Chapter 4

Atomic Structure

4.1 Electron Orbital Structure

Fermi Statistics

Atomic transitions will all involve the different quantum energy states of the electrons in an atom.

An important consideration in determining the arrangement of these states is that electrons are Fermions (particles having a half-integer spin, in this case, s=1/2, for a spin angular momentum of $\hbar/2$). Electrons then obey Fermi-Dirac statistics, which here basically just means they follow the Pauli Exclusion principle: no two electrons can occupy the same energy state of an atom.

Energy States

A typical way to visualize energy states (which we will see again when we talk later about rotational and vibrational energy states) is a diagram in which the y axis represents the energy (this can be shown schematically, with energy increasing with increasing y, or quantitatively, where the y axis has values in terms of eV or K). The x axis does not have a quantitative meaning, but instead is generally used to separate energy levels corresponding to different quantum numbers.
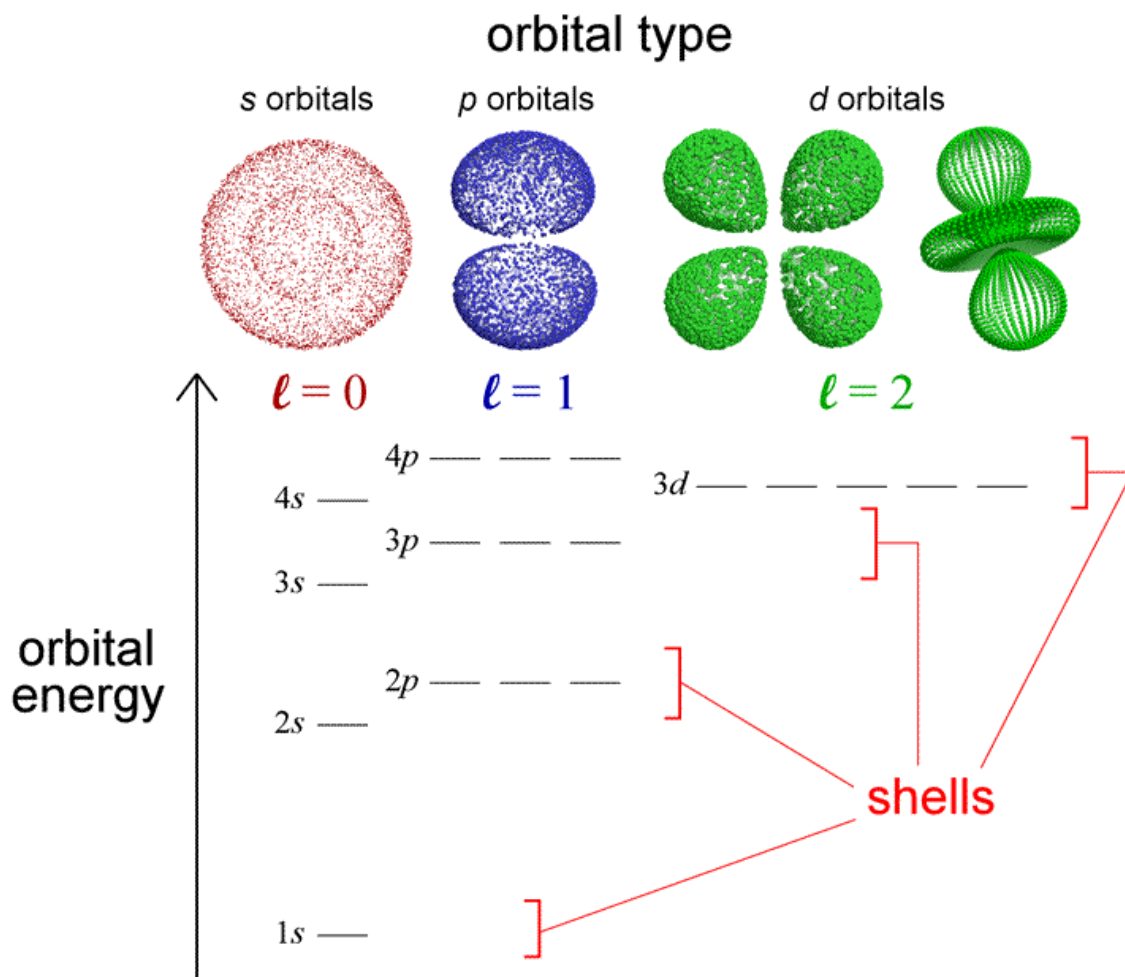
Figure 4.1: *orbital_energy_and_type_diagram.png*

In this figure, you can more clearly see the ordering of the electron orbitals by increasing energy, as given in the text: 1s, 2s, 2p, 3s, 3p, 4s, 4d and so on. In this diagram, each dashed line segment represents an electron pair: the s-orbitals can hold 2 electrons, the p-orbitals can hold 6 electrons, and the d-orbitals can hold 10 electrons.

Quantum Numbers

The orbitals in the figure above are organized by two of the principal quantum numbers we will deal with for atoms. Increasing up the y-axis we have n, the principal quantum number. n is determined by the electron wave function, and corresponds generally to the energy of the electron (bottom diagram) and its most likely distance from the nucleus (e.g., the size of the shell in the top image). The lowest value of n is 1, and it can (in theory though not in practice) be infinitely large.

Increasing to the right on the x-axis we have l which is the orbital angular momentum quantum number. The orbital angular momentum of an electron is $l\hbar$ and this is different from the intrinsic spin angular momentum (which is also quantized, with a spin magnetic quantum number m_s, which can only take two values: $\pm\frac{1}{2}$, corresponding to the orientation of the electron spin relative to the spin of the nucleus). Note that s, p, and d are not actually quantum numbers, but are simply

ways of referring to the $l = 0$, $l = 1$, and $l = 2$ states. So, the $4p$ orbital has quantum numbers $n = 4$ and $l = 1$.

l can have values ranging from 0 to $n - 1$ (which is why, for example, there is no $1p$ state). l determines the number of subshells in an orbital (e.g., for $n = 1$, the only possible l value is 0, so there is just one subshell: $1s$. For $n = 2$, l can now take on the values of 0 and 1, so there are two subshells: $2s$ and $2p$).

The final quantum number, which sets the total number of independent quantum states in a subshell and thus the number of electrons in that subshell, corresponds to the projection of the angular momentum of the electron along the z-axis of the atom. This quantum number (denoted m_l, the magnetic quantum number) then has to do with the orientation of the electron relative to the atom– or basically, which suborbital the electron is located within. , which is usually most important when we are discussing a situation in which the atom is in a magnetic field. m_l takes values of $\pm l$.

Taking all of these quantum numbers together, we can finally define the number of electrons in a given subshell l: $2(2l + 1)$. Checking this: for $l = 0$, there is only one possible value of m_l The two possible states in which an electron can exist are then set by its two possible intrinsic spin values, $m_s = \pm\frac{1}{2}$. We also see that the number of electrons in a subshell does not depend on n, so the number of electrons in any s, p, or d subshell is always the same.

4.2 Spectroscopic Terms

Because the relative orientation of the intrinsic and orbital electron spins is important (vectors!), it isn't always enough to just specify an energy state by these quantum numbers. To deal with this, we introduce the additional concept of 'Terms', which are (quantum-mechanically-allowed) combinations of the total spin and orbital angular momentum of the whole-atom system.

The total spin angular momentum of an atom is the vector sum of the individual spin angular momenta of the electrons (each one having $\pm\frac{1}{2}\hbar$). This total value is denoted as $S\hbar$. Similarly, the total orbital angular momentum is given as $L\hbar$, the sum of all the $\pm l\hbar$ values for all electrons (as with the spin, the plus/minus convention corresponds to the direction of the orbit).

A term (L, S) is written as $^{2S+1}\mathcal{L}$.

Note that like we did for l, we denote specific values of the total orbital angular momentum quantum number with (now capital) letters: $\mathcal{L} = $ S, P, D corresponds to $L = 0, 1, 2$

You may notice that a horrible thing happens here in Draine: the total spin quantum number S is incredibly and unfortunately similar to the $L = 0$ total angular momentum state, S. Such is our lot.

To illustrate how terms are constructed, let's consider the Hydrogen atom, a one-electron system. Depending on its energy, this single electron can occupy any of the orbitals we have defined so far. The lowest-energy state that it can occupy is the $n = 1$, $1s$ orbital. The total orbital angular momentum L is 0, and the total spin angular momentum S is just the spin of a single electron ($S = 1/2$). We can then write the term for this state as ^2S. Note that the term by itself contains no information on the excitation of the atom (the n quantum number of the electron). As there is one term, this state is called a singlet (although actually, as we will find, this state has hyperfine

structure due to slight differences in the energies between different configurations of the spins of the electron and the proton).

4.3   Fine Structure (Spin-Orbit Coupling)

Of course things get a lot fancier than the ground state of a single-electron atom.

Once we are considering both spin and orbital angular momentum, the total electronic angular momentum of an atom (J) is useful to define. J is the vector sum of L (all the orbital angular momentums) and S (all the spin angular momentums). This information can be added to our notation for a term, which is now written as $^{2S+1}\mathcal{L}_J$

We can use this to rewrite the term for the ground state of hydrogen. The orbital angular momentum of the electron is zero, so the net angular momentum J for the whole atom is just the total spin: $J = S = 1/2$. The full ground state of the hydrogen atom is then sometimes written as $^2S_{1/2}$.

A much more illustrative case of the role of J is the next-highest excited state of the Hydrogen atom is $n = 2$. We find that considering the placement of just a single electron in this orbital results in two different possibilities for the total angular momentum J. For an electron in the $2s$ orbital, we again have no orbital angular momentum and a net angular momentum $J = 1/2$. Like the ground state, the term for this state would be written as $^2S_{1/2}$. However, the electron could also be in the $2p$ orbital, in which case it would have $L = 1$. Depending on the orientation of its spin relative to its orbit, the total angular momentum could be $J = L + S = 3/2$ or $J = L - S = 1/2$. We thus find that, in total, there are three different terms for the $n = 2$ state: $^2S_{1/2}$, $^2P_{1/2}$ and $^2P_{3/2}$. As there are only two distinct values of J among these terms, this state is called a doublet.

This doublet represents not just two distinct angular momentum states of the hydrogen atom, but due to spin-orbit coupling it also represents two distinct energy states. This can be shown, with a bunch of tedious quantum mechanics, to be the result of the different interactions of the magnetic dipole of the electron (due to its intrinsic spin) as it orbits in the electric field of the nucleus. As a result, the $n = 2$ orbital energy level is split into two slightly different energies. The difference in wavelength of a photon emitted as an electron transitions between one or the other of these energy states can be observed with sufficiently high resolution spectroscopy.

The fine structure splitting of the $n = 2$ state of the hydrogen atom is shown in this figure. On the left are the energy levels one would expect with a simple Bohr 'shell' model of an atom (in which the electron does not have an assumed intrinsic spin). On the right is the observed splitting in a 'Dirac' model that includes the spin of the electron as an additional quantum number. The transition from $n = 2$ to $n - 1$ is known as the "Lyman α" transition.

Note that in most (but not all!) astronomical situations, the Bohr approximation is sufficient to define the observed transitions: because the line splitting is so small, the fine structure or hyperfine structure is much less than the observed doppler broadening or pressure broadening of the line. We often think of a spectral line as arising from just a transition between different n orbitals.
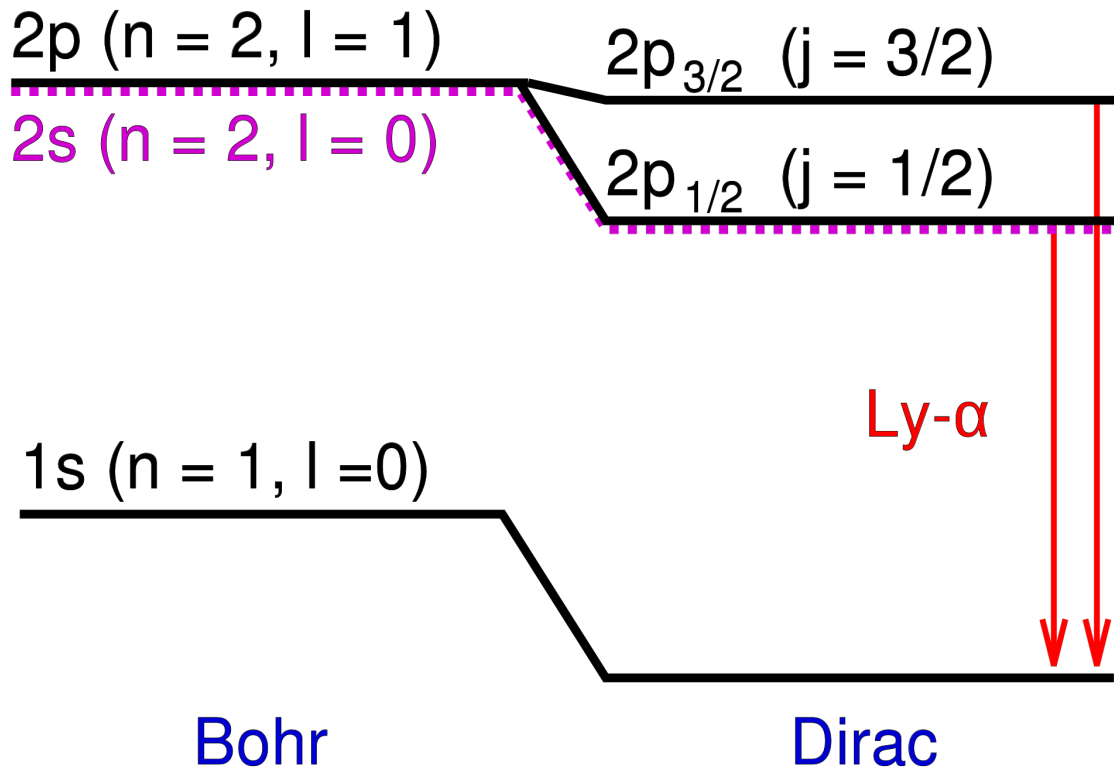
Figure 4.2: *Hydrogen_fine_structure.png*

4.4 Parity, Degeneracy, and Multiplicity (oh my)

Now that we have a way to describe the full angular momentum properties of a given configuration of electrons in an atom (which corresponds to an energy level or an excitation state) as a set of terms, we can turn to some different ways to classify these terms.

The parity of an energy level (which is determined by the symmetry of the wave function: whether or not it changes sign when reflected about the origin, see figure below) can be determined to be odd or even based on the sum of all of the l quantum numbers.

The parity is even if $\sum_i l_i$ is even

The parity is odd if $\sum_i l_i$ is odd
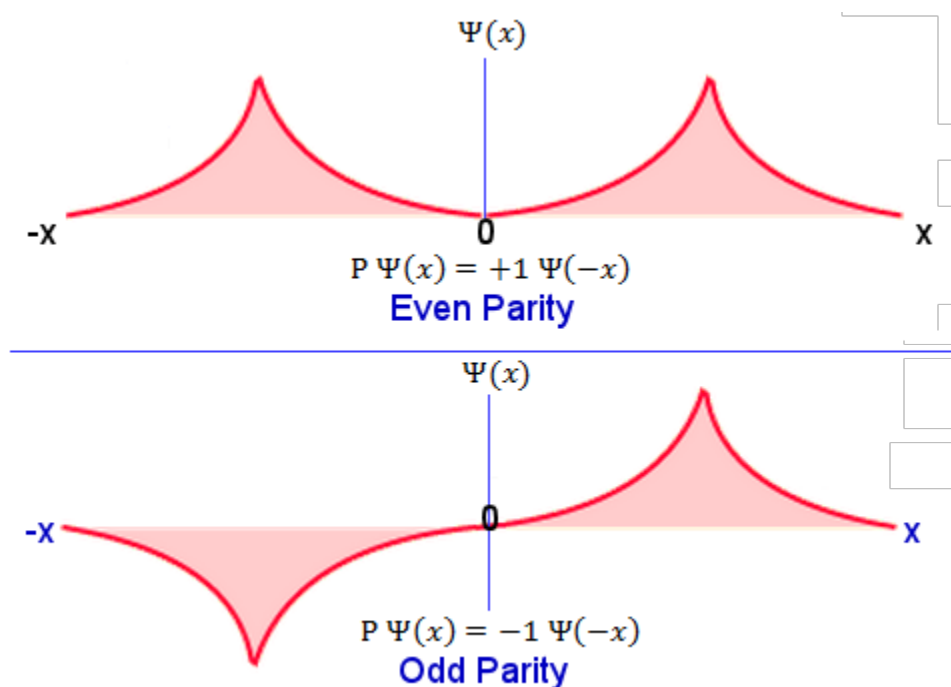
Figure 4.3: *parity.png*

Given all of the different possible combinations of L and S, especially for many-electron atoms, we also have to consider which of these are actually distinct energy levels– or conversely, for a given energy level, how many different quantum angular momentum states it encompasses.

The multiplicity describes the total number of different angular momentum states in an energy level. This is given by $g = (2S + 1) \times (2L + 1)$. For the ^2P term of the $n = 2$ hydrogen orbital, with $S = 1/2$ and $l = 1$ we would calculate a multiplicity of 6.

The degeneracy, while a very similar concept, refers to the number of different angular momentum states which correspond to unique values of the total angular momentum ($J = 1/2$ and $J = 3/2$). This is basically the remaining multiplicity once you account for whether a line is a singlet, doublet, triplet, etc. due to the fine structure splitting resulting from spin-orbit coupling. Mathematically, the degeneracy of these states is given by $g = 2J + 1$

For the fine structure splitting of the ^2P term of the $n = 2$ hydrogen orbital, the degeneracies of the two doublet states are 2 (for $J = 1/2$) and 4 (for $J = 3/2$).

4.5   Selection Rules and Forbidden Transitions

What is the likelihood that we can observe the transition of an electron from one energy state to another? Here, we are going to focus on radiative transitions, and specifically on the emission of a photon resulting from an electron transitioning from a higher energy state to a lower energy state. Note that there are other possible ways for the electron to transition between energy states (for example, increasing its energy due to the absorption of a photon of the correct energy, or moving up or down in energy due to the exchange of energy from the collision of an atom with another particles). We will discuss all of these in a future lecture.

For now, it turns out there are a lot of rules that govern how likely (if at all) an electron is to move from one orbital to a lower one by way of emitting a photon.

Fundamentally, to understand these rules it helps to think of a state transition as the electron physically moving in the electromagnetic potential of the atom. There are then several relevant terms that can be defined, and we will have to dig a bit into quantum mechanics to really get to the meat of what is going on.

First, we need to characterize the distribution of charges in the atom. To do this, we define the dipole moment μ as $\mu = \sum_j q_j r_j$ where the q_j are all the charges in the system (electrons and nucleus) and the r_j are the position vectors, representing their relative location in the atom. The dipole moment describes the electrical polarity of the system. Note however that it is just an approximation: the dipole term is the lowest order term to consider: there are also higher-order perturbations (the quadrupole and even octopole moments).

Now, by moving the electron relative the the electric (magnetic) field of the atom, the total energy of the system changes. We can define the energy for a given state as $E = -\mu \cdot \epsilon$ where ϵ is the electric field of the atom.

What we really want to characterize is the transition between two of these energy states: what is the dipole moment of this change? (we call this the transition dipole moment or μ_T). Because this is a quantum-mechanical and so probabilistic process, what we need to find is the expectation value of this quantity. We can start with the expectation value for the energy that it takes to transition between these two states, which we denote with an initial (ψ_i^*) and final (ψ_f) wave function:

$$\langle E \rangle = \int \psi_i^* (-\mu \cdot \epsilon) \psi_f dV$$

We will assume the electric field is constant on the size scale of the atom, which leaves us to evaluate

$$\mu_T = \langle \mu \rangle_T = \int \psi_i^* (\hat{\mu}) \psi_f dV$$

Long story short (a few matrix evaluations later) – if μ_T is nonzero, then the transition has an electric dipole moment, and is an "allowed" transition. However, if μ_T is zero, there is no electric dipole moment for the transition, and the transition is "forbidden" or "semiforbidden". This does not mean that no transition is possible! It just means that you would have to go to higher-order terms (the transition may have a nonzero magnetic dipole moment or electric quadrupole moment).

In general however such transitions are much less likely, and so statistically will take longer to occur. In terrestrial environments, it is likely that a collision wil de-excite an atom waiting to make this transition before it gets the chance to decay via radiating a photon, hence the initial surprise at seeing "forbidden" lines in the ISM: they only become viable in the low-density environment of space. In general, a good takeaway from all of this is that electric dipole transitions are the strongest and most likely type of transitions to see (and we will return to this theme when we talk about rotational transitions in molecules).

All that wave function math can be a bit tedious, so we can use some patterns in the results to define a set of selection rules that tell us when electric dipole transitions can and cannot happen.

(1) The parity of the initial and final state must be different

(2) $\Delta L = 0$, or ± 1

(3) $\Delta J = 0$, or ± 1 but $J = 0 - 0$ is not allowed

(4) $\Delta l = \pm 1$ and only one single-electron wave function nl can change

(5) $\Delta S = 0$: Spin does not change

Transitions that satisfy all of these selection rules are allowed, and are written with no brackets around the species name, e.g., NII $^3P_0 - {}^3D_1$ at 108.4 nm

A transition that only violates (5) is known as semi-forbidden (or intersystem). Such transitions are written with a single brackett, e.g., NII] $^3P_2 - {}^5S_2$ at 214.3 nm

Forbidden transitions violate at least one of rules (1)-(4), typically occurring via a magnetic dipole interaction (e.g., [NII] $^3P_1 - {}^1D_2$ at 654.99 nm) or electric quadrupole interaction (e.g., [NII] $^1D_2 - {}^1S_0$ at 575.62 nm).

(Consider also as an example of parity selection: the Lyman alpha doublet shown in the figure in an above cell. As a strong line, it must come from a transition between the $2p$ and $1s$ orbitals. Even though the $2s$ orbital has the same energy as one of the $2p$ terms, the transition $2s$-$1s$ would not result in a change in parity, and so is not allowed by electron dipole selection rules).

4.6   Hyperfine Structure

If the nucleus of an atom has nonzero spin, then it has a magnetic moment. This results in additional splitting of those fine structure levels which also have a nonzero total spin. Essentially, the interaction of the magnetic moments is slightly different, depending on the directionality of the electron spin (whether it is parallel or antiparallel to the spin of the nucleus). The difference in orientation results in an (extremely small!) energy difference, and the single "fine structure" energy level splits into several distinct "hyperfine" energy levels.

4.7   Applications

Why bother learning all of this? It turns out that atomic transitions are ubiquitous in the ISM, and radiation from these transitions is used for many important diagnostics of gas conditions. Many atomic lines like those from hydrogen (Hα) occur within the visible range of wavelengths, and have become key tracers of the ISM by virtue of their brightness and ease of observation. Atomic line radiation is also one of the most important mechanisms for radiatively cooling the ISM (especially the hot ISM). Finally, the quantum structure of atoms is also important when considering molecules. We will revisit many of these concepts (e.g., hyperfine structure) in a molecular context. We also will have to consider the population of the outermost electron orbital (valence electrons) when determining chemical reactivity. An example of this unique to the ISM is a class of molecules called radicals, which have unpaired valence electrons. These molecules are extremely reactive, and in the high-density conditions of terrestrial chemistry, are extremely short-lived. However, in the low-density environment of interstellar space, these molecules can survive for long periods of times, and radicals like OH are commonly observed.