

Physics 228, Lecture 15
Monday, March 21, 2005

Atomic States and Spectra. Ch. 41.2–5, Ch 38:6

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1 Orbital Quantum Numbers

We saw in Bohr's model that he imposed a quantization condition $L = n\hbar$ on the angular momentum of an electron. Later, we saw that as de Broglie suggested a wavelength is associated with momentum, $\lambda \sim h/p$, an electron in a circular orbit with quantized angular momentum,

$$L = rp = \frac{hr}{\lambda} = \hbar \frac{2\pi r}{\lambda} = \hbar n,$$

can be interpreted as requiring an integer number of wavelengths to fit in the circumference of the orbit.

Now, as we have seen, the Bohr model is not quite correct, but the idea that the electron's wavefunction must return to its original phase if one follows it around a circle is correct in the full quantum mechanical theory, and angular momentum is, in fact, quantized, though the form is a bit more complex than we have discussed. The angular momentum is a vector. To discuss quantization, we need to pick out one particular direction, generally taken to be the z -direction. Then the quantization conditions are

$$\begin{aligned} L_z &= m_\ell \hbar, & -\ell \leq m_\ell \leq \ell, \\ |L| &= \sqrt{\ell(\ell+1)} \hbar. \end{aligned}$$

As we mentioned for spin, the fact that we choose the z axis to discuss states of quantized L_z is arbitrary, but if we specify L_z there is a kind of uncertainty condition which prevents us from knowing L_x or L_y exactly (unless $L^2 = 0$).

The electron has a magnetic moment due to the current it produces going around in a loop (Eq. 28.26), and it also has a spin magnetic moment which can be thought of as due to its rotation about its own axis. The total magnetic moment is

$$\vec{\mu} = -\frac{e}{2m_e} (\vec{L} + 2\vec{S}).$$

One can understand the fact that the spin angular momentum \vec{S} produces twice as much magnetic moment per angular momentum as does the orbital angular momentum, but only by studying relativistic quantum mechanics¹, as proposed by Dirac in 1928. That theory actually discovered the spin variable, which popped out unexpectedly from the mathematics.

Like the orbital angular momentum, the spin is quantized along one axis, generally chosen to be the z -axis, and always has the same magnitude,

$$|S| = \sqrt{3/4} \hbar, \quad S_z = \pm \frac{1}{2} \hbar = m_s \hbar.$$

If the atom is in a uniform applied magnetic field \vec{B} , the electron's magnetic moment has an interaction energy with the magnetic field $U = -\vec{\mu} \cdot \vec{B}$, (Eq. 27.27), so if we choose z in the direction of the field, the electron's potential energy due to the field is

$$U = \frac{e\hbar B}{2m_e}(m_\ell + 2m_s) = (m_\ell + 2m_s)\mu_B B,$$

where

$$\mu_B = \frac{e\hbar}{2m_e} = 5.8 \times 10^{-5} \text{ eV/T} \text{ is called the } \mathbf{Bohr \ magneton}.$$

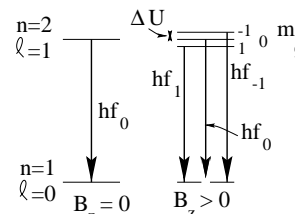
Atoms have a number of electrons, and their magnetic moments add up, as vectors. As the state of the atom depends on how the L and S add up, the magnitude of μ is fixed for each state of the atom, and it is often zero because the electrons pair up in ways their L and S cancel with each other.

1.1 Zeeman effect

Can this magnetic energy be detected? Consider atoms giving off light by making a transition, say, from the 2p to the 1s state. In the absence of an external field, all three m_ℓ states in the 2p subshell have the same energy, so

¹Actually, the factor of 2 needs to be corrected to 2.0023193044 (experimentally) due to effects of relativistic quantum field theory. This correction, known as the anomalous magnetic moment of the electron, has also been calculated, giving 2.0023193048 with an uncertainty that just about covers the difference. This is probably the most accurately known physical constant in all of science.

the photons produced when they relax to the 1s state all have exactly the same energy, frequency and wavelength. But if the atom is in a magnetic field, the 3 states in the 2p subshell have slightly different energies. As $e\hbar/2m_e = 5.8 \times 10^{-5}$ eV/T, and one tesla is a pretty big field, we are talking about energy differences around 10^{-4} eV, while visible photons have energies of about 2 eV. Thus the three states will give off light of three slightly different energies, frequencies and wavelengths. this is known as the **Zeeman effect**.



1.2 Detecting Spin

Another way the magnetic moment of an atom can be detected is by its interaction with a **non**-uniform magnetic field. We saw in Ch. 27 that a uniform field exerts only a torque, and not a net force, on a current loop, but a nonuniform field will exert a force. One way to see that is that the potential energy $U(\vec{r}) = -\vec{\mu} \cdot \vec{B}(\vec{r})$ will then vary with position, so its gradient will create a force. Stern and Gerlach (1921) passed beams of silver and then other atoms through a field with a \vec{B} and its gradient in the z direction, perpendicular to the beam, so that there would be a bending of the beam proportional to μ_z . Because of “space-quantization” of the angular momentum, in which L_z can take on $2\ell + 1$ discrete values, we might expect to get an odd number of beams emerging from the region of nonuniform field. But in many cases one gets two beams, even when $\ell = 0$ is expected, as in the silver atoms Stern and Gerlach first used, or for hydrogen in its ground state. These experiments helped establish the concept of electron spin.

2 Exclusion Principle and the Periodic Table

We have given a lot of attention to just one atom, the hydrogen atom, which has a nucleus and just one electron. We did mention that all our analysis can be easily generalized to hydrogen-like ions, nuclei with charge greater than one unit but with all but one electrons removed. An example is He^+ , which is found in the prominences of the Sun.

But all other atoms and ions have more than one electron, and so the classical motion, taking into account the mutual repulsion of the electrons, is much more complicated. Nonetheless, the idea that each electron can be in any one of a discrete set of states, indexed by the quantum numbers n , ℓ , m_ℓ and m_s is still valid. It is no longer true that all states of the same n have the same energy, but energies still increase with n . We can describe the state of the whole atom by specifying how many electrons are occupying each of the possible electronic states.

An **orbital** is defined as the set of electronic states with given values of n , ℓ , and m_ℓ . As this specifies everything except m_s , which always has two possible values $\pm 1/2$, there are two quantum states associated with each orbital.

At room temperature most atoms are in the lowest possible energy state. So what state is that? We might expect that the lowest state would be when all the electrons in the atom were in the lowest energy orbital, $n = 1, \ell = 0$. Fortunately, that does not happen, for if it did chemistry wouldn't work. Instead, electrons obey the **Pauli exclusion principle**:

No two electrons can occupy the same quantum state.

Imagine taking a heavy nucleus and dropping in electrons one at a time, each going into the lowest possible state. The first goes into either of the two spin states in the K shell,

$$n = 1, \ell = 0, m_\ell = 0, m_s = \pm \frac{1}{2},$$

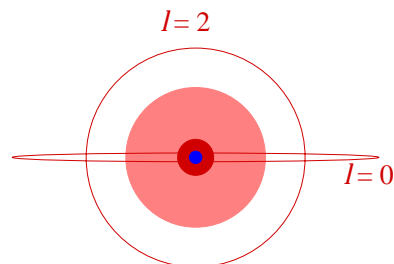
and the second electron will go into the other one. But the third electron cannot go into an $n = 1$ state, because they are all filled. The best it can do is go into the $n = 2$ shell. Thus in Lithium, with $Z = 3$, the third electron cannot fit into the K shell, and must settle for an $n = 2$ orbital in the L shell. There are two possible choices for ℓ , the $2s$ orbital with $\ell = 0$ or the $2p$ orbital with $\ell = 1$. The $2s$ has slightly lower energy than the $2p$, even

though it is much higher than the K shell energy. Thus in the lowest energy, or ground, state of lithium, there are two tightly bound electrons in the $n = 1$ shell and one not very happy electron in the $n = 2$ shell, in the $2s$ state. For higher Z nuclei, the next electron goes into the $2s$ with the opposite spin,

	1s	2s	2p	
H	↑			$1s^1$
He	↑↓			$1s^2$
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	↑↓	↑↓	↑↑↑↑↑	$1s^2 2s^2 2p^6$

and then electrons start filling up the $2p$ states, those with $n = 2, \ell = 1$.

In general, for states of the same n , the lower angular momentum states have the lower energy. The reason is that they spend more time closer to the nucleus. The outer electrons, for the most part, see a spherical charge distribution which consists of the positive nucleus “screened” by the spherical negative charge distribution of the electrons in lower shells. So they are attracted only by a net charge much smaller than Ze . But to the extent that they penetrate within the lower shells, they see only the charge closer to the nucleus, so less screened. This gives them a greater binding energy.



Now the maximum ℓ orbital for each shell can be thought of as a circular orbit, while the $\ell = 0$ orbital can be thought of as a very narrow ellipse for which \vec{r} and \vec{p} are nearly parallel (so $L = 0$). Thus we see that the lower ℓ states spend more time penetrating the nucleus.

Thus the $2s$ orbital fills up before the $2p$.

When we get to carbon, with $Z = 6$, we are first faced with the question of which m_ℓ and m_s . Each of the 3 $2p$ orbitals have the same energy, and in this case **Hund’s rule** applies:

In filling orbitals of equal energy, the electrons try to keep their spins unpaired.

As the charge of the nucleus increases, the binding energy of each shell increases, so while the electron entering the L shell ($n = 2$) in Lithium was only weakly bound, the last electron that can enter that shell in Ne ($Z = 10$) is quite tightly bound. Thus atoms with all occupied shells filled are uninterested in chemically relating to others, and these are the “noble” or “inert” gases. He and Ne are the first two. But after that, the order in which subshells are filled begins to mix. The $4s$ subshell fills before the $3d$, so we get a noble gas by filling up just the s and p states of the M shell ($n = 3$) requires 2 additional electrons for the $3s$ subshell, 6 for the $3p$, on top of the 10 for Neon, giving Argon, with $Z = 18$.

In fact, a better rule for the order in which orbitals fill up is this:

- Look for an unfilled orbital with the lowest value of $n + \ell$.
- among those, choose the one with the lowest n .

Thus potassium, with $Z = 19$, puts its 19th electron in the $4s$ orbital, with $n + \ell = 4$, rather than the unoccupied $3d$ state, with $n + \ell = 5$.

We saw last time that each shell's wavefunctions were predominantly based further out. So in considering the states above a filled shell, as for example the 11th electron in sodium (Na), we can think of the electron as orbiting around a spherical charge including 11 protons and 10 electrons, with a net charge of $+e$. Atoms in this group, with one electron more than a noble gas, are very willing to give it up and become a positive ion. These are the Alkali metals. On the other hand, any atom short by one electron of a full shell is quite willing to accept one, and become a negative ion. These are the halogens, fluorine, chlorine, bromine, *etc.*

3 Atomic Spectra

As we mentioned earlier, atoms in states which are not the lowest possible energy state will “deexcite” by giving off a photon and transitioning to a state of lower energy. These transitions are not equally likely, however. It is much more likely for an **allowed transition**, one for which the change in ℓ and m_ℓ satisfy

$$\Delta\ell = \pm 1, \quad \text{and} \quad \Delta m_\ell = 0, \pm 1.$$

This is because the photon itself has a spin, but unlike an electron, the values of the spin are $\pm\hbar$ rather than $\pm\frac{1}{2}\hbar$.

While a full calculation of the energies of the different electron states is very complicated due to the interactions of the electrons, there are two cases where we can make reasonable approximations. As we mentioned, outside a full shell the orbit is outside most of the other electrons, and we can treat nucleus together with the full shell as an effective nucleus with an effective charge Z_{eff} , and the possible states with $n > n_{\text{shell}}$ having energies

$$E_n = -13.6 \frac{Z_{\text{eff}}^2}{n^2} \text{ eV}.$$

Only states with n higher than that of the shell are accessible. Another energy we can reasonably approximate is the energy of the $n = 1$ state and of the $n = 2$ state of atoms for which a $1s$ electron is missing. These are important because a prominent X-ray emission line comes about if one of the $1s$ electrons is knocked out of an atom, and subsequently a L electron fills in

the empty orbital. The one remaining $1s$ electron shields one of the charges, so

$$E_L = -\frac{13.6}{2^2} (Z - 1)^2 \text{ eV}, \quad E_K = -13.6 (Z - 1)^2 \text{ eV},$$

so the X-ray will have an energy of approximately $10.2 (Z - 1)^2$ eV. The $L \rightarrow K$ transition produces an X-ray known as the K_α line.

The X-ray machine your dentist uses shoots a beam of electrons with energies around 50 KeV onto a metal surface. These collide with the electrons deep inside atoms and knock them out of the atom, leaving an unoccupied tightly bound orbital. Then one of the electrons in a higher energy orbital notices the empty spot and makes the transition, emitting the X-ray.

4 Atomic Transitions

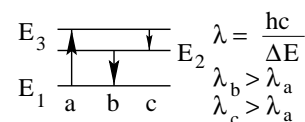
The deexcitation we have discussed occurs **spontaneously**. That is, an atom in an excited state will eventually emit a photon of frequency $f = \Delta E/h$ and relax to a lower energy state. But the same transition can happen more rapidly if it is **stimulated** by the presence of other photons of the appropriate frequency. The presence of such electromagnetic oscillations facilitates transitions in either direction. When photons of frequency f cause a transition from the higher to the lower state, an *additional* photon is emitted in the same direction and frequency, in a process known as **stimulated emission**. The incident photons are not absorbed, so there is an increase by one in the number of photons of a given momentum.

Of course if the energy of the incident photon is equal to the energy difference between two atomic states, it can also be **absorbed** by an atom in the lower state transitioning to the higher state. Normally, in thermal equilibrium, atoms are more likely in lower energy states than higher energy ones, so photons with $hf = \Delta E$ are more likely to be absorbed than to stimulate the emission of another photon. If somehow a collection of atoms can be forced to have more atoms in the higher energy state than the lower, we call this **population inversion**. In this situation, more transitions will occur releasing a photon of the right frequency than absorbing one, and a chain reaction of release of light occurs, all with the same energy and direction. This stimulated emission is the basis of a **laser**² (for visible light) or a maser (for **microwaves**).

²Light amplification by stimulated emission of radiation.

Another effect worth mentioning occurs when an atom is excited to a highly excited state from which it can relax more easily in several steps than in one. It will then emit several photons, each of which has less energy than the one which made the transition to the excited state initially. This is called **fluorescence**. In fluorescent lights, electrons accelerated by the voltage difference between the two ends of the tube collide with atoms and cause excitation into high energy states. These relax, either in the gas or in a fluorescent coating, in a sequence of decays each of which emits visible light, rather than the ultraviolet light which would have been emitted had the deexcitation occurred in one step. In fluorescent materials, incident light of short wavelength λ_a can excite atoms from a state of energy E_1 to a state of much higher energy E_3 , with $E_3 = E_1 + hc/\lambda_a$.

Then an electron from a state of intermediate energy E_2 may transition to E_1 , giving off a photon of wavelength $\lambda_b = hc/(E_2 - E_1)$, which is longer than the incident wavelength λ_a because the energy difference is smaller. After that, the electron in E_3



can transition to the now empty state E_2 , giving off another photon with wavelength $\lambda_c = hc/(E_3 - E_2)$, which is again longer than the incident light. Thus an ultraviolet photon can be converted into two visible photons.

Show
fluorescent
rocks.

If some of the states along the chain of deexcitation are long-lived, or **metastable**, the emitted light can come a considerable time after the initial excitation. This is the basis of **phosphorescence**.

Show
phosphorescent
objects, turn out
light.