LECTURE 5

The One–Electron Atom

The problem with Bohr's theory is that it postulates an electron whizzing around the nucleus with a velocity v and centripetal acceleration v^2/r. Classical electromagnetic theory tells us that when a charged particle is accelerated, it must radiate and lose energy. So Bohr's electron should be radiating and losing energy which doesn't sound very stable. To treat the electron properly, we need to use quantum mechanics. Let's start by writing down Schrodinger's equation:

$$H\psi = E\psi \tag{1}$$

(I'm going to drop the little hat on H. Just remember that it's an operator.) Let's just consider a one electron atom so that we don't have to worry about the interactions between electrons. The Hamiltonian is

$$H = \frac{p^2}{2m} - \frac{Ze^2}{r} \tag{2}$$

where r is the distance from the nucleus, Z is the number of protons (i.e., the atomic number), and m is the mass of the electron. The first term is the kinetic energy of the electron and the second term is the potential energy of the electron interacting with the nucleus via the Coulomb interaction. Since p is an operator (see lecture 1), we can write

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \tag{3}$$

It's always a good idea to look for symmetries before plunging into a problem. So let's do that. The potential produced by the nucleus is spherically symmetric. It is called a central potential. The spherical symmetry means that we should use spherical coordinates θ and ϕ. Spherical symmetry means that orbital angular momentum will be associated with good quantum numbers ℓ and m. So we expect to be able to label the different ψ's with ℓ and m. Here m is the z-component of ℓ. It turns out that if you write (3) in spherical coordinates, it is separable into 3 differential equations: one for r, one for θ, and one for ϕ. Let $R(r)$, $\Theta(\theta)$, and $\Phi(\phi)$ be the solutions of these three equations. Then the total wavefunction can be written as a product:

$$\psi(\vec{r}) = AR(r)\Theta(\theta)\Phi(\phi) \tag{4}$$

where A is a constant. We won't go through all the math needed to solve the Schrodinger equation. Rather I'll just write down the answer. The energy eigenvalues are

$$E_n = -\frac{mZ^2e^4}{2\hbar^2 n^2} \tag{5}$$

Notice that the energy eigenvalues are quantized. n is called the *principal quantum number.* $n = 1,\ 2,\ 3, ...$ It is associated with the radial part of the wavefunction. n can be thought of as labeling the atomic orbital shells; the larger n is, the farther away the shell is from the nucleus. The radius of a shell is roughly na where a is very close to the Bohr radius in size. The radial part of the wavefunction has an exponential factor:

$$R_{n\ell}(r) \sim e^{-Zr/na} \tag{6}$$

Notice that the exponential factor means that the probability that an electron is located beyond a distance na falls off exponentially. When $Z = 1$ and $n = 1$, eq. (5) reduces to –1 Rydberg:

$$E_0 = -\frac{me^4}{2\hbar^2} = -13.6 \text{ eV } = -1 \text{ Rydberg} \tag{7}$$

This is a good energy to remember. It sets an upper bound for how tightly electrons are bound to a nucleus.

The energy eigenfunctions are

$$u_{nlm} = A_{n\ell m} R_{n\ell}(r) P_\ell^m(\cos\theta) e^{\pm im\phi} \tag{8}$$

The actual functions for various values of n, ℓ, and m are given in Eisberg and Resnick on page 243. Here we see that the orbital angular momentum quantum numbers are associated with the angular part of the wavefunction. For a given value of n, the values of ℓ are

$$\ell = 0, 1, 2, 3, ...(n-1) \tag{9}$$

By convention the $\ell = 0$ sublevel corresponds to an s orbital, $\ell = 1$ to a p orbital, $\ell = 2$ to a d orbital, and $\ell = 3$ to an f orbital. These spectroscopic notations are the initial letters of adjectives formerly used to describe spectral lines: sharp, principal, diffuse, and fundamental. The spectral lines were discovered before people realized where the lines came from. For ℓ values larger than 3, the letters used proceed alphabetically: g, h, i, k, l, etc. (Note that j is omitted.) For each value of ℓ there are $(2\ell + 1)$ values of m:

$$m = -\ell, -\ell + 1, ..., \ell - 1, \ell \tag{10}$$

Notice that the energy eigenvalues (5) are independent of ℓ and m. This means that for a given value of n, there n^2 degenerate orbitals which differ in their values of ℓ and m. Various effects which we haven't included in the Hamiltonian can split this degeneracy. For example, if the atom is in a magnetic field, the m levels are split. This is known as the Zeeman effect and m is known as the magnetic quantum number. If we include the spin of the electron, the maximum number of electrons that can reside in a given energy level is $2n^2$.

Let's look at the shapes of these various orbitals. The energy eigenfunctions are orthogonal and this helps to determine the shapes they can have. By orthogonal, I mean that they must satisfy

$$\int d^3r u^*_{n\ell m}(\vec{r}) u_{n'\ell' m'}(\vec{r}) = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'} \tag{11}$$

where $\delta_{nn'} = 1$ if $n = n'$ and $\delta_{nn'} = 0$ if $n \neq n'$. (The fact that the eigenfunctions are normalized to unity means that they are actually orthonormal.) The $n = 1$ level has a single $1s$ orbital that is a spherically symmetric ball with no nodes. (It's a nonzero constant at $r = 0$.) The $2s$ orbital is also spherically symmetric but it has a node at $r = 2a/Z$ due to orthogonality. (A node is a place where the wavefunction is zero.) There are three $2p$ orbitals, and each has a nodal plane passing through the nucleus at the origin. Each p orbital consists of two lobes that may be considered to be oriented along the x, y, or z axis; hence, they have the designations $2p_x$, $2p_y$, and $2p_z$. The $2p_z$ orbital corresponds to the $n = 2$, $\ell = 1$, $m = 0$ orbital. The $2p_x$ and $2p_y$ orbitals correspond to symmetric and antisymmetric linear combinations of the $n = 2$, $\ell = 1$, $m = 1$ and $n = 2$, $\ell = 1$, $m = -1$ orbitals. For $n = 3$, there is a $3s$ orbital, three $3p$ orbitals, and five $3d$ orbitals ($3d_{x^2-y^2}$, $3d_{z^2}$, $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$). The shape of the $3d_{z^2}$ orbital is different from the others, but all these orbitals are energetically equivalent.

Each electronic state is labelled by 4 quantum numbers: n, ℓ, m, and s_z. The Pauli exclusion principle prohibits 2 electrons from having the same set of quantum numbers. If 2 electrons have the same n, ℓ, m, then one is spin up and the other is spin down.

Spin–Orbit Coupling

Spin–orbit coupling refers to the coupling between the spin of an electron in an atom and its orbital angular momentum. It arises from relativistic effects and leads to a slight splitting of the degenerate energy levels for a given value of n. There are 2 contributions to spin–orbit coupling. The first comes from the fact that the spin of the electron is associated with a magnetic moment $\vec{\mu}$ (see lecture 2) that couples to any magnetic fields that might be present. As the electron moves through the nuclear electric field, it sees both a magnetic and an electric field. Special relativity says that an electric field in a stationary reference frame looks like an electric and a magnetic field in a moving frame.

$$\vec{B}' = -\frac{1}{c}\vec{v} \times \vec{E} \qquad \text{(cgs)} \tag{12}$$

This magnetic field couples to the electron's magnetic moment and the magnetic moment precesses about the magnetic field that it sees. This is Larmor precession. This is one way that orbital motion couples to the electron's spin.

The other way is called Thomas precession. It too is a relativistic effect. Because of time dilation an observer at the nucleus and an observer at rest on the electron would disagree about the amount of time it takes for one particle to make a complete revolution about the other. If the observer on the electron calls this time interval T, then an observer on the nucleus will find it to be $T' = \gamma T$, where $\gamma = (1 - v^2/c^2)^{-1/2}$ and v is the speed of the electron about the nucleus. Now, in the rest frame of the electron, the spin vector maintains its direction in space, so that to the observer on the nucleus, this spin vector appears to precess at a rate equal to the difference between the two angular velocities $2\pi/T$ and $2\pi/T'$. The Thomas precession frequency turns out to be half that of the Larmor precession frequency and of the opposite sign.

Both of these effects couple the electron spin to its orbital motion. Putting these two effects together leads to a spin–orbit coupling term in the Hamiltonian:

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} + \frac{Ze^2}{2m^2c^2r^3}\vec{S}\cdot\vec{L} \tag{13}$$

where $\vec{S}\cdot\vec{L}$ is an operator with units of angular momentum squared ($\hbar^2$). This extra term in the Hamiltonian splits the degenerate energy level for a given value of n into several degenerate levels. The splittings are of order 1 part in 10^4. ($\Delta E \sim |E_n|\alpha^2$, where the fine structure constant $\alpha = e^2/\hbar c \approx 1/137$. So $\alpha^2 \approx 1/20,000$.) These small splittings lead to *fine structure* in the spectral lines.

Because spin and orbital angular momentum are coupled together L_z and S_z are not conserved, though L^2 and S^2 are conserved. ($[S^2, H] = [L^2, H] = 0$ but $[S_z, H] \neq 0$ and $[L_z, H] \neq 0$). So ℓ and s are good quantum numbers, but m_ℓ and m_s are not. But the *total* angular momentum $\vec{J} = \vec{L} + \vec{S}$ is conserved and therefore, j and m_J are good quantum numbers. (see lecture 2)

Many Electron Atom

Other sources of energy level splitting

There are several other sources of electron level splitting. For example, there is also another small relatistic correction to the energy due to the fact that in special relativity, the energy

$$E = \sqrt{p^2c^2 + m^2c^4} \tag{14}$$

This shifts the energy levels by the same order of magnitude as spin–orbit coupling.

When there are many electrons, dipole–dipole (spin–spin) interactions between the electrons as well as the electrostatic Coulomb interactions between them lead to energy splittings.

Russell–Saunders or LS Coupling

The relative strengths of these effects varies depending on what kind of atom we have. In some cases spin–orbit effects are quite small compared to spin–spin and electrostatic interactions between the electrons. In this case LS or Russell–Saunders coupling is a good place to start. In this coupling it is assumed that the individual orbital angular momenta ℓ_i are quite strongly coupled together, as are the individual spin angular momenta s_i. So ℓ_i and s_i are not good quantum numbers. (Here ℓ_i is the orbital angular momentum of the ith electron and s_i is the spin angular momentum of the ith electron.) However, the total orbital angular momentum $\vec{L} = \sum_i \ell_i$ of all the electrons and the total spin angular momentum $\vec{S} = \sum_i s_i$ of all the electrons are close to being good quantum numbers. The resultant $\vec{L}$ and $\vec{S}$ are less strongly coupled to each other and their resultant is $\vec{J}$.

Hund's Rule

Atomic levels may have the same electron configuration (e.g., $4p$ $4d$) but different total L and S. Hund's rule is an empirical principle concerning the relative position of levels with the same configuration but different L and S: *The term with the greatest possible value of S (for the given electron configuration) and the greatest possible value of L (for this S) has the lowest energy.* In other words, Hund's rule states that electrons are distributed among the orbitals of a subshell in a way that gives the maximum number of unpaired electrons with parallel spins, and the maximum value of the orbital angular momentum L consistent with this S. The value of the total angular momentum J is equal to $|L-S|$ when the shell is less than half full and to $L+S$ when the shell is more than half full. When the shell is exactly half full, the maximization of the S gives $L=0$, so that $J=S$.

For example, suppose there are four equivalent d electrons outside the closed shells in an atom. The magnetic quantum number of each d electron can take five values: 0, ±1, ±2. Hence all four electrons can have the same spin component $m_s=1/2$, and the maximum possible total spin is $S=2$. Now we must assign the maximum value of $M_L=\sum_\ell m_\ell$, namely $m_\ell=2,1,0,-1$. This implies that $M_L=2$. Thus the maximum value of L for $S=2$ is also 2. The shell is less than half full (there can be up to 10 d electrons), so $J=|L-S|=0$.

Another example would be nitrogen which has 3 electrons in the $2p$ orbitals. The electronic configuration is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. Notice that the electrons distribute themselves among the p orbitals rather than bunching up in, say, $2p_x^2\ 2p_y^1\ 2p_z^0$. The standard way to write the electronic configuration of nitrogen is $1s^2\ 2s^2\ 2p^3$ where it is understood that the electrons will spread out among the orbitals.

To understand why S should be as large as possible, let us suppose that the total wavefunction ψ for the electrons can be written as the product of a spin wavefunction χ_s and a space wavefunction ϕ_r.

$$\psi(1,2,...,N)=\chi_s(s_1,s_2,...,s_N)\phi_r(r_1,r_2,...,r_N) \tag{15}$$

where s_i is the spin coordinate of the ith electron and r_i is the spatial coordinate of the ith electron. Since electrons are fermions, ψ must be antisymmetric under the interchange of any 2 particles.

$$\psi(1,2,...,r,...,s,...,N)=-\psi(1,2,...,s,...,r,...,N) \tag{16}$$

We can satisfy this by having χ_s symmetric and ϕ_r antisymmetric or vice–versa. For example, if we have 2 electrons, they can be in a singlet ($S=0$) or a triplet ($S=1$) state. The triplet state has a symmetric spin wavefunction and an antisymmetric spatial wavefunction.

$$\begin{aligned}
\chi_{S=1,m_s=1} &= \uparrow\uparrow \\
\chi_{S=1,m_s=0} &= \frac{1}{\sqrt{2}}[\uparrow\downarrow+\downarrow\uparrow] \\
\chi_{S=1,m_s=-1} &= \downarrow\downarrow
\end{aligned}$$

and

$$\phi_r=\frac{1}{\sqrt{2}}(\phi_a(r_1)\phi_b(r_2)-\phi_a(r_2)\phi_b(r_1)) \tag{17}$$

The singlet state has an antisymmetric spin wavefunction and a symmetric spatial wavefunction.

$$\chi_{S=0,m_s=0} = \frac{1}{\sqrt{2}}[\uparrow\downarrow - \downarrow\uparrow] \tag{18}$$

and

$$\phi_r = \frac{1}{\sqrt{2}}(\phi_a(r_1)\phi_b(r_2) + \phi_a(r_2)\phi_b(r_1)) \tag{19}$$

The nodes in the antisymmetric spatial wavefunction of the triplet helps to keep the electrons apart and reduce the Coulomb repulsion much more than the symmetric spatial wavefunction of the singlet. This tends to be true in general since larger spin tends to be associated with more nodes in the spatial wavefunction.

Spectroscopic Notation

The energy eigenstates of almost all atoms can be described in terms of a quantum number L which defines the net orbital angular momentum of all the electrons, a quantum number S which defines the net spin angular momentum of all of the electrons, and a quantum number J which defines the total angular momentum $\vec{J} = \vec{L} + \vec{S}$. L is always an integer, and S is integral or half–integral depending upon whether the total number of electrons in the atom is even or odd. In this general case the multiplicity of the level is equal to $2S + 1$ or $2L + 1$, whichever is smaller.

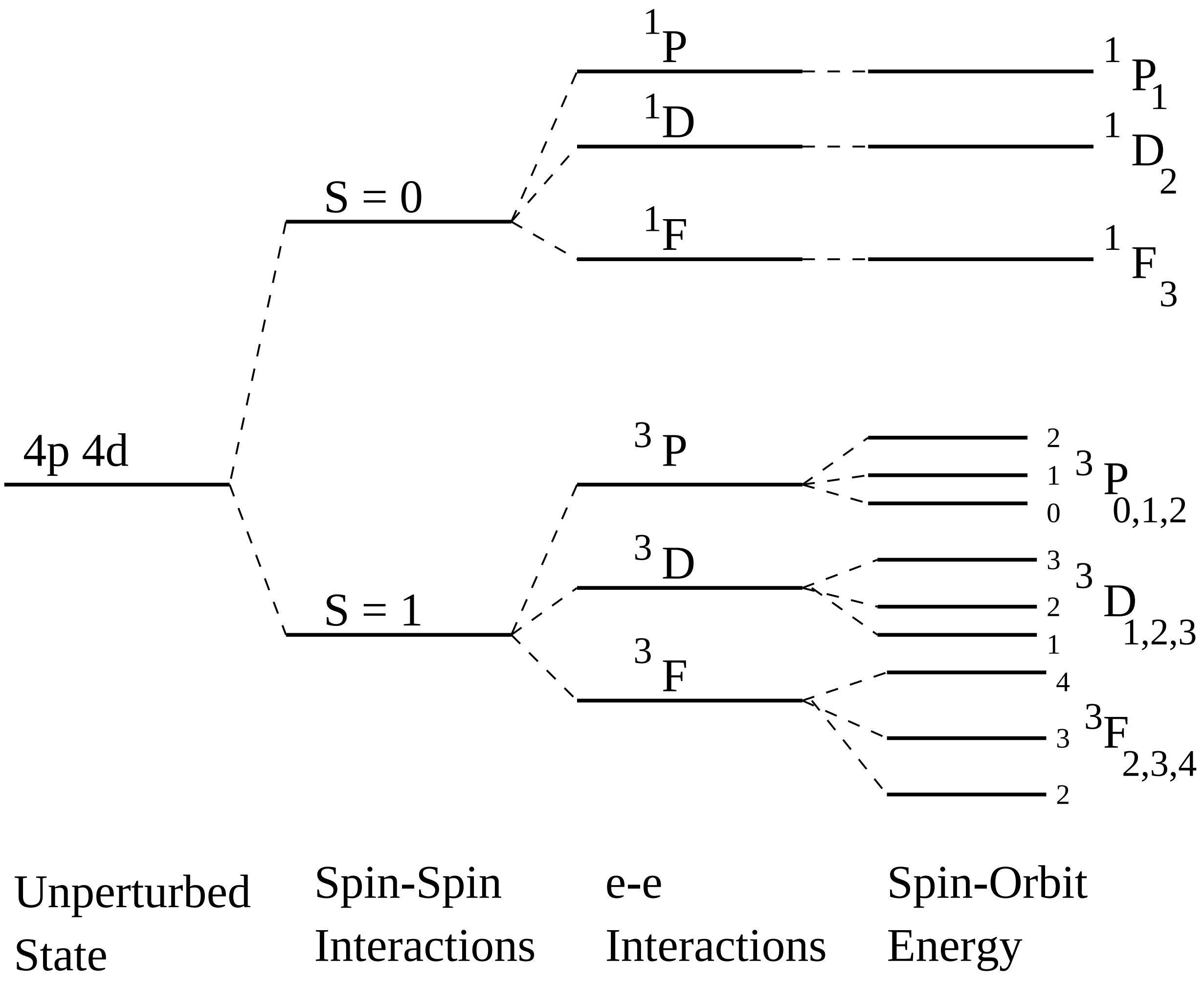
Spectroscopic notation for labeling the energy eigenstates has the following form:

$$^{2S+1}(L)_J \tag{20}$$

Since it is most often the case that S is smaller than L, so that the multiplicity is equal to $2S+1$, the preceding superscript has come to be always associated with S. This index is always equal to $2S + 1$, and is equal to the true multiplicity of the level only if S is less than, or equal to, L. The value of the total angular momentum J for a given level is indicated by the subscript. The numerical values of L are correlated with the letter notation according to the table:

L	0	1	2	3	4	5	6	7	8	9	10
Letter	S	P	D	F	G	H	I	K	L	M	N

For an example consider the 4 equivalent d electrons that we showed had $L = S = 2$ and $J = 0$. The spectroscopic notation for this is state is $^5D_0$. Another example is shown in the figure


1P
1D
1F
1 P1
1 D2
1 F3
S = 0
4p 4d
S = 1
3 P
3 D
3 F
2
1
0
3 P0,1,2
3
2
1
3 D1,2,3
4
3
2
3F2,3,4
Unperturbed State
Spin-Spin Interactions
e-e Interactions
Spin-Orbit Energy