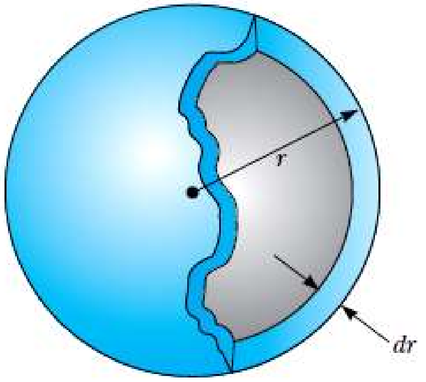


Figure 8.9 $P(r)\ dr$ is the probability that the electron will be found in the volume of a spherical shell with radius r and thickness dr. The shell volume is just $4\pi r^2\ dr$.

For all "hydrogen like" ions, i.e. He^+, Li^{++}, …

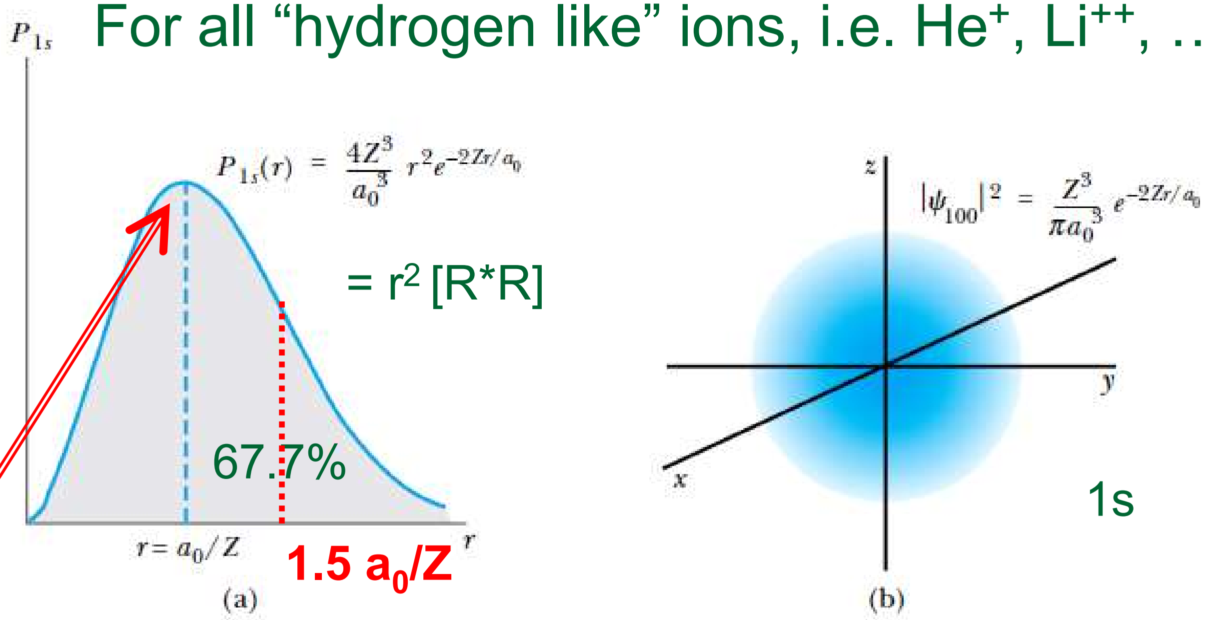


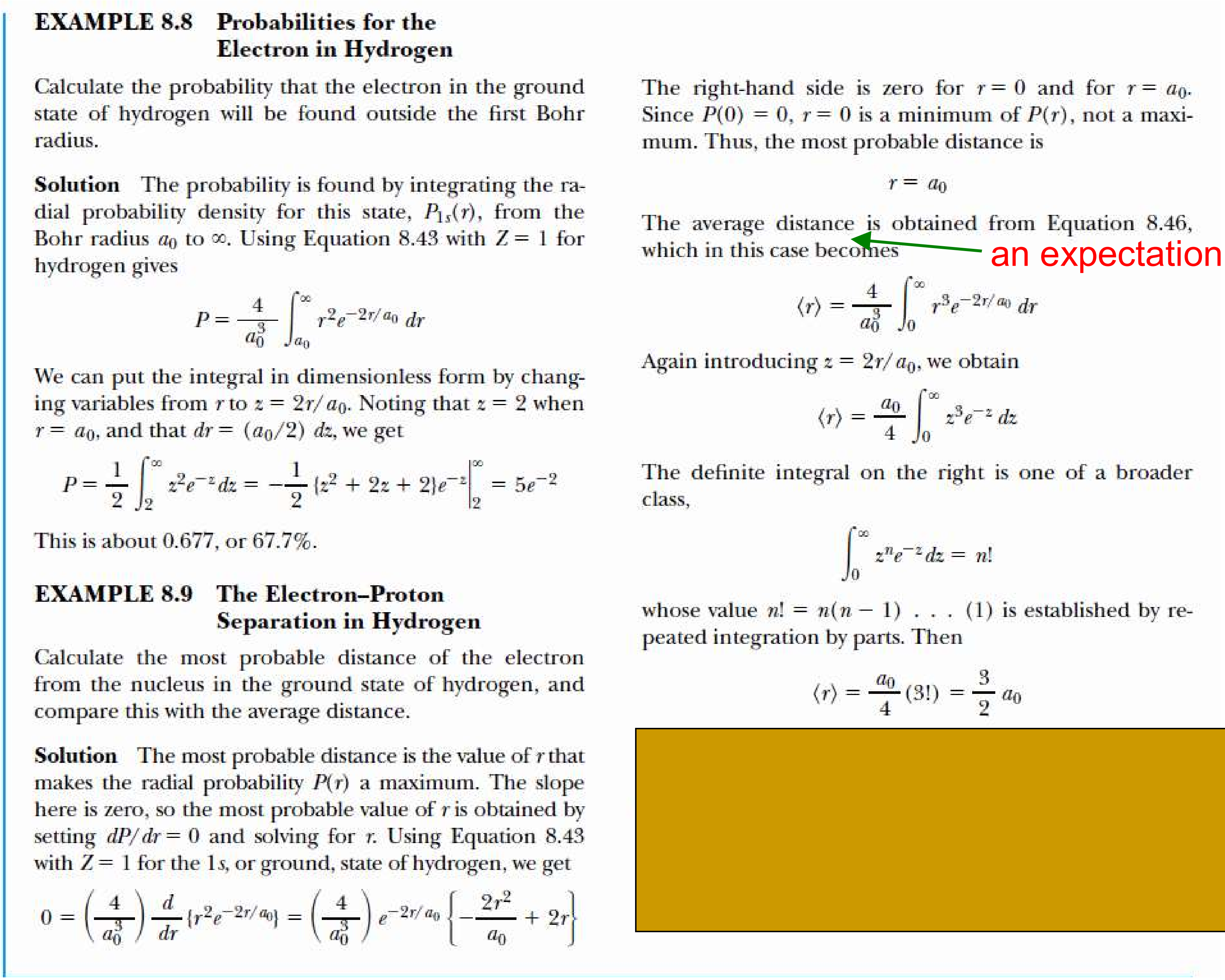
Figure 8.10 (a) The curve $P_{1s}(r)$ representing the probability of finding the electron as a function of distance from the nucleus in a 1s hydrogen-like state. Note that the probability takes its maximum value when r equals a_0/Z. (b) The spherical electron "cloud" for a hydrogen-like 1s state. The shading at every point is proportional to the probability density $|\psi_{1s}(\mathbf{r})|^2$.

First Bohr radius, maximum of probability density for n = 1, $\ell = 0$

Max of P_{1s} $\qquad$ $dP_{1s} / dr = 0$

$$\langle r \rangle_{n,l} = \int_0^\infty r P(r)\ dr$$

Is the expectation value of the smallest radius in the hydrogen atom also the Bohr radius, i.e. the length scale with the highest probability density?



EXAMPLE 8.8 Probabilities for the Electron in Hydrogen

Calculate the probability that the electron in the ground state of hydrogen will be found outside the first Bohr radius.

Solution The probability is found by integrating the radial probability density for this state, $P_{1s}(r)$, from the Bohr radius a_0 to ∞. Using Equation 8.43 with $Z = 1$ for hydrogen gives

$$P = \frac{4}{a_0^3} \int_{a_0}^{\infty} r^2 e^{-2r/a_0}\, dr$$

We can put the integral in dimensionless form by changing variables from r to $z = 2r/a_0$. Noting that $z = 2$ when $r = a_0$, and that $dr = (a_0/2)\, dz$, we get

$$P = \frac{1}{2} \int_{2}^{\infty} z^2 e^{-z}\, dz = -\frac{1}{2} \{z^2 + 2z + 2\} e^{-z} \Big|_{2}^{\infty} = 5e^{-2}$$

This is about 0.677, or 67.7%.

EXAMPLE 8.9 The Electron–Proton Separation in Hydrogen

Calculate the most probable distance of the electron from the nucleus in the ground state of hydrogen, and compare this with the average distance.

Solution The most probable distance is the value of r that makes the radial probability $P(r)$ a maximum. The slope here is zero, so the most probable value of r is obtained by setting $dP/dr = 0$ and solving for r. Using Equation 8.43 with $Z = 1$ for the $1s$, or ground, state of hydrogen, we get

$$0 = \left(\frac{4}{a_0^3}\right) \frac{d}{dr} \{r^2 e^{-2r/a_0}\} = \left(\frac{4}{a_0^3}\right) e^{-2r/a_0} \left\{-\frac{2r^2}{a_0} + 2r\right\}$$

The right-hand side is zero for $r = 0$ and for $r = a_0$. Since $P(0) = 0$, $r = 0$ is a minimum of $P(r)$, not a maximum. Thus, the most probable distance is

$$r = a_0$$

The average distance is obtained from Equation 8.46, which in this case becomes

an expectation value

$$\langle r \rangle = \frac{4}{a_0^3} \int_{0}^{\infty} r^3 e^{-2r/a_0}\, dr$$

Again introducing $z = 2r/a_0$, we obtain

$$\langle r \rangle = \frac{a_0}{4} \int_{0}^{\infty} z^3 e^{-z}\, dz$$

The definite integral on the right is one of a broader class,

$$\int_{0}^{\infty} z^n e^{-z}\, dz = n!$$

whose value $n! = n(n-1) \ldots (1)$ is established by repeated integration by parts. Then

$$\langle r \rangle = \frac{a_0}{4} (3!) = \frac{3}{2} a_0$$

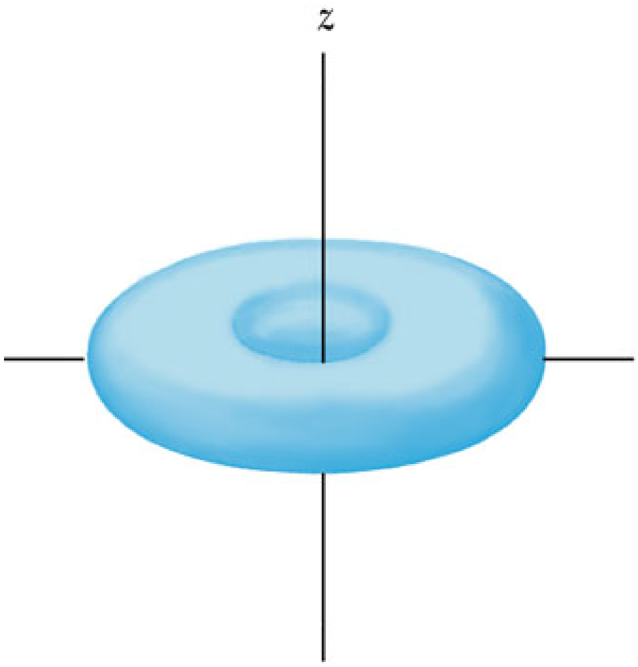
[redacted]

Full Probability Distribution Functions

- orbitals, complex conjugate squares of full wavefunctions

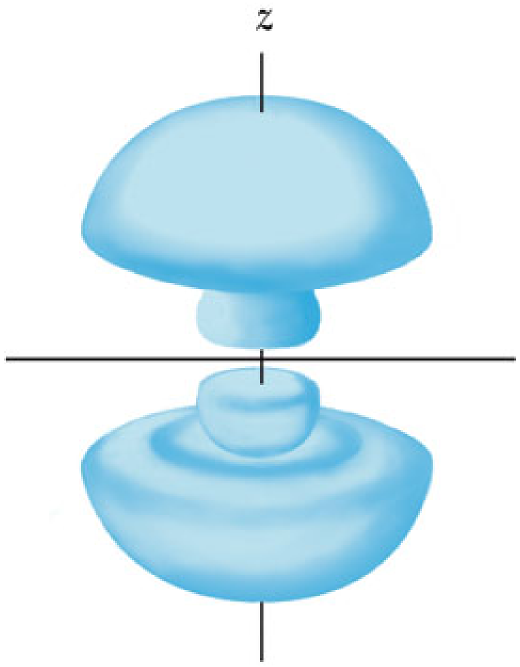
$$P = \int \psi^*(r,\theta,\phi)\cdot\psi(r,\theta,\phi)\cdot d\tau$$

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



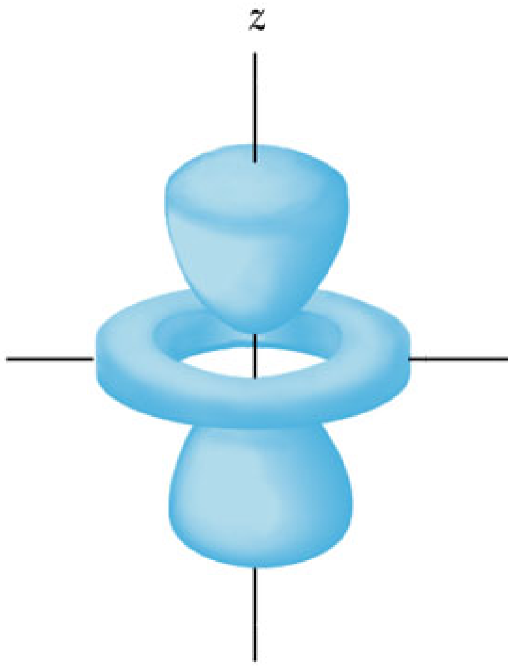
2p

$n = 2$
$\ell = 1$
$m_\ell = \pm 1$



3p

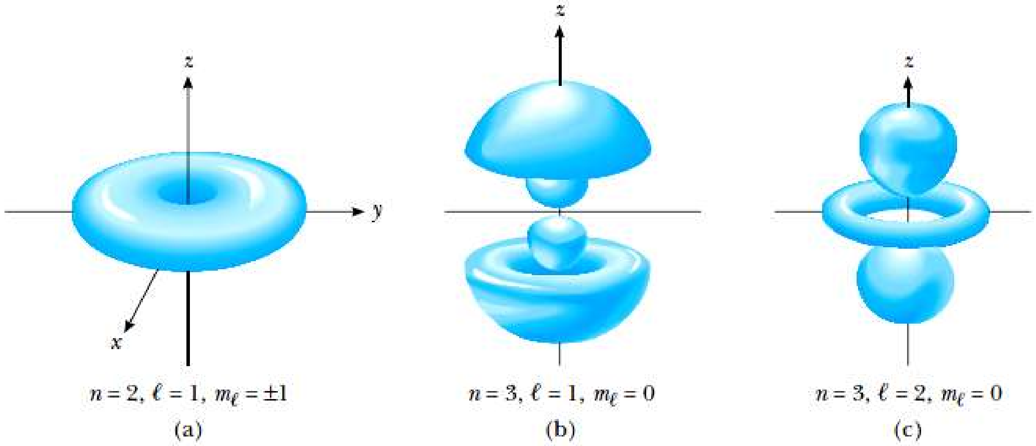
$n = 3$
$\ell = 1$
$m_\ell = 0$



3d

$n = 3$
$\ell = 2$
$m_\ell = 0$

Probabilities per unit volume fall of monotonically as *r* gets large, zero at infinity, so isolated hydrogen atom has no real size



$n = 2, \ell = 1, m_\ell = \pm 1$
(a)

$n = 3, \ell = 1, m_\ell = 0$
(b)

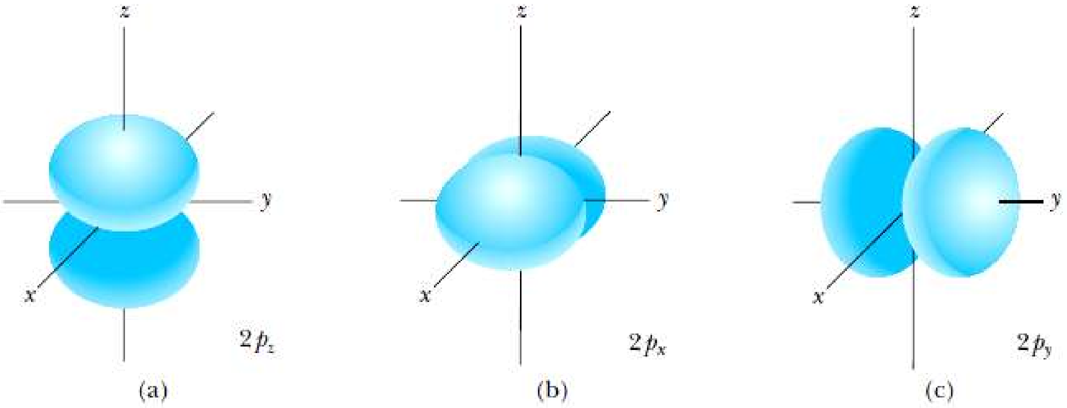
$n = 3, \ell = 2, m_\ell = 0$
(c)

Figure 8.12 (a) The probability density $|\psi_{211}|^2$ for a hydrogen-like $2p$ state. Note the axial symmetry about the z-axis. (b) and (c) The probability densities $|\psi(\mathbf{r})|^2$ for several other hydrogen-like states. The electron "cloud" is axially symmetric about the z-axis for all the hydrogen-like states $\psi_{n\ell m_\ell}(\mathbf{r})$.

These orbital models are just for some fixed value of probability density, e.g. 85 %, some other books may show them for 90 %

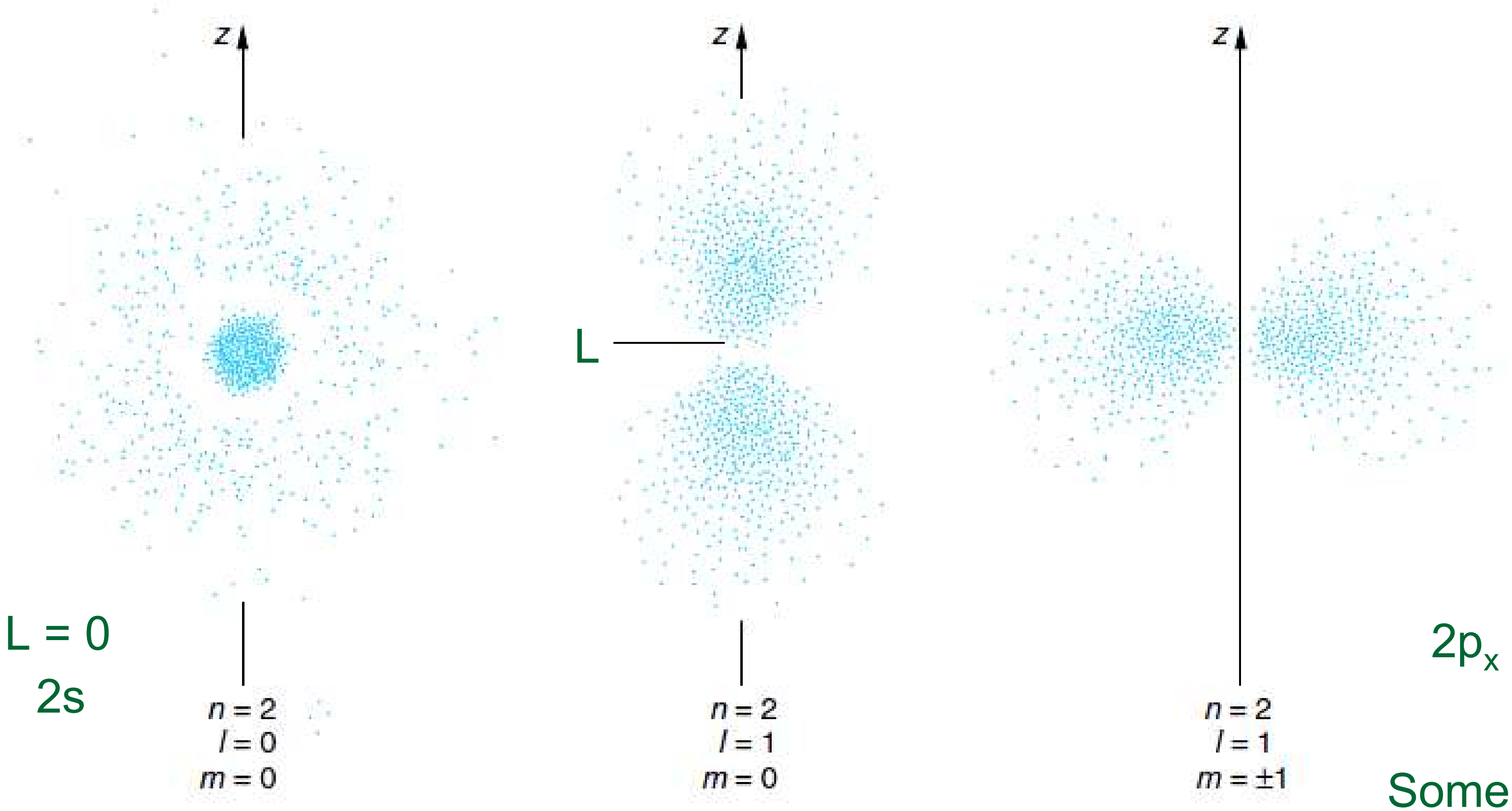
$$[\psi_{2p}]_y = \frac{1}{\sqrt{2}}\{\psi_{211} - \psi_{21-1}\}$$

Any two wavefunctions can be added to give another wavefunction (linearity of the Schrödinger equation)



(a) (b) (c)

Figure 8.13 (a) Probability distribution for an electron in the hydrogenlike $2p_z$ state, described by the quantum numbers $n = 2$, $\ell = 1$, $m_\ell = 0$. (b) and (c) Probability distributions for the $2p_x$ and $2p_y$ states. The three distributions $2p_x$, $2p_y$, and $2p_z$ have the same structure, but differ in their spatial orientation.



$2p_x$ and $2p_y$

Some books drop the index l on the m

Figure 7-11 Probability densities $\psi^*\psi$ for the $n = 2$ states in hydrogen. The probability is spherically symmetric for $\ell = 0$. It is proportional to $\cos^2\theta$ for $\ell = 1, m = 0$, and to $\sin^2\theta$ for $\ell = 1, m = \pm 1$. The probability densities have rotational symmetry about the z axis. Thus, the three-dimensional charge density for the $\ell = 1, m = 0$ state is shaped roughly like a dumbbell, while that for the $\ell = 1, m = \pm 1$ states resembles a doughnut, or toroid. The shapes of these distributions are typical for all atoms in S states ($\ell = 0$) and P states ($\ell = 1$) and play an important role in molecular bonding. [*This computer-generated plot courtesy of Paul Doherty, The Exploratorium.*]

You can rotate these figures around the z axis in your head in order to get the orbitals back

So far the H atom model with a central Coulomb potential energy function, how does it hold up experimentally?

Measurements of spectral line are energy-level measurements, can be pretty accurate, many more than a single atoms is typically involved, so we get statistical results, later on we deal with that kind of thing with statistical physics

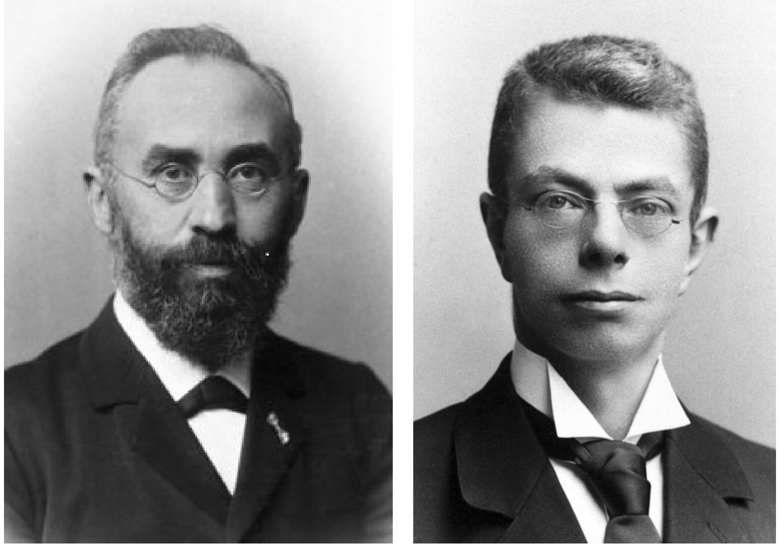
7.4: Magnetic effect on hydrogen atom spectra

- The Dutch physicist Pieter Zeeman (and 1902 physics Nobelist) observed with a state of the art spectrometer of the time, (which we would now consider pretty crude) that many spectral lines split in a magnetic field into **three** (and more) spectral lines, one stays at the original position, the spacing of the other two depends linearly on the strength of the magnetic field. It is called the **Zeeman effect**.
- A good theory of the hydrogen atom needs to explain this !!

Normal Zeeman effect, which is actually **not** observed with modern spectrometers, historically "normal" because of easy explanation

Model the electron in the H atom as a small permanent magnet.

- Think of an electron as an orbiting circular current loop of $I = dq / dt$ around some nucleus (that was not known to exist at that time).
- The current loop has a magnetic moment μ and the period $T = 2\pi r / v$. (don't confuse this μ *with reduced mass)*
- $\vec{\mu} = -\frac{e}{2m}\vec{L}$ where $L = mvr$ is the magnitude of the orbital angular momentum for a circular path.



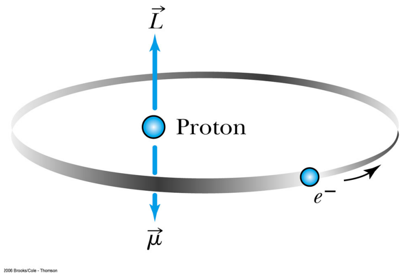
Born: 25 May 1865

The Nobel Prize in Physics 1902 was awarded jointly to Hendrik Antoon Lorentz and Pieter Zeeman *"in recognition of the extraordinary service they rendered by their researches into the influence of magnetism upon radiation phenomena."*

Lorentz was postulating the existence of electrons in atoms well before they were actually discovered by J.J. Thomson in 1897 and before there was physical evidence of the existence of atoms by Einstein, 1905 (only clever combination of literature values), experiments done in 1907 by Perrin at higher level confirms atoms, nucleus 1913 (Rutherford’s group)

The "Normal" Zeeman Effect

We initially ignore space quantization and the uncertainty principle for the sake of the (essentially wrong) argument



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- When there is no magnetic field to align them, $\vec{\mu}$ doesn't have an effect on total energy. In an external magnetic field a dipole has a potential energy

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

If there is a magnetic field $\vec{B}$ in direction z, it will act on the magnetic moment, this brings in an (extra) potential energy term into the Hamiltonian operator

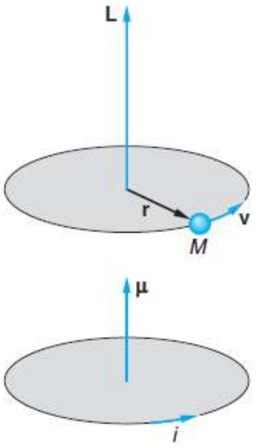


Figure 7-12 A particle moving in a circle has angular momentum **L**. If the particle has a positive charge, the magnetic moment due to the current is parallel to **L**.

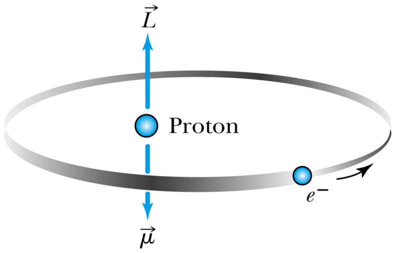
For electron opposite direction

- So an external magnetic field should have an effect on atoms, spectral lines are "fingerprint" characteristics of atoms, in an external magnetic field, each spectral line should be splitting into three lines, distance between two extra lines proportional to the strength of the magnetic field, tested by experiment, observed, part of Nobel prize

Back to quantum mechanics: as |L| magnitude and z-component of L vector are both quantized in hydrogen

$$\mu_z = \frac{e\hbar}{2m} m_\ell = -\mu_B m_\ell$$

$\mu_B = e\hbar / 2m$ is called a **Bohr magneton ≈ 5.7858 10^{-5} eV T^{-1}**. (depends on the reduced mass)

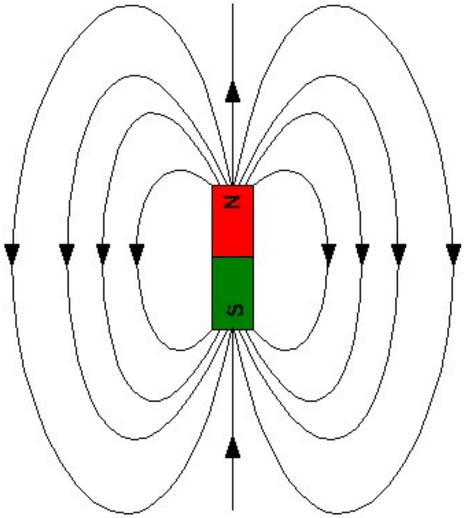


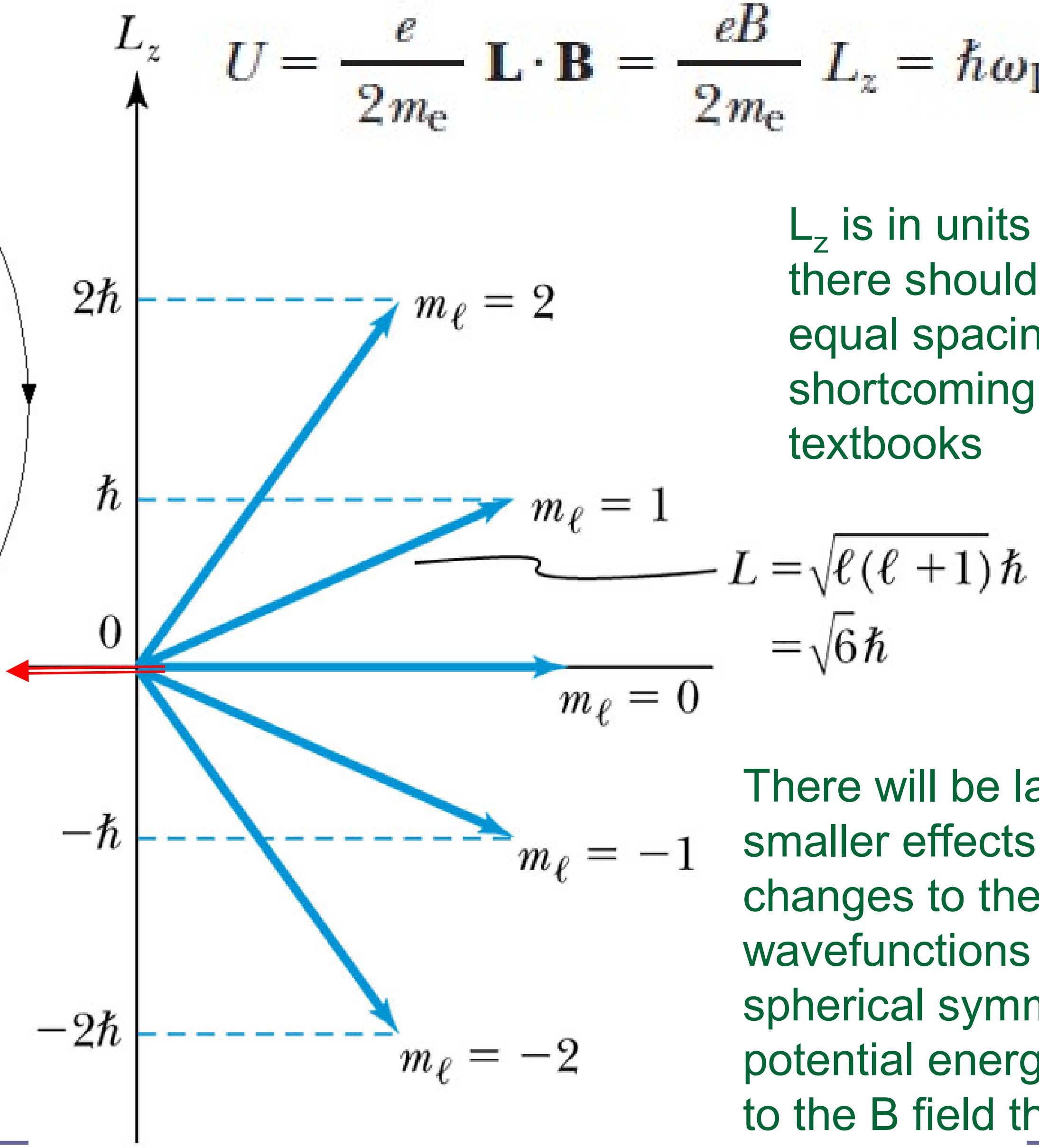
$$\vec{\mu} = -\mu_B \vec{L} / \hbar$$

We get quantized contribution to the potential energy (in the Hamiltonian), combined with space quantization, m_l being a positive, zero, or negative integer

m is mass of the electron, better to use its reduces mass, depends on the nucleus

$$U = \frac{e}{2m_e}\mathbf{L}\cdot\mathbf{B} = \frac{eB}{2m_e}L_z = \hbar\omega_L m_\ell$$





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L_z is in units of h-bar, there should be an equal spacing, typical shortcoming of textbooks

External magnetic field acts on magnetic moments of different m_l states for the same magnitude of L-vector differently, no effect for m_l = 0 state

There will be larger and smaller effects, forces, changes to the wavefunctions for a spherical symmetric potential energy function due to the B field that is conveniently oriented along the z-axis

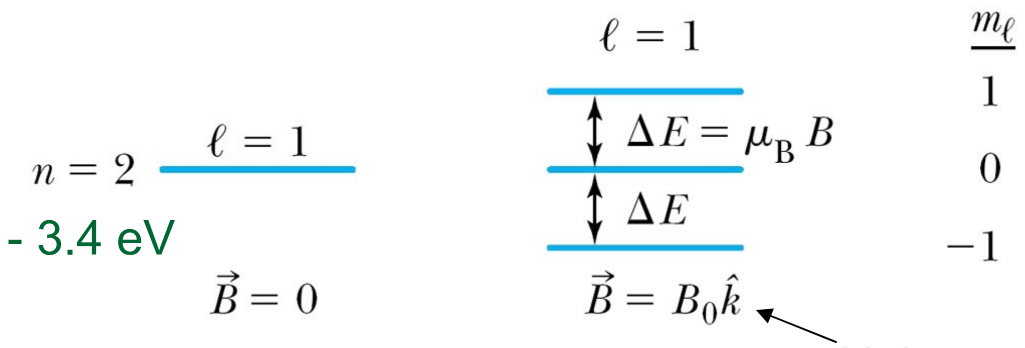
The “Normal” Zeeman Effect for Hydrogen

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

$$V_B = -\mu_z B = +\mu_B m_\ell B$$

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

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



- 3.4 eV

Unit vector in z-direction

$\mu_B = e\hbar / 2m$ is called a **Bohr magneton, ≈ 9.27 10^{-24} Ws T^{-1}**.

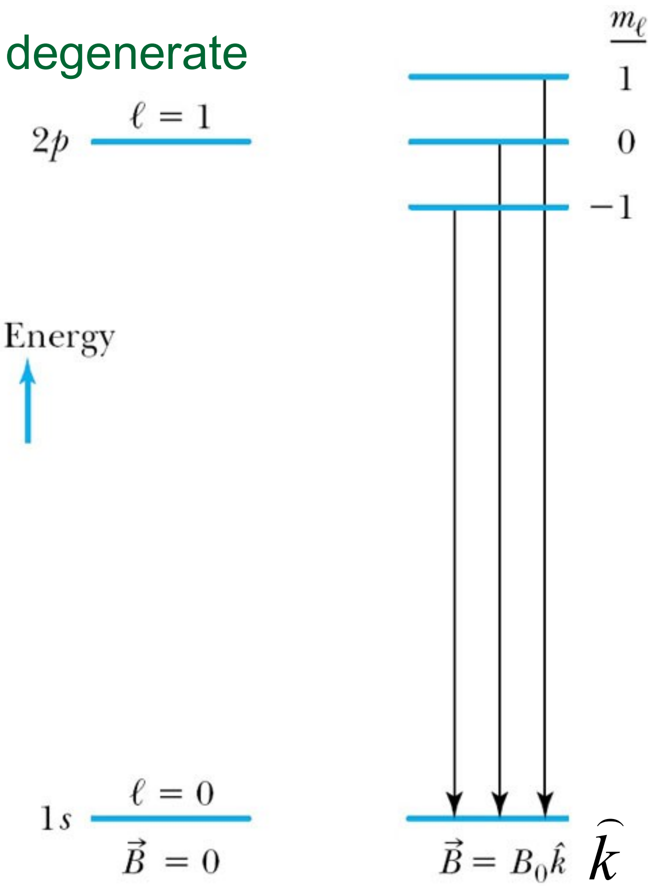
Don’t confuse $\vec{\mu}$ with the reduced mass of the electron μ

The “Normal” Zeeman Effect

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

$\Delta E = 2\,\mu_B\,B$

All degenerate



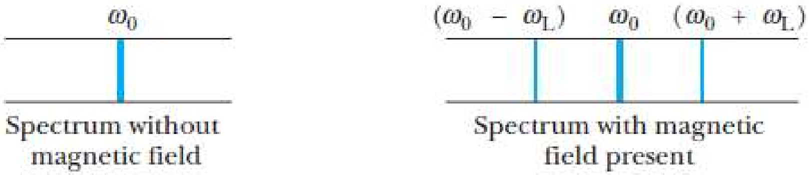
$\hat{k}\_parallel\_\vec{z}$

The larger B, the larger the splitting, if B is switched off suddenly, the three lines combine as if nothing ever happened, total intensity of lines remains constant in the splitting

Larmor frequency

B strength dependent

$$U = \frac{e}{2m_e}\mathbf{L}\cdot\mathbf{B} = \frac{eB}{2m_e}L_z = \hbar\omega_L m_\ell$$



Spectrum without magnetic field

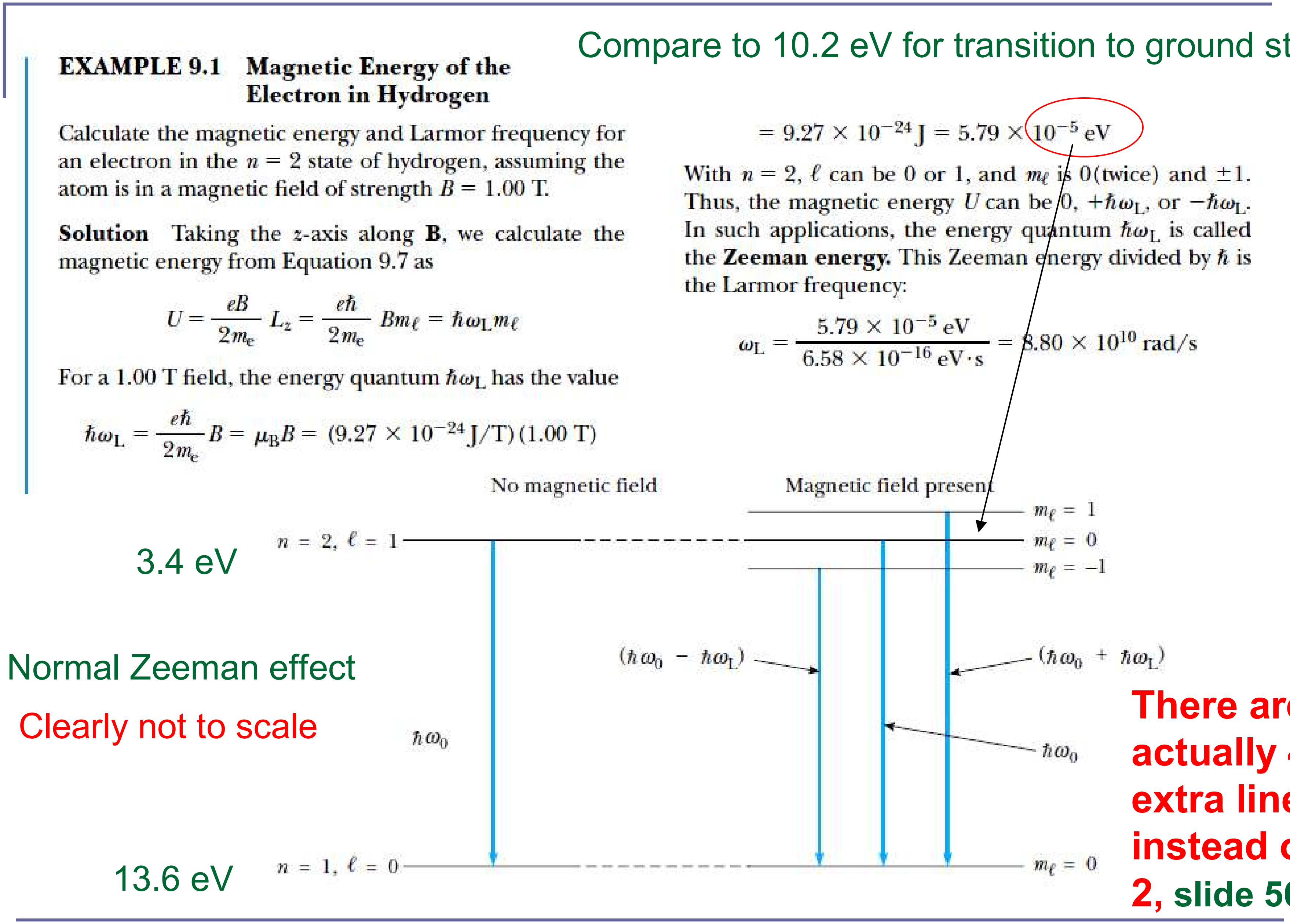
Spectrum with magnetic field present

$$E = E_0 + \hbar\omega_L m_\ell$$

Agrees with “Schrödinger H-atom prediction” assuming spin effects are too small to be observed

What is really observed with good spectrometers: there are a lot more lines in atomic spectra when they are in a magnetic field ! So called **Anomalous Zeeman effect**, which is the only one observed with good spectrometers !!.

Compare to 10.2 eV for transition to ground state



EXAMPLE 9.1 Magnetic Energy of the Electron in Hydrogen

Calculate the magnetic energy and Larmor frequency for an electron in the $n = 2$ state of hydrogen, assuming the atom is in a magnetic field of strength $B = 1.00$ T.

Solution Taking the z-axis along **B**, we calculate the magnetic energy from Equation 9.7 as

$$U = \frac{eB}{2m_e} L_z = \frac{e\hbar}{2m_e} B m_\ell = \hbar\omega_L m_\ell$$

For a 1.00 T field, the energy quantum $\hbar\omega_L$ has the value

$$\hbar\omega_L = \frac{e\hbar}{2m_e} B = \mu_B B = (9.27 \times 10^{-24}\ \text{J/T})(1.00\ \text{T})$$

$$= 9.27 \times 10^{-24}\ \text{J} = 5.79 \times \boxed{10^{-5}\ \text{eV}}$$

With $n = 2$, ℓ can be 0 or 1, and m_ℓ is 0(twice) and ± 1. Thus, the magnetic energy U can be 0, $+\hbar\omega_L$, or $-\hbar\omega_L$. In such applications, the energy quantum $\hbar\omega_L$ is called the **Zeeman energy.** This Zeeman energy divided by $\hbar$ is the Larmor frequency:

$$\omega_L = \frac{5.79 \times 10^{-5}\ \text{eV}}{6.58 \times 10^{-16}\ \text{eV} \cdot \text{s}} = 8.80 \times 10^{10}\ \text{rad/s}$$

3.4 eV

Normal Zeeman effect

Clearly not to scale

13.6 eV

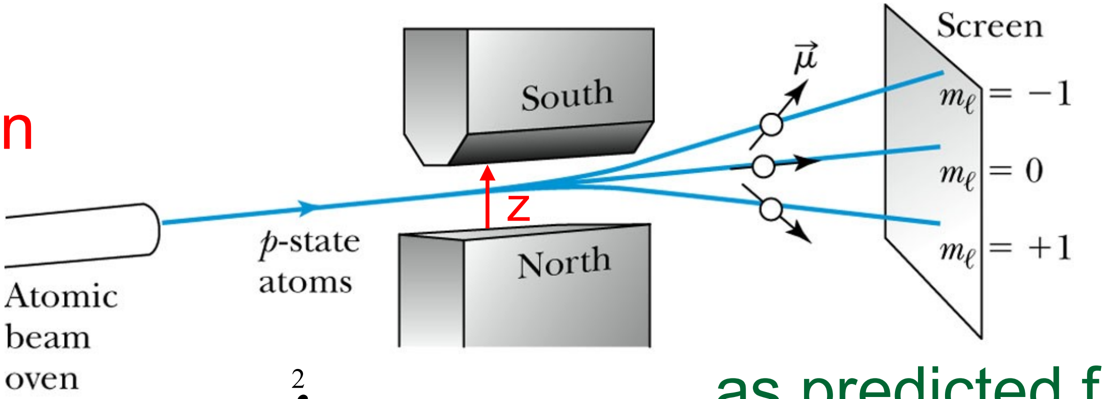
There are actually 4 extra lines, instead of 2, slide 56

1 Tesla = 10,000 Gauss, magnetic field of earth surface: 0.3 to 0.6 Gauss

The Stern – Gerlach experiment early 1920s

- a beam of Ag (or H atoms) in the ℓ = 1 state passes through an inhomogeneous magnetic field along the *z* direction

designed to test space quantization and getting something else



but 6 instead of 3 observed

- $V_B = -\mu_z B$ $\quad V_{B2} - V_{B1} = -\int_1^2 F_z \cdot dz$
- $F_z = -(dV_B / dz) = \mu_z (dB / dz)$

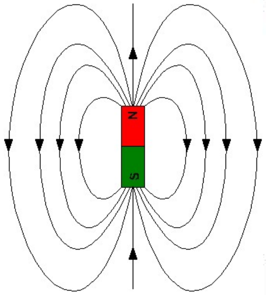
as predicted from what we have learned so far

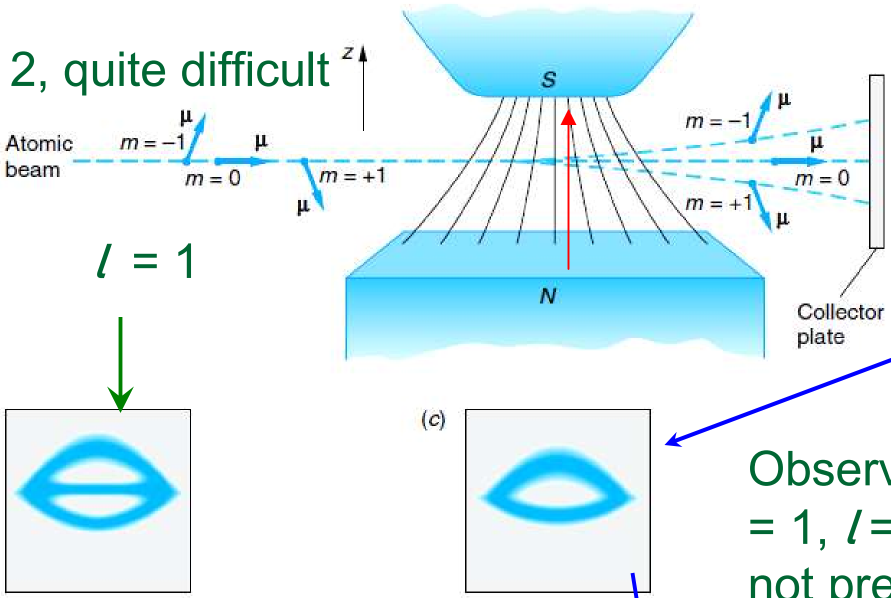
- The m_ℓ = +1 state will be deflected down, the m_ℓ = −1 state up, and the m_ℓ = 0 state will not be deflected.
- If the space quantization were due to the magnetic quantum number m_ℓ, and the total number of m_ℓ states is always odd (2ℓ + 1) the experiment should always produced an odd number of lines.

BUT always an even number of spots is observed !!!

n = 2, quite difficult

Easier: one outer *s* electron in ground state



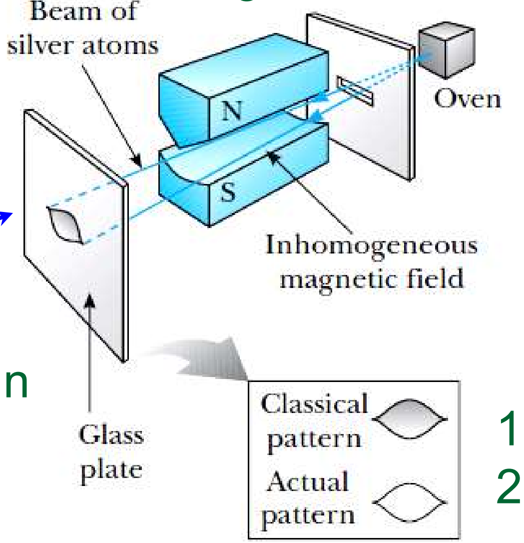


l = 1

Predicted but not observed

Observed for n = 1, *l* = 0, but not predicted

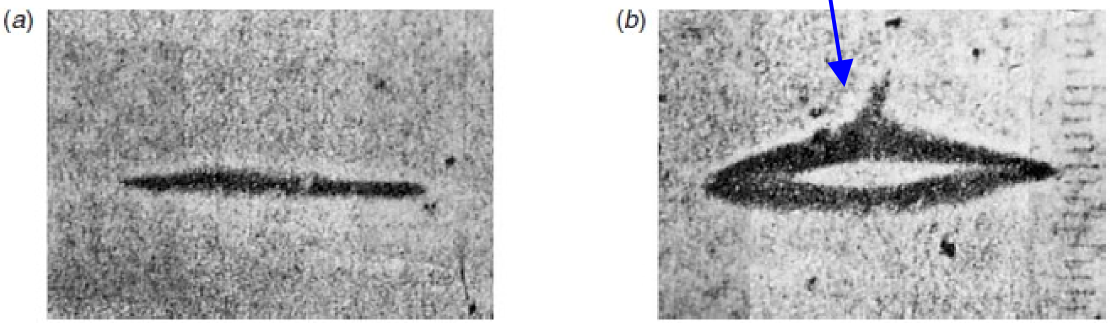
Figure 7-15 (*a*) In an inhomogeneous magnetic field the magnetic moment μ experiences a force F_z whose direction depends on the direction of the *z* component μ_z of μ and whose magnitude depends on those of μ_z and dB/dz. The beam from an oven (not shown) is collimated into a horizontal line. (*b*) The pattern for the ℓ = 1 case illustrated in (*a*). The three images join at the edges and have different detailed shapes due to differences in the field inhomogeneity. (*c*) The pattern observed for silver and hydrogen.



1
2

Spacing one Bohr magneton

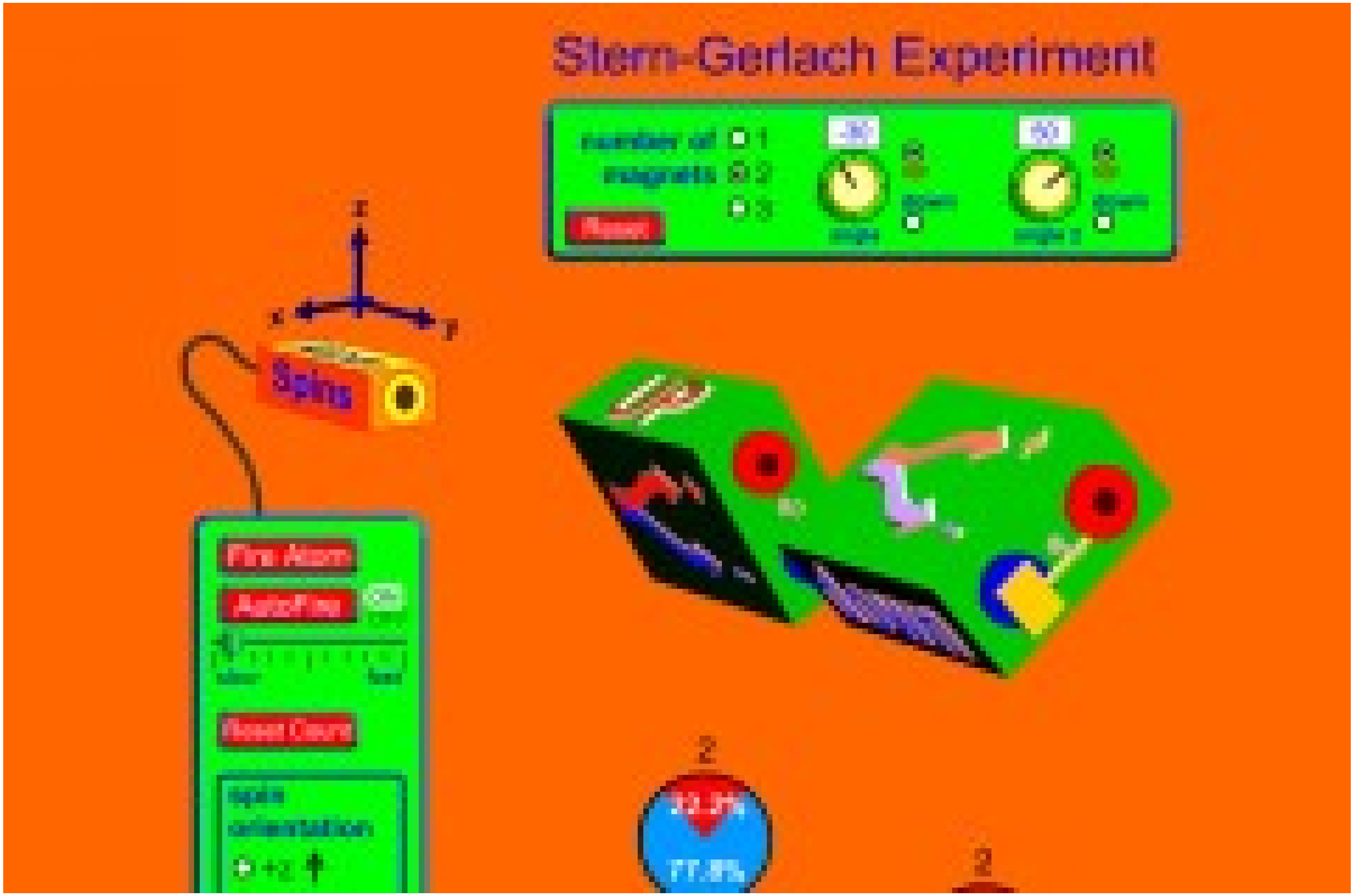
For the 1s state !!! *l* = 0, but also two !!!



Photographs made by Stern and Gerlach with an atomic beam of silver atoms. (*a*) When the magnetic field is zero, all atoms strike in a single, undeviated line. (*b*) When the magnetic field is nonzero, the atoms strike in upper and lower lines, curved due to differing inhomogeneities. [*From O. Stern and W. Gerlach, Zeitschr. f. Physik* **9**, *349 (1922).*]

$5s^1$

There are more things in heaven and earth, **Horatio**, than are dreamt of in your philosophy. - Hamlet (1.5.167-8)



https://www.cengage.com/physics/phet/sims/stern-gerlach/stern-gerlach_en.html

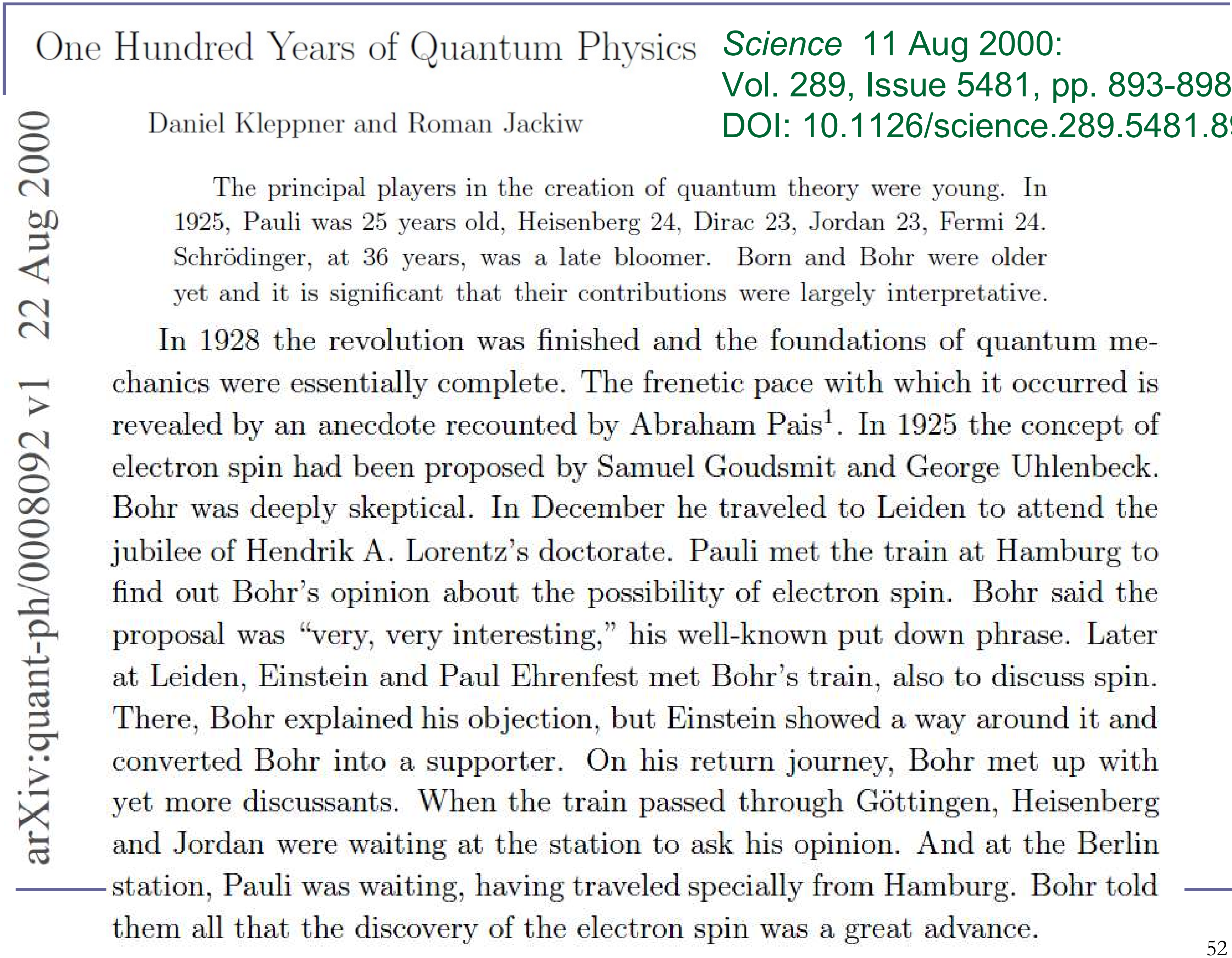
7.5: Intrinsic Spin / internal degree of freedom

- Samuel Goudsmit and George Uhlenbeck (working with Paul Ehrenfest in Leiden) proposed in 1925 that *the electron must have an intrinsic angular momentum* and a magnetic moment on its own (it was identified later as a fermion). Internal degree of freedom – from the outside it looks like a magnetic moment which is just about **twice** as strong as usual)

- Paul Ehrenfest showed that the surface of the spinning electron should be moving faster than the speed of light if it were a little sphere (not difficult to show)

- In order to explain experimental data on the anomalous Zeeman effect, Goudsmit and Uhlenbeck proposed that the electron must have an **intrinsic spin quantum number** s = ½ , associated intrinsic angular momentum, intrinsic magnetic momentum, everything worked out fine

- Wolfgang Pauli's assistant Ralph Kronig, considered essentially the same idea a year earlier, but Pauli said it was ludicrous and then used it in 1925 to derived his exclusion principle on its basis … "*Kronig had almost invented spin / if Pauli had not frightened him.*"



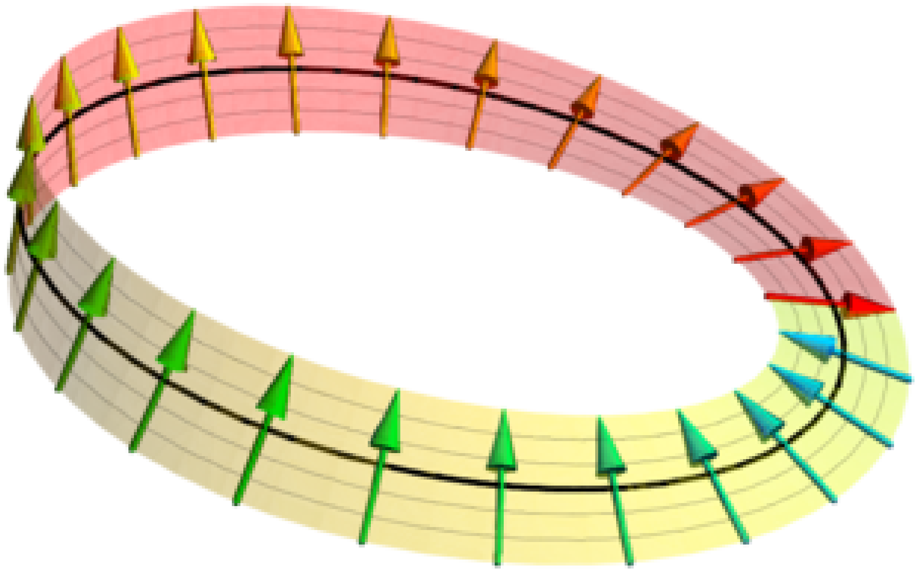
One Hundred Years of Quantum Physics

Science 11 Aug 2000:
Vol. 289, Issue 5481, pp. 893-898
DOI: 10.1126/science.289.5481.893

Daniel Kleppner and Roman Jackiw

The principal players in the creation of quantum theory were young. In 1925, Pauli was 25 years old, Heisenberg 24, Dirac 23, Jordan 23, Fermi 24. Schrödinger, at 36 years, was a late bloomer. Born and Bohr were older yet and it is significant that their contributions were largely interpretative.

In 1928 the revolution was finished and the foundations of quantum mechanics were essentially complete. The frenetic pace with which it occurred is revealed by an anecdote recounted by Abraham Pais[1]. In 1925 the concept of electron spin had been proposed by Samuel Goudsmit and George Uhlenbeck. Bohr was deeply skeptical. In December he traveled to Leiden to attend the jubilee of Hendrik A. Lorentz's doctorate. Pauli met the train at Hamburg to find out Bohr's opinion about the possibility of electron spin. Bohr said the proposal was "very, very interesting," his well-known put down phrase. Later at Leiden, Einstein and Paul Ehrenfest met Bohr's train, also to discuss spin. There, Bohr explained his objection, but Einstein showed a way around it and converted Bohr into a supporter. On his return journey, Bohr met up with yet more discussants. When the train passed through Göttingen, Heisenberg and Jordan were waiting at the station to ask his opinion. And at the Berlin station, Pauli was waiting, having traveled specially from Hamburg. Bohr told them all that the discovery of the electron spin was a great advance.



$s = ½$

Spin is mathematically described by a spinor, very loosely speaking some kind of a "square root" of a vector, one has to make two full turns to reach the same state for fermions

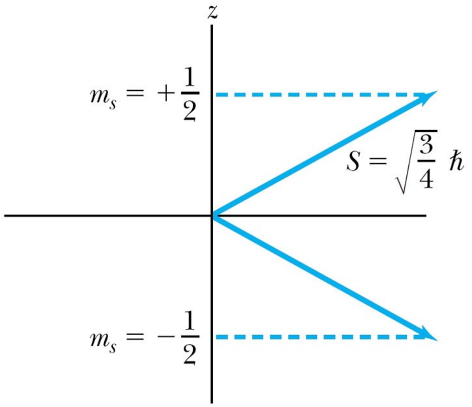
Crucial in Dirac’s special relativity compliant version of the Schrödinger equation

Intrinsic Spin / Internal degree of freedom

- The "spinning" electron reacts in a magnetic field *similarly* to an orbiting electron.
- We should try to find its analogs to L, L_z, ℓ, and m_ℓ.
- The **magnetic spin quantum number** m_s has only two values, $m_s = \pm\frac{1}{2}$.

Nope, uncertainty principle !

The electron's spin will be either "up" or "down" (again space quantization) and can never be "spinning" with its magnetic moment μ_s exactly along the z axis. There is no preferred z-axis, so this must be true about any axis !!!



$$\left|\vec{S}\right| = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$$

$$\boxed{S_z = m_s\hbar} \qquad \text{where } m_s = \tfrac{1}{2} \text{ or } -\tfrac{1}{2}$$

Only two values, so no Bohr correspondence principle, spin corresponds to nothing we are used to in classical physics, it's something in 4D space time

Intrinsic Spin

Slightly larger than **2** (2.0023..), effect of virtual particles that are allowed by the uncertainty principle, remember the Casimir force, Feynman's quantum electro-dynamics

- 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 a consequence of special relativity applied to quantum mechanics

New selection rule, there will later be another one due to a coupling of spin and orbital angular momentum

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

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

$\Delta m_s = 0$

Error in 3rd edition, eq. 7.34b, Thornton-Rex corrected in 4th edition

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

  → there is still space quantization due to the intrinsic spin.

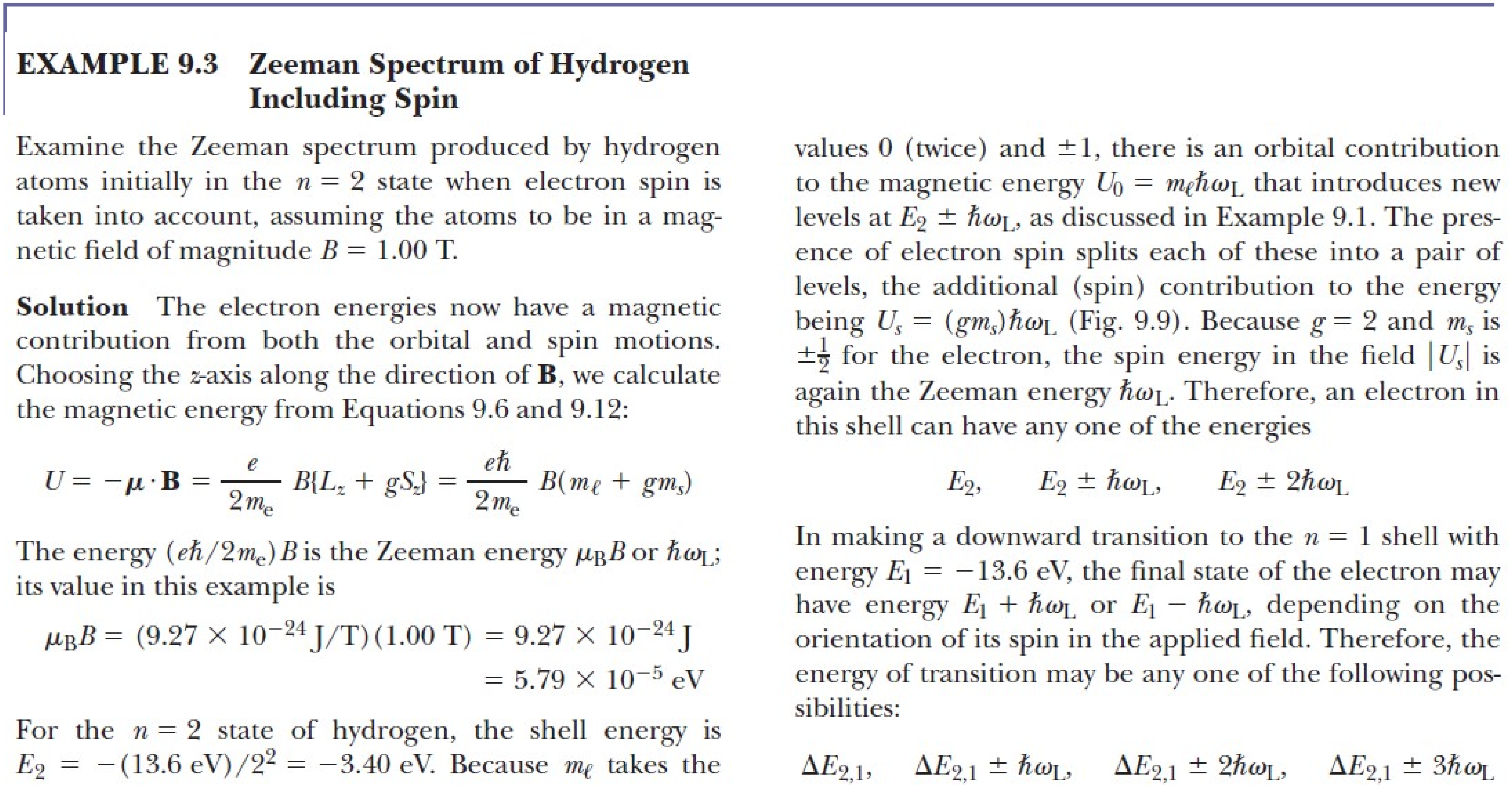
$m_s = \pm 1/2$

- Apply m_s and the corresponding potential energy becomes

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

B external magnetic field

Helps explaining what is really observed in atomic spectra with good spectrometers ***instead*** of the ***"normal"*** Zeeman effect



EXAMPLE 9.3 Zeeman Spectrum of Hydrogen Including Spin

Examine the Zeeman spectrum produced by hydrogen atoms initially in the $n = 2$ state when electron spin is taken into account, assuming the atoms to be in a magnetic field of magnitude $B = 1.00$ T.

Solution The electron energies now have a magnetic contribution from both the orbital and spin motions. Choosing the z-axis along the direction of $\mathbf{B}$, we calculate the magnetic energy from Equations 9.6 and 9.12:

$$U = -\boldsymbol{\mu}\cdot\mathbf{B} = \frac{e}{2m_e}B\{L_z + gS_z\} = \frac{e\hbar}{2m_e}B(m_\ell + gm_s)$$

The energy $(e\hbar/2m_e)B$ is the Zeeman energy $\mu_B B$ or $\hbar\omega_L$; its value in this example is

$$\mu_B B = (9.27\times10^{-24}\ \mathrm{J/T})(1.00\ \mathrm{T}) = 9.27\times10^{-24}\ \mathrm{J}$$
$$= 5.79\times10^{-5}\ \mathrm{eV}$$

For the $n = 2$ state of hydrogen, the shell energy is $E_2 = -(13.6\ \mathrm{eV})/2^2 = -3.40$ eV. Because m_ℓ takes the values 0 (twice) and ±1, there is an orbital contribution to the magnetic energy $U_0 = m_\ell\hbar\omega_L$ that introduces new levels at $E_2 \pm \hbar\omega_L$, as discussed in Example 9.1. The presence of electron spin splits each of these into a pair of levels, the additional (spin) contribution to the energy being $U_s = (gm_s)\hbar\omega_L$ (Fig. 9.9). Because $g = 2$ and m_s is $\pm\frac{1}{2}$ for the electron, the spin energy in the field $|U_s|$ is again the Zeeman energy $\hbar\omega_L$. Therefore, an electron in this shell can have any one of the energies

$$E_2, \qquad E_2 \pm \hbar\omega_L, \qquad E_2 \pm 2\hbar\omega_L$$

In making a downward transition to the $n = 1$ shell with energy $E_1 = -13.6$ eV, the final state of the electron may have energy $E_1 + \hbar\omega_L$ or $E_1 - \hbar\omega_L$, depending on the orientation of its spin in the applied field. Therefore, the energy of transition may be any one of the following possibilities:

$$\Delta E_{2,1}, \quad \Delta E_{2,1} \pm \hbar\omega_L, \quad \Delta E_{2,1} \pm 2\hbar\omega_L, \quad \Delta E_{2,1} \pm 3\hbar\omega_L$$

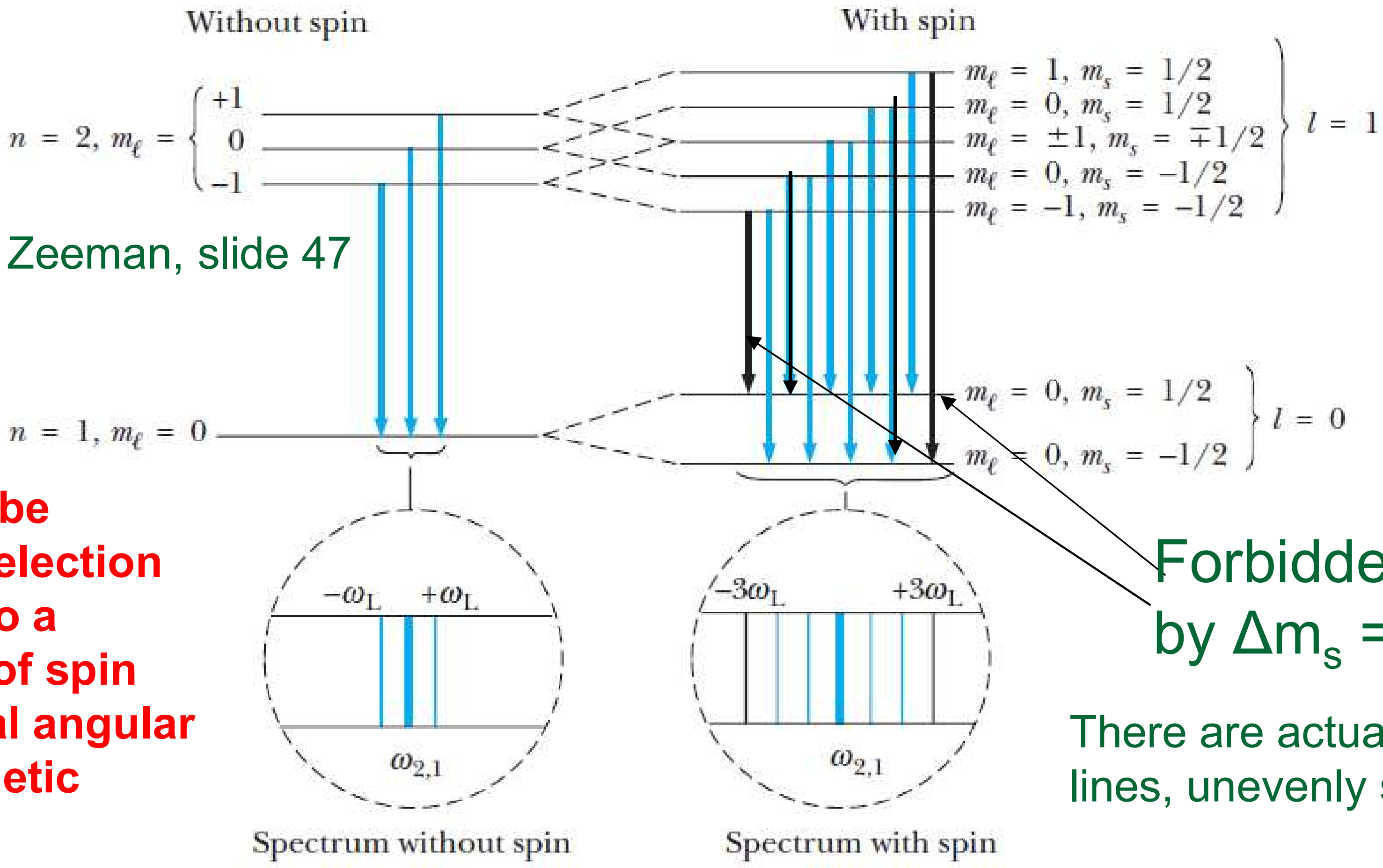
To be continued on slide 58, would be better to make calculation for 10 T

Five spectral lines observed instead of 7, because an extra selection rule needs to be obeyed

$\Delta m_s = 0$

Distinctions between strong magnetic fields some ten times larger than effect of spin-orbit coupling effects and weak magnetic fields where spin-orbit coupling contributes even more lines, **g ≈ 2**

Normal Zeeman, slide 47



there will be another selection rule due to a coupling of spin and orbital angular and magnetic momenta

Forbidden by $\Delta m_s = 0$

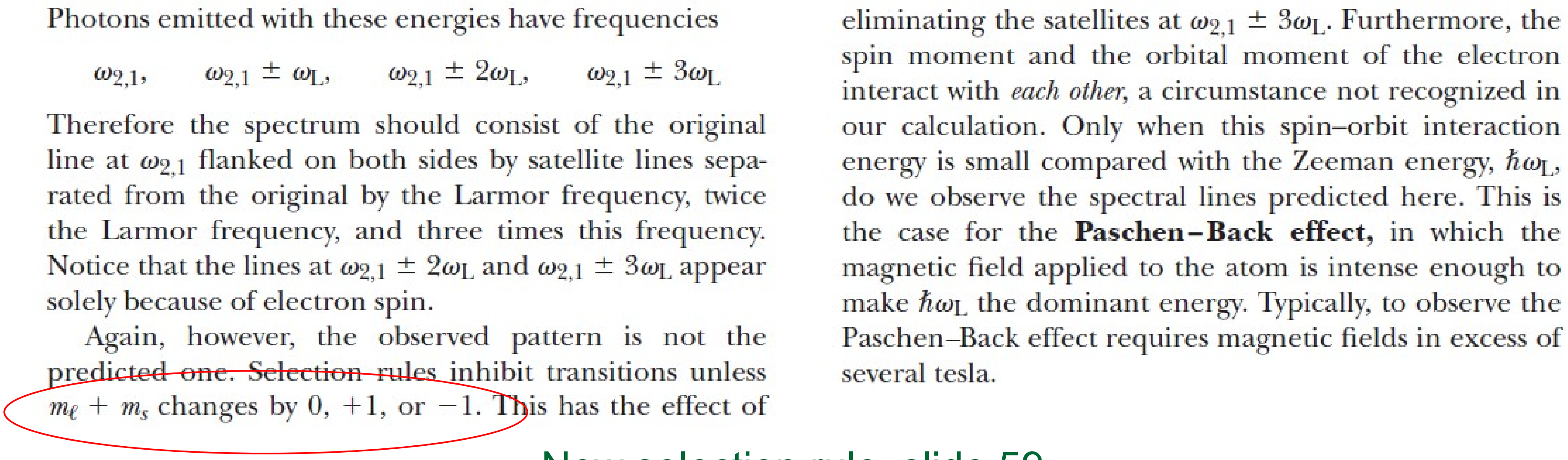
There are actually 10 lines, unevenly spaced

Figure 9.9 (Example 9.3) Predicted Zeeman pattern and underlying atomic transitions for an electron excited to the $n = 2$ state of hydrogen, when electron spin is taken into account. Again, selection rules prohibit all but the colored transitions. Because of the neglect of the spin–orbit interaction, the effect shown here (called the Paschen–Back effect) is observed only in very intense applied magnetic fields.

Very strong external magnetic field, several Tesla, spin-orbit coupling neglected

Continuation from slide 56

when external magnetic fields are rather strong



Photons emitted with these energies have frequencies

$$\omega_{2,1}, \qquad \omega_{2,1} \pm \omega_{\mathrm{L}}, \qquad \omega_{2,1} \pm 2\omega_{\mathrm{L}}, \qquad \omega_{2,1} \pm 3\omega_{\mathrm{L}}$$

Therefore the spectrum should consist of the original line at $\omega_{2,1}$ flanked on both sides by satellite lines separated from the original by the Larmor frequency, twice the Larmor frequency, and three times this frequency. Notice that the lines at $\omega_{2,1} \pm 2\omega_{\mathrm{L}}$ and $\omega_{2,1} \pm 3\omega_{\mathrm{L}}$ appear solely because of electron spin.

Again, however, the observed pattern is not the predicted one. Selection rules inhibit transitions unless $m_\ell + m_s$ changes by 0, +1, or −1. This has the effect of eliminating the satellites at $\omega_{2,1} \pm 3\omega_{\mathrm{L}}$. Furthermore, the spin moment and the orbital moment of the electron interact with *each other*, a circumstance not recognized in our calculation. Only when this spin–orbit interaction energy is small compared with the Zeeman energy, $\hbar\omega_{\mathrm{L}}$, do we observe the spectral lines predicted here. This is the case for the **Paschen–Back effect,** in which the magnetic field applied to the atom is intense enough to make $\hbar\omega_{\mathrm{L}}$ the dominant energy. Typically, to observe the Paschen–Back effect requires magnetic fields in excess of several tesla.

New selection rule, slide 59

In a zero magnetic field, we will also see the splitting of spectral lines due to spin-orbit coupling

In a relatively weak magnetic field, say < 0.1 T, we will have both, the anomalous Zeeman effect and spectral line splitting due to spin-orbit coupling

$\Delta m_s = 0$ because spin results in a magnetic effect, the selection rules are due to electric dipole transitions, oscillating expectation value for an electron (one negative charge), necessity to conserve angular momentum by emitting or absorbing one photon

Spin-orbit coupling, angular momenta interact

$$\boldsymbol{\mu} = \underset{\text{or } l}{\boldsymbol{\mu}_0} + \boldsymbol{\mu}_s = \frac{-e}{2m_e}\{\mathbf{L} + g\mathbf{S}\} \qquad (9.12)$$

g = 2 Dirac

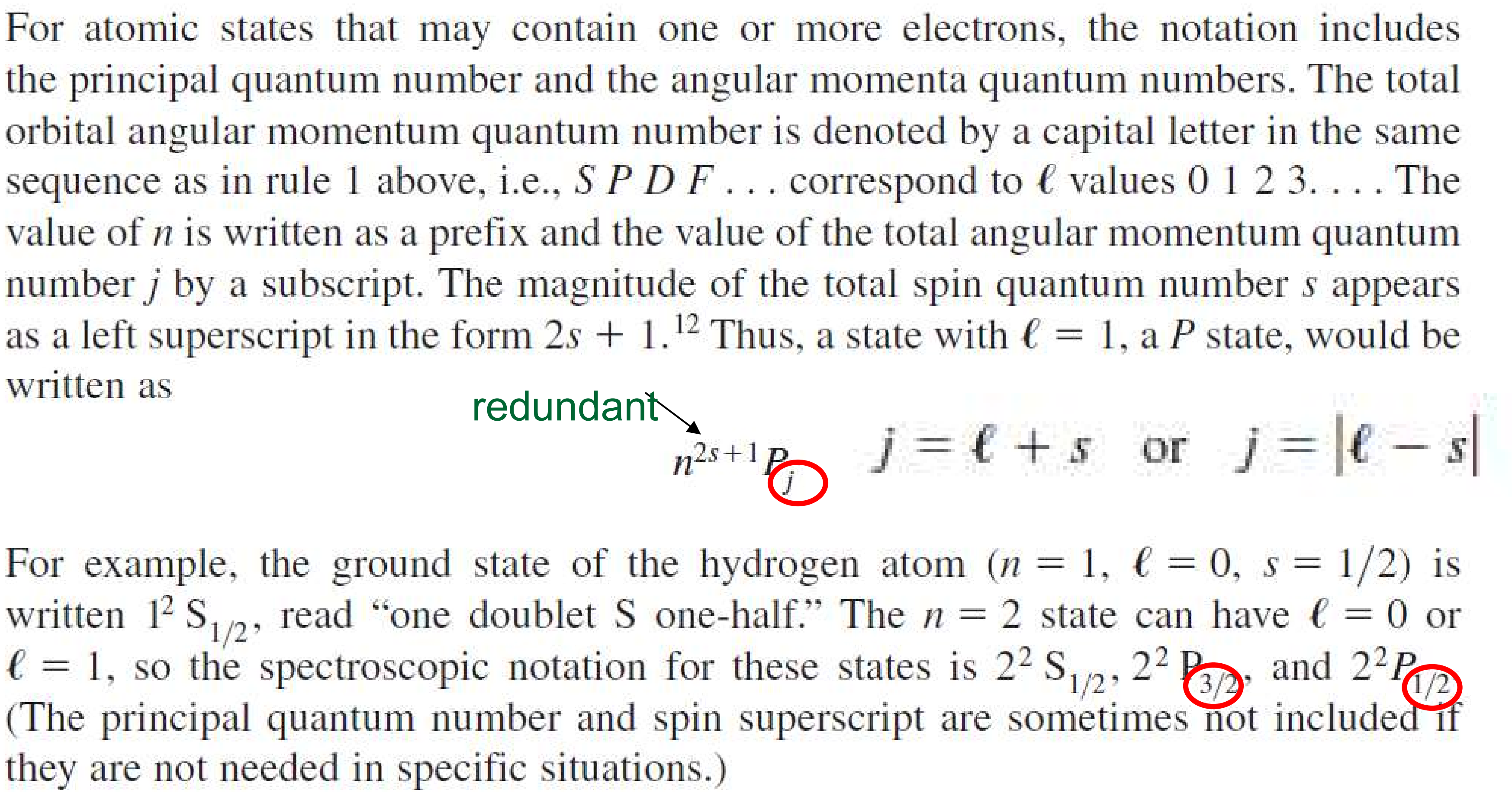
The total magnetic moment of an electron

Their magnetic moments also do interact !! Vector sums. We don’t need an external magnetic field in order to lift many of the degeneracies. This will have observable consequences, anomalous Zeeman effects explains all spectral lines of isolated hydrogen for strong and weak external magnetic fields, Schrödinger model quantitatively very good – basis for the structure of all other atoms – but qualitatively a blunder as 4D space time and special relativity neglected

A 5th quantum number leading to a new selection rule

$$j = \ell + s \quad \text{or} \quad j = |\ell - s|$$

Spectroscopy notation for experimental spectra of heavier atoms with more electrons



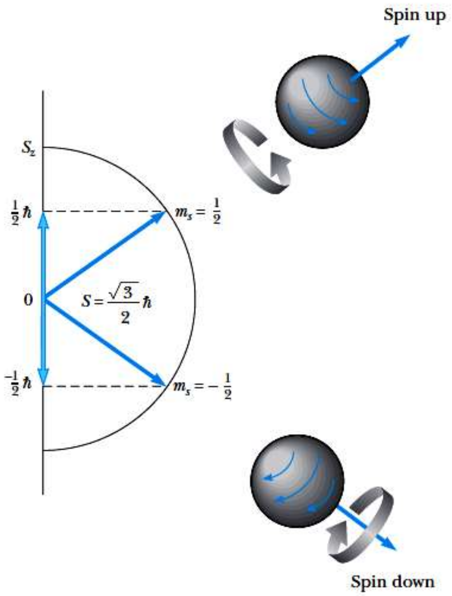
For atomic states that may contain one or more electrons, the notation includes the principal quantum number and the angular momenta quantum numbers. The total orbital angular momentum quantum number is denoted by a capital letter in the same sequence as in rule 1 above, i.e., *S P D F* . . . correspond to ℓ values 0 1 2 3. . . . The value of n is written as a prefix and the value of the total angular momentum quantum number j by a subscript. The magnitude of the total spin quantum number s appears as a left superscript in the form $2s + 1$.[12] Thus, a state with $\ell = 1$, a *P* state, would be written as

redundant

$$n^{2s+1}P_j \qquad j = \ell + s \quad \text{or} \quad j = |\ell - s|$$

For example, the ground state of the hydrogen atom ($n = 1$, $\ell = 0$, $s = 1/2$) is written $1^2\,\mathrm{S}_{1/2}$, read "one doublet S one-half." The $n = 2$ state can have $\ell = 0$ or $\ell = 1$, so the spectroscopic notation for these states is $2^2\,\mathrm{S}_{1/2}$, $2^2\,\mathrm{P}_{3/2}$, and $2^2P_{1/2}$. (The principal quantum number and spin superscript are sometimes not included if they are not needed in specific situations.)

Figure 9.8 The spin angular momentum also exhibits space quantization. This figure shows the two allowed orientations of the spin vector **S** for a spin $\frac{1}{2}$ particle, such as the electron.



Half of the hydrogen atoms have spin up, the other half spin down after a measurement, there is a superposition of both states before measurement

Two electrons in same state will lead to cancellation of spin, as one has spin up and the other spin down

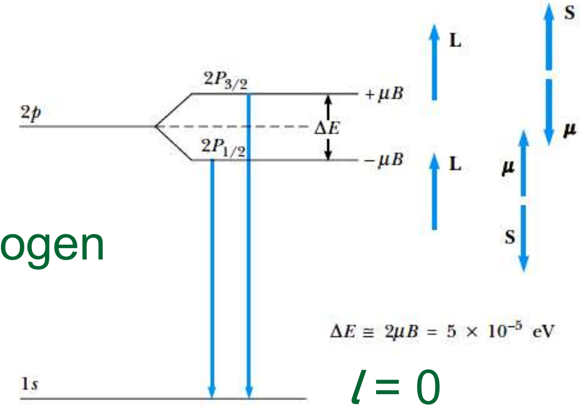
Spin-orbit coupling

$$\mu = \underset{\text{or } l}{\mu_0} + \mu_s = \frac{-e}{2m_e}\{\mathbf{L} + g\mathbf{S}\}$$

g ≈ 2

$l = 1$

Hydrogen



$l = 0$

Figure 9.11 The $2p$ level of hydrogen is split by the spin–orbit effect into a doublet separated by the spin–orbit energy $\Delta E = 5 \times 10^{-5}$ eV. The higher energy state is the one for which the spin angular momentum of the electron is "aligned" with its orbital angular momentum. The 1s level is unaffected, since no magnetic field arises for orbital motion with zero angular momentum.

total (orbital plus spin) angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$

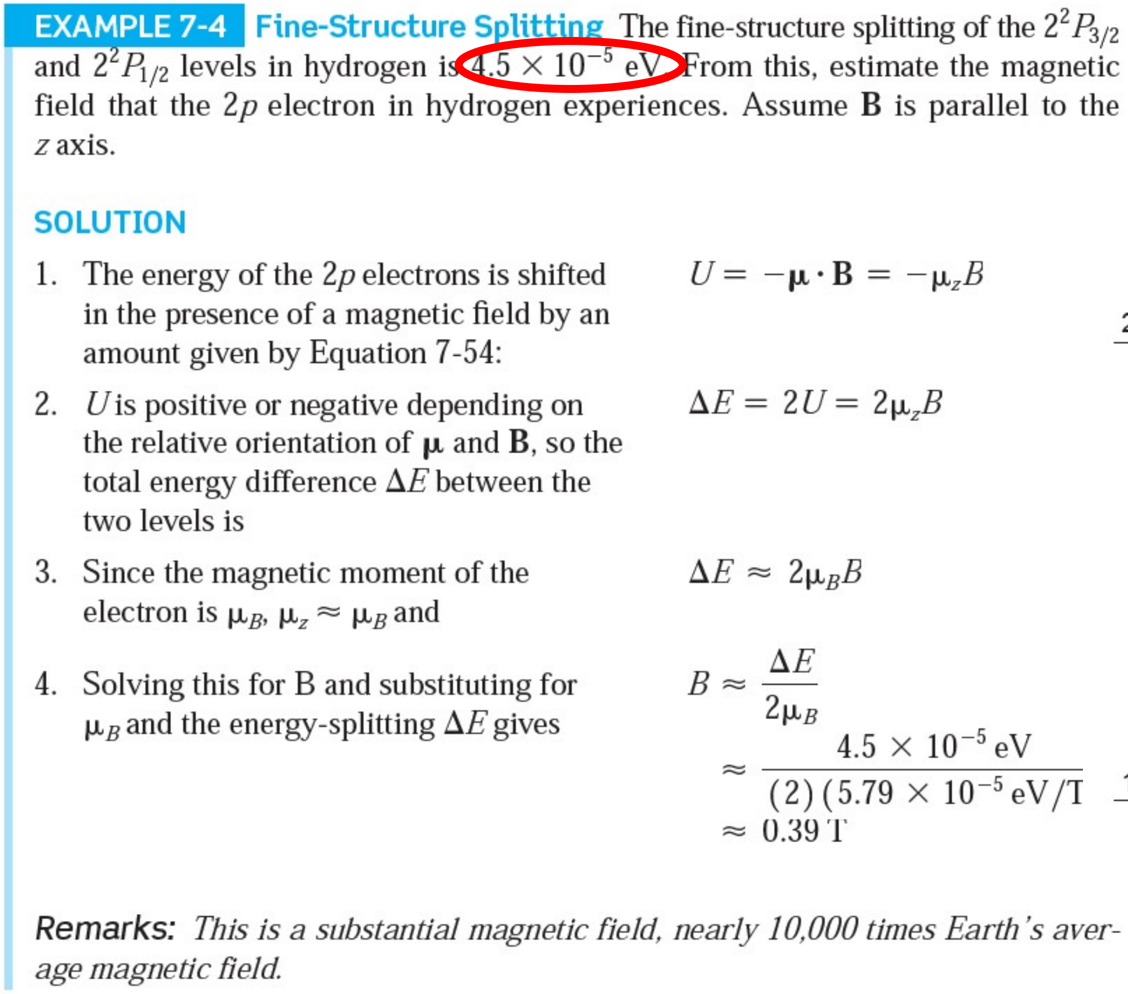
$$|\mathbf{J}| = \sqrt{j(j+1)}\,\hbar \qquad j = \ell + s \quad \text{or} \quad j = |\ell - s|$$

$$J_z = m_j\hbar \qquad \text{with } m_j = j, j-1, \ldots, -j$$

ΔE ≈ 0.45 10^{-4} eV caused by internal magnetic field, next slide

New selection rules: $\Delta m_j = 0, \pm 1$, $\Delta j = 0, \pm 1$ (all single-electron atom/ions) in addition to $\Delta\ell = \pm 1$

We will have a lot of spin-orbit coupling with heavier atoms, e.g. Na



EXAMPLE 7-4 **Fine-Structure Splitting** The fine-structure splitting of the $2^2P_{3/2}$ and $2^2P_{1/2}$ levels in hydrogen is 4.5×10^{-5} eV. From this, estimate the magnetic field that the $2p$ electron in hydrogen experiences. Assume **B** is parallel to the z axis.

SOLUTION

1. The energy of the $2p$ electrons is shifted in the presence of a magnetic field by an amount given by Equation 7-54: $U = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B$
2. U is positive or negative depending on the relative orientation of $\boldsymbol{\mu}$ and **B**, so the total energy difference ΔE between the two levels is $\Delta E = 2U = 2\mu_z B$
3. Since the magnetic moment of the electron is μ_B, $\mu_z \approx \mu_B$ and $\Delta E \approx 2\mu_B B$
4. Solving this for B and substituting for μ_B and the energy-splitting ΔE gives

$$B \approx \frac{\Delta E}{2\mu_B} \approx \frac{4.5 \times 10^{-5}\ \text{eV}}{(2)(5.79 \times 10^{-5}\ \text{eV/T})} \approx 0.39\ \text{T}$$

Remarks: *This is a substantial magnetic field, nearly 10,000 times Earth's average magnetic field.*

Half of the hydrogen atoms have spin up, the other half spin down

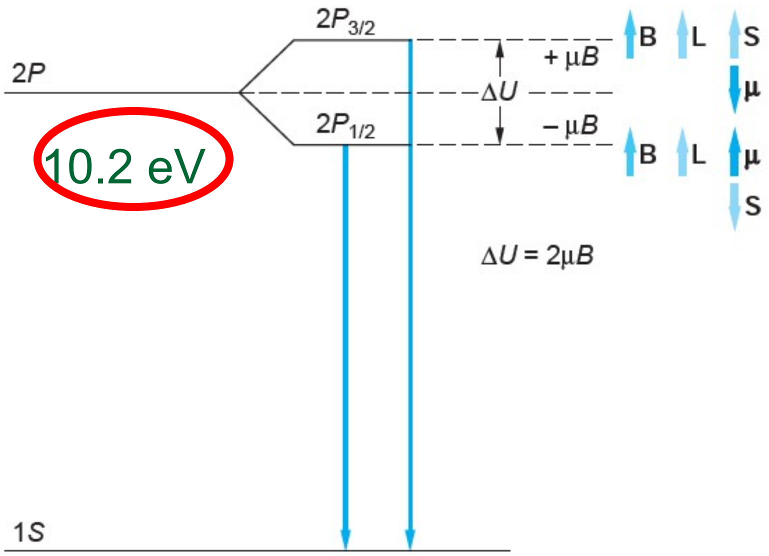


FIGURE 7-18 Fine-structure energy-level diagram. On the left, the levels in the absence of a magnetic field are shown. The effect of the magnetic field due to the relative motion of the nucleus is shown on the right. Because of the spin-orbit interaction, the magnetic field splits the $2P$ level into two energy levels, with the $j = 3/2$ level having slightly greater energy than the $j = 1/2$ level. The spectral line due to the transition $2P \rightarrow 1S$ is therefore split into two lines of slightly different wavelengths. (Diagram is not to scale.)

No external magnetic field, but spectral line doublet

Fine structure is due to spin-orbit coupling, there is also a contribution due to the movement of the proton about the common center of mass with the electron, angular momenta interact, so will magnetic momenta

Total Angular Momentum is a vector sum

- If j and m_j are quantum numbers for the single electron (hydrogen atom).

$$J = \sqrt{j(j+1)}\hbar$$

$$J_z = m_j\hbar$$

- Quantization of the magnitudes.

$$L = \sqrt{\ell(\ell+1)}\hbar$$

$$S = \sqrt{s(s+1)}\hbar$$

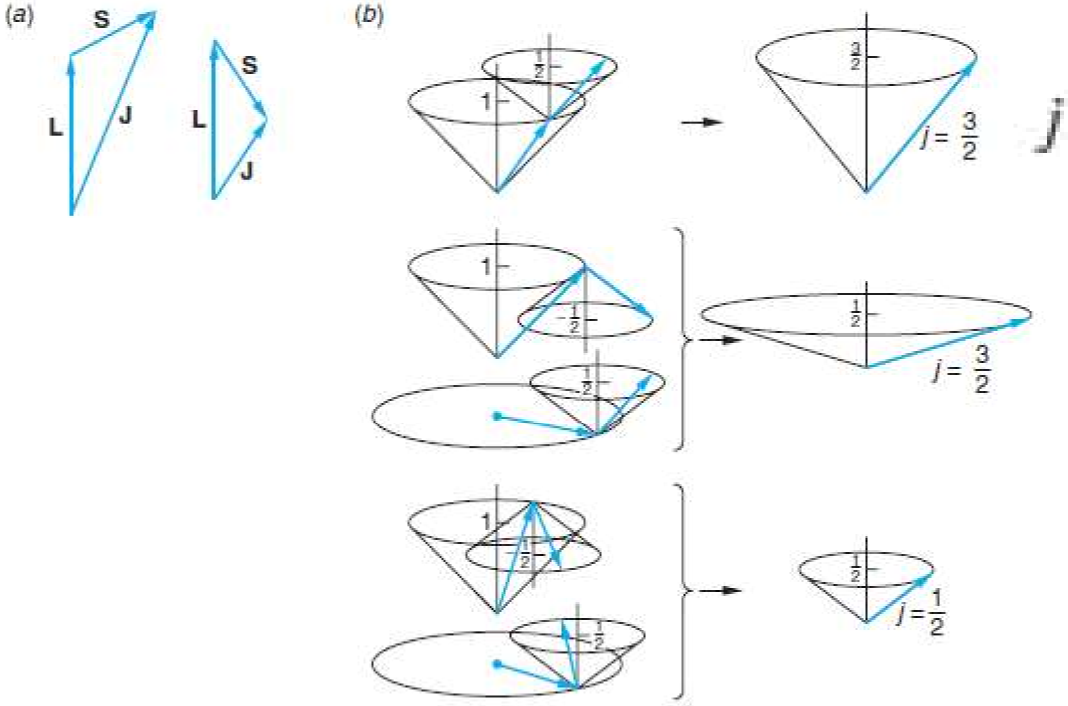
$$J = \sqrt{j(j+1)}\hbar$$

- The total angular momentum quantum number for the single electron can only have the values

$$j = \ell + s \quad \text{or} \quad j = |\ell - s|$$

e.g. index ½ after S or P, $^{3}/_{2}$ after P from last slide

New selection rules: $\Delta m_j = 0, \pm 1$ $\Delta m_s = 0$ $\Delta j = 0, \pm 1$

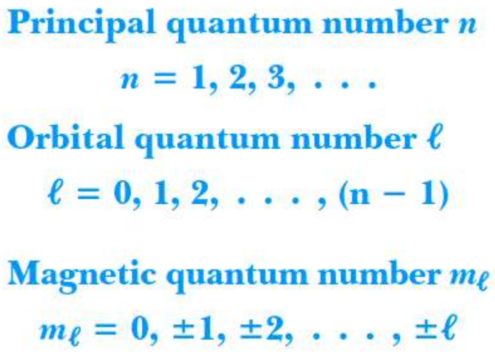


$$j = \ell + s \quad \text{or} \quad j = |\ell - s|$$

http://enjoy.phy.ntnu.edu.tw/data/458/www/simulations/simsb6fb.html?sim=SternGerlach_Experiment

Figure 7-16 (*a*) Simplified vector model illustrating the addition of orbital and spin angular momenta. The case shown is for $\ell = 1$ and $s = \frac{1}{2}$. There are two possible values of the quantum number for the total angular momentum: $j = \ell + s = \frac{3}{2}$ and $j = \ell - s = \frac{1}{2}$. (*b*) Vector addition of the orbital and spin angular momenta, also for the case $\ell = 1$ and $s = \frac{1}{2}$. According to the uncertainty principle, the vectors can lie anywhere on the cones, corresponding to the definite values of their *z* components. Note in the middle sketch that there are two ways of forming the states with $j = \frac{3}{2}$, $m_j = \frac{1}{2}$ and $j = \frac{1}{2}$, $m_j = \frac{1}{2}$.

As one h-bar needs to be taken away by an emitted photon, $\Delta\ell = \pm1$, spin-orbit coupling "modifies" the selection rules of the Schrödinger model of H-atom !



Principal quantum number n

$n = 1, 2, 3, \ldots$

Orbital quantum number ℓ

$\ell = 0, 1, 2, \ldots, (n - 1)$

Magnetic quantum number m_ℓ

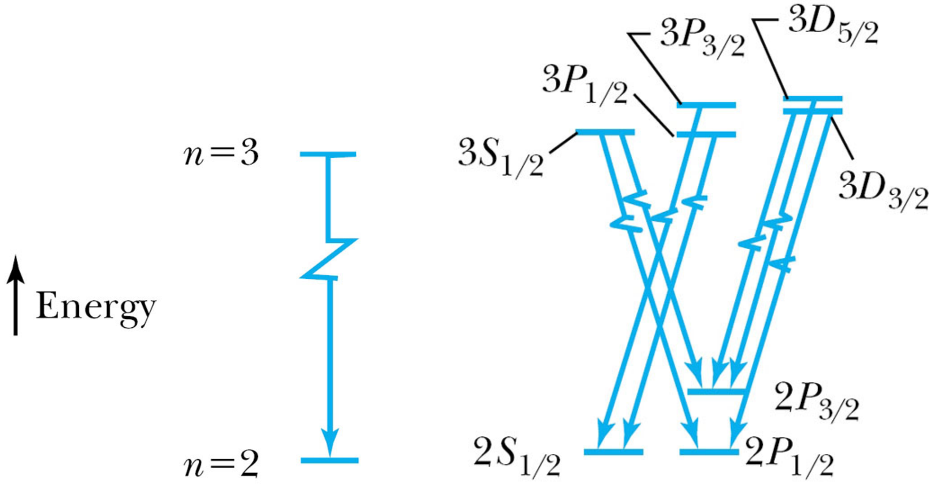
$m_\ell = 0, \pm1, \pm2, \ldots, \pm\ell$

m_s quantum number: ½, -½ , but s = ½

The hydrogen wave functions serve as approximations for the wave functions of all other atoms !!!

Spectral line splitting due to total angular momentum

- Now the selection rules for a single-electron atom become
  - **Δn = anything** **$\Delta \ell = \pm 1$** $\Delta m_\ell = 0, \pm 1$ $\Delta m_s = 0$
  - $\Delta m_j = 0, \pm 1$ $\Delta j = 0, \pm 1$
- Hydrogen energy-level diagram for $n = 2$ and $n = 3$ with the spin-orbit splitting.



Unperturbed Fine structure due to spin-orbit coupling gets observed

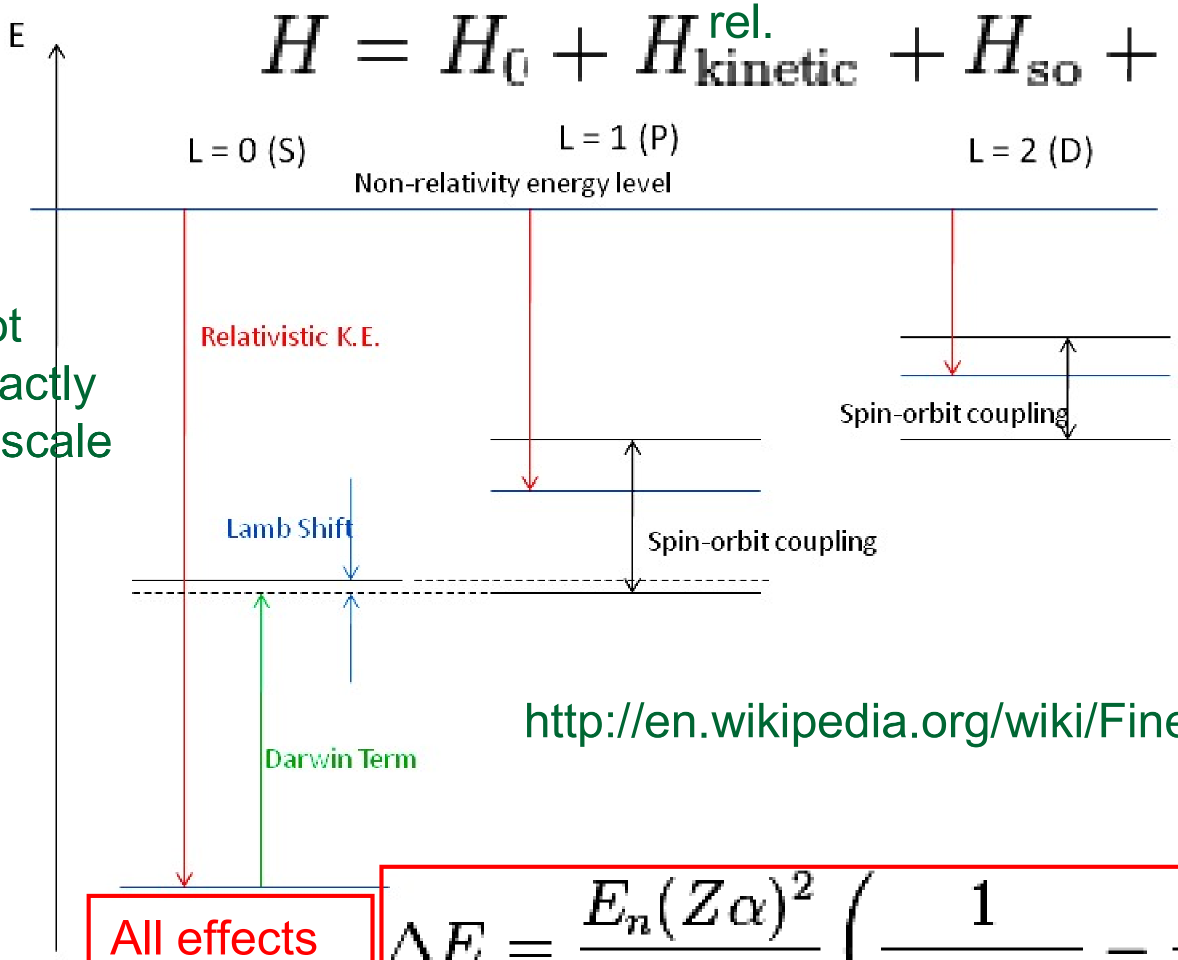
(a) (b)

Reminder: selection rules make sure photon carries away one unit of angular momentum = h-bar

Fine structure of spectrum of hydrogen atom is explained by the eigenfunctions of a more complicated Hamiltonian operator

Charles Galton Darwin

$$H = H_0 + H^{\text{rel.}}_{\text{kinetic}} + H_{\text{so}} + H_{\text{Darwinian}}.$$



Not exactly to scale

Correction for relativistic kinetic energy ***only***

n = 1, ΔE =

$$-9.056 \times 10^{-4}\ \text{eV}$$

so Schrödinger equation is pretty good approximation

(13.6 eV ground state)

http://en.wikipedia.org/wiki/Fine_structure

All effects combined

$$\Delta E = \frac{E_n (Z\alpha)^2}{n} \left(\frac{1}{j + 1/2} - \frac{3}{4n} \right)$$

$j = 1/2$ if $l = 0$

$j = l \pm 1/2$ otherwise

There is also ultra-fine (or hyper-fine) structure in an isolated hydrogen atom, it arises form interactions between the spins of the proton and electron

We use the same orbital notation for all atoms

EXAMPLE 9.4 The Sodium Doublet

The famed sodium doublet arises from the spin–orbit splitting of the sodium $3p$ level, and consists of the closely spaced pair of spectral lines at wavelengths of 588.995 nm and 589.592 nm. Show on an energy-level diagram the electronic transitions giving rise to these lines, labeling the participating atomic states with their proper spectroscopic designations. From the doublet spacing, determine the magnitude of the spin–orbit energy.

Solution The outer electron in sodium is the first electron to occupy the $n = 3$ shell, and it would go into the lowest-energy subshell, the $3s$ or $3S_{1/2}$ level. The next-highest levels belong to the $3p$ subshell. The $2(2\ell + 1) = 6$ states of this subshell are grouped into the $3P_{1/2}$ level with two states, and the $3P_{3/2}$ level with four states. The spin–orbit effect splits these levels by the spin–orbit energy. The outer electron, once it is excited to either of these levels by some means (such as an electric discharge in the sodium vapor lamp), returns to the $3S_{1/2}$ level with the emission of a photon. The two possible transitions $3P_{3/2} \to 3S_{1/2}$ and $3P_{1/2} \to 3S_{1/2}$ are shown in Figure 9.13. The emitted photons have nearly the same energy but differ by the small amount ΔE representing the spin–orbit splitting of the initial levels. Since $E = hc/\lambda$ for photons, ΔE is found as

$$\Delta E = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = \frac{hc(\lambda_2 - \lambda_1)}{\lambda_1 \lambda_2}$$

For the sodium doublet, the observed wavelength difference is

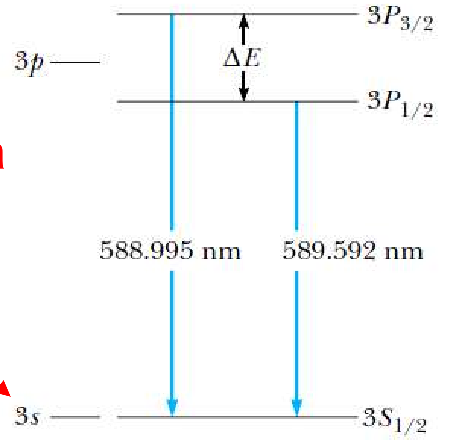
$$\lambda_2 - \lambda_1 = 589.592\text{ nm} - 588.995\text{ nm} = 0.597\text{ nm}$$

Using this with $hc = 1240\text{ eV}\cdot\text{nm}$ gives

≈ 0.1%

$$\Delta E = \frac{(1240\text{ eV}\cdot\text{nm})(0.597\text{ nm})}{(589.592\text{ nm})(588.995\text{ nm})} = 2.13 \times 10^{-3}\text{ eV}$$

Ground state Sodium, a single 3s electron

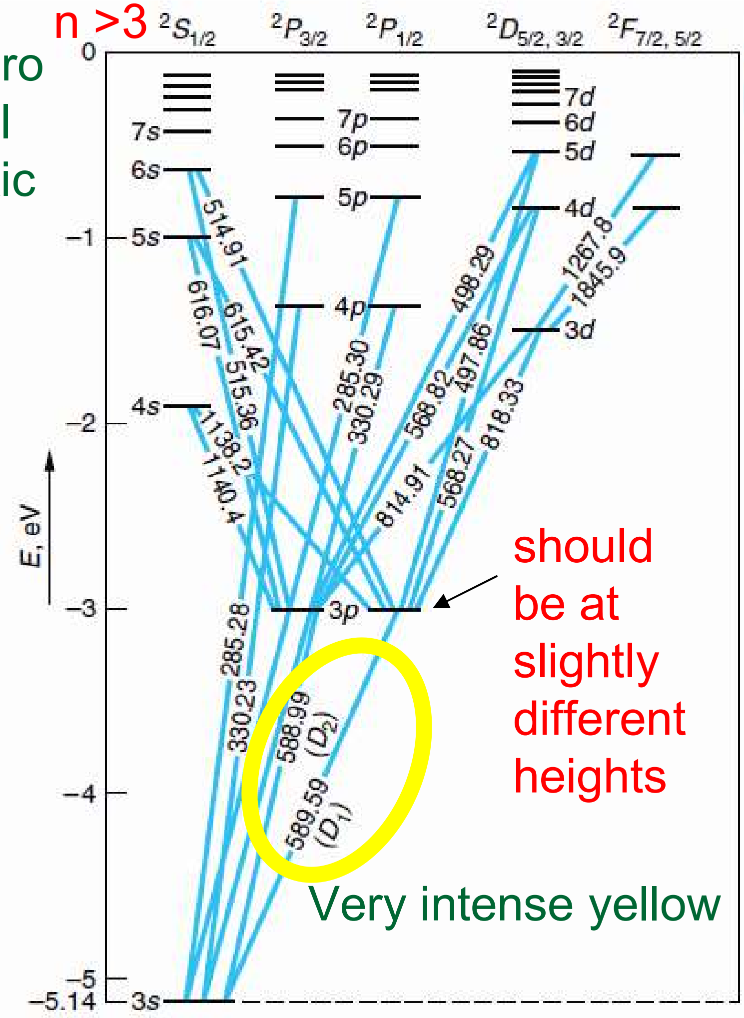


Half of these atoms spin up, half of them spin down for $3s^1$ ground state

Figure 9.13 (Example 9.4). The transitions $3P_{3/2} \to 3S_{1/2}$ and $3P_{1/2} \to 3S_{1/2}$ that give rise to the sodium doublet. The $3p$ level of sodium is split by the spin–orbit effect, but the $3s$ level is unaffected. In the sodium vapor lamp, electrons normally in the $3s$ level are excited to the $3p$ levels by an electric discharge.

Because there is no spin-orbit effect in s sub-shell, as $l = 0$

With zero external magnetic field



n >3

should be at slightly different heights

Very intense yellow

Figure 7-22 Energy-level diagram for sodium (Na) with some transitions indicated. Wavelengths shown are in nanometers. The spectral lines labeled D_1 and D_2 are very intense and are responsible for the yellow color of lamps containing sodium. The energy splittings of the D and F levels, also doublets, are not shown.

More

Tradition tells us that Mrs. Bohr encountered an obviously sad young Wolfgang Pauli sitting in the garden of Bohr's Institute for Theoretical Physics in Copenhagen and asked considerately if he was unhappy. His reply was, "Of course I'm unhappy! I don't understand the anomalous Zeeman effect!" On the home page we explain *The Zeeman Effect* so you, too, won't be unhappy: www.whfreeman.com/tiplermodernphysics5e. See also Equations 7-70 through 7-74 and Figures 7-28 through 7-31 here.

Pauli's exclusion principle empirical: the quantum state that a single electron occupies has a distinct set of 4 quantum numbers, n, ℓ, m_l, and m_s (½ up or down) - no other electron in the same system can have the same distinct set

Later: electrons are fermions, only two of them with different spin state can occupy each state that is determined by a set of three quantum numbers

Overview transitions / selection Rules

- We use the wave functions to calculate transition probabilities for the electron to change from one state to another. These probabilities are proportional to the intensity of the spectral lines

Allowed transitions:

- Electrons absorbing or emitting photons to change states when $\Delta\ell = \pm1$ that corresponds to one unit of angular momentum and is the spin of the photon, it's a boson, spin is 1

Forbidden transitions:

- Other transitions possible if system is disturbed but occur with much smaller probabilities when $\Delta\ell \neq \pm1$.

$\Delta n =$ positive integer > 0 for downward transition

$\Delta\ell = \pm 1$ $\Delta m_s = 0$

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

Because of these rules, Rydberg atoms, n ≈ 100 or more are quite stable in outer space

$\Delta m_j = 0, \pm 1$ For single electron atoms and ions

TOPIC	RELEVANT EQUATIONS AND REMARKS	
1. Schrödinger equation in three dimensions	The equation is solved for the hydrogen atom by separating it into three ordinary differential equations, one for each coordinate r, θ, ϕ. The quantum numbers n, ℓ, and m_ℓ arise from the boundary conditions to the solutions of these equations.	
2. Quantization		
Angular momentum	$\lvert \mathbf{L} \rvert = \sqrt{\ell(\ell + 1)}\hbar$ for $\ell = 0, 1, 2, 3, \ldots$	7-22
z component of **L**	$L_z = m\hbar$ for $m = 0, \pm 1, \pm 2, \ldots, \pm \ell$ $= m_\ell$	7-23
Energy	$E_n = -\left(\frac{kZe^2}{\hbar}\right)^2 \frac{\mu}{2n^2} = -13.6\frac{Z^2}{n^2}\,\text{eV}$ also for He^+, Li^{++}	7-24
3. Hydrogen wave functions	$\Psi_{n\ell m} = C_{n\ell m} R_{n\ell}(r) Y_{n\ell m}(\theta, \phi)$ where $C_{n\ell m}$ are normalization constants, $R_{n\ell}$ are the radial functions, and $Y_{\ell m}$ are the spherical harmonics.	
4. Electron spin	The electron spin is not included in Schrödinger's wave equation.	
Magnitude of **S**	$\lvert \mathbf{S} \rvert = \sqrt{s(s + 1)}\hbar \quad s = \frac{1}{2}$	7-36
z component of **S**	$S_z = m_s \hbar \quad m_s = \pm\frac{1}{2}$	
Stern-Gerlach experiment	This was the first direct observation of the electron spin.	
5. Spin-orbit coupling	**L** and **S** add to give the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, whose magnitude is given by $\lvert \mathbf{J} \rvert = \sqrt{j(j + 1)}\hbar$ where $j = \ell + s$ or $\lvert \ell - s \rvert$. This interaction leads to the fine-structure splitting of the energy levels.	7-53
6. Exclusion principle	No more than one electron can occupy a given quantum state specified by a particular set of the single-particle quantum numbers n, ℓ, m_ℓ, and m_s.	

Table 8.4 The Radial Wavefunctions $R_{n\ell}(r)$ of Hydrogen-like Atoms for $n = 1$, 2, and 3

n	ℓ	$R_{n\ell}(r)$
1	0	$\left(\frac{Z}{a_0}\right)^{3/2} 2e^{-Zr/a_0}$
2	0	$\left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	$\left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{\sqrt{3}\,a_0} e^{-Zr/2a_0}$
3	0	$\left(\frac{Z}{3a_0}\right)^{3/2} 2\left[1 - \frac{2Zr}{3a_0} + \frac{2}{27}\left(\frac{Zr}{a_0}\right)^2\right] e^{-Zr/3a_0}$
3	1	$\left(\frac{Z}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3} \frac{Zr}{a_0}\left(1 - \frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$
3	2	$\left(\frac{Z}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

$$\Psi(r, \theta, \phi, t) = R(r)\, Y_\ell^{m_\ell}(\theta, \phi)\, e^{-i\omega t}$$

Table 8.3 The Spherical Harmonics $Y_\ell^{m_\ell}(\theta, \phi)$

$$Y_0^0 = \frac{1}{2\sqrt{\pi}}$$

$$Y_1^0 = \tfrac{1}{2}\sqrt{\frac{3}{\pi}} \cdot \cos\theta$$

$$Y_1^{\pm 1} = \mp\tfrac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot \sin\theta \cdot e^{\pm i\phi}$$

$$Y_2^0 = \tfrac{1}{4}\sqrt{\frac{5}{\pi}} \cdot (3\cos^2\theta - 1)$$

$$Y_2^{\pm 1} = \mp\tfrac{1}{2}\sqrt{\frac{15}{2\pi}} \cdot \sin\theta \cdot \cos\theta \cdot e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \tfrac{1}{4}\sqrt{\frac{15}{2\pi}} \cdot \sin^2\theta \cdot e^{\pm 2i\phi}$$

$$Y_3^0 = \tfrac{1}{4}\sqrt{\frac{7}{\pi}} \cdot (5\cos^3\theta - 3\cos\theta)$$

$$Y_3^{\pm 1} = \mp\tfrac{1}{8}\sqrt{\frac{21}{\pi}} \cdot \sin\theta \cdot (5\cos^2\theta - 1) \cdot e^{\pm i\phi}$$

$$Y_3^{\pm 2} = \tfrac{1}{4}\sqrt{\frac{105}{2\pi}} \cdot \sin^2\theta \cdot \cos\theta \cdot e^{\pm 2i\phi}$$

$$Y_3^{\pm 3} = \mp\tfrac{1}{8}\sqrt{\frac{35}{\pi}} \cdot \sin^3\theta \cdot e^{\pm 3i\phi}$$

All normalized, ready for use

Table 6.1 Normalized Wave Functions of the Hydrogen Atom for $n = 1, 2,$ and 3*

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\, a_0^{3/2}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\, a_0^{3/2}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\, a_0^{3/2}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0} \cos\theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0} e^{-r/3a_0} \sin\theta\, e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4}(3\cos^2\theta - 1)$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}(3\cos^2\theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin\theta\cos\theta\, e^{\pm i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2\theta\, e^{\pm 2i\phi}$

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.292 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

$$\psi(\mathbf{r}) = \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$P(r) = |g(r)|^2 = r^2|R_{n\ell}(r)|^2 \qquad (8.44)$$

$P(r)\,dr$ is the probability that the electron will be found at a distance between r and $r + dr$ from the nucleus. The most probable distance is the one that maximizes $P(r)$ and generally differs from the average distance $\langle r \rangle$, calculated as

$$\langle r \rangle = \int_0^\infty rP(r)\ dr \qquad (8.46)$$

The most probable values are found to coincide with the radii of the allowed orbits in the Bohr theory. For the states with the maximal possible angular momentum

---

$$\Psi_{n\ell m_\ell m_s} = R_{n\ell} Y_{\ell m_\ell} X_{m_s}$$

4 quantum numbers at last for hydrogen in 4D space time

where $R_{n\ell}$ is the radial wave function, $Y_{\ell m_\ell}$ is the spherical harmonic, and X_{m_s} is the spinwave function

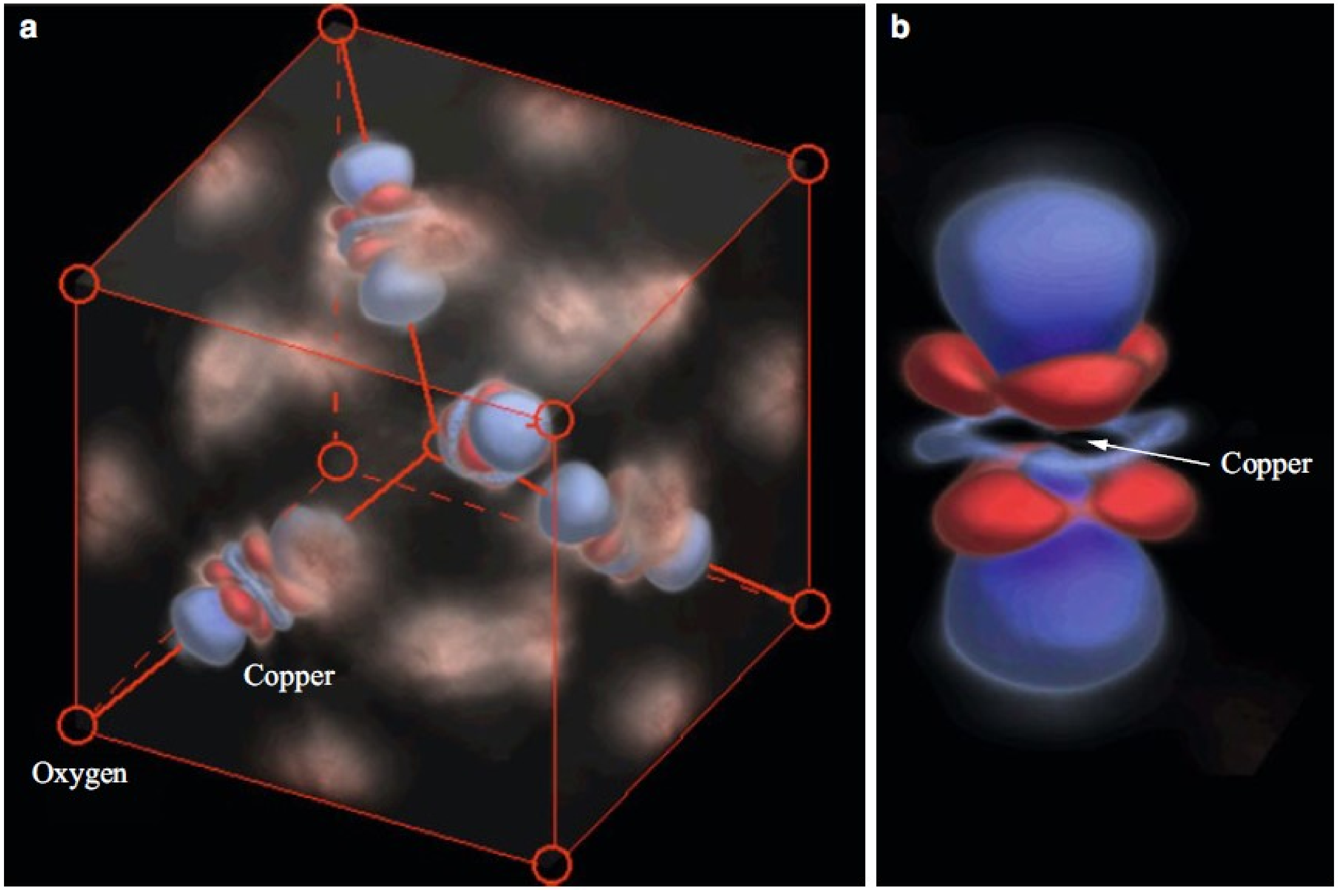
So all we have learned in 3D is valid when spin wave function is multiplied in

"The best that most of us can hope to achieve in physics is simply to misunderstand at a deeper level."

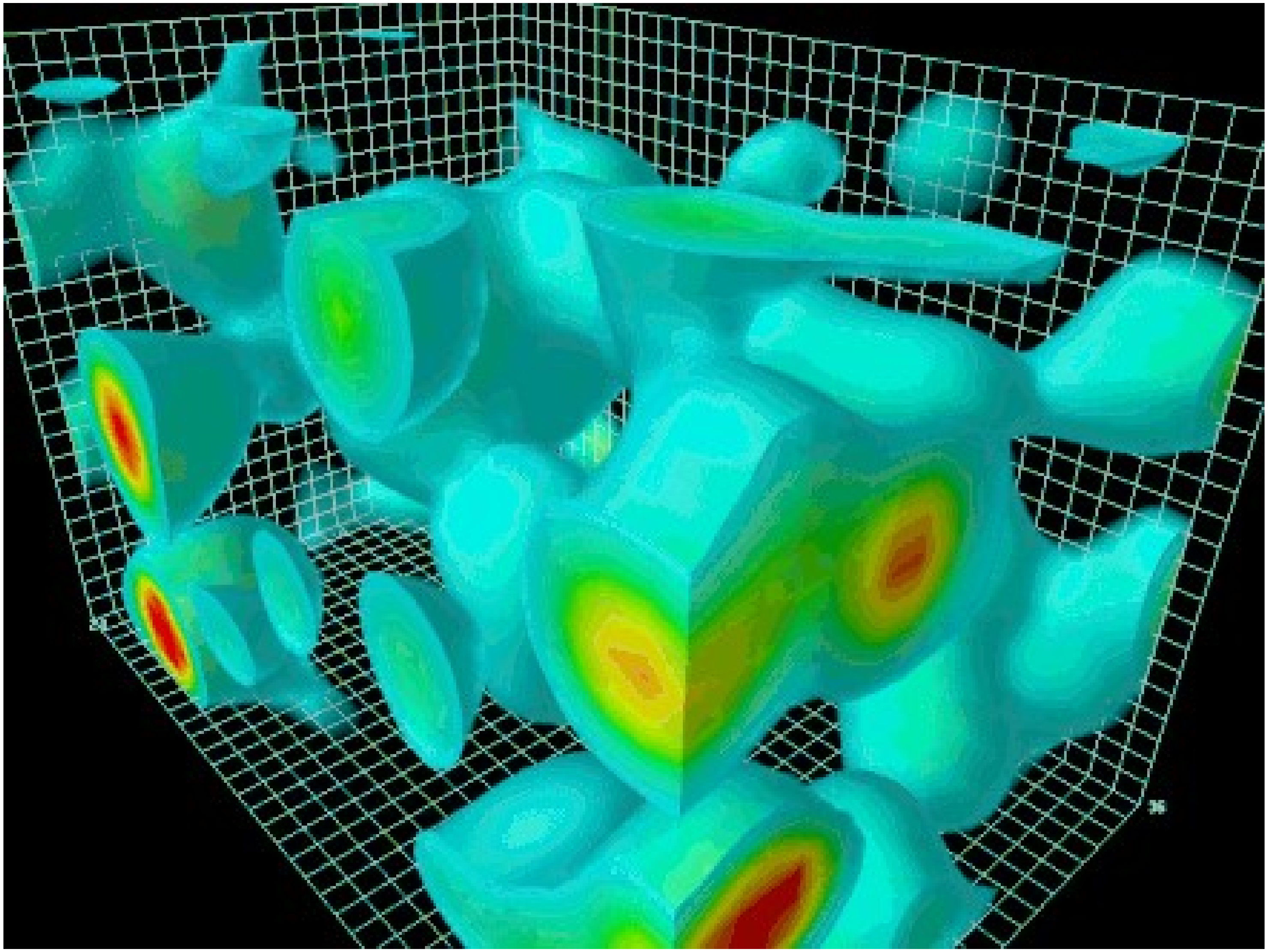
Wolfgang Pauli

https://doi.org/10.1007/978-3-319-26651-0_5

Fig. 5.6 a Measured surfaces of constant charge-density difference in Cu_2O (cuprite). *Blue* shows less charge than MCDF ions (producing 'holes' in the shape of $d_z{}^2$ orbitals), *red* is more. Note metal–metal bonds at center of copper tetrahedra. (The coppers form an FCC lattice.) If cuprite were purely ionic (Cu + O--) this picture would be blank (Zuo et al. 1999). **b** Measured surfaces of constant charge-density difference in Cu_2O along the (vertical) copper–oxygen bond. *Blue* shows less charge than MCDF ions (producing a $d_z{}^2$ 'hole'), *red* is more

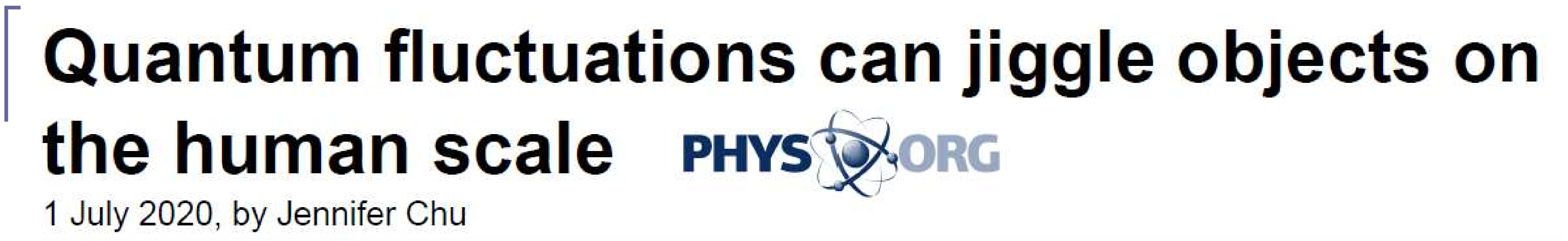


Experimental shape very close to what is predicted by the Schrödinger model of the hydrogen atom and its 4s orbital, i.e. the outermost electron in Cu



3D visualization of quantum fluctuations of the QCD vacuum

http://www.physics.adelaide.edu.au/theory/staff/leinweber/VisualQCD/ImprovedOperators/index.html



Quantum fluctuations can jiggle objects on the human scale

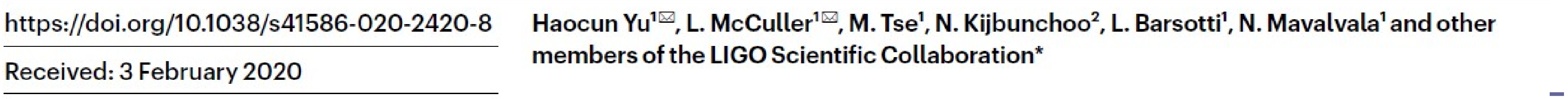
PHYS.ORG

1 July 2020, by Jennifer Chu

"What's special about this experiment is we've seen quantum effects on something as large as a human," says Nergis Mavalvala, the Marble Professor and associate head of the physics department at MIT. *"We too, every nanosecond of our existence, are being kicked around, buffeted by these quantum fluctuations. It's just that the jitter of our existence, our thermal energy, is too large for these quantum vacuum fluctuations to affect our motion measurably. With LIGO's mirrors, we've done all this work to isolate them from thermally driven motion and other forces, so that they are now still enough to be kicked around by quantum fluctuations and this spooky popcorn of the universe."*

Quantum correlations between light and the kilogram-mass mirrors of LIGO

40 kg mass in LIGO experiments moves by 10^{-20} m due to quantum noise, just as predicted from the uncertainty principle



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