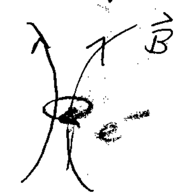
Magnetic Dipole Moments, Spin, and Transition Rates

Eisberg + Resnick, Chapter 8.

Finally we come to grips with how we measure some of this stuff, like the z component of angular momentum. In many cases we do it by putting the atom in a magnetic field + looking at its response.

Orbital Magnetic Dipole Moments

Recall back in E+M when the magnetic dipole moment was introduced. We calculated the magnetic field due to a current loop w/current I + area A and found that we could write it in terms of a magnetic dipole moment $\vec{\mu}$ where



$$|\vec{\mu}| = IA$$

and the direction is perpendicular to the plane of the loop.

Now if we pretend the electron in an atom is in a circular Bohr orbit of radius r, then we can define a magnetic dipole moment for it.

[Aside Of course we shouldn't take the orbit idea literally; it's simply a picture that lets us imagine the physical situation a little better and happens to give the right answer. TO do the derivation for real requires quantum electrodynamics, which is beyond our scope. So we'll try to motivate the ideas and then explore the results.

end of aside

Since current is charge/unit time, and the time for the charge $-e$ to pass by a point on the orbit is just the period $T = \frac{v}{2\pi r}$, the current is

$$I = \frac{ev}{2\pi r},$$

which gives a magnetic moment

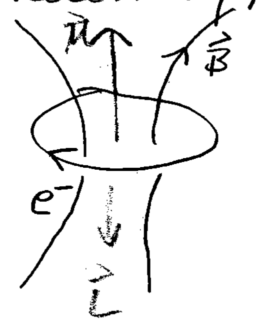
$$\mu = IA = \frac{ev}{2\pi r}\pi r^2 = \frac{evr}{2}$$

Now we can't take this orbit stuff literally, so we don't want an expression for the magnetic moment to have v + r in it (e is okay). We'll express μ in terms of the classical angular momentum and then postulate that it works if we use the quantum angular momentum. (It does work - you get the same thing as you would if you did the QED calculation) Classically,

$$L = mvr$$

and now we're using m instead of μ for the reduced mass ($\simeq m_e$) because now μ is magnetic moment.

Now, $\vec{L}$ is a vector, and its direction is opposite $\vec{\mu}$ because the electron's charge is negative. Remember the right-hand rule for $\vec{L}$ and for $\vec{B}$: $\vec{\mu}$ points parallel to $\vec{B}$, and $\vec{B}$ is given by the right hand rule (thumb in direction of motion of charge $\Rightarrow$ fingers curl in direction of $\vec{B}$, but then reverse it for the − sign. Equivalently, thumb in direction of motion of positive charge + no reversal necessary.).



For angular momentum, just curl fingers in direction of motion and thumb points in direction of $\vec{L}$.

One more notational thing: this magnetic moment is associated with orbital angular momentum, so we're going to call it μ_ℓ, to distinguish it from another kind of magnetic moment (associated with spin, or intrinsic angular momentum) to be discussed later.

So $\mu_\ell = \frac{evr}{2}$ and $L = mvr$. We can get rid of the explicit orbital stuff by writing

$$\mu_\ell = \frac{e}{2m} L$$

$$= \frac{g_\ell \mu_b L}{\hbar}$$ ← standard notation that follows from QED derivation

where $\mu_b = \frac{e\hbar}{2m} = 0.927 \times 10^{-23}$ amp-m^2
= "Bohr magneton"

$g_\ell = 1$
= "orbital g factor"

The orbital g factor seems superfluous but we'll find another g factor that's different from 1.
Finally, combining all this and writing it in terms of vectors, we have for the electron

$$\boxed{\vec{\mu}_\ell = -\frac{g_\ell \mu_b}{\hbar} \vec{L}}$$

and it's all expressed in terms of fundamental constants along with the angular momentum, which we now interpret to be quantum mechanical, i.e. $|\vec{L}| = \hbar\sqrt{\ell(\ell+1)}$

Now there are several more results from classical E+M for the behavior of magnetic moments in magnetic fields that will have quantum analogies. They are

- Torque + energy assoc. w/ orientation
  A magnetic dipole in a magnetic field feels a torque:

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

and there's an associated potential energy that depends on the orientation of the dipole

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

so the lowest energy is for $\vec{\mu}$ parallel to $\vec{B}$. Note this also means that energy must be either absorbed or emitted for $\vec{\mu}$ to change its orientation in the field.

Ex: Suppose a mag. dipole is in an external field in the lowest energy state, i.e. parallel to $\vec{B}$. How much energy do you have to provide to turn the dipole antiparallel to the field? Assume $\mu = 1$ Bohr magneton + $B = 1$ Tesla

$F = qv \times B$

$$E_f - E_i = \mu B - (-\mu B) = 2\mu B$$

$$= 2 * 0.927 \times 10^{-23} \text{ amp m}^2 * 1T$$

$$T = \frac{N}{\text{Coul} \cdot \frac{m}{sec}} = \frac{N}{\text{amp-m}}$$

$$= 1.85 \times 10^{-23} \text{ amp m}^2 \frac{N}{\text{amp m}}$$

→

$$= 1.85 \times 10^{-23}\ Nm = \frac{1.85 \times 10^{-23}\ J}{1.602 \times 10^{-19}\ J/eV}$$

$$= 1.16 \times 10^{-4}\ eV$$

$\Rightarrow$ Small compared to typical atomic energies (cf 13.6 eV for H ground state)

- Larmor precession

Remember that since the magnetic force is

$$\vec{F} = q\vec{v} \times \vec{B}$$

and the force is perpendicular to the velocity, a magnetic force doesn't change the energy of a charged particle (+ we can carry that over to apply to a dipole & hence a magnetic moment).

So the magnetic field can't change the energy, which means it can't change the angle between it and the mag. moment. But it still exerts a torque on $\vec{\mu}$, which results in $\vec{\mu}$ precessing about $\vec{B}$ such that their orientation (and hence $\vec{\mu} \cdot \vec{B}$) is fixed.

To find the <u>precession frequency</u>, note from classical mechanics that

$$\vec{\tau} = \vec{\mu}_\ell \times \vec{B} = -\frac{g_\ell \mu_b}{\hbar} \vec{L} \times \vec{B}$$

but $\vec{\tau} = \frac{d\vec{L}}{dt} = +\vec{L} \times \vec{\omega}$, $\boxed{\vec{\omega} = \frac{g_\ell \mu_b \vec{B}}{\hbar}}$

Whenever you have an eqn of motion

7) $$\frac{d\vec{A}}{dt} = \vec{A} \times \vec{\omega},$$

the solution is a rotation of $\vec{A}$ about $\vec{\omega}$ with angular frequency $|\vec{\omega}|$. To see this, let $\vec{\omega} = \omega\hat{z}$.

The eq'n becomes

$$\frac{dA_x}{dt} = \omega A_y, \quad \frac{dA_y}{dt} = -\omega A_x, \quad \frac{dA_z}{dt} = 0$$

Combining the 1st two eq'ns,

$$\frac{d}{dt}\underbrace{(A_x + iA_y)} = \omega(A_y - iA_x) = -i\omega\underbrace{(A_x + iA_y)}$$

or $$\frac{da}{dt} = -i\omega a$$

The sol'n is an exponential:

$$a = a_0 e^{-i\omega t}$$

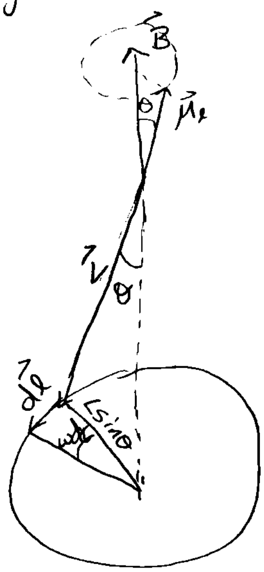
or $$A_x + iA_y = A_{x0}\cos\omega t - iA_{y0}\sin\omega t$$

so $$A_x = A_{x0}\cos\omega t \qquad \left(\text{Note } A_z = A_{z0}\right)$$
$$A_y = -A_{y0}\sin\omega t$$

and this is just a rotation in the plane perpendicular to ω.

So $\vec{L} \to \vec{A}$ and $\vec{L}$ thence $\vec{\mu}$ precesses about $\vec{B}$ with angular frequency ω

That was an algebraic derivation. A more geometrical derivation is given in the text in figure 8-2 (p.270). We have again



$$\frac{d\vec{L}}{dt} = \vec{\tau} = -\frac{g_\ell \mu_b}{\hbar} \vec{L} \times \vec{B}$$

In time dt, $|d\vec{L}| = \underbrace{(L\sin\theta)}_{\text{radius}}\underbrace{\omega\, dt}_{\text{angle}}$

but

$$\left|\frac{d\vec{L}}{dt}\right| = \frac{g_\ell \mu_b L |\vec{B}| \sin\theta}{\hbar}$$

$$\Rightarrow \quad \vec{\omega} = -\frac{g_\ell \mu_b \vec{B}}{\hbar}$$

* the − sign is for $\vec{L}$, but $\vec{\mu}$ precesses w/ $+\frac{g_\ell \mu_b \vec{B}}{\hbar}$

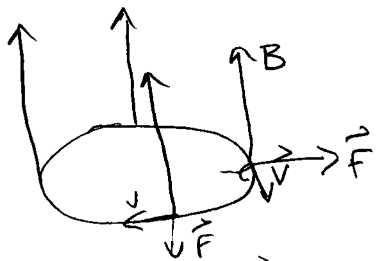
This was classical but quantum-mechanically you get the same result, only with expectation values

– Force in a non-uniform $\vec{B}$ field.

It turns out that you can get something besides precession: if the $\vec{B}$ field isn't uniform, you can get a translational force. That's because in different parts of, for example, a Bohr orbit, you don't get a cancellation if $\vec{B}$ is different of all the components of the force.

See for example Fig 8-3 (p. 271)

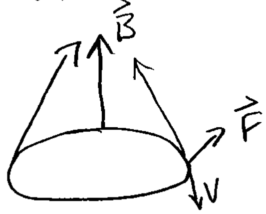
uniform:



$\vec{F}$ is always radially outward

Note that we can't just have $\vec{B} = B(z)\hat{z}$ w/ $B(z)$ increasing because $\nabla \cdot \vec{B}$ must $= 0$.

Converging B



$\vec{F}$ has component upward

It turns out the average force is, in terms of the magnetic moment

$$\overline{F_z} = \frac{\partial B_z}{\partial z} \mu_{\ell_z}$$

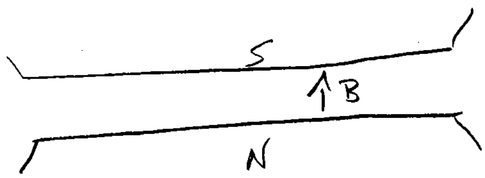
The net effect is a <u>drift</u> in the direction of the change in B.

Spin

We can use the last result about nonuniform fields to get yet another simple phenomenon that classical mechanics gets wrong and quantum gets right. Consider a long magnet designed to have a nonuniform field, such that $\vec{B}$ increases in the z direction (cf. fig 8-5 on p. 272).

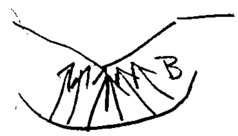
(5.10)

Side view



$\uparrow z$ $\vec{B}$ gets more intense

end view



so $\frac{\partial B}{\partial z} \neq 0$

Now take some hydrogen atoms + send a beam through this apparatus. They'll feel a force

$$\bar{F}_z = \frac{\partial B_z}{\partial z} \mu_{\ell z}$$

in the $\pm z$ direction according to the sign of $\mu_{\ell z}$, i.e. according to the sign of L_z.

<u>Classically</u>, the z component of L can take on any value between $+|\vec{L}|$ + $-|\vec{L}|$ so if we have a random beam of H atoms, they'll feel a continuum of forces, + if we collect them on a detector when they come out we'll get a continuous smear.

<u>Quantum mechanically</u>, $L_z = \hbar m_\ell$ where $m_\ell = -\ell, \ldots +\ell \Rightarrow$ can only take on discrete values. That means the forces will be quantized as well, and the atoms will

be deflected in bundles, so you should see bands on the detector plate.

- Result: You get bands, and quantum mechanics wins. Note that for a given l, you have $2l+1$ (an odd number) of bands, including one in the middle for $m_l = 0$.

  Now prepare a beam of hydrogen atoms in the ground state, $n=1$, $l=0$, $m_l=0$. No angular momentum $\Rightarrow$ no magnetic moment $\Rightarrow$ no force $\Rightarrow$ no deflection: a single band right in the middle. Right?

- Surprise!! You get two bands, with nothing in the middle! How does that happen?!

Turns out there's another kind of angular momentum, besides the orbital ang. mom. we've been talking about, that's intrinsic to the electron. It's called **spin**, but there's nothing actually spinning. Mathematically it's a lot like orbital angular momentum, except for the actual values it takes on. Let's be specific. We have a new intrinsic angular momentum

$$\vec{S} = \text{spin} = \text{intrinsic ang. mom.}$$

- and associated is a quantum numbers

analogous to l, so

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

and $S_z = m_s \hbar$

but for the electron we only have

$$s = \frac{1}{2}$$ ← [illegible] electron a [illegible] particle

$$m_s = -\frac{1}{2},\ +\frac{1}{2}$$

and there's a spin magnetic moment

$$\vec{\mu}_s = -\frac{g_s \mu_b}{\hbar}\vec{S}$$

$$\text{+} \quad \mu_{s_z} = -\frac{g_s \mu_b}{\hbar} S_z$$

Now we know where the two bands came from. There's no orbital magnetic moment, but the spin magnetic moment of the atoms responded to the magnetic field gradient. In fact we can calculate the expected displacement of the bands, and when we measure them that tells us that

$$g_s = 2$$

The g-factor for spin is twice that for orbital angular momentum.

Comments:

- The apparatus + experiment described above was originally devised by Stern + Gerlach, although they used silver atoms in their original 1922 experiment. The actual hydrogen experiment was done in 1927 by Phipps + Taylor. The idea of spin was introduced/worked out by Goudsmit and Uhlenbeck in 1925. It took a while for the evidence to build up so people believed spin was real. Not surprising, because the idea doesn't work in a literal sense — if the electron is literally spinning, then to get the right magnetic moment it either has to be bigger than an atom or its surface would have to be moving faster than the speed of light.

- The Stern-Gerlach apparatus, or any external mag. field provides a way to pick a z axis, i.e. to pick a direction of quantization. You get the same results for any orientation of the magnet.

- How ~~else~~ do we know about spin? Zeeman effect. Use the fact that even in a uniform $\vec{B}$ field, a magnetic moment feels a torque and there's an associated energy. So for an H atom in the ground state, even though $l=0$, the degeneracy in spin can be broken by an external magnetic field.

We have

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

$$= -\mu_{s_z} B \qquad \text{let } z \text{ be direction of } \vec{B}$$

$$= g_s \mu_b m_s B$$

$$= \pm g_s \mu_b B/2$$

So the groundstate energy gets shifted up + down, + if you look at the hydrogen spectrum in a $\vec{B}$ field you see that the spectral line corresponding to the ground state is split into two lines.

This is called the <u>Zeeman</u> <u>effect</u>.

We'll see below that there's a splitting even without an external field.

But first, more comments about spin:

- The state of an electron in an atom is now specified by 4 quantum numbers

$$n, l, m_e, m_s$$

(We don't include s because it's always ½.)

Classically we expect 3 (takes 3 to specify electron's location in space). Spin is a purely quantum effect

- When Dirac did his relativistic version of the Schr. Eq'n, the eq'n he got automatically described a particle with intrinsic angular momentum given by $s = 1/2$. Spin comes automatically from the relativistic theory.

- Are there any more angular momentum surprises in store? Am I going to tell you that there's yet another kind of angular momentum with quantum number $1/3$? Nope. It's beyond our scope, but there's some fascinating math called group theory and abstract algebra that tells us something about angular momentum. In particular it says that spin can be described mathematically in terms of the group SU(2). ← 2 dimensions

  Special Unitary

  In technical terms, the different possible angular momenta (values of s, ℓ) are described by different "representations" (a technical math term) of SU(2). A consequence is that angular momenta have to be integer multiples of $\frac{1}{2}$.

- Do other particles besides electrons have spin? Yes. Here's the spin of the elementary particles in the Standard Model

quarks: $\begin{pmatrix} u \\ d \end{pmatrix} \begin{pmatrix} c \\ s \end{pmatrix} \begin{pmatrix} t \\ b \end{pmatrix}$ spin $1/2$

Leptons $\begin{pmatrix} \nu_e \\ e^- \end{pmatrix} \begin{pmatrix} \nu_\mu \\ \mu^- \end{pmatrix} \begin{pmatrix} \nu_\tau \\ \tau^- \end{pmatrix}$ spin $1/2$

gauge bosons $\left.\begin{array}{l} \gamma \text{ photon} \\ W^\pm, Z^0 \text{ weak bosons} \\ g \text{ gluon} \end{array}\right\}$ spin 1

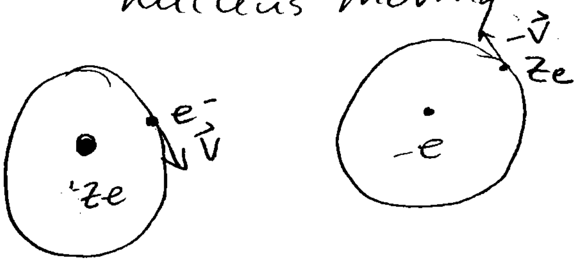
Higgs boson h spin 0
(never seen)

Composite particles, like the proton and neutron which are made up of combinations of quarks, have spin that depends on what they're made of and how it's combined. Protons + neutrons have spin $1/2$.

Spin-orbit interaction

So an electron in an atom has spin, with an associated magnetic moment. If we put the electron in a magnetic field, then, the electron will feel a torque and there will be an associated interaction energy.

But an electron in an atom is already in a magnetic field! Why? Because of its motion – the electron is moving w.r.t. the nucleus (picture Bohr orbits). That means if you're the electron, you see the nucleus moving about you:



But a moving charge is a current, and currents give magnetic fields. Therefore

> An electron in an atom experiences an internal magnetic field due to the relative motion of the electron and the nucleus.

Furthermore, the magnetic field can be expressed in terms of the electron's <u>orbital</u> angular momentum. The interaction of this field with the electron's spin is therefore called the

<u>spin-orbit interaction.</u>

To see how the interaction works, recall that the interaction energy (the orientational potential energy) is

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

$$= \frac{g_s \mu_b}{\hbar} \vec{S} \cdot \vec{B} \Big|_{\text{rest frame of nucleus}}$$

We're going to write $\vec{B}$ in terms of the electron's orbital angular momentum and the Coulomb potential for the electromagnetic interaction.

But there's a catch. The orientation energy above assumes we're in a frame where the nucleus is at rest.* But it's easiest to find $\vec{B}$ in the frame where the e- is at rest. We'll do that, then throw in an extra factor to account for switching back to the nucleus frame. So let's find $\vec{B}_{\text{e-frame}}$

The B the electron sees is due to the motion of the nucleus, and since the nucleus has charge Ze and velocity $-\vec{v}$ the field is

$$\vec{B}_{\text{e frame}} = \frac{\mu_0}{4\pi} Ze \frac{(-\vec{v} \times \vec{r})}{r^3}$$

* And that's the normal frame we'd have for making measurements. It's easier to keep the nucleus at rest...

Now, if we can express this in terms of the electric field, that's the same as writing it in terms of the electrical force, which we can write in terms of a derivative of the potential. It's straightforward. The electric field of the nucleus at the position of the electron is
$$\vec{E} = \frac{Ze}{4\pi\epsilon_0}\frac{\hat{r}}{r^2} = \frac{Ze\,\vec{r}}{4\pi\epsilon_0 r^3}$$

Comparing, we see
$$\vec{B}_{eframe} = -\epsilon_0\mu_0\vec{v}\times\vec{E}$$
$$= -\frac{1}{c^2}\vec{v}\times\vec{E}$$

The latter relation, is the one we need and, actually, using relativity you can derive it in general — it's the magnetic field felt by a particle moving with velocity $\vec{v}$ relative to the electric field $\vec{E}$.

Now we use $\vec{E} = \frac{\vec{F}}{-e}$

where $\vec{F}$ is the electric force on the electron.

We also have $\vec{F} = -\vec{\nabla}V = -\frac{dV(r)}{dr}\hat{r} = -\frac{dV(r)}{dr}\frac{\vec{r}}{r}$

for a radial potential. (Note: If you plug the

Coulomb potential into this expression for $\vec{F}$ and multiply by $-e$, you get back the $\vec{E}$ on p. 5.19). So plugging all this into $\vec{B}$:

$$\vec{B}_{eframe} = -\frac{1}{c^2}\,\vec{v}\times\vec{E}$$

$$= +\frac{1}{ec^2}\,\vec{v}\times\vec{F}$$

$$= -\frac{1}{ec^2}\,\frac{1}{r}\frac{dV(r)}{dr}\,\underbrace{\vec{v}\times\vec{r}}_{=\frac{-\vec{L}}{m}}$$

since $\vec{L} = \vec{r}\times\vec{p}$
$= -m\vec{v}\times\vec{p}$

$$= \frac{1}{emc^2}\,\frac{1}{r}\,\frac{dV(r)}{dr}\,\vec{L}$$

Now we just have to know what the expression is for ΔE when we've evaluated $\vec{B}$ in the e^- rest frame. It's a complicated relativistic thing called the Thomas Precession, beyond the scope of this course. Fortunately it gives a simple result: an extra factor of $\frac{1}{2}$:

$$\Delta E\Big|_{\substack{\text{rest frame}\\ \text{of nucleus}}} = \frac{1}{2}\,\frac{g_s\mu_b}{\hbar}\,\vec{S}\cdot\vec{B}_{eframe}$$

fr/ Thomas precession

So, finally,

$$\Delta E = \frac{g_s \mu_b}{2emc^2\hbar} \frac{1}{r} \frac{dV(r)}{dr} \vec{S} \cdot \vec{L}$$

$$\boxed{\Delta E = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{S} \cdot \vec{L}}$$ since $g_s = 2$ + $\mu_b = \frac{e\hbar}{2m}$

Spin-orbit interaction

Remember that $\vec{S}$ and $\vec{L}$ are the spin and orbital angular momentum of the electron.

Notice that there's no splitting for the ground state, $n=1$, because $l=0$ in that state and there is no orbital angular momentum.

__Ex__ Estimate this ΔE for hydrogen for the $n=2$, $l=1$ state.

$$\Delta E = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV}{dr}(r) \vec{S} \cdot \vec{L}$$

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$ ($Z_1 = 1$ for hydrogen)

so $$\frac{dV}{dr} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r^2}$$

$$\Rightarrow \Delta E = \frac{e^2}{4\pi\epsilon_0 m^2c^2} \frac{1}{r^3} \vec{S} \cdot \vec{L}$$

Here's where the estimation comes in. We say $\vec{S} \cdot \vec{L} \sim \hbar^2$, each one being $\sim \hbar$, and the expectation value of $\frac{1}{r^3}$ for $n=2$ is approx $\frac{1}{(3a_0)^3}$. Plugging + chugging (see p. 280) we get

$$|\Delta E| \sim 10^{-23} J \sim 10^{-4} eV$$

Comments: The $n=2$ energy is $-3.4 eV$ so the splitting is about 1 part in 10^4. This is about what's needed to describe the "fine structure" in hydrogen, a small splitting seen in the spectral lines.

Ex: From $|\Delta E|$ above, estimate the B field

Since $\Delta E = -\mu_s \cdot \vec{B}$,

$|\Delta E| \sim \mu_b B$ + we took $\mu_s \sim \mu_b \sim 10^{-23}$ amp-m²

so $B = \frac{\mu_b}{|\Delta E|} \sim \frac{10^{-23} J}{10^{-23} amp\text{-}m^2} \sim 1$ Tesla

So the B field used in the example on p. 5.5 was actually typical for an internal atomic field. We said this was a big field. Recall

$$\vec{B} = \frac{1}{c^2} \vec{v} \times \vec{E}$$

So we get a big field because the electron is moving fast in the strong nuclear field.

Total angular momentum

So the total angular momentum for our hydrogen atom has two contributions; orbital and spin. The way they combine is a bit complicated. The total angular momentum is called J. So

$$\vec{J} = \vec{L} + \vec{S}$$

It turns out that $\vec{J}$ & $\vec{J}_z$ are quantized in a manner similar to $\vec{L}$ and $\vec{S}$. There is a quantum number j s.t.

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

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

Now, as you might guess, j is related to l & s, but not just from simple addition. The formalism associated with addition of angular momentum will be saved for P246, so we'll just give an idea of how it works. We <u>do</u> have

$$J_z = L_z + S_z$$

which implies $\quad m_{j\,max} = m_{l\,max} + \frac{1}{2} = l + \frac{1}{2}$

That means in turn that

$$j_{max} = l + \tfrac{1}{2}$$

You can show (see argument in book, p. 283) that

$$j_{min} = l - \tfrac{1}{2}$$

+ since the j's differ by integers (in analogy w/ l), we have

$$j = l + \tfrac{1}{2},\ l - \tfrac{1}{2}$$

+ if $l = 0$, we have $j = \tfrac{1}{2}$ only since $j > 0$.

So for example, for the $l = 2$ state of the hydrogen atom (for any $n \geq 3$), the possible values of j + m_j are

$$j = 2 + \tfrac{1}{2} = \tfrac{5}{2} \qquad m_j = -\tfrac{5}{2}, -\tfrac{3}{2}, -\tfrac{1}{2}, +\tfrac{1}{2}, \tfrac{3}{2}, \tfrac{5}{2}$$

$$j = 2 - \tfrac{1}{2} = \tfrac{3}{2} \qquad m_j = -\tfrac{3}{2}, -\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{3}{2}$$

Now, if the atom is in free space, w/no external mag. field the total angular momentum is conserved. The internal magnetic field acts on the electron an gives a torque on its spin. The torque depends on $\vec{L}$. So we have the coupling as described above, + both $\vec{L}$ + $\vec{S}$ precess. Turns out they precess about their sum, i.e. about $\vec{J}$.

So L_z + S_z don't have fixed values, but J_z does

$\Rightarrow m_s + m_l$ are no longer good quantum numbers

Now notice that something interesting happens. Since $j = l \pm 1/2$, different values of l can correspond to the same j. For example:

$$n = 3 \Rightarrow l = 0 \Rightarrow j = +\tfrac{1}{2}$$
$$1 \Rightarrow j = +\tfrac{1}{2}$$
same j, $l = 0, 1$
$$+\tfrac{3}{2}$$
$$2 \Rightarrow j = +\tfrac{3}{2}$$
same j, $l = 1, 2$
$$+5/2$$

This will have some interesting consequences when we look at the spin-orbit interaction + hydrogen energy levels.

Fine structure: Spin-orbit interaction + H energy levels

So now we know that because of the spin-orbit interaction and its associated energy, the energy levels of hydrogen get shifted, depending on what $\vec{S} \cdot \vec{L}$ is. In fact we can write the interaction energy in terms of the total angular momentum. With

$$\vec{J} = \vec{L} + \vec{S}$$

We then note

$$J^2 = (\vec{L}+\vec{S})^2$$
$$= L^2 + S^2 + 2\vec{S}\cdot\vec{L}$$

or $\boxed{\vec{S}\cdot\vec{L} = \frac{1}{2}(J^2 - L^2 - S^2)}$

but $J^2 = \hbar^2 j(j+1)$, $L^2 = \hbar^2 \ell(\ell+1)$ $S^2 = \hbar^2 s(s+1)$

for a quantum state described by j, ℓ, s, so

$$\vec{S}\cdot\vec{L} = \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right] \quad \left(\text{+ of course } s = \tfrac{1}{2}\right)$$

That means, for a given hydrogen state the expectation value for the associated spin-orbit interaction is (cf. p. 5.21)

$$\overline{\Delta E} = \frac{\hbar^2}{4m^2c^2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]\overline{\frac{1}{r}\frac{dV(r)}{dr}}$$

Where the expectation value on the right is the usual

$$\int_0^\infty \frac{1}{r}\frac{dV}{dr}P(r)\,dr$$

Where $P(r) = 4\pi r^2 |R_{n\ell}|^2$.

So performing this calculation for all n, ℓ + adding to the ground state gives the energy w/ the spin-orbit correction. To do a proper job, we'd have to use the Dirac eq'n (beyond our scope) and there's an additional relativistic effect that's comparable in magnitude to the spin-orbit effect (comparable for hydrogen, anyway; for higher Z atoms the spin-orbit effect gets bigger. Taken together these effects give the fine structure of the atom, and now the energy levels for hydrogen are

reduced mass

$$\boxed{E = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right]}$$

Comments

- The first term is the regular old H energy from the Schrödinger eq'n
- The second and third terms are small because

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137} \quad \text{"fine structure const"}$$

is small, and α^2 is even smaller. In fact α^2 by itself tells you the effect is $\mathcal{O}(10^{-4})$ compared to the main one

- The correction depends on angular momentum only through j, the total ang. mom. quantum number, not on l or m_l or m_s

- The degeneracy (same energy for all ang. mom. states of a given n) is now split; the energy is different for each j. But there is still some degeneracy left, because different l can have the same j (as mentioned above and shown below).

- The shift in energy is determined by the sign of the term in parentheses

$$\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)$$

& note that since the overall sign is negative, if this term is $>0 \Rightarrow$ decrease in energy
$<0 \Rightarrow$ increase in energy

Now for $n=1$, $j=\frac{1}{2}$, $(\,)=\frac{1}{4}$

$n=2$: $j=\frac{1}{2}$ $(\,)=\frac{5}{8}$ energy decrease

$\frac{3}{2}$ $(\,)=\frac{1}{8}$

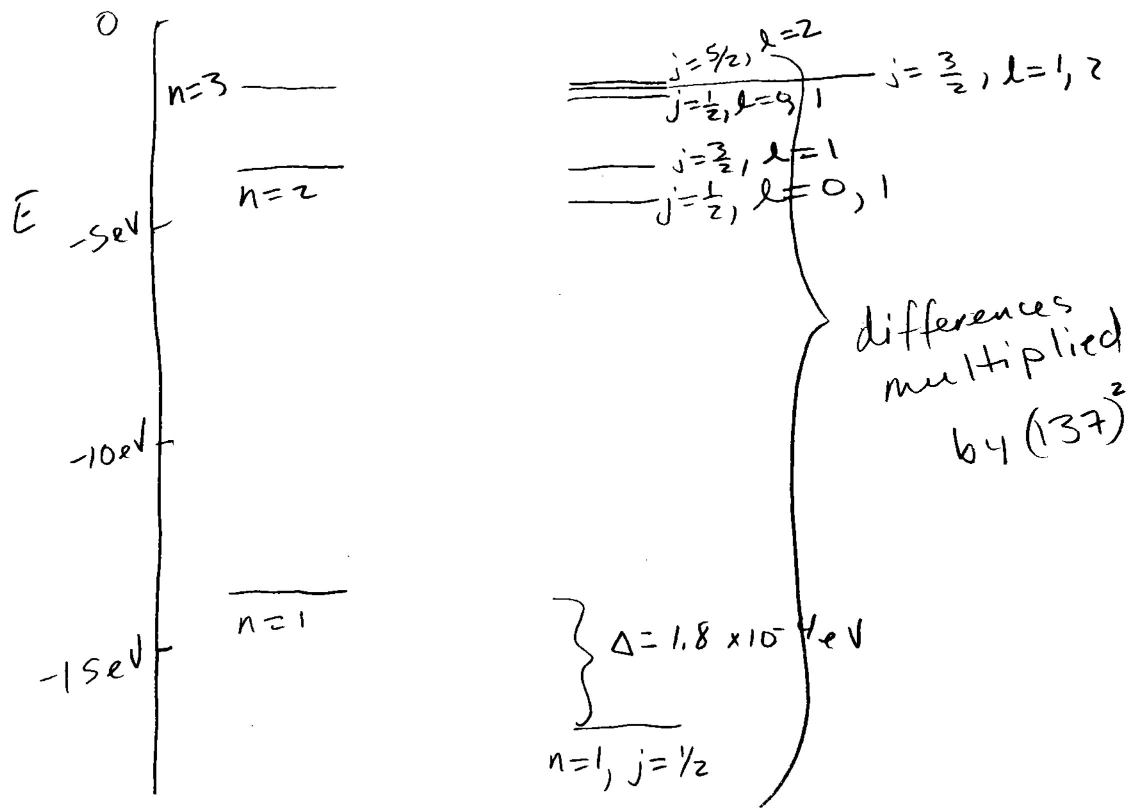
$n=n$: $j_{min}=\frac{1}{2}$ $(\,)=1-\frac{3}{4n}$

$\vdots$

$j_{max}=l_{max}+\frac{1}{2}$ $(\,)=\frac{1}{n}-\frac{3}{4n}=\frac{1}{4n}$
$=n-\frac{1}{2}$

So the energy always shifts down, with the biggest shift for the smallest j.

This is illustrated by an energy level diagram:



- The energies are split into <u>n levels</u>, 1 for each value of j ($= \frac{1}{2}, \ldots n - \frac{1}{2}$), but there's still <u>degeneracy</u> for some j with different l (every j except the max and min values, in fact).

This l degeneracy actually produces a (<u>very</u> small) splitting of its own, also predicted by Dirac's theory, ← actually QED called the Lamb shift, which we won't discuss further.

Finally, if the nucleus has a spin, then its spin magnetic moment can interact with the $\vec{B}$ field due to the electron, so we can get further splitting still. This is the *hyperfine splitting*, and it's several orders of magnitude smaller than the fine structure splitting (because of the large mass of the nucleus).

Transition Rates + Selection Rules

The last topic in our discussion of the hydrogen atom takes us back to the beginning of the semester, when we talked about some of the original motivations for quantum mechanics.

Recall that one motivation was the pattern of atomic spectra, that is, the sets of wavelengths (or frequencies) emitted by atoms. We now understand that each spectral line corresponds to a transition between energy eigenstates. So for example, the Balmer series in hydrogen is given by transitions to the $n=2$ state from higher n:

$$\frac{hc}{\lambda} = h\nu = E_i - E_f = -\frac{\mu^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2}\left(\frac{1}{n^2} - \frac{1}{4}\right)$$