

# Class Notes for Modern Physics, Part 3

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# Quantum Mechanics in 3D

There are a lot of issues regarding coordinate systems and spatial symmetries of the potential or physical configuration that enter into the three-dimensional situation.

In the 3D case,

$$\Psi = \Psi(\vec{r}, t) = \Psi(x, y, z, t), \quad P(\vec{r}, t) = |\Psi(\vec{r}, t)|^2 \quad (1)$$

where  $P(\vec{r}, t)dV$  = the probability to find the particle in a volume element of size  $dV$  about  $\vec{r}$  at time  $t$ .

What is the 3D version of the SE? Start from

$$E = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + U(x, y, z). \quad (2)$$

Then multiply by  $\Psi$  and use operator substitutions of

$$\hat{E} = i\hbar \frac{\partial}{\partial t}, \quad \hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}, \quad \hat{p}_y = \frac{\hbar}{i} \frac{\partial}{\partial y}, \quad \hat{p}_z = \frac{\hbar}{i} \frac{\partial}{\partial z}. \quad (3)$$

The resulting SE is

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi + U\Psi \quad (4)$$

where  $\vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ . For the situation considered, where  $U$  has no explicit time dependence, we again use a separation of variables approach by writing

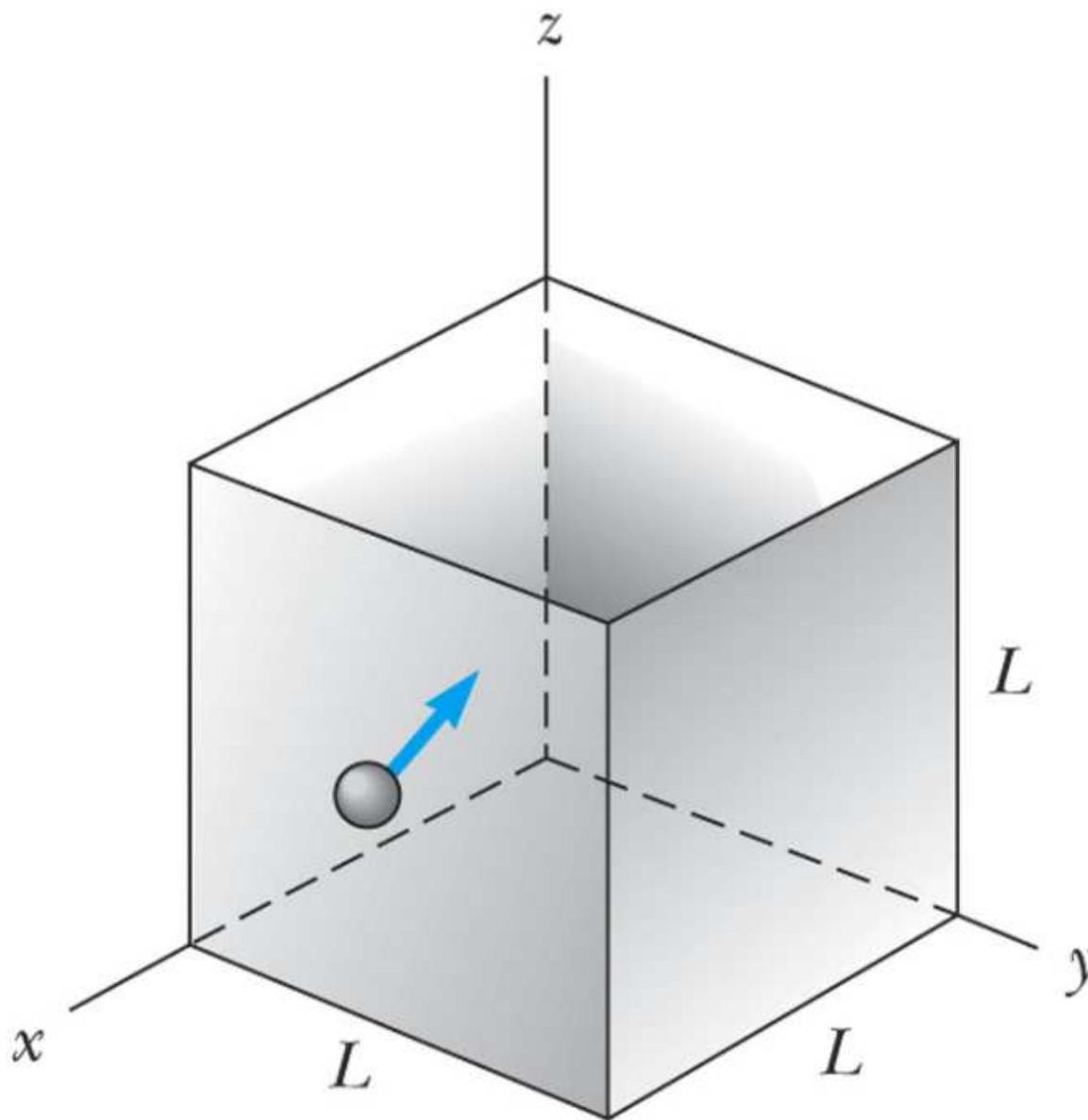
$$\Psi(\vec{r}, t) = \psi(\vec{r})\phi(t) = \psi(\vec{r})e^{-i\omega t}, \quad (5)$$

where  $i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, t) = \hbar\omega\Psi(\vec{r}, t) = E\Psi(\vec{r}, t)$  and consistency with the SE requires the time-independent SE:

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{r}) + U(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}). \quad (6)$$

### Cubical symmetry case

The simplest case is that of a cube with infinite potential at the sides of the cube. This is analogous to our infinite well in one dimension. The picture is below.



Inside the box where  $U = 0$ , the time-independent SE reduces to

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{r}) = E\psi(\vec{r}), \quad (7)$$

while outside the box  $U = \infty$  and  $\psi = 0$ . Given the symmetry of the situation, it is appropriate to further separate variables by writing

$$\psi(\vec{r}) = \psi_1(x)\psi_2(y)\psi_3(z). \quad (8)$$

If we substitute this form into the 3D SE, we get ( $\partial \rightarrow d$  is ok)

$$-\frac{\hbar^2}{2m} \left( \frac{d^2\psi_1(x)}{dx^2} \psi_2\psi_3 + \psi_1 \frac{d^2\psi_2(y)}{dy^2} \psi_3 + \psi_1\psi_2 \frac{d^2\psi_3(z)}{dz^2} \right) = E\psi_1\psi_2\psi_3. \quad (9)$$

We may then divide both sides of this equation by  $\psi_1\psi_2\psi_3$  to obtain:

$$-\frac{\hbar^2}{2m} \left( \frac{\frac{d^2\psi_1(x)}{dx^2}}{\psi_1} + \frac{\frac{d^2\psi_2(y)}{dy^2}}{\psi_2} + \frac{\frac{d^2\psi_3(z)}{dz^2}}{\psi_3} \right) = E. \quad (10)$$

At this point, we note that each of the terms depends only on one coordinate  $x$ ,  $y$  or  $z$ . The only way the above equation can hold for all  $x, y, z$  is if

$$-\frac{\hbar^2}{2m} \left[ \frac{\frac{d^2\psi_1}{dx^2}}{\psi_1(x)} \right] = E_1 \quad \dots \quad (11)$$

where the  $E_1$ ,  $E_2$ ,  $E_3$  are all constants and  $E_1 + E_2 + E_3 = E$ . Each of these individual equations is then solved just like in the  $1D$  case.

Using a coordinate set up where the cubical box runs from  $0$  to  $L$  in each of the three spatial coordinates, it should be clear from the one-dimensional case that vanishing of  $\psi_1$  at  $x = 0$  and  $x = L$ , and so forth, implies

$$\begin{aligned} \psi_1(x) &\propto \sin k_1 x, & \text{with } k_1 &= \frac{n_1 \pi}{L} \\ \psi_2(y) &\propto \sin k_2 y, & \text{with } k_2 &= \frac{n_2 \pi}{L} \\ \psi_3(z) &\propto \sin k_3 z, & \text{with } k_3 &= \frac{n_3 \pi}{L}. \end{aligned} \quad (12)$$

If we now take these forms and plug into the SE, using, for example,

$$\frac{d^2}{dx^2}[\psi_1(x)\psi_2(y)\psi_3(z)] = \left[ \frac{d^2}{dx^2}\psi_1(x) \right] \psi_2(y)\psi_3(z) = -k_1^2[\psi_1(x)\psi_2(y)\psi_3(z)], \quad (13)$$

we obtain

$$E = E_1 + E_2 + E_3 = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2). \quad (14)$$

Note that each of the squared momenta are “sharp” variables in that they have definite eigenvalues: for example,

$$\hat{p}_x^2 \psi(\vec{r}) = \hbar^2 k_1^2 \psi(\vec{r}) = \frac{\hbar^2 n_1^2 \pi^2}{L^2} \psi(\vec{r}). \quad (15)$$

Normalization is a straightforward generalization of the 1D case: writing  $\psi = A \sin k_1 x \sin k_2 y \sin k_3 z$ , we require

$$\begin{aligned} \int |\psi|^2 dV &= A^2 \int |\psi_1|^2 dx \int |\psi_2|^2 dy \int |\psi_3|^2 dz = A^2 \left(\frac{2}{L}\right)^3 = 1, \\ \Rightarrow A &= \left(\frac{2}{L}\right)^{3/2}. \end{aligned} \quad (16)$$

The lowest state is  $n_1 = n_2 = n_3 = 1$ . (None of the  $n_i$ 's can be 0, or the wave function vanishes. More correctly, to have  $\frac{d^2 \psi_1}{dx^2} = 0$  would

require  $\psi_1 = a + bx$ . But then,  $a = 0$  is required for  $\psi_1 = 0$  at  $x = 0$  and then  $b = 0$  is required for  $\psi_1 = 0$  at  $x = L$ .) This lowest state has energy

$$E_{111} = \frac{\pi^2 \hbar^2}{2mL^2} (3). \quad (17)$$

The first excited state can be achieved in 3 ways:

$$\begin{aligned} n_1 = 2, \quad n_2 = 1, \quad n_3 = 1 \\ n_1 = 1, \quad n_2 = 2, \quad n_3 = 1 \\ n_1 = 1, \quad n_2 = 1, \quad n_3 = 2 \end{aligned} \quad (18)$$

for which

$$E_{211} = E_{121} = E_{112} = \frac{\pi^2 \hbar^2}{2mL^2} (4 + 1 + 1 = 6). \quad (19)$$

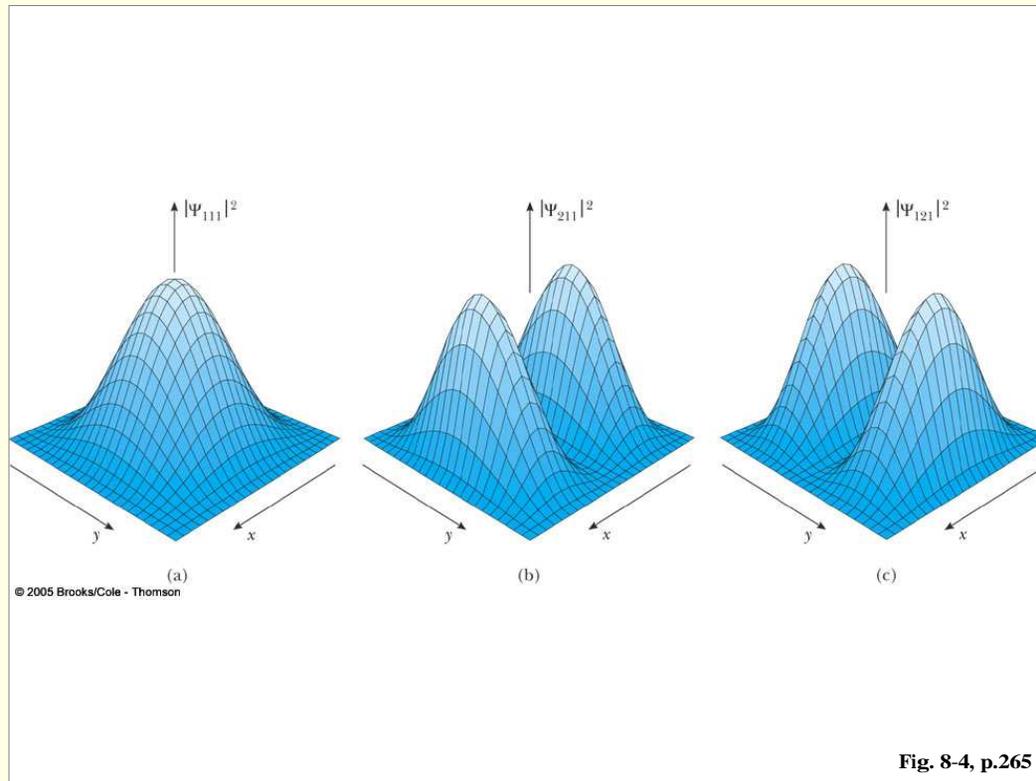
A situation in which the same total energy can be achieved in more than one way, is call **degeneracy**. The above energy level is said to have a 3-fold degeneracy. Similarly, we have

$$E_{221} = E_{212} = E_{122} = \frac{\pi^2 \hbar^2}{2mL^2} (4 + 4 + 1 = 9)$$

$$E_{311} = E_{131} = E_{113} = \frac{\pi^2 \hbar^2}{2mL^2} (9 + 1 + 1 = 11)$$

$$E_{222} = \frac{\pi^2 \hbar^2}{2mL^2} (4 + 4 + 4 = 12). \quad (20)$$

Note that the **222** state is again non-degenerate. That energy can only be achieved in one way.



**Figure 1: Pictures of the 111, 211 and 121 cubic box  $|\psi|^2$  shapes.**

## Spherical Symmetry Case

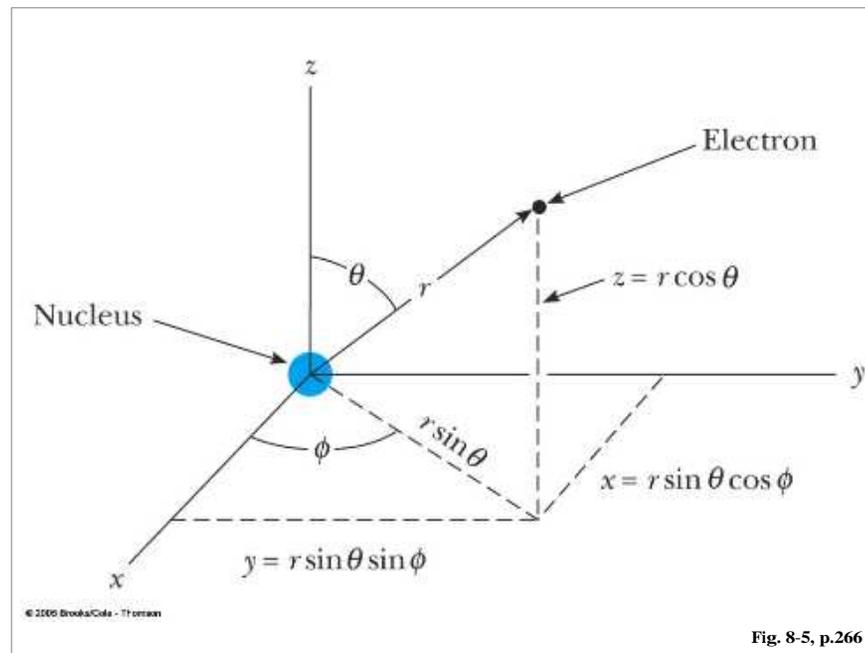


Figure 8.5 The central force on an atomic electron is one directed toward a fixed point, the nucleus. The coordinates of choice here are the spherical coordinates  $r$ ,  $\theta$ ,  $\phi$ , centered on the nucleus.

**Figure 2: Spherical coordinate system with nucleus at center.**

This is the case where we have a **central force**, so that  $U = U(r)$  where  $r = |\vec{r}|$ .

In this case, it is best to employ spherical coordinates:  $r$ ,  $\theta$ , and  $\phi$ , where

$$z = r \cos \theta, \quad x = r \sin \theta \cos \phi, \quad y = r \sin \theta \sin \phi. \quad (21)$$

If  $U$  has no explicit time dependence, then we again separate coordinates by writing

$$\Psi(\vec{r}, t) = \psi(\vec{r})e^{-i\omega t}, \quad E = \hbar\omega. \quad (22)$$

Now we input some additional ideas from classical central forces.

You should recall that for a central potential, in classical mechanics one finds that the angular momentum is conserved. So we can choose a given value of  $\vec{L}$  (all three components) and it will not change.

In QM, it is no longer possible to fix all three components of  $\vec{L}$  at the same time. It is a dilemma related to the HUP.

1. Indeed, if  $\vec{L}$  were known exactly (all components), the particle would be confined to the orbital plane  $\perp$  to  $\vec{L}$ .
2. In particular, its coordinate along the  $\vec{L}$  direction would be known *exactly*.

3. The HUP then says that the  $\vec{p}$  along  $\vec{L}$  would be completely unknown.
4. So, then how can we say that all of  $\vec{p}$  is  $\perp$  to  $\vec{L}$ ?
5. In fact, it is impossible (according to the HUP) to specify more than one component of  $\vec{L}$ !

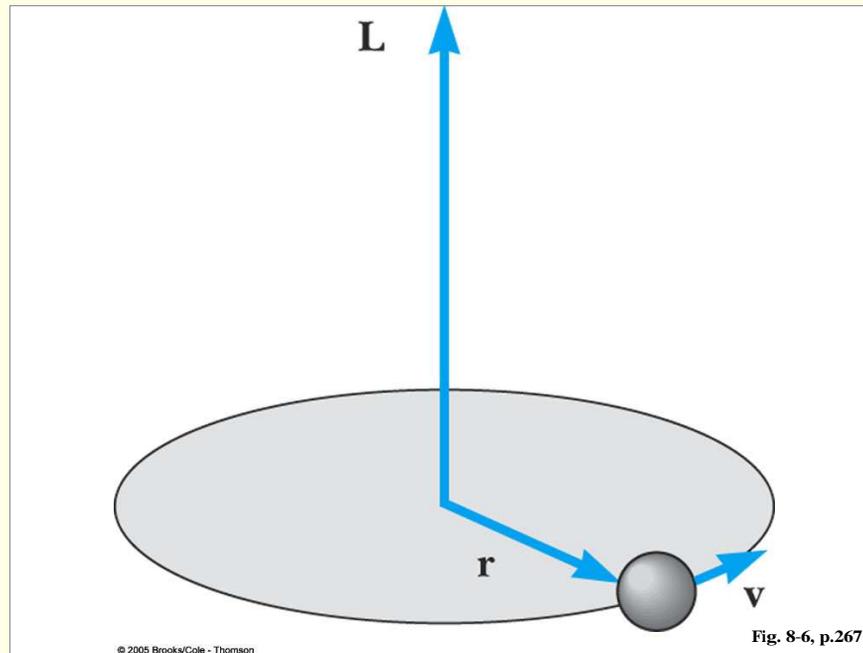


Figure 3: Fixed  $\vec{L}$  picture.

It is conventional to choose to fix  $L_z = xp_y - yp_x$ . In addition, the magnitude  $|\vec{L}|$  can also be fixed, where

$$|\vec{L}|^2 = L_x^2 + L_y^2 + L_z^2. \quad (23)$$

In QM, we can recognize when there is a conflict between *exactly* specifying two different quantities associated with operators  $\hat{O}_1$  and  $\hat{O}_2$  by checking whether or not  $[\hat{O}_1, \hat{O}_2] \equiv \hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1 = 0$ .

If the order of the operators does not matter, then we say they **commute** and then precise values for  $O_1$  and  $O_2$  can be simultaneously specified.

In the language of eigenvalues, it is only consistent for our wave function to be such that both  $\hat{O}_1\psi = o_1\psi$  and  $\hat{O}_2\psi = o_2\psi$  if  $[\hat{O}_1, \hat{O}_2] = 0$ : equivalently,

$$[\hat{O}_1, \hat{O}_2]\psi = \hat{O}_1\hat{O}_2\psi - \hat{O}_2\hat{O}_1\psi = \hat{O}_1(o_2\psi) - \hat{O}_2(o_1\psi) = o_2o_1\psi - o_1o_2\psi = 0 \quad (24)$$

if  $\psi$  is an eigenstate for both operators.

If the **commutator**  $[\hat{O}_1, \hat{O}_2] \neq 0$ , then we cannot simultaneously have precise values for both operators.

Our previous example of this was  $\hat{x} = x$  and  $\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$ . We found

$$[\hat{x}, \hat{p}_x] = i\hbar, \quad (25)$$

which is equivalent to the HUP which says  $\Delta x \Delta p_x \geq \frac{1}{2}\hbar$ . In the case of

angular momentum, it is easy to check that, for example,

$$[\hat{L}_z, \hat{L}_x] \neq 0, \quad \text{and} \quad [\hat{L}_z, \hat{L}_y] \neq 0, \quad (26)$$

where

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = x\frac{\hbar}{i}\frac{\partial}{\partial y} - y\frac{\hbar}{i}\frac{\partial}{\partial x}, \quad (27)$$

and cyclic permutations thereof. In contrast, one finds that

$$[\hat{L}_z, \widehat{|\vec{L}|^2}] = [\hat{L}_z, (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2)] = 0, \quad (28)$$

implying that these two operators can be simultaneously fixed, that is they can simultaneously have precise eigenvalues.

This is particularly easy to recognize in spherical coordinates for which

we have  $\widehat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$ <sup>1</sup> and

$$\widehat{L}^2 = -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \csc^2 \theta \frac{\partial^2}{\partial \phi^2} \right]. \quad (30)$$

We see that

$$[\widehat{L}_z, \widehat{L}^2] = 0 \quad (31)$$

by virtue of the fact that the only  $\phi$  dependence in  $\widehat{L}^2$  is in the form of  $\frac{\partial^2}{\partial \phi^2}$  which commutes with the  $\frac{\partial}{\partial \phi}$  appearing in  $\widehat{L}_z$  — it doesn't matter which order partial derivatives of exactly the same form are done in.

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<sup>1</sup>Let's check by using the chain rule for partial derivatives:

$$\begin{aligned} \frac{\partial}{\partial \phi} &= \frac{\partial x}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \phi} \frac{\partial}{\partial z} = \frac{\partial(r \sin \theta \cos \phi)}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial(r \sin \theta \sin \phi)}{\partial \phi} \frac{\partial}{\partial y} + \frac{\partial(r \cos \theta)}{\partial \phi} \frac{\partial}{\partial z} \\ &= -r \sin \theta \sin \phi \frac{\partial}{\partial x} + r \sin \theta \cos \phi \frac{\partial}{\partial y} + 0 = -y \frac{\partial}{\partial x} + x \frac{\partial}{\partial y} \end{aligned} \quad (29)$$

## The wave functions

The wave functions with sharp values of  $|\vec{L}|$  and  $L_z$  are of the form

$$\psi(\vec{r}) = \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (32)$$

Earlier, we noted that in spherical coordinates

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = \frac{\hbar}{i} \frac{\partial}{\partial \phi}. \quad (33)$$

This means that if we specify  $\hat{L}_z\psi = L_z\psi$ , then it should turn out that  $\phi$  should be completely unknown. To see this explicitly, we note that the  $\Phi$  which obeys the above equation is

$$\Phi(\phi) = e^{+iL_z\phi/\hbar}, \quad (34)$$

for which  $|\Phi|^2 = 1$  is indeed completely independent of  $\phi$ .

But, this is not the end of the story. As you have learned,  $\psi$  should be a single valued function. For this to be the case, it has to be that

$$\Phi(\phi) = \Phi(\phi + 2\pi). \quad (35)$$

Applying this to the specific form given above, we have the requirement:

$$e^{iL_z 2\pi} = 1, \quad \Rightarrow \quad L_z = m_l \hbar, \quad m_l = 0, \pm 1, \pm 2, \dots \quad (36)$$

The quantity  $m_l$  is called the **magnetic quantum number**.

So, let us now return to the full SE:

$$-\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi(\vec{r}) + U(r)\psi(\vec{r}) = E\psi(\vec{r}). \quad (37)$$

To make use of the spherical symmetry, we must rewrite  $\vec{\nabla}^2$  in spherical coordinates  $r, \theta, \phi$ . I hope that this is something with which you are familiar (you use the change rule as we did for  $\hat{L}_z$ ). The correct result is

$$\begin{aligned} \vec{\nabla}^2 &= \frac{\partial^2}{\partial r^2} + \left(\frac{2}{r}\right) \frac{\partial}{\partial r} + \frac{1}{r^2} \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \\ &= \frac{\partial^2}{\partial r^2} + \left(\frac{2}{r}\right) \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\hat{L}^2}{\hbar^2}. \end{aligned} \quad (38)$$

Note how the  $r, \theta, \phi$  derivatives appear in separate terms. This means that a separation of variables is again possible. So, we proceed by plugging  $\psi(\vec{r}) = R(r)\Theta(\theta)\Phi(\phi)$  in the SE with the above form of  $\vec{\nabla}^2$  and then divide by  $-\hbar^2\psi(\vec{r})/2m$ . The result is ( $\partial \rightarrow d$  ok)

$$\left\{ \frac{r^2}{R} \left[ \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right] - \frac{2mr^2}{\hbar^2} [U(r) - E] \right\} + \left\{ \frac{1}{\Theta} \left[ \frac{d^2 \Theta}{d\theta^2} + \cot \theta \frac{d\Theta}{d\theta} \right] + \csc^2 \theta \left[ \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \right] \right\} = 0. \quad (39)$$

The  $r, \theta$  and  $\phi$  groupings must each give a constant value in order for this equation to be satisfied. We already have set things up so that  $\Phi(\phi) = e^{im_l\phi}$ , so that

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m_l^2. \quad (40)$$

We next want to have

$$\frac{1}{\Theta} \left[ \frac{d^2 \Theta}{d\theta^2} + \cot \theta \frac{d\Theta}{d\theta} \right] - m_l^2 \csc^2 \theta = -\frac{|\vec{L}|^2}{\hbar^2}, \quad (41)$$

where the constant is the eigenvalue of  $\widehat{\vec{L}}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2$  whose operator

form in spherical coordinates was given earlier and took precisely the form implicit in Eqs. (39) and (41). We have argued that  $|\widehat{\vec{L}}|^2$  can take on a sharp eigenvalue, and we are calling the eigenvalue  $|\vec{L}|^2$ , which is supposed to be a particular numerical constant.

The solutions of this equation are called the Legendre Polynomials and the products  $\Theta\Phi = Y_l^{m_l}(\theta, \phi)$  are called the spherical harmonic functions. These functions are only consistent (*i.e.* single valued, etc.) if

$$\frac{|\vec{L}|^2}{\hbar^2} = l(l + 1), \quad l = 0, 1, 2, 3, \dots \quad \text{and} \quad l \geq |m_l|. \quad (42)$$

The quantity  $l$  is called the **orbital quantum number**. The use of “quantum number” for  $m_l$  and  $l$  is in close analogy to Bohr’s original usage. We will see Bohr’s quantum number emerge in a moment. A picture of the  $|\vec{L}|$  and  $L_z$  quantization is below.

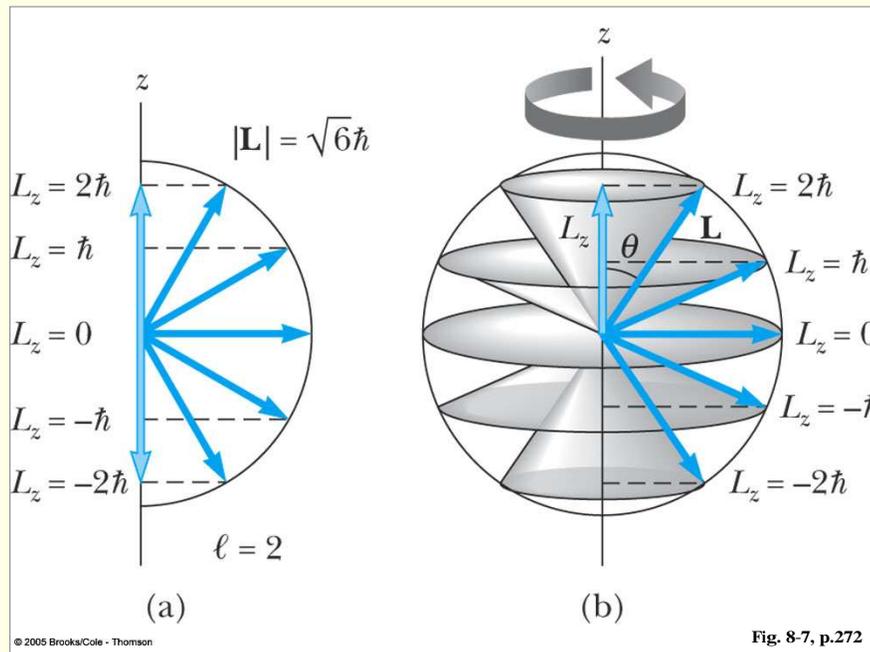


Figure 4:  $l = 2$  picture showing  $|\vec{L}|^2 = l(l + 1)\hbar^2 = 6\hbar^2$  and different  $L_z$  and associated orientations.

What we see is that the angle of  $\vec{L}$  with respect to the  $z$  axis is fixed by  $m_l$ ;  $\vec{L}$  can be thought of as rotating (really smeared) around the  $z$  axis at this fixed angle so that neither  $L_x$  nor  $L_y$  is fixed. The angles of  $\vec{L}$  wrp to  $z$  can only take on certain precise values:

$$\cos \theta = \frac{L_z}{|\vec{L}|} = \frac{m_l}{\sqrt{l(l + 1)}}. \quad (43)$$

Note that  $\vec{L}$  cannot be fully aligned with the  $z$  axis since  $|m_l| \leq l < \sqrt{l(l+1)}$ . Classically, any angle would be allowed. The book calls the quantization of these angles **space quantization**.

This kind of quantization is intrinsically related to the wave point of view. This quantization arises from the  $3D$  analogue of fitting an integer number of wavelengths around the Bohr atom circumference. Waves must reinforce one another in a standing wave pattern. This “reinforcement” is equivalent to the earlier requirement that  $\Phi$  be a unique function as  $\phi \rightarrow \phi + 2\pi$ . This only happens for precisely quantized configurations.

In fact, we can refine this analogy a bit further for  $L_z$ . Suppose the particle has tangential velocity about the  $z$  axis of  $v_t$ . The associated tangential momentum and wavelength would then be  $p = mv_t$  and  $\lambda = \frac{h}{p} = \frac{h}{mv_t}$ . Requiring  $2\pi r = m_l \lambda$  is equivalent to requiring

$$L_z = mv_t r = mv_t \left( \frac{m_l \lambda}{2\pi} \right) = mv_t \left( \frac{m_l \frac{h}{mv_t}}{2\pi} \right) = m_l \hbar. \quad (44)$$

The restriction to precise values of  $l$  is more complicated to explain. We have a certain differential equation to solve and there are always

solutions to this differential equation for any value of the rhs constant. However, only for the given  $l(l + 1)$  type of rhs constant are these solutions well-behaved. For other values, they would have a divergent type of behavior.

It is not clear that this  $m_l$  has much to do with the Bohr quantization condition. In fact, it doesn't, as we shall see.

### An example

Suppose the minimum angle between  $|\vec{L}|$  and the  $z$  axis is  $30^\circ$ . What is  $|\vec{L}|$ .

Answer: the minimal angle occurs when  $m_l = l$ . In this case,

$$\cos \theta = \frac{l}{\sqrt{l(l+1)}} = \sqrt{\frac{l}{l+1}}. \quad (45)$$

For  $\theta = 30^\circ$ , this leads to

$$\cos 30^\circ = 0.866 = \sqrt{\frac{l}{l+1}} \quad (46)$$

which is satisfied for  $l = 3$ .

## Examples of $\Theta\Phi$

Let us give the first few solutions of these  $\Phi$  and  $\Theta$  equations and check that they really do look consistent and do satisfy the differential equations. Well, of course, we already know that  $e^{im_l\phi}$  satisfies

$$\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -m_l^2. \quad (47)$$

We need only check the  $\Theta$  equation:

$$\frac{1}{\Theta} \left[ \frac{d^2\Theta}{d\theta^2} + \cot\theta \frac{d\Theta}{d\theta} \right] - m_l^2 \csc^2\theta = -\frac{|\vec{L}|^2}{\hbar^2} = -l(l+1) \quad (48)$$

- $l = 0, m_l = 0$ .

For this case the solution is  $\Phi = 1$  and  $\Theta = 1$ . Clearly the latter solves the  $\Theta$  equation. Note that no matter how hard you tried, you would not have found a well-behaved solution to the  $\Theta$  equation above for  $l = 0$  with  $m_l = \pm 1$ , for example.

- $l = 1, m_l = 0.$

For this case,  $\Phi = 1$  and  $\Theta = \cos \theta$ . If we substitute this  $\Theta$  into the  $\Theta$  equation, we get

$$\frac{1}{\cos \theta} [-\cos \theta + \cot \theta (-\sin \theta)] - 0 \stackrel{?}{=} -2, \quad (49)$$

which is indeed ok.

- $l = 1, m_l = 1.$

For this case,  $\Phi = e^{i\phi}$  and  $\Theta = \sin \theta$ . To check that the latter works, we again substitute to see if

$$\frac{1}{\sin \theta} [-\sin \theta + \cot \theta \cos \theta] - \frac{1}{\sin^2 \theta} = -1 + \frac{\cos^2 \theta - 1}{\sin^2 \theta} \stackrel{?}{=} -2. \quad (50)$$

Once again we see that this is consistent.

- $l = 2, m_l = 0.$

$$\Theta = P_{2,0} = \frac{1}{2}(3 \cos^2 \theta - 1) \quad (51)$$

can easily be checked.

- $l = 2, m_l = 1.$

$$\Theta = P_{2,1} = 3 \cos \theta \sin \theta \quad (52)$$

can easily be checked.

- $l = 2, m_l = 2.$

$$\Theta = P_{2,2} = 3 \sin^2 \theta \quad (53)$$

can easily be checked. We do this one explicitly. The  $\Theta$  equation requires:

$$\begin{aligned} & \frac{1}{3 \sin^2 \theta} [(6 \cos^2 \theta - 6 \sin^2 \theta) + \cot \theta (6 \sin \theta \cos \theta)] - \frac{4}{\sin^2 \theta} \\ = & \frac{2}{\sin^2 \theta} [\cos^2 \theta - \sin^2 \theta + \cos^2 \theta - 2] \stackrel{?}{=} -6, \end{aligned} \quad (54)$$

which is, in fact, true.

Note the general notation above of  $P_{l,m_l}$  for the associated Legendre polynomials that are the solutions of the  $\Theta$  equations.

It is conventional to normalize the above  $\Theta\Phi$  products so that

$$\int d \cos \theta d \phi \Theta^2 |\Phi|^2 = 2\pi \int d \cos \theta \Theta^2 = 1, \quad (55)$$

where the  $d \cos \theta d \phi$  comes from what you know from calculus is the spherical form of the volume element:

$$dxdydz = r^2 dr d \cos \theta d \phi. \quad (56)$$

The resulting  $\Theta\Phi$  functions are the Spherical Harmonics  $Y_l^{m_l}(\theta, \phi)$  examples of which are:

$$\begin{aligned} Y_0^0 &= \frac{1}{2\sqrt{\pi}} \\ Y_1^0 &= \frac{1}{2}\sqrt{\frac{3}{\pi}} \cos \theta \\ Y_1^{\pm 1} &= \mp \frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi} \\ Y_2^0 &= \frac{1}{4}\sqrt{\frac{5}{\pi}} (3 \cos^2 \theta - 1) \end{aligned}$$

$$\begin{aligned}
Y_2^{\pm 1} &= \mp \frac{1}{2} \sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{\pm i\phi} \\
Y_2^{\pm 2} &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{\pm 2i\phi}.
\end{aligned} \tag{57}$$

## The Radial Wave Equation

So now we must return to Eq. (39), which I repeat below:

$$\begin{aligned}
&\left\{ \frac{r^2}{R} \left[ \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right] - \frac{2mr^2}{\hbar^2} [U(r) - E] \right\} \\
&+ \left\{ \frac{1}{\Theta} \left[ \frac{d^2 \Theta}{d\theta^2} + \cot \theta \frac{d\Theta}{d\theta} \right] + \csc^2 \theta \left[ \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \right] \right\} = 0. \tag{58}
\end{aligned}$$

We have learned that the  $\Theta$  part of this gives a valid solution if it equals  $-l(l+1)$ . So, that means we must solve

$$\left\{ \frac{r^2}{R} \left[ \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right] - \frac{2mr^2}{\hbar^2} [U(r) - E] \right\} - l(l+1) = 0 \tag{59}$$

This we rewrite in the form:

$$-\frac{\hbar^2}{2m} \left[ \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right] + \frac{\hbar^2 l(l+1)}{2mr^2} R(r) + U(r)R(r) = ER(r). \quad (60)$$

Now, you will note that while it is very likely that the allowed (presumably discrete) values of  $E$  will depend on  $l$ , it is clear that even at fixed  $l$  there will be a series of degenerate states characterized by the  $2l + 1$  different values of  $m_l$ ,  $\Rightarrow (2l + 1)$ -fold degeneracy. This degeneracy applies for any spherically symmetric potential.

You will notice that the  $\frac{\hbar^2 l(l+1)}{2mr^2} R$  term enters like an extra potential or energy in addition to  $U(r)$ . It can be understood as the energy associated with orbital motion:

$$\begin{aligned} K^{orb} &= \frac{1}{2} m v_{orb}^2 \\ &= \frac{1}{2} m \left( \frac{|\vec{L}|}{mr} \right)^2 \quad \text{using } |\vec{L}| = m v_{orb} r \\ &= \frac{1}{2} m \left( \frac{\hbar^2 l(l+1)}{m^2 r^2} \right) \quad \text{using } |\vec{L}|^2 = \hbar^2 l(l+1) \end{aligned}$$

$$= \frac{\hbar^2 l(l+1)}{2mr^2}.$$

### Application to atoms

This is the most important application. We will discuss the Bohr-like situation where there is a single  $e^-$  bound to a nucleus of charge  $Ze$  for which

$$U(r) = \frac{k(Ze)(-e)}{r} = -k\frac{Ze^2}{r}. \quad (61)$$

We will be using our separated form

$$\Psi(r, \theta, \phi, t) = R(r)Y_l^{m_l}(\theta, \phi)e^{-i\omega t} \quad (62)$$

that is a suitable solution with definite  $|\vec{L}|^2$  and  $L_z$ . There is one more manipulation that will simplify things, which is to take Eq. (60) and substitute  $g(r) = rR(r)$ . The utility of this substitution follows from

$$\frac{d^2(rR)}{dr^2} = r \left[ \frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} \right]. \quad (63)$$

Making this substitution, the radial equation becomes

$$-\frac{\hbar^2}{2m} \frac{d^2 g(r)}{dr^2} + U_{eff}(r)g(r) = E g(r) \quad (64)$$

where

$$U_{eff} = \frac{|\vec{L}|^2}{2mr^2} + U(r) = \frac{\hbar^2 l(l+1)}{2mr^2} - k \frac{Ze^2}{r} \quad (65)$$

is an effective radial potential and the  $-\frac{\hbar^2}{2m} \frac{d^2}{dr^2}$  is an effective radial kinetic energy in operator form.

We will not actually go through the general techniques for solving this equation in this course. However, you have perhaps come to anticipate the fact that acceptable solutions for  $g(r)$  are only found for certain discrete values of  $E$ . (Acceptable means normalizable and well-behaved at  $r \rightarrow 0$  and  $r \rightarrow \infty$ .) These  $E$  values are the ones you are already familiar with:

$$E = -\frac{ke^2 Z^2}{2a_0 n^2}, \quad n = 1, 2, 3, \dots \quad (66)$$

*i.e.* just like the Bohr result, but a very different derivation. Further, the

solutions are acceptable only if

$$(l + 1) \leq n. \quad (67)$$

The difference  $n - l - 1$  is equal to the number of nodes or zeroes of the radial function  $R$  and must physically be  $\geq 0$ . Thus, the solutions are labeled as  $R_{nl}$ .

Note that we now have an additional degeneracy:  $E$  depends only on  $n$  and not on  $l$  which can take any value  $l \leq n - 1$ . And, of course, there is still the  $(2l + 1)$  degeneracy associated with the possible  $m_l$  values at any fixed  $l$  among the possible choices.

Independence of  $m_l$  for  $E$  was automatic for any  $U(r)$  and, recall, comes from the spherical symmetry of the problem.

That  $E$  does not depend on  $l$  at fixed  $n$  is a special feature of the single- $e^-$  atom situation. It does not apply in general. There is an extra symmetry (that we do not discuss) that one can identify as being

responsible for this additional degeneracy.

### Some terminology

States of definite  $n$  form a **shell**.

$n = 1$  is the  $K$  shell.

$n = 2$  is the  $L$  shell.

$n = 3$  is the  $M$  shell.

States having the same  $n$  and  $l$  form a **sub-shell**. The different sub-shell's for a given  $n$  are denoted as follows.

$l = 0$  is denoted by  $s$ .

$l = 1$  is denoted by  $p$ .

$l = 2$  is denoted by  $d$ .

$l = 3$  is denoted by  $f$ .

Of course, for  $n = 1$ , we only have the  $s$  subshell, whereas for  $n = 2$ , the  $s$  and  $p$  subshells are both allowed, and so forth.

So, let us count the number of states with  $n = 3$ . We have  $l = 0$  (the  $s$  state) and there is only 1. We have  $l = 1$ , with  $m_l = -1, 0, 1$ , or 3 states. Finally, we have  $l = 2$  with  $m_l = -2, -1, 0, 1, 2$ , or 5 states. Total number of states =  $1 + 3 + 5 = 9$ . All have the same energy of  $E_3 = -(13.6 \text{ eV}) \frac{Z^2}{3^2}$ .

Bohr?

So, we have seen that Bohr's quantization  $L = n\hbar$  is certainly not actually correct. In fact, we have found that  $l = 0$  will be ok for any  $n$ .

If we try to reinterpret Bohr's condition as  $L_z = n\hbar$ , this also fails. In fact, we have found that  $E_n$  as specified for some radial solution with  $n - 1$  nodes is actually independent of  $m_l$ .

Understanding the result for  $|\vec{L}|^2$

Since there is no preferred direction, we expect that

$$\langle L_x^2 \rangle = \langle L_y^2 \rangle = \langle L_z^2 \rangle. \quad (68)$$

This should apply even though the wave functions with definite  $L_z$  are

not eigenstates of  $\widehat{L}_y^2$  and  $\widehat{L}_x^2$ . Using the above equality, we find that

$$\langle |\vec{L}|^2 \rangle = |\vec{L}|^2 = 3 \langle \widehat{L}_z^2 \rangle = 3 \langle L_z^2 \rangle = 3 \frac{1}{2l+1} \sum_{m_l=-l}^l m_l^2 \hbar^2 = l(l+1) \hbar^2 \quad (69)$$

where the last result is simply a result of the indicated calculation.

And, of course, the range of  $m_l$  is determined by the fact that  $L_z \geq \sqrt{\langle |\vec{L}|^2 \rangle}$  is not allowed. Had we gone up to  $m_l = l + 1$ , we would have violated this condition.

### The wave functions

It is useful to display a few of the solutions  $R_{nl}$ . Those for  $n = 1, 2, 3$  appear in Table 5. You will note that the number of nodes is  $n - l - 1$  as stated earlier. Also note the exponential fall off as controlled by  $e^{-Zr/na_0}$ .

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

$n$	$\ell$	$R_{n\ell}(r)$
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	$\left(\frac{Z}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

Table 8-4, p.280

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**Figure 5: Radial wave functions  $R_{nl}(r)$  for  $n = 1, 2, 3$ .**

**The rules for photon emission are more complicated than originally**

understood at the beginning. Since the photon actually has a spin (something we shall come to) of 1, conservation of total angular momentum (atom+ photon) is only possible if the initial and final states of the atom differ by exactly one unit of  $l$ :

$$|l_f - l_i| = 1, \quad \text{or} \quad \Delta l = \pm 1. \quad (70)$$

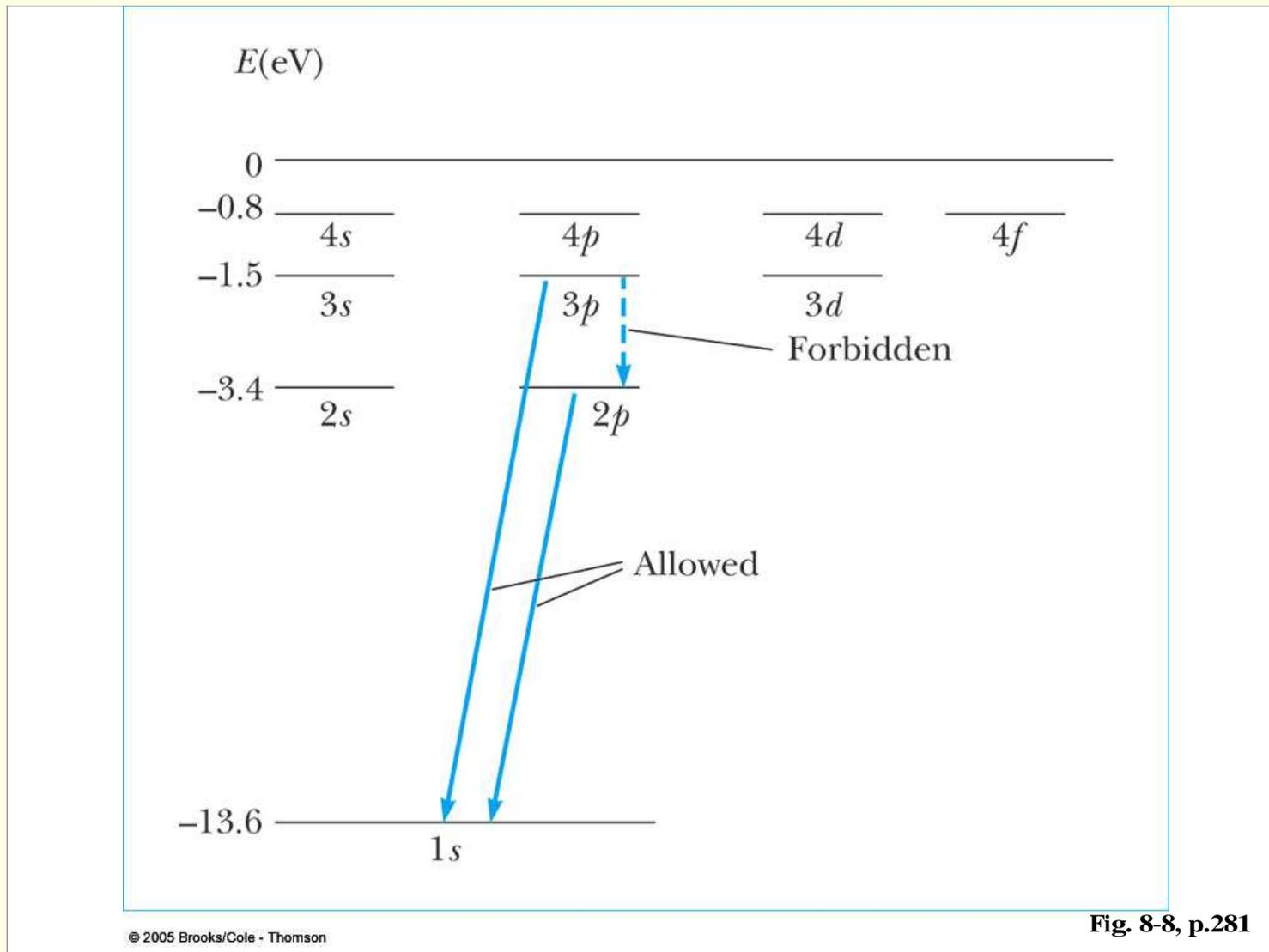
This is an example of a selection rule. Transitions that obey the above are said to be **allowed** while transitions that violate the above are very much less likely and are termed **forbidden**.

(Actually,  $\Delta l = 0$  is allowed by angular momentum conservation, but forbidden by “parity” conservation.)

Thus, for example, the  $3p \rightarrow 1s$  and  $2p \rightarrow 1s$  are both allowed, whereas  $3p \rightarrow 2p$  is forbidden as is  $3s \rightarrow 2s$ .

In addition, since the photon has maximum  $L_z$  of 1, allowed transitions all have  $\Delta m_l = 0, \pm 1$ .

Examples of allowed and forbidden transitions appear in Fig. 6.



**Figure 6: Some allowed and forbidden transitions.**

**What is most dramatically different from the Bohr picture is the actual probability distribution describing where an electron is to be found in the**

atom.

Consider the  $n, l, m_l = 1, 0, 0$  state. We have

$$\psi_{100} = R_{10}Y_0^0 = \pi^{-1/2}(Z/a_0)^{3/2}e^{-Zr/a_0}, \quad (71)$$

which is normalized so that

$$\int |\psi_{100}|^2 dV = 1. \quad (72)$$

Now, it is useful to write  $dV = r^2 dr d\cos\theta d\phi$ , and carry out the angular integrals to define a radial probability distribution  $P(r)$  such that

$$\int |\psi|^2 r^2 dr d\cos\theta d\phi = \int P(r) dr. \quad (73)$$

In the present case of a spherically symmetric wave function,

$$P(r)dr = |\psi|^2 4\pi r^2 dr \quad (74)$$

which for the  $1s$  state gives

$$P_{1s}(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0} = |g(r)|^2 = r^2 |R(r)|^2. \quad (75)$$

The normalization condition is then

$$\int P(r) dr = 1 \quad (76)$$

and average values of  $r$ -dependent quantities are computed using  $P(r)$ . For example,

$$\langle r \rangle = \int r P(r) dr. \quad (77)$$

A one-dimensional plot of  $P_{1s}(r)$  and a three-dimensional plot of  $|\psi_{100}|^2$  appear in Fig. 7.

You should take particular note of the  $3D$  picture. The electron is a spherical smear of probability with a most probable value of  $r$  given by the point where  $P(r)$  is a maximum.

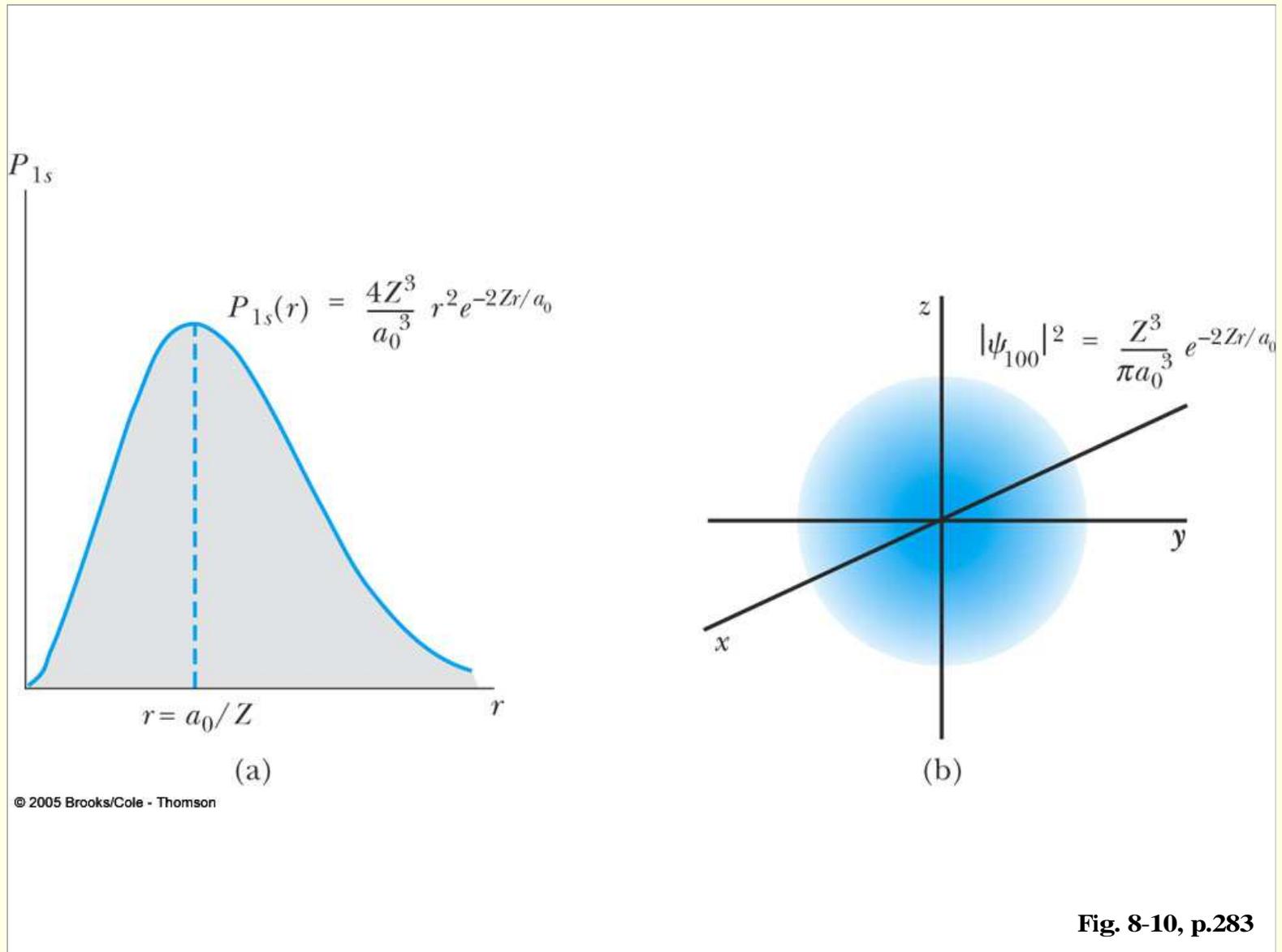


Fig. 8-10, p.283

Figure 7: The  $1s$  radial and full wave function.

Computing  $dP(r)/dr$  using  $P_{1s}$  of Eq. (75), we find

$$\frac{dP_{1s}}{dr} \propto \frac{d}{dr} \left[ r^2 e^{-2r/a_0} \right] = e^{-2r/a_0} \left[ -\frac{2r^2}{a_0} + 2r \right] = 0 \quad \text{for } r = a_0. \quad (78)$$

Thus,  $a_0$  is not *the* radius of the Bohr orbit, but rather the most probable value of  $r$  of some spherical distribution. Also, the average distance and most probable distance are not the same:  $\langle r \rangle = (3/2)a_0$ .

If we move on to higher states, the  $s$  states are all spherically symmetric and have  $n - 1$  nodes. The most probable distance for the  $2, 0, 0$  state is  $\sim 5a_0$  ( $Z = 1$ ) and is not simply the Bohr result of  $2^2 a_0$ . As  $n$  increases, the nodes push the main part of the wave function out to larger and larger radii. Thus, the  $2p$  state with no nodes has a smaller value for the most probable radius than does the  $2s$  state. In general

$$\langle r_n^s \rangle > \langle r_n^p \rangle > \langle r_n^d \rangle \dots \quad (79)$$

where the series ends when  $l = n - 1$ . For example, compare the  $3s$ ,  $3p$  and  $3d$  plots in the upcoming figure.

A picture of the  $P(r)$ 's for the  $s$ ,  $p$  and  $d$  states with low values of  $n$  is given in Fig. 8.

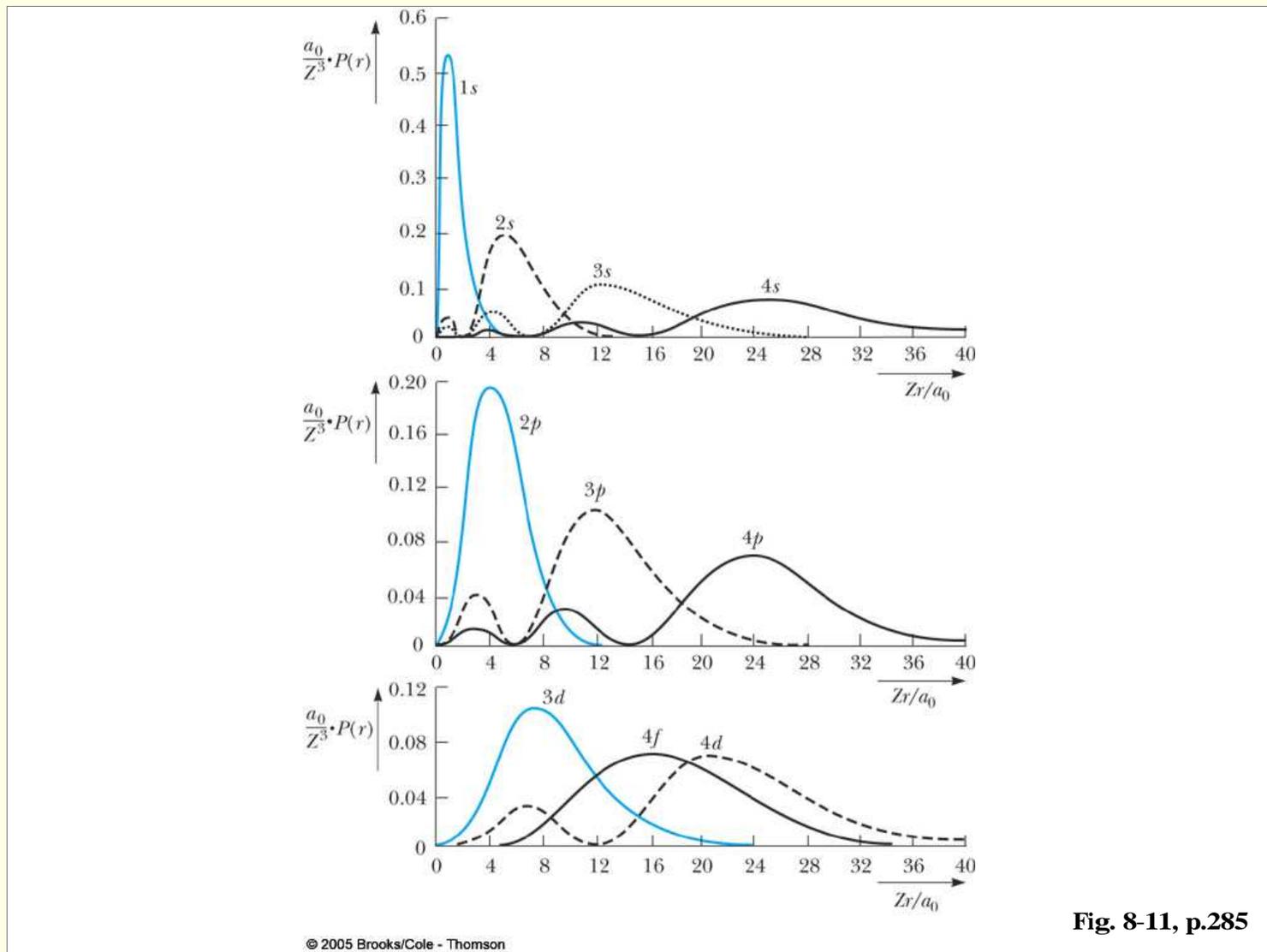


Fig. 8-11, p.285

Figure 8: The  $P(r)$  distributions for some low-lying states. Note how quickly the most likely value of  $r$  increases with  $n$ .

What is equally important to realize is that for  $l \neq 0$ , the wave functions have a complicated  $3D$  structure. Some examples of the corresponding

probability densities,  $|\psi|^2$ , are shown in Fig. 9. The 3D structure is controlled by the number of radial nodes and the behavior of the appropriate  $Y_l^{m_l}$ .

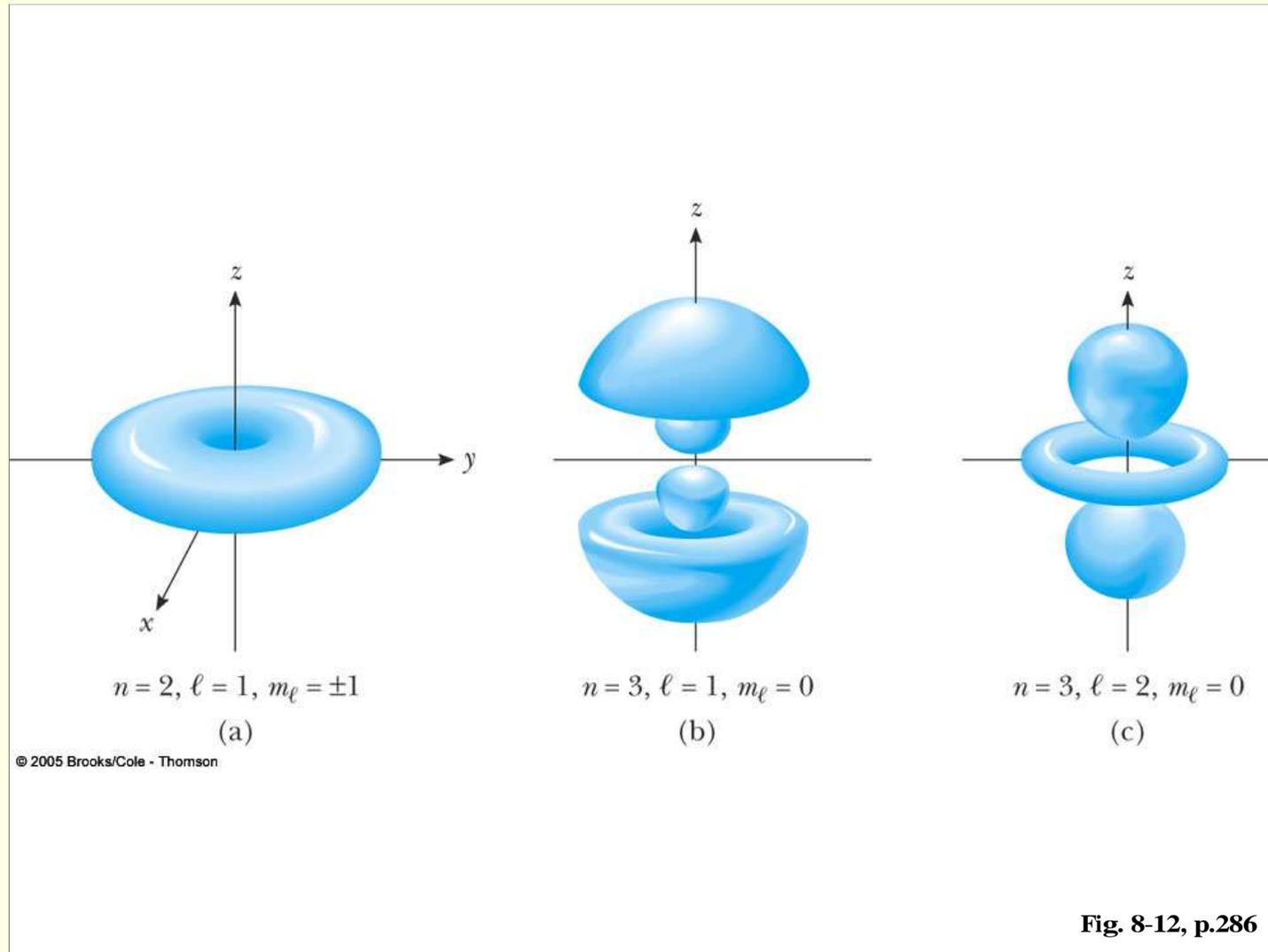


Figure 9: Three-dimensional pictures of some  $l \neq 0$  probability densities.

For example, the first picture is for the

$$\psi_{211} = R_{21}(r)Y_1^1 = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{8a_0}\right) e^{-Zr/2a_0} \sin \theta e^{i\phi} \quad (80)$$

state. You see that  $|\psi|^2$  is largest near the  $x, y$  plane and the single radial node creates a donut kind of probability distribution.

I have always found it remarkable that very different wave functions can have exactly the same energy. For example, the two  $n = 3$  wave functions in the preceding figure both have  $E_3 = -13.6/9 \text{ eV}$ .

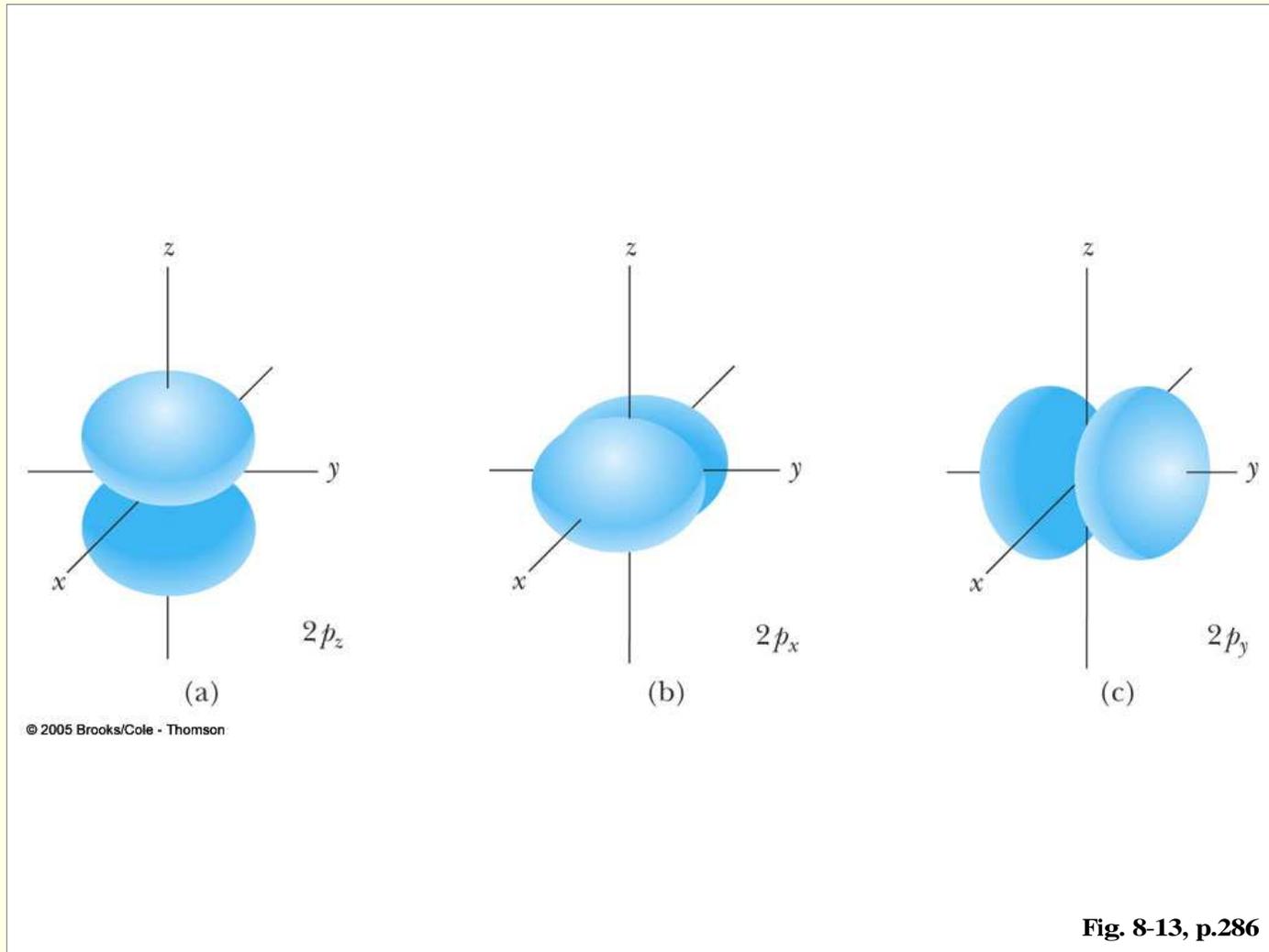
An atom can also be in a state of definite energy that is a combination of the different (degenerate) angular momentum states. These can be set up to have orientations that lie primarily along the  $x$  and  $y$  axes. Interesting cases are

$$\begin{aligned} [\psi_{2p}]_x &= \frac{1}{\sqrt{2}}[\psi_{211} + \psi_{21-1}] \\ [\psi_{2p}]_y &= \frac{1}{\sqrt{2}}[\psi_{211} - \psi_{21-1}] \end{aligned}$$

which have distributions along the  $x$  and  $y$  axes much like that of

$$[\psi_{2p}]_z = \psi_{210} \quad (81)$$

along the  $z$  axis. Pictures of these states are below.



**Figure 10: Three-dimensional pictures of some  $2p$  state oriented densities.**

Such wave functions with a highly directional character play an important role in chemical bonding.

### General result for degeneracy and implications

We have discussed how there is a large degeneracy associated with a given  $n$ . The general formula for degeneracy is

$$\sum_{l=0}^{n-1} (2l + 1) = n^2 . \quad (82)$$

What this means is that the  $n$ 'th shell associated with a nucleus of charge  $Z$  can hold  $n^2$  electrons if there are no other considerations. (Of course, there are other considerations, but this degeneracy is the most important aspect to consider first.)

In fact, this is not the whole story. Each  $e^-$  actually can have two spin orientations (we will come shortly to the concept of spin). As a result, level  $n$  can hold  $2n^2$  electrons.

You might ask why we cannot put more than 2 electrons into each  $n, l, m_l$  quantum state. This has to do with **Fermi statistics** and the

**Fermi exclusion principle.** This is a very important physical law that says that every electron must be in a distinct quantum state (as identified using all possible characteristics of that state — the characteristics here being  $n, l, m_l$  and  $s$ .)

So, this brings us to the next chapter of the story on magnetic moments, spin and the exclusion principle.

A particularly nice thing will be that we can actually see certain characteristics of the wave functions for a given  $n$  that will allow us to actually verify that the different  $l$  and, in particular,  $m_l$  values are really all present.

# More Atomic Structure: Zeeman Effect, Spin, Exclusion Principle

Multi-electron atoms are more complicated in many ways compared to the single electron type atom or ion that we have been considering.

1. The electrons repel.
2. The electrons have **spin** that is elemental.
3. Electrons cannot occupy the same quantum state.
4. The atom interacts in many ways with an external magnetic field.

We will be giving short shrift to all these topics.

## Orbital Magnetism

You know that a planar current loop creates a magnetic moment  $\vec{\mu} = IA\hat{n}$ , where  $I$  is the current,  $A$  is the area of the loop, and the direction  $\hat{n}$  of  $\vec{\mu}$  is given by the right-hand rule.

A charge  $q$  circulating around a nucleus will create a current and this current will, in turn, give rise to a  $\vec{\mu}$ .

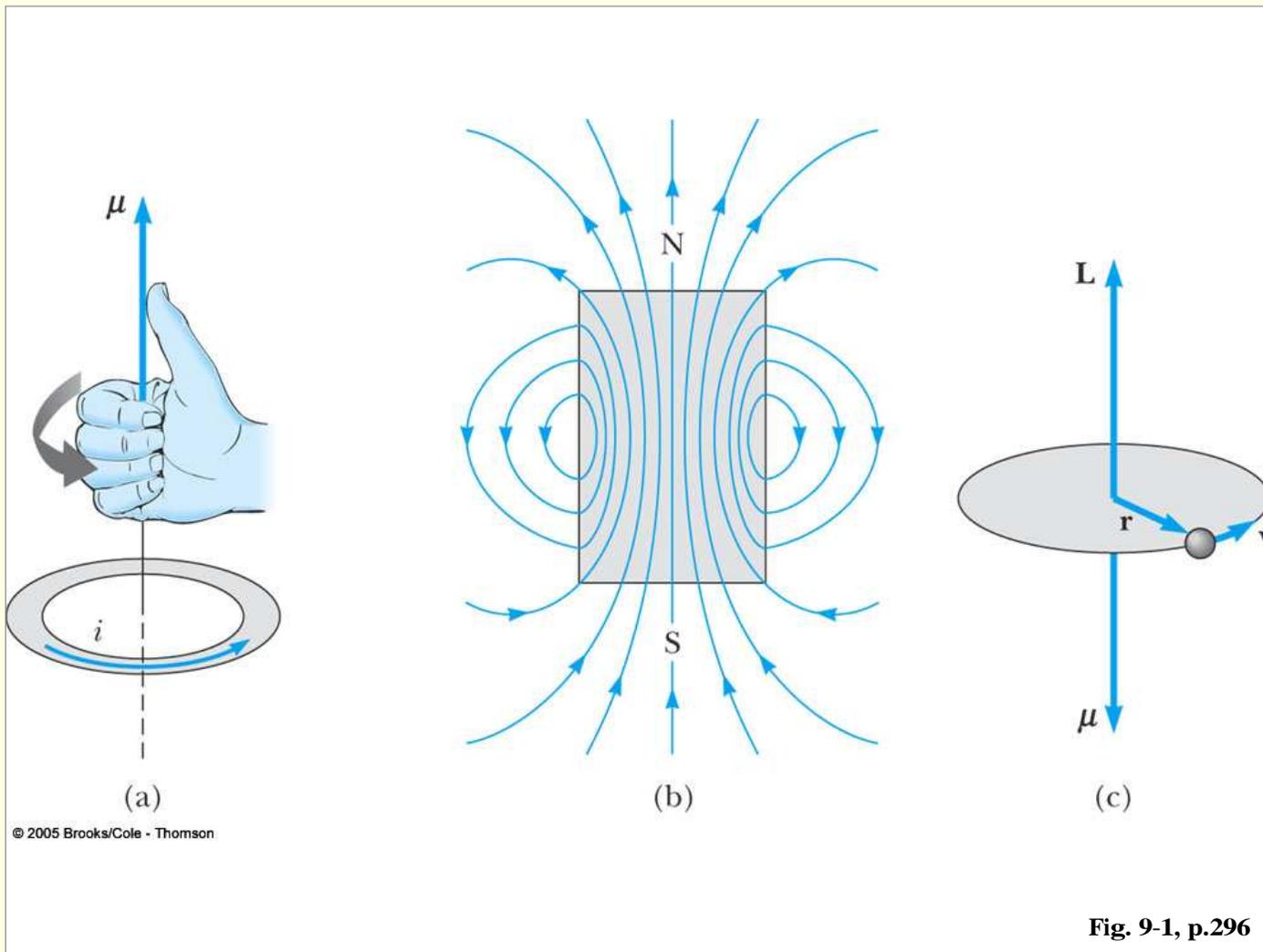


Fig. 9-1, p.296

Figure 11: Magnetic moment from a current loop or circulating charge.

Classically, we have

$$L = mvr = m \left( \frac{2\pi r}{T} \right) r = 2m \left( \frac{\pi r^2}{T} \right) = 2m \frac{A}{T}, \quad (83)$$

where  $T$  is the orbital period. We also have

$$I = \frac{q}{T} \quad \text{from current} = \text{charge through given location/sec.} \quad (84)$$

This leads to

$$Lq = 2m \frac{A}{T} q = 2mIA = 2m\mu. \quad (85)$$

This leads to

$$\vec{\mu} = \frac{q}{2m} \vec{L} \equiv g\vec{L}, \quad (86)$$

where  $g = \frac{q}{2m} \equiv$  **gyromagnetic ratio**. For  $e^-$ 's,  $q = -e$  so that  $\vec{\mu}$  is actually opposite in direction to  $\vec{L}$ .

Now, for an atomic electron, we know that  $|\vec{L}|$  and  $L_z$  are quantized in units of  $\hbar$ . Thus, it is natural to define

$$\mu_B \equiv \text{Bohr magneton} = \frac{e\hbar}{2m} = 9.274 \times 10^{-24} \text{ J/T} = 5.79 \times 10^{-9} \text{ eV/G}, \quad (87)$$

where  $T$  stands for Tesla and  $G$  stands for Gauss. In particular, we will have

$$\mu_z = -\frac{e}{2m} L_z = -\mu_B m_l \quad \text{using } L_z = \hbar m_l. \quad (88)$$

The magnetic moment will come at certain fixed angles with respect to the  $z$  axis, in fact the same fixed angles as for  $\vec{L}$ .

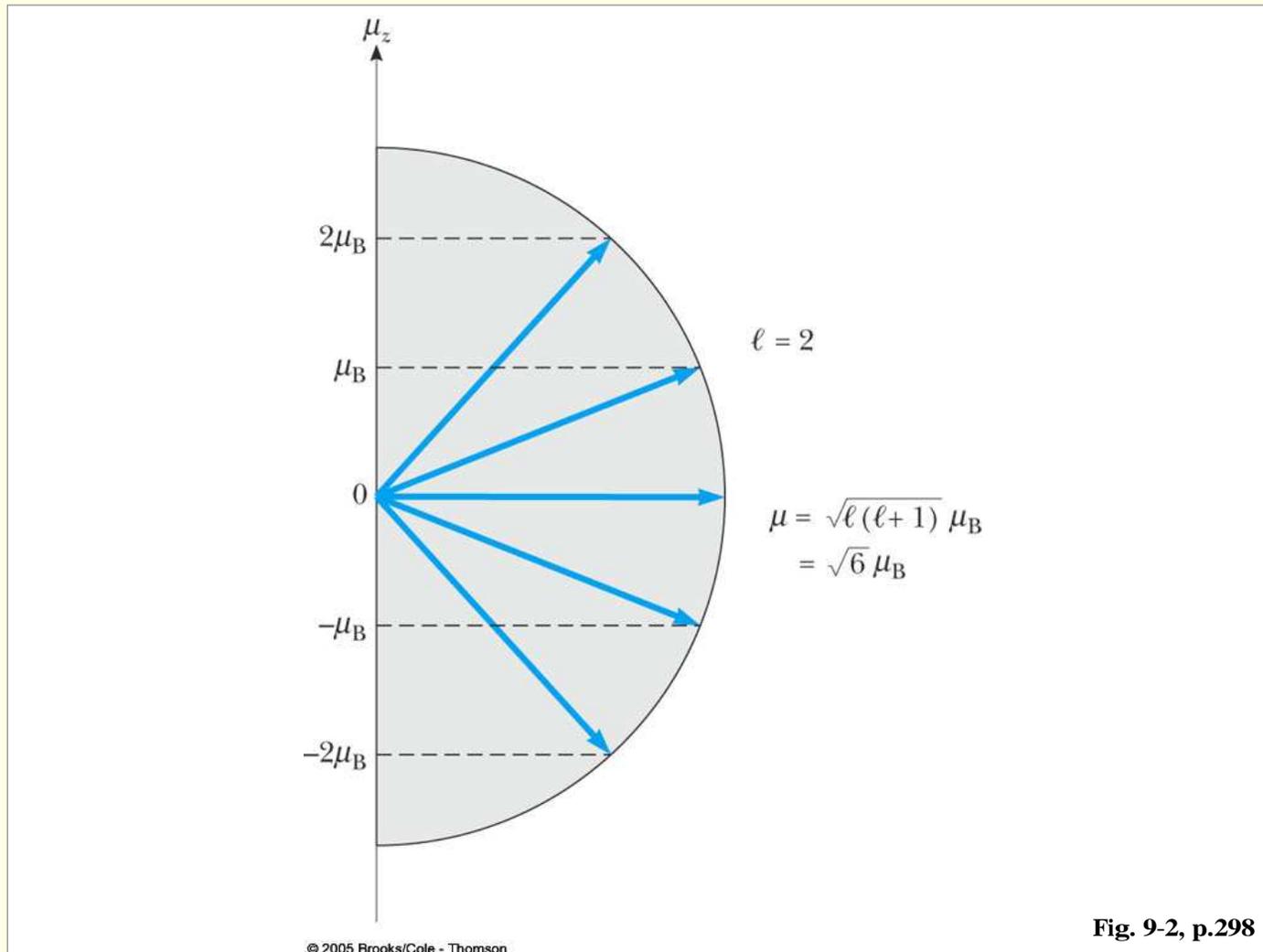


Figure 12: Quantized  $\vec{\mu}$  angles with respect to  $z$  axis.

This magnetic moment will interact with a  $\vec{B}$  field. I hope you know that the result is a torque given by

$$\vec{\tau} = \vec{\mu} \times \vec{B}. \quad (89)$$

Classically,  $\vec{\mu}$  will precess around a fixed  $\vec{B}$  field direction according to

$$\frac{d\vec{L}}{dt} = \vec{\tau} \quad (90)$$

which is to say that  $d\vec{L}$  is perpendicular to both  $\vec{L}$  and  $\vec{B}$ . This is referred to as **Larmor precession**.

Using the picture shown, where  $\phi$  is the precession angle in the plane perpendicular to  $\vec{B}$ , we have (using  $|\vec{\mu}| = \frac{e}{2m}|\vec{L}| = \frac{eL}{2m}$  and  $|\vec{\tau}| =$

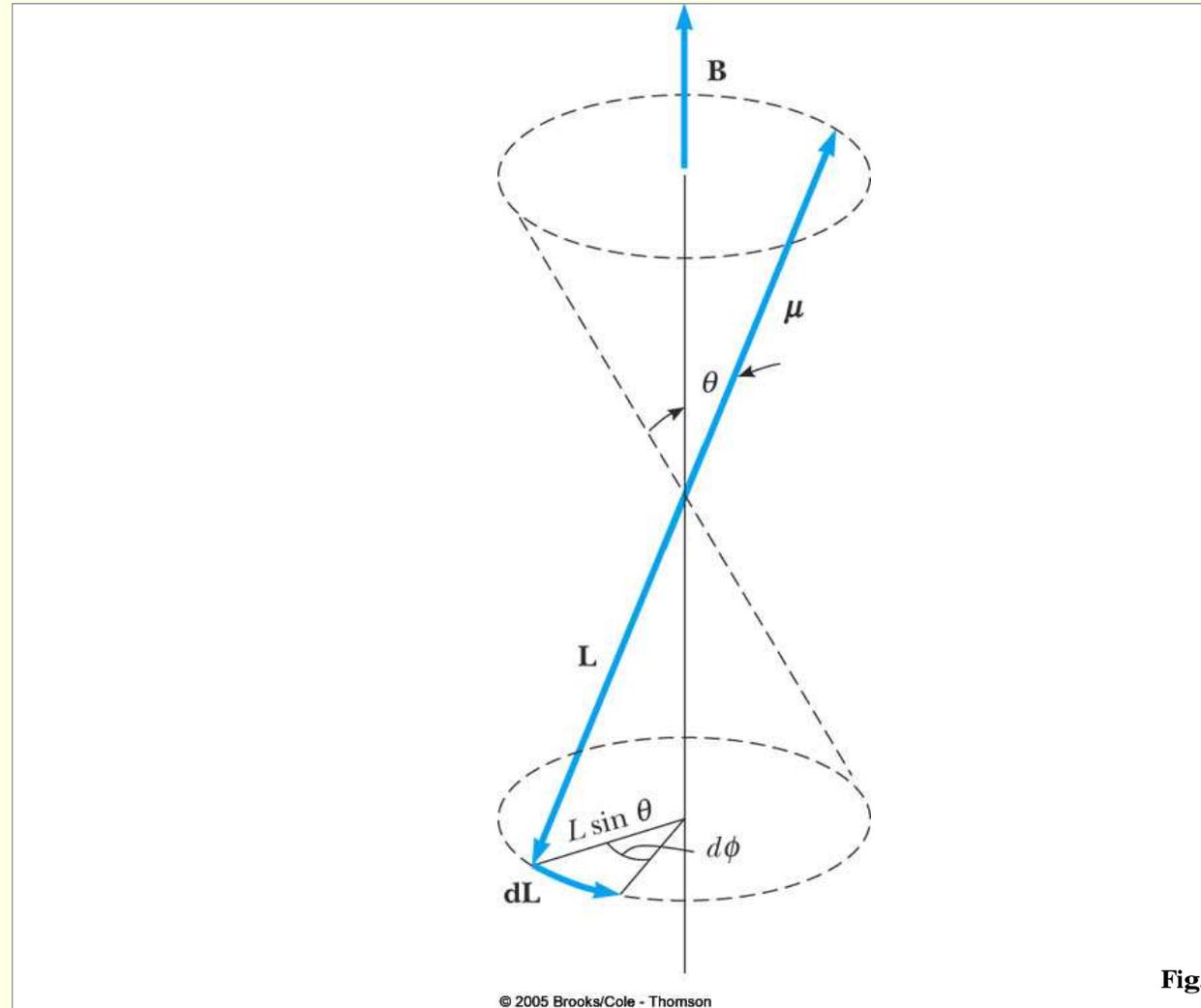


Figure 13: Precession of  $\vec{\mu}$  about  $\vec{B} = \hat{z}B$ .

$$|\vec{\mu} \times \vec{B}| = |\vec{\mu}||\vec{B}| \sin \theta$$

$$d\phi = \frac{|\vec{dL}|}{L \sin \theta} = \frac{|\vec{\tau}| dt}{L \sin \theta} = \frac{\left(\frac{eL}{2m} B \sin \theta\right) dt}{L \sin \theta} = \frac{e}{2m} B dt. \quad (91)$$

The result is a precession angular frequency given by

$$\omega_L = \frac{d\phi}{dt} = \frac{e}{2m} B, \quad (92)$$

called the **Larmor frequency**.

Now consider the work required to reorient  $\vec{\mu}$  in the presence of  $\vec{B}$ . Such work becomes part of the potential energy:  $dU = dW$ , where  $dW$  is the work done *against* the torque. In the present set up, you must do work to increase  $\theta$ . Equivalently,  $\vec{\tau}$  is trying to decrease  $\theta$ .

In more detail, let us first write the work done *by*  $\tau$  if  $\theta$  is allowed to change without resistance. One has:

$$dW_{\text{with } \vec{\tau}} = \tau d\theta_{\text{RH rule}} = -\tau d\theta_{\text{of picture}}. \quad (93)$$

So,

$$dU = dW_{\text{against } \tau} = -dW_{\text{with } \tau} = \tau d\theta_{\text{picture}}. \quad (94)$$

Now input  $\tau = \mu B \sin \theta$  which gives

$$dU = \mu B \sin \theta d\theta, \quad \Rightarrow \quad U = -\mu B \cos \theta + \text{constant} = -\vec{\mu} \cdot \vec{B}, \quad (95)$$

where we determined the constant by the convention that  $U = 0$  when  $\theta = \pi/2$ . The final result says that  $\vec{\mu}$  likes to be parallel to  $\vec{B}$ .

Now, since the possible orientations for  $\vec{L}$  and hence  $\vec{\mu}$  are quantized, if we choose  $\vec{B}$  to be in the  $\hat{z}$  direction we get (using  $\vec{\mu} = \frac{-e}{2m}\vec{L}$ )

$$U = -\vec{\mu} \cdot \vec{B} = \frac{e}{2m}\vec{L} \cdot \vec{B} = \frac{eB}{2m}L_z = \omega_L \hbar m_l. \quad (96)$$

Thus, in the presence of a magnetic field, the energy associated with a given atomic state will change according to  $m_l$ :

$$E_{B \neq 0}(n, m_l) = E_{B=0}(n) + \hbar \omega_L m_l \quad (97)$$

$\Rightarrow$  the magnetic field breaks the degeneracy by destroying the spherical symmetry.

## An aside on details

Now, although the energies depend on  $m_l$  in the presence of  $\vec{B}$ , the wave functions do not. Classically, this is understood since  $\vec{B}$  only causes precession about the direction of  $\vec{B}$ . But, such precession is already implicit in our semi-classical picture of  $e^-$  orbits being smeared out over a kind of precession cone. Placing such a precession “smear” into a  $\vec{B}$  field does not change the smear.

In more detail, the precession when  $\vec{B} \neq 0$  appears as follows. Whereas  $\langle L_x \rangle = \langle L_y \rangle = 0$  at all times when  $\vec{B} = 0$ , when  $\vec{B} = \hat{z}B \neq 0$  one finds

$$\frac{d^2}{dt^2} \langle L_x \rangle = -\omega_L^2 \langle L_x \rangle \quad (98)$$

and similarly for  $\langle L_y \rangle$ . So, what precesses is the average angular momentum in the perpendicular directions.

In still more detail, classically we have (recall that  $\omega_L = \frac{eB}{2m_e} = gB$ )

$$\begin{aligned} \frac{dL_x}{dt} &= \tau_x = (\vec{\mu} \times \vec{B})_x = \mu_y B_z = gL_y B_z = \omega_L L_y \\ \frac{dL_y}{dt} &= \tau_y = (\vec{\mu} \times \vec{B})_y = -\mu_x B_z = -gL_x B_z = -\omega_L L_x \end{aligned}$$

$$\frac{d^2 L_x}{dt^2} \Rightarrow \omega_L \frac{dL_y}{dt} = -\omega_L^2 L_x, \quad \text{and} \quad \frac{d^2 L_y}{dt^2} = -\omega_L \frac{dL_x}{dt} = -\omega_L^2 L_y$$

In QM, these equations remain true for the *average values*.

Note also that all this is consistent with  $|\vec{L}|^2$  remaining unchanged. In more detail, we have the classical equations

$$\frac{dL_x^2}{dt} = 2L_x \frac{dL_x}{dt} = 2L_x(\omega_L L_y), \quad \frac{dL_y^2}{dt} = 2L_y \frac{dL_y}{dt} = 2L_y(-\omega_L L_x) \quad (99)$$

Taking the sum of these equations, we have

$$\frac{d}{dt}(L_x^2 + L_y^2) = 0 \quad (100)$$

both classically and quantum mechanically. And, of course,  $L_z^2$  does not change in the presence of  $\vec{B} = \hat{z}B$ . So,  $\frac{d}{dt}(\vec{L})^2 = 0$ , both classically and quantum mechanically.

## Back to the Spectra

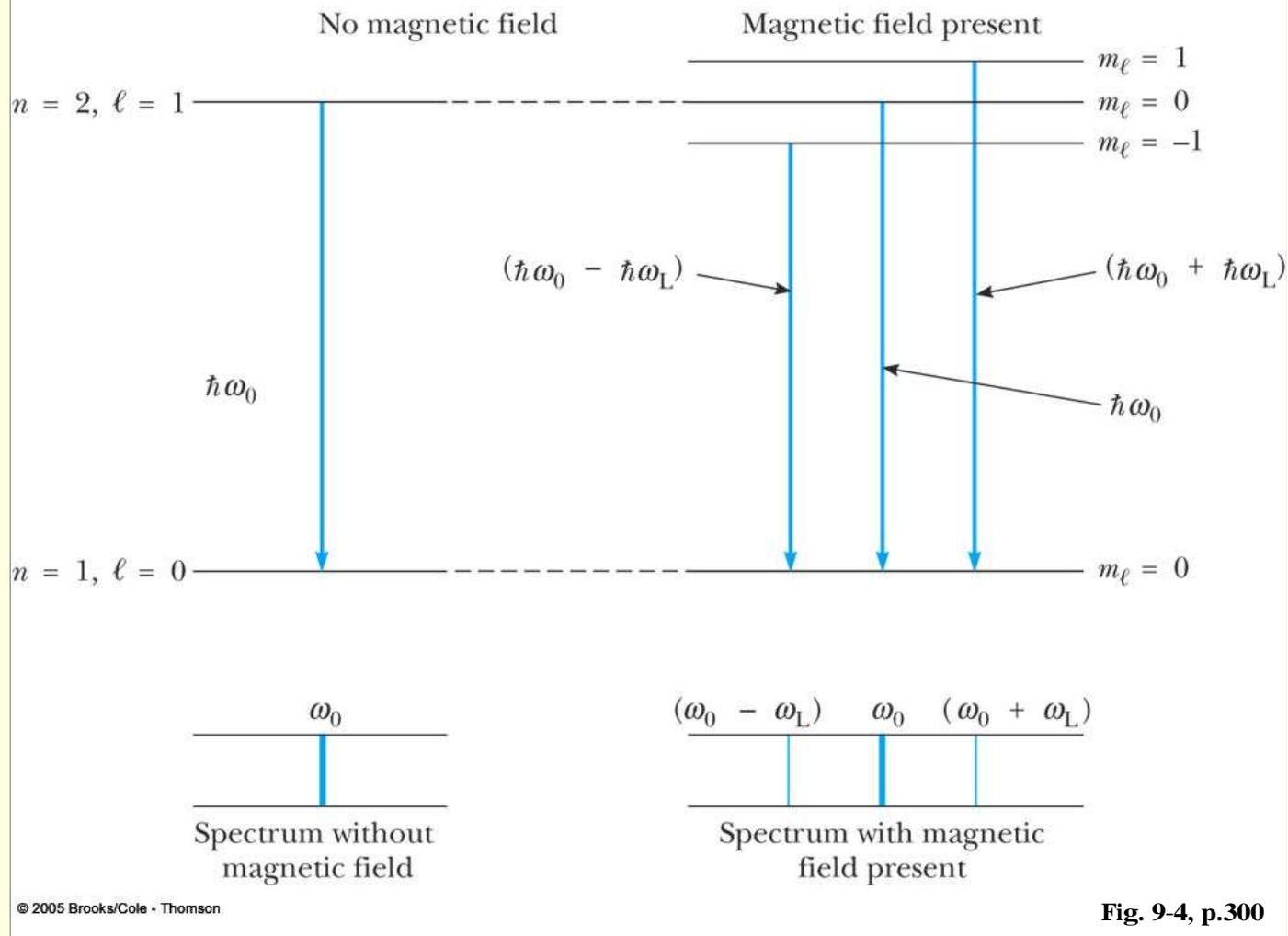
So, if

$$E_{B \neq 0}(n, m_l) = E_{B=0}(n) + \hbar\omega_L m_l \quad (101)$$

we should be able to actually “see” the different  $m_l$  states by placing the atom in a  $\vec{B}$  field and looking at the new atomic spectra compared to the old. For every single spectral line we had before turning on  $\vec{B}$ , we get a series of spectral lines with frequency separated by  $\omega_L$  relative to the original  $\omega_0$ .

**And, we do see these spectral line separations.** However, the spectra are complicated by the effects of electron spin, to which we shall come. We temporarily ignore this complication in the following discussion.

The simplest case to illustrate is the  $n = 2, l = 1$  to  $n = 1, l = 0$  transitions. These are depicted in the following figure.



**Figure 14:** Energy levels and possible transitions from  $n = 2$  to  $n = 1$ .

In more complicated cases, you might think you get an enormous number of lines:  $\omega_0, \omega_0 \pm \omega_L, \omega_0 \pm 2\omega_L, \dots$ . But, in fact only  $\omega_0$  and  $\omega_0 \pm \omega_L$  will be present. This is the result of the  $\Delta m_l = 0, \pm 1$  selection rule required by conservation of angular momentum and the fact that the emitted photon carries spin 1.

Example:  $n = 3$  to  $n = 2$  transitions (see figure).

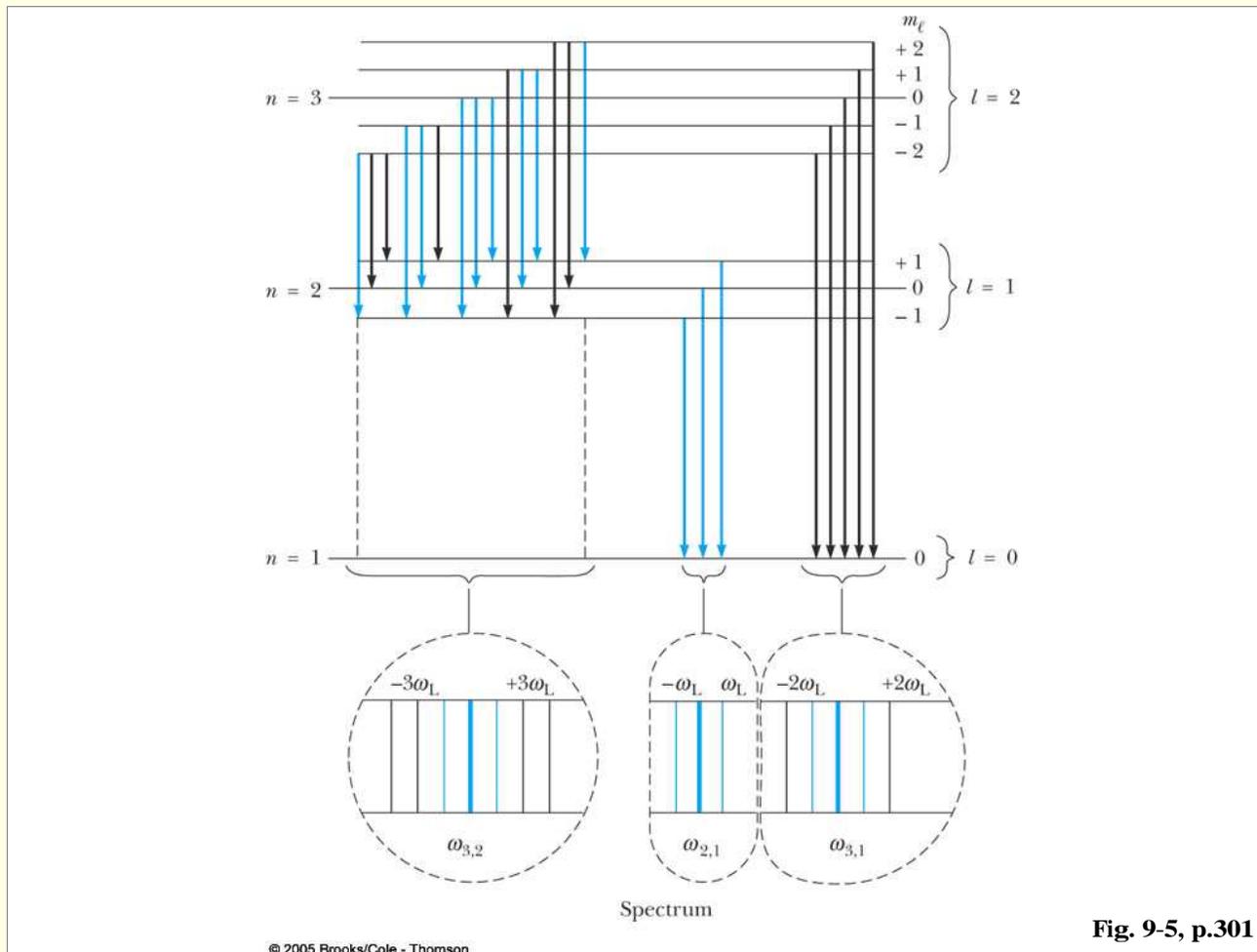


Figure 15: Spectral lines for  $n = 3$  to  $n = 2$  transitions. Black lines are forbidden by  $\Delta l = \pm 1$  and/or  $\Delta m_l = 0, \pm 1$  selection rules. Blue lines show the allowed transitions. We will be focusing on the 6th and 9th blue lines in the left hand group, which give the blue lines to either side of the central line in the lower circled picture.

Consider a hydrogen atom with an electron in an  $n = 3$ ,  $l = 2$  state with  $m_l = 2$  or  $m_l = 0$ . Suppose the atom decays by emitting a photon and moving to a  $n = 2$  state with  $l = 1$  and  $m_l = 1$ . By how much will the frequencies  $f$  of the emitted photons differ assuming a  $1\text{ T}$   $\vec{B}$  field oriented along the  $\hat{z}$  axis?

First, we should note that I carefully chose  $m_l$  values and  $l$  values so that both transitions are allowed by the  $\Delta l = \pm 1$  and  $\Delta m_l = 0, \pm 1$  selection rules.

Now to the numbers. We need first of all the value of the **Zeeman energy**

$$\begin{aligned} \hbar\omega_L &= \frac{e\hbar}{2m_e}B = \mu_B B \\ &= (9.27 \times 10^{-24} \text{ J/T})(1.00 \text{ T}) = 9.27 \times 10^{-24} \text{ J} \\ &= 5.79 \times 10^{-5} \text{ eV}. \end{aligned} \tag{102}$$

Next, we recall the  $\vec{B} = 0$  energy levels:

$$E_3 = -\frac{13.6 \text{ eV}}{3^2} = -1.511 \text{ eV}, \quad E_2 = -\frac{13.6 \text{ eV}}{2^2} = -3.4 \text{ eV},$$

$$\Rightarrow E_3 - E_2 = 1.899 \text{ eV} . \quad (103)$$

The  $n = 3, l = 2, m_l = 2$  to  $n = 2, l = 1, m_l = 1$  energy difference is then

$$\Delta E_1 \equiv (E_3 + 2\hbar\omega_L) - (E_2 + \hbar\omega_L) = 1.899 \text{ eV} + 5.79 \times 10^{-5} \text{ eV} . \quad (104)$$

The  $n = 3, l = 2, m_l = 0$  to  $n = 2, l = 1, m_l = 1$  energy difference is then

$$\Delta E_2 \equiv (E_3 + 0\hbar\omega_L) - (E_2 + \hbar\omega_L) = 1.899 \text{ eV} - 5.79 \times 10^{-5} \text{ eV} . \quad (105)$$

The two transitions then have

$$\Delta E_1 - \Delta E_2 = 11.58 \times 10^{-5} \text{ eV} . \quad (106)$$

The photon frequencies are given by  $\Delta E = hf$  and thus

$$\Delta f = \frac{\Delta E_1 - \Delta E_2}{h} = \frac{11.58 \times 10^{-5} \text{ eV}}{4.136 \times 10^{-15} \text{ eV} \cdot \text{s}} = 2.80 \times 10^{10} \text{ s}^{-1} . \quad (107)$$

Note that the small fractional energy change means that a highly precise measurement of the frequencies of the two photons is needed to see this “normal” **Zeeman effect** named after the first person to observe it.

## Electron Spin

In fact, the spectral line arrangement is even more complicated in the presence of a  $\vec{B}$  field than discussed above. The extra complication arises from the fact that the electron itself has **spin**.

Spin is an intrinsic angular momentum of the electron itself. Just like regular orbital motion of a charge gives rise to a magnetic moment, if the electron is spinning (which implies that its charge is, in some sense, spinning) we can expect that the electron will have its own magnetic moment.

A picture of this sort of classical point of view regarding the connection between a spinning charged body and the resulting magnetic moment is below.

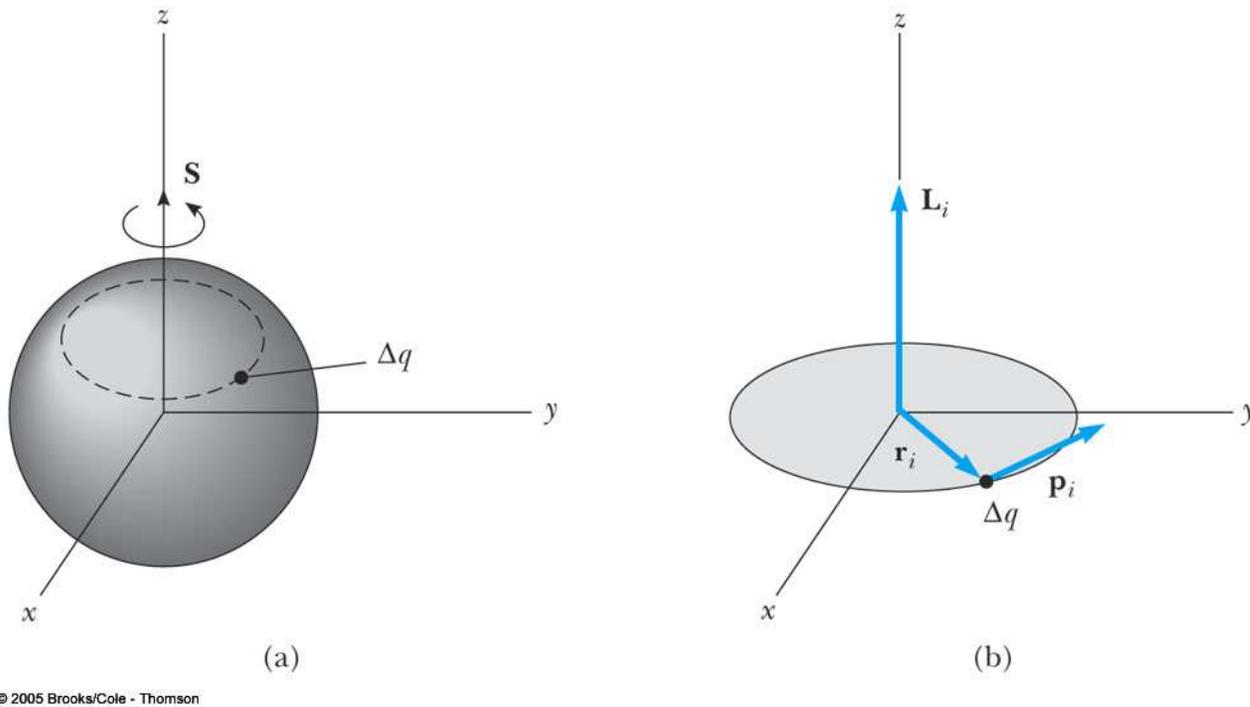


Figure 16: A spinning charge distribution and its  $\vec{\mu}$ . Fig. 9-6, p.302

If the charged body has a uniform charge to mass ratio throughout some effective size, then one finds

$$\vec{\mu}_s = \frac{q}{2m_e} \vec{S}, \quad (108)$$

where  $\vec{S}$ , or spin, is just our special name for the intrinsic angular

momentum of the electron. In fact, such a picture does not really apply to an elementary point-like electron and so we should not be surprised that it is wrong. In fact, we find for an electron that

$$\vec{\mu}_s = g_e \frac{-e}{2m_e} \vec{S}, \quad (109)$$

where the **gyromagnetic ratio** is  $g_e \simeq 2$ ,  $|\vec{S}|^2 = \hbar^2 s(s+1)$  with  $s = 1/2$  and  $S_z = \pm \frac{1}{2} \hbar$ .

How do we know that the above statements are true? For example, how do we know that the  $e^-$  has only two possible  $S_z$  values and therefore has  $s = 1/2$ ?

First, there are the atomic spectra measurements in a strong  $\vec{B}$  field that must be explained by accounting for electron spin, which we shall return to. And, there is also the historically important Stern-Gerlach experiment.

### Stern-Gerlach Experiment

In this experiment, a beam of silver atoms was sent through a magnetic field. Silver was originally chosen because it has net  $\vec{L} = 0$  and therefore should have no magnetic moment. The same result to be described was

later found for the  $l = 0$  ground state of the simple hydrogen atom, which obviously has  $\vec{L} = 0$  and, therefore,  $\vec{\mu} = 0$ .

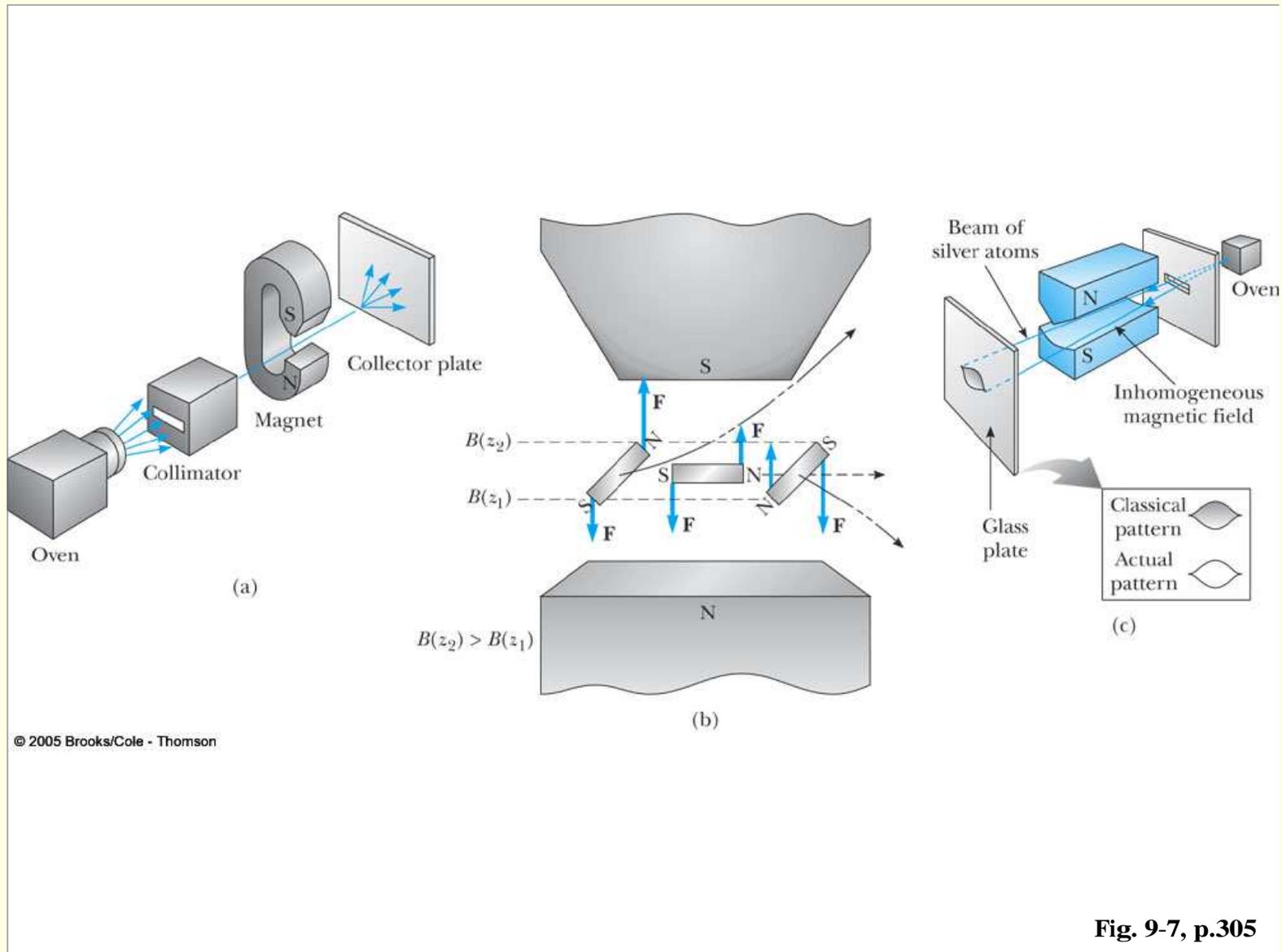


Figure 17: The Stern-Gerlach experimental set up.

The result of passing the beam through a **non-uniform** magnetic field would be to actually move the beam up or down if the particles in the beam have  $\vec{\mu} \neq 0$ .

(If  $\vec{B}$  is uniform, then only torque is produced which rotates but does not deflect the particle in the beam.)

If  $\vec{\mu} \neq 0$ , the prediction is a deflection that depends on the precise orientation of the  $\vec{\mu}$ . This orientation would be a continuous distribution classically, implying a continuum of possible deflections.

For silver, which has no  $\vec{L}$ , it was anticipated that nothing would be seen. However, deflection was seen, and not a continuum of deflections but rather the beam was split into **two** distinct components.

This meant that there were precisely two possible (quantized) orientations of the  $\vec{\mu}$  and they had to come from something other than  $\vec{L}$  of the orbital motion.

The explanation is to introduce **spin** ( $\vec{S}$ ) for the  $e^-$  with two (and only two) orientations. Because  $S_z$  would be expected to be quantized like

$L_z$  and  $|\vec{S}|^2$  quantized like  $|\vec{L}|^2$ , the natural choice is

$$S_z = \pm \frac{1}{2} \hbar \equiv m_s \hbar, \quad |\vec{S}|^2 = \hbar^2 s(s+1) = \hbar^2 \frac{1}{2} \left( \frac{1}{2} + 1 \right) = \frac{3}{4} \hbar^2, \quad (110)$$

as pictured below.

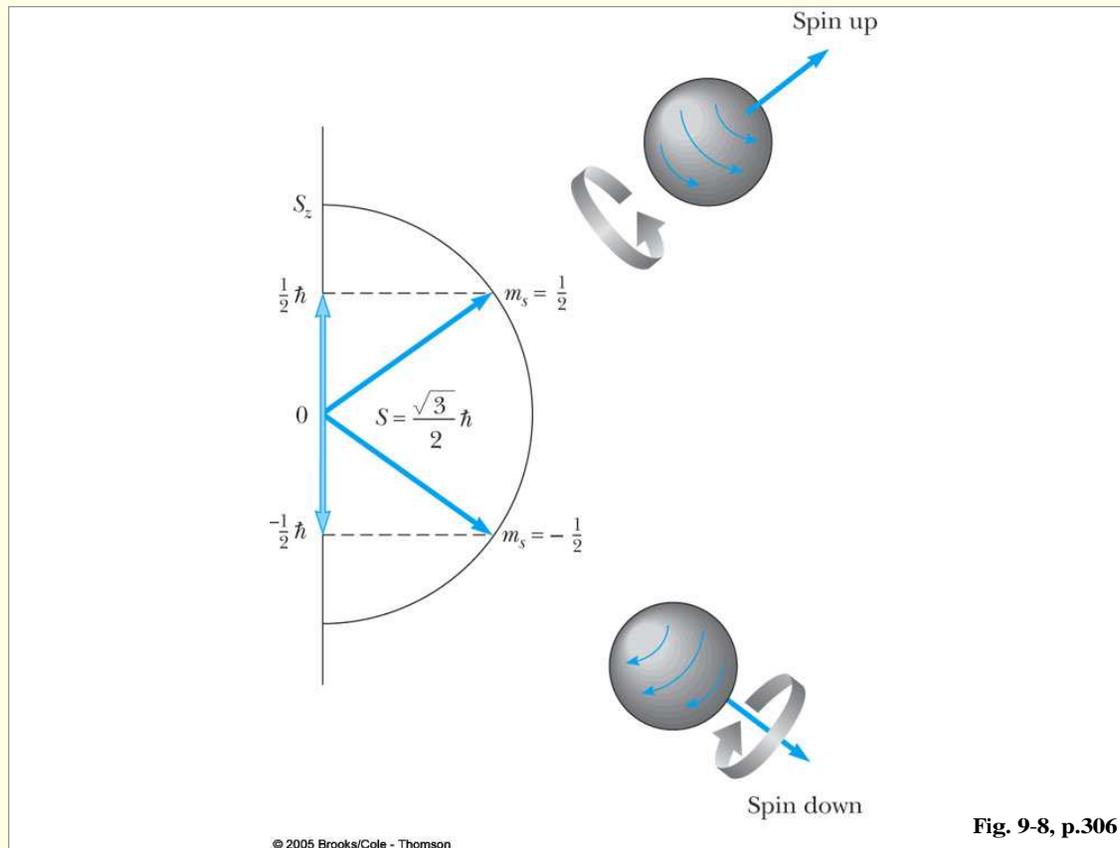


Figure 18: Picture of  $e^-$  spin.

Let us recall why if we have  $S_z = \pm \frac{1}{2}\hbar$  then we must have  $s = 1/2$  in the formula for  $|\vec{S}|^2$ . We have

$$\begin{aligned} |\vec{S}|^2 &= \langle S_z \rangle^2 + \langle S_y^2 \rangle + \langle S_x^2 \rangle = 3\langle S_z^2 \rangle = 3\frac{\frac{1}{4}\hbar^2 + \frac{1}{4}\hbar^2}{2} = \frac{3}{4}\hbar^2, \\ \text{if } &= \hbar^2 s(s+1) \Rightarrow s = 1/2. \end{aligned} \quad (111)$$

Now, you still might ask why one could not have  $S_z = \pm\hbar$  (*i.e.*  $m_s = \pm 1$  (and, correspondingly,  $s = 1$ ) and simply insist that the  $S_z = 0$  (*i.e.*  $m_s = 0$ ) orientation is removed. (This would be nice in that the observed  $\vec{\mu}_s$  for the  $e^-$  would be possible with  $g_e = 1$  instead of 2.)

Theoretically, this is impossible unless the electron is massless. Experimentally, we can prove that this possibility does not apply on the basis of what the atomic spectra look like.

### Atomic Spectra and Spin

In fact, atomic spectra in a magnetic field had already implied that the electron had to have this kind of quantized spin.

Indeed, even if  $\vec{B} = 0$ , the spectral lines of the hydrogen atom have a

**fine structure** to them (*i.e.* they are split apart by tiny amounts).

In addition, there is the **anomalous Zeeman effect** that is present when  $\vec{B} \neq 0$ . We will focus on the latter first.

As we have already said,  $\vec{S}$  gives rise to  $\vec{\mu}_s$ . And,

$$(\vec{\mu}_s)_z \simeq \left( g_e \frac{-e}{2m_e} \right) S_z = \left( 2 \left( -\frac{e}{2m_e} \right) \left( \pm \frac{1}{2} \hbar \right) \right) \quad (112)$$

gives rise to an additional energy

$$- (\vec{\mu})_z B_z = \pm \left( \frac{e B_z}{2m_e} \right) \hbar \quad (113)$$

in a magnetic field.

Combining with the  $\vec{\mu}$  from orbital motion, the general formule are

$$(\vec{\mu})_z = (\vec{\mu}_L + \vec{\mu}_S)_z = -\frac{e}{2m_e} (L_z + g_e S_z), \quad \text{with} \quad L_z = m_l \hbar \quad S_z = m_s \hbar, \quad (114)$$

and

$$\Delta E = -\vec{\mu} \cdot \vec{B} = \frac{e\hbar}{2m_e}(m_l + g_e m_s)B_z = \hbar\omega_L(m_l + g_e m_s). \quad (115)$$

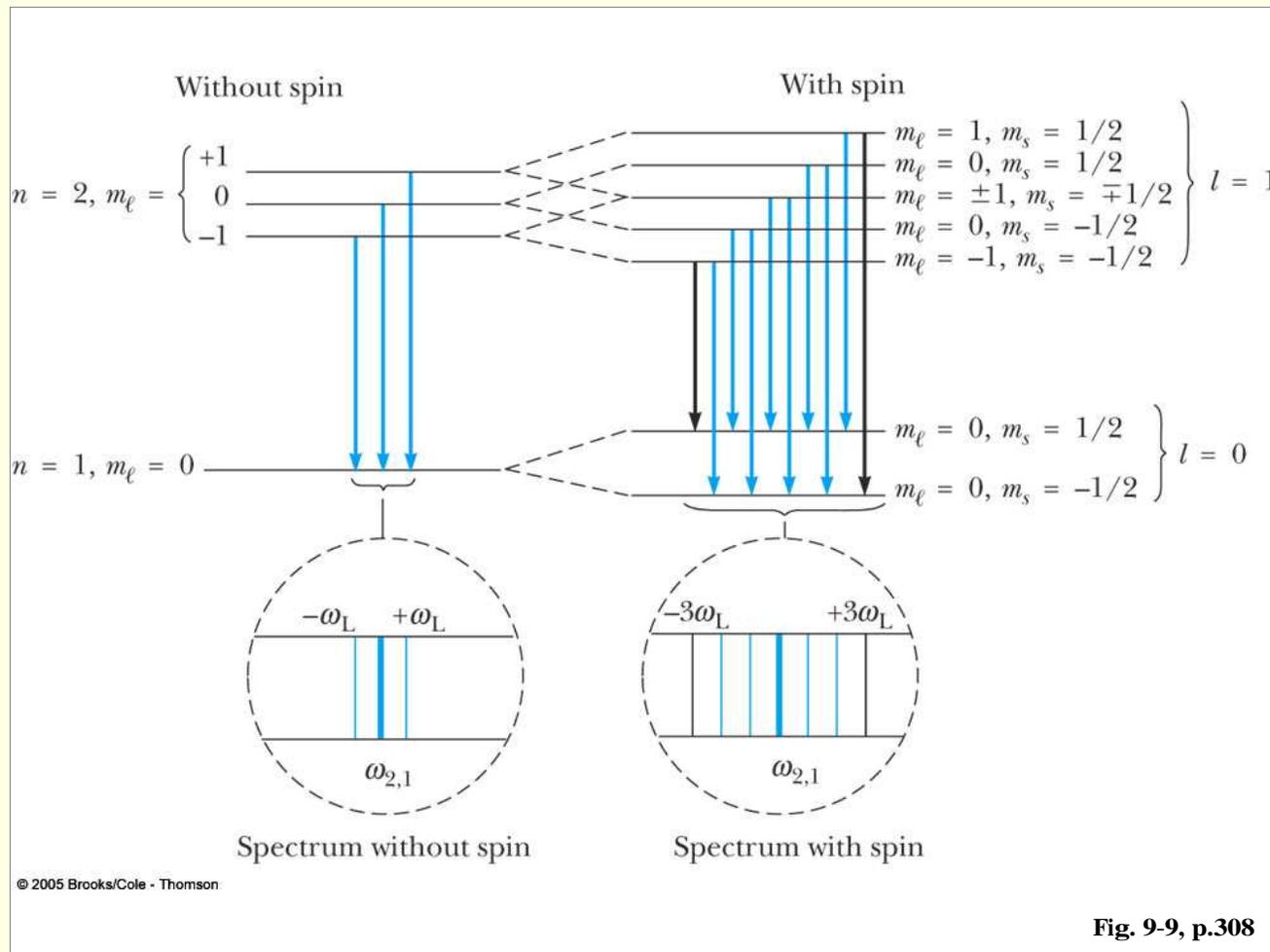
The resulting additional, originally unexpected structure in the spectral lines (called the **Anomalous Zeeman Effect**) is most easily isolated in the case of hydrogen. The picture is below.

In the upcoming picture, note how the

$$\begin{aligned} m_l = 1, m_s = 1/2 &\rightarrow m_l = 0, m_s = -1/2 && \text{and} \\ m_l = -1, m_s = -1/2 &\rightarrow m_l = 0, m_s = +1/2 \end{aligned} \quad (116)$$

transitions are forbidden because the net change in  $J_z = L_z + S_z$  is  $-2$  and  $+2$  respectively, while the photon can only carry one unit of  $J_z$ : including electron spin, we have the selection rule  $\Delta(m_l + m_s) = 0, \pm 1$ .

The spectra predicted and pictured below require the use of electron spin and are actually observed. These spectra were the first reason that we came to know that the electron has spin and that this spin has only  $S_z = \pm \frac{1}{2}\hbar$  values corresponding to two quantized orientations.



**Figure 19: Spectral lines in presence of electron spin. We will be discussing the next to last two blue lines on the right hand side that originate from the  $m_l = 0, m_s = \frac{1}{2}$  state.**

**Example:**

**Can  $s = 1/2$  with  $g_e = 2$  explain the anomalous Zeeman Effect in the case of  $n = 2, l = 1, m_l = 0 \rightarrow n = 1, l = 0, m_l = 0$  transitions?**

First note that since  $\Delta l = 0$  and  $\Delta m_l = 0$  this is an allowed transition according to the (old, pre-spin) selection rules.

Now, introduce  $m_s$  to see what we expect. Consider in particular the transitions

$$\begin{aligned} n = 2, l = 1, m_l = 0, m_s = \frac{1}{2} &\rightarrow n = 1, l = 0, m_l = 0, m_s = \frac{1}{2} \\ n = 2, l = 1, m_l = 0, m_s = \frac{1}{2} &\rightarrow n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2} \end{aligned}$$

in the presence of  $\vec{B} = \hat{z}B$ . Without the magnetic moment associated with spin, these transitions should yield a photon with the same energy. But, if electron spin is actually present, and the  $\vec{\mu}_s$  that goes with it, we have

$$E_{\vec{\mu}} = -\vec{\mu} \cdot \vec{B} = \hbar\omega_L(m_l + g_e m_s) = \hbar\omega_L(m_l + 2m_s). \quad (117)$$

Then, we have

$$\begin{aligned} (n = 2) \quad n = 2, l = 1, m_l = 0, m_s = \frac{1}{2} &\Rightarrow E_{\vec{\mu}} = \hbar\omega_L \\ (n = 1, a) \quad n = 1, l = 1, m_l = 0, m_s = \frac{1}{2} &\Rightarrow E_{\vec{\mu}} = \hbar\omega_L \\ (n = 1, b) \quad n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2} &\Rightarrow E_{\vec{\mu}} = -\hbar\omega_L \end{aligned}$$

Thus, you would get

$$E^{(2)} - E^{(1b)} = \text{normal} + 2\hbar\omega_L, \quad E^{(2)} - E^{(1a)} = \text{normal}. \quad (118)$$

In particular, the shift or  $2\hbar\omega_L$  in the  $2 \rightarrow 1b$  transition is twice what you could get for any  $m_l$  arrangement (since  $\Delta m_l = 0, \pm 1$ ) in the absence of spin.

Finally, let us return to why we could not insist that  $S_z = \pm\hbar$  with  $S_z = 0$  missing.

The answer is implicit in the

$$\begin{aligned} n = 2, l = 1, m_l = 0, m_s = \frac{1}{2} &\rightarrow n = 1, l = 0, m_l = 0, m_s = \frac{1}{2} \\ n = 2, l = 1, m_l = 0, m_s = \frac{1}{2} &\rightarrow n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2} \end{aligned}$$

transitions we just discussed. Since  $m_l = 0$  both for the initial state and for the final state, when the photon is emitted it must be the electron spin that compensates for the  $z$  component of the photon's spin. If the 2nd transition were actually what would be envisioned for  $S_z = \pm\hbar$ , that

is

$$n = 2, l = 1, m_l = 0, m_s = +1 \rightarrow n = 1, l = 0, m_l = 0, m_s = -1, \quad (119)$$

this would mean that the photon would have to carry away two units of spin,  $\Delta m_s = 2$ . Since the photon carries spin 1, this would be impossible and this transition (and others like it) would be missing from the spectrum. We need the  $m_s = \frac{1}{2} \rightarrow m_s = -\frac{1}{2}$  type of transition to explain the observed spectra.

**Summary:** To understand atomic spectra fully, one must say that the state of an  $e^-$  in the presence of the nuclear Coulomb force must be specified by **4 quantum numbers** (at least):  $n, l, m_l, m_s$ .

We have no time to go into the  $\vec{B} = 0$  fine structure of spectra that can also be explained in this way. Suffice it to say that  $\mu_{\vec{L}}$  creates a magnetic field (just like a bar magnet) which  $\mu_{\vec{S}}$  then “feels”. This interaction affects the energy levels and creates a very fine structure for the atomic spectra relative to the results obtained without considering electron spin.

## More on Electron Spin

As we have already said, **spin must be viewed as an intrinsic property of an elementary  $e^-$** . That is, it is probably not associated with any sort of charge distribution of a spinning body of finite radius.

In fact, experiments imply  $r_{e^-} \leq 10^{-17} \text{ m}$  or less. If we try to write (crudely)  $S = mvr = \frac{1}{2}\hbar$  with such a small radius, one would need  $v \gg c!$ .

So, any classical (even if relativistic) model fails.

However, modern physics is still happy with this situation in a more advanced context.

If you combine

1. Relativity
2. Quantum Mechanics
3. Causality
4. Locality (no action at a distance)

then one finds that the SE-like wave equations can only be consistently written for very definite choices of  $s$ .

$$s = 0, \quad s = \frac{1}{2}, \quad s = 1, \quad s = \frac{3}{2}, \quad \dots \quad (120)$$

The electron has chosen the 2nd option.

Further, for  $s = 1/2$ , the advanced theory *predicts* that  $g_e = 2$ .

This prediction that  $g_e = 2$  has nothing to do with any sort of structure or size of the electron. It is rather purely a prediction that follows from the special relativistic wave equation (called the Dirac equation) that the electron must satisfy.

Finally, if the Dirac equation is placed in the context of **Quantum Field Theory — QFT** one predicts that spin- $1/2$  particles should obey the **Fermi Exclusion principle**, to which we now turn.

### The Pauli Exclusion Principle

How many  $e^-$ 's can we fit into a given quantum state of definite  $n, l, m_l, m_s$ ? The answer is **exactly 1** and no more.

This is called the **Pauli Exclusion Principle**. Without it, all of chemistry would be changed. In fact, all  $e^-$ 's would occupy the state of lowest possible energy, the  $1s$  state.

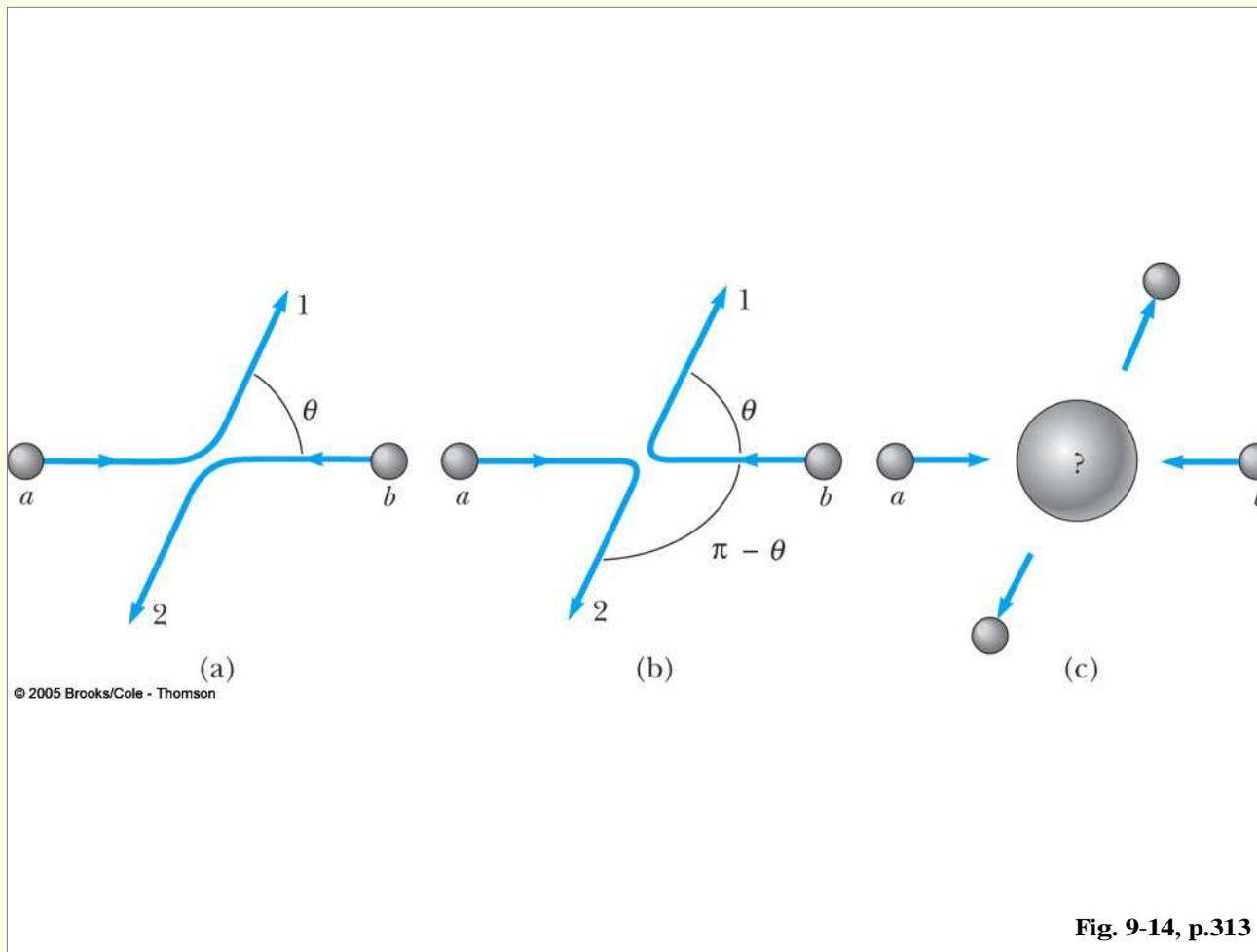
As stated above, the Pauli exclusion principle applies to particles with half-integer spin, but not to particles with integer spin. So far, you only know about particles with half integer spin.

The mere possibility of something like an exclusion principle is a purely QM phenomenon.

First, you must really accept that any two  $e^-$ 's are identical.

We must understand why this is important.

Classically, the two possible scatterings depicted below can be distinguished even if the electrons are identical particles. You just focus your microscope on one of the electrons. But, note how this measurement/observation means in a QM sense that you have made the  $e^-$ 's non-identical.



**Figure 20: Indistinguishable scatterings.**

If there is truly nothing to distinguish, who says which  $e^-$  goes where? You can't follow the classical paths — the  $e^-$ 's blend together in the collision region in a wave sense.

**This indistinguishability of  $e^-$ 's is best understood in the important**

context of  $2 - e^-$  atoms, that is the *He* atom. We will ignore the Coulomb interaction between the  $e^-$ 's in what follows.

We have

$$E = K_1 + V_1 + K_2 + V_2 \quad (121)$$

and we convert to the Schroedinger equation in the usual way, except that now we have locations and derivatives for each of the electrons:

$$-\frac{\hbar^2}{2m} \vec{\nabla}_1^2 \Psi + V_1 \Psi - \frac{\hbar^2}{2m} \vec{\nabla}_2^2 \Psi + V_2 \Psi = E \Psi \quad (122)$$

where  $\Psi = \Psi(\vec{r}_1, \vec{r}_2, t)$  describes the simultaneous wave function of the two  $e^-$ 's.

Consider the solutions of this equation that can be separated as

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi_a(\vec{r}_1) \psi_b(\vec{r}_2) e^{-i\frac{E}{\hbar}t}, \quad (123)$$

with

$$-\frac{\hbar^2}{2m} \vec{\nabla}_1^2 \psi_a(\vec{r}_1) + V_1 \psi_a(\vec{r}_1) = E_a \psi_a \quad -\frac{\hbar^2}{2m} \vec{\nabla}_2^2 \psi_b(\vec{r}_2) + V_2 \psi_b(\vec{r}_2) = E_b \psi_b \quad (124)$$

where  $a$  and  $b$  denote some quantum state for an electron and  $E_a + E_b = E$ . The new feature is that for any such solution an equally good solution with exactly the same energy is provided by  $\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)$ .

And, in QM wave theory, we believe that we should be able to superimpose the two solutions of the same energy and write

$$\psi(\vec{r}_1, \vec{r}_2) = c\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + d\psi_b(\vec{r}_1)\psi_a(\vec{r}_2). \quad (125)$$

**Pauli says “not so fast”.** He says that  $d = -c$  ( $= 1/\sqrt{2}$  for normalization) is required. QFT says the same thing.

Why the  $-$ ? The minus sign is required by the Pauli exclusion principle which says that two electrons cannot occupy exactly the same state. In the present context, the two electrons would be in the same state if  $a = b$ . By requiring the minus sign, the wave function automatically vanishes if  $a = b$ , *i.e.* violation of the Pauli exclusion principle is automatically prevented. This is the situation for all **Fermions** ( $s = 1/2, 3/2, \dots$ ).

Note that if we were talking about **Bosons** ( $s = 0, 1, 2, \dots$ ), one would instead have a plus sign between the two pieces of the full wave function.

With  $-$  sign firmly in place, the form of the wavefunction

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)] . \quad (126)$$

implies that it is truly impossible to say which  $e^-$  is in which state (*i.e.*  $a$  or  $b$ ).

Another way to approach the Boson and Fermion possibilities is to start out with the form

$$\psi(\vec{r}_1, \vec{r}_2) = c\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + d\psi_b(\vec{r}_1)\psi_a(\vec{r}_2) . \quad (127)$$

and require indistinguishability in the form

$$P(\vec{r}_1, \vec{r}_2) = P(\vec{r}_2, \vec{r}_1) . \quad (128)$$

Substituting in  $P = |\psi|^2$ , this requirement becomes

$$\begin{aligned}
& |c|^2 |\psi_a(\vec{r}_1)|^2 |\psi_b(\vec{r}_2)|^2 + 2c^* d \psi_a(\vec{r}_1) \psi_b^*(\vec{r}_1) \psi_a^*(\vec{r}_2) \psi_b(\vec{r}_2) \\
& + 2cd^* \psi_a^*(\vec{r}_1) \psi_b(\vec{r}_1) \psi_a(\vec{r}_2) \psi_b^*(\vec{r}_2) + |d|^2 |\psi_b(\vec{r}_1)|^2 |\psi_a(\vec{r}_2)|^2 \\
= & \\
& |c|^2 |\psi_a(\vec{r}_2)|^2 |\psi_b(\vec{r}_1)|^2 + 2c^* d \psi_a(\vec{r}_2) \psi_b^*(\vec{r}_2) \psi_a^*(\vec{r}_1) \psi_b(\vec{r}_1) \\
& + 2cd^* \psi_a^*(\vec{r}_2) \psi_b(\vec{r}_2) \psi_a(\vec{r}_1) \psi_b^*(\vec{r}_1) + |d|^2 |\psi_b(\vec{r}_2)|^2 |\psi_a(\vec{r}_1)|^2
\end{aligned} \tag{129}$$

This equality requires

$$|c|^2 = |d|^2, \quad \text{and} \quad cd^* = c^*d. \tag{130}$$

If you satisfy the first equation above by writing  $c = \rho e^{i\theta_c}$  and  $d = \rho e^{i\theta_d}$ , then the 2nd equality requires

$$\rho^2 e^{i(\theta_c - \theta_d)} = \rho^2 e^{i(\theta_d - \theta_c)}, \quad \Rightarrow \quad \theta_c - \theta_d = \theta_d - \theta_c + 2\pi n \tag{131}$$

which in turn can be rewritten as

$$2(\theta_c - \theta_d) = 0, \pm 2\pi, \dots, \quad \Rightarrow \quad \theta_c - \theta_d = 0, \pm\pi, \pm 2\pi, \dots \tag{132}$$

which is to say that  $c = \pm d$  are the only two possibilities.

## The Periodic Table

Armed with our understanding of energy levels, spin quantization and the exclusion principle, we can now understand the structure of the periodic table.

In complicated atoms, one fills a succession of levels with increasing energy (exclusion means can't put all electrons into the lowest level).

It is then the outermost electrons that are primarily responsible for the chemical properties of a given atom.

The technical phrase that goes with this procedure is **the central field approximation**.

The procedure in more detail is:

- a) Add one  $e^-$  after another into the lowest state possible taking into account the exclusion principle.
- b) Assume all electrons already present just give (along with the nucleus) a certain  $V(r)$  central kind of potential (this ignores among other things the "spin-orbit" interaction that we mentioned earlier but did not study).

In this approximation, the energy levels are a function of  $n$  (as for hydrogen), but, now, also of  $l$ .

- The  $l$  dependence of  $E_{n,l}$  comes from the fact that low  $l$  wavefunctions tend to have more nodes and therefore more eccentric wavefunction distributions that can penetrate further towards the nucleus and therefore experience less shielding due to already-present electrons and therefore more attraction from the nucleus; *i.e.* smaller  $l$  implies that there are fewer electrons in between the electron about to be put in and the nucleus.

We still have degeneracy of the energy with respect to  $m_l$  and  $m_s$ , which implies that each  $E_{n,l}$  level has a  $2(2l + 1)$  degeneracy.

- c) Of course, you should note that if the “next”  $e^-$  is added to a non-minimum energy level then it would naturally fall to the minimum allowed (by exclusion principle) energy level.
- d) The chemical properties are determined by the  $e^-$ 's in the outermost shell(s). Remember a shell is specified by  $n$ .
- If the last shell is filled by the last electron, then the element is inert.
  - If the last shell is mostly empty, then the electrons in this last shell are easily given up to a neighboring atom.
  - If the last shell is mostly full, then it can easily grab an electron from a neighboring atom.

## The Ground State Configurations

### Example

It is interesting to consider in detail the *He* atom with nuclear charge  $Z = 2$ .

The first  $e^-$  placed will go into the  $n = 1, l = 0, m_l = 0$  state

$$\psi_{100} = \pi^{-1/2} (2/a_0)^{3/2} e^{-2r/a_0}. \quad (133)$$

To this wave function we should append a spin label ( $\pm$ ) indicating the direction of the  $e^-$  spin. We might then call the net label  $a = (1, 0, 0, +)$  or  $b = (1, 0, 0, -)$ . The energy will not depend upon this spin orientation:

$$E_a = E_b = -(2^2/1^2)(13.6 \text{ eV}) = -54.4 \text{ eV}. \quad (134)$$

We now bring in the 2nd  $e^-$ . We assume that it will come in to the same energy state to first approximation (which neglects repulsion between the two  $e^-$ 's).

The net wave function must be antisymmetric as described above and

would be written

$$\psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\psi_{100+}(\vec{r}_1)\psi_{100-}(\vec{r}_2) - \psi_{100-}(\vec{r}_1)\psi_{100+}(\vec{r}_2)] . \quad (135)$$

The two components have exactly the same spatial dependence, but differ with regard to the spin orientation. The first component has spin up for  $e_1^-$  and down for  $e_2^-$ , and the 2nd component has the reverse. We could denote these two configurations by  $|+ - \rangle$  and  $|- + \rangle$ , in which case we could write

$$\psi(\vec{r}_1, \vec{r}_2) = \pi^{-1}(2/a_0)^3 e^{-2(r_1+r_2)/a_0} \frac{1}{\sqrt{2}} [|+ - \rangle - |- + \rangle] \quad (136)$$

Of course, this approximation does not take into account the shielding of one electron by the other nor their mutual repulsion, but it gives you an idea of how things work.

The above shielding and repulsion means that the ground state energy is not simply  $E = E_a + E_b = -2(54.4 \text{ eV}) = -108.8 \text{ eV}$ . It is something substantially less negative:  $-79.0 \text{ eV}$ .

Closely related is the fact that to remove the first electron from the *He* atom only takes  $24.6 \text{ eV}$  rather than a full  $54.4 \text{ eV}$ . The  $e^-$  being

left behind **screens** the nuclear charge making the attraction felt as the 2nd  $e^-$  is removed much less than that of the full nuclear charge.

### **Hund's Rule**

Before going on to fill in a table of configurations, we note a final fairly general rule:

If there are two electrons in the same  $n, l$  state (with  $l > 0$  so that there are several  $m_l$  values), they tend to go into different  $m_l$  states rather than the same  $m_l$  state with opposite spins.

This reduces the repulsion between the two  $e^-$ 's since wavefunctions with different  $m_l$  values do not overlap nearly as much as two wavefunctions with the same  $m_l$  value.

## Table of Atomic Configurations

Atom	Filled States	Denoted by
$H^+$ :	$n = 1, l = 0, m_s = \pm \frac{1}{2}$	$1s$
$He^{++}$ :	$n = 1, l = 0, m_s = +\frac{1}{2}$ $n = 1, l = 0, m_s = -\frac{1}{2}$	$1s^2$
$Li^{+++}$ :	$n = 1, l = 0, m_s = +\frac{1}{2}$ $n = 1, l = 0, m_s = -\frac{1}{2}$ $n = 2, l = 0, m_s = \pm \frac{1}{2}$	$1s^2 2s$
for last $e^-$ , $l = 0$ has slightly lower $E$ than $l = 1$		
$Be^{4+}$ :	$n = 1, l = 0, m_s = +\frac{1}{2}$ $n = 1, l = 0, m_s = -\frac{1}{2}$ $n = 2, l = 0, m_s = +\frac{1}{2}$ $n = 2, l = 0, m_s = -\frac{1}{2}$	$1s^2 2s^2$
not inert since $2p$ shell so nearby in $E$		
$B^{5+}$ :	$n = 1, l = 0, m_s = +\frac{1}{2}$ $n = 1, l = 0, m_s = -\frac{1}{2}$ $n = 2, l = 0, m_s = +\frac{1}{2}$ $n = 2, l = 0, m_s = -\frac{1}{2}$ $n = 2, l = 1, m_s = \pm \frac{1}{2}$	$1s^2 2s^2 2p^1$

Atom	1s	2s	2p			Electron configuration
Li						$1s^2 2s^1$
Be						$1s^2 2s^2$
B						$1s^2 2s^2 2p^1$
C						$1s^2 2s^2 2p^2$
N						$1s^2 2s^2 2p^3$
O						$1s^2 2s^2 2p^4$
F						$1s^2 2s^2 2p^5$
Ne						$1s^2 2s^2 2p^6$

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Fig. 9-15, p.321

Figure 21: Electronic Configurations.

Of course, various complexities develop as you go to more complex atoms. For example, the transition metals and the like are tricky. We do not have time to discuss these more complex cases.

### A Final Example

This is the example that you should use to study for the Monday quiz. If you can do this example and have memorized the way in which the shells get filled, then the quiz will be easy.

Consider the element *Ge*, which has nuclear charge of  $Z = 32$ . The outer shell configuration is  $3d^{10}4s^24p^2$ .

1. Give the full configuration for the remaining inner shell electrons.

First, you should note that there are an additional 18 electrons whose configurations must be specified. They are in the configurations

$$1s^2, 2s^22p^6, 3s^23p^6 \quad (137)$$

2. In “box” notation, lay out the outer-shell configuration given for *Ge* above.

I will only try to describe. All boxes are maximally filled except the  $4p$  boxes. There are 3 such boxes, and the two electrons go into separate boxes (Hund’s rule).

3. What is the  $Z$  value such that the  $4d$  and  $5s$  shells as well as all

inner shells are also filled.

There is a little bit of trickery as to exactly what order they get filled in but there is no doubt as to the final result which is that we must go from  $3d^{10}4s^24p^2$  to  $3d^{10}4s^24p^64d^{10}5s^2$ , which means an additional 16 electrons taking us to  $Z = 48$  (which is *Cd* — see Table 9.2 in the book).