Many-Electron Atomic States, Terms, and Levels

5th May 2009

I. Hartree-Fock with Antisymmetrized Wavefunctions

Recall the earlier discussion of the Hartree-Fock self-consistent method. For the purposes of that introduction, we used trial wavefunctions that were simple products of single-electron orbitals. We did not account for antisymmetry and Pauli exclusion. Here, we will briefly formulate the Hartree-Fock method with anti-symmetric wavefunctions. The results of this analysis will give rise to the already determined orbital energies and electron-electron repulsion terms (Coulomb integral), as well as a new term arising from the antisymmetric nature of the wavefunction—exchange integral. Keep in mind that the following does still not consider explicitly effects of electron correlation (though, depending on the source, the exchange term is thought to contribute some amount to correlation).

The N-electron Slater determinantal wavefunction form, recall, is:

$$\Psi(\mathbf{r}_1,\sigma_1,\mathbf{r}_2,\sigma_2,...,\mathbf{r}_N,\sigma_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} u_1(\mathbf{r}_1,\sigma_1) & u_2(\mathbf{r}_1,\sigma_1) & \dots & u_N(\mathbf{r}_1,\sigma_1) \\ u_1(\mathbf{r}_2,\sigma_2) & u_2(\mathbf{r}_2,\sigma_2) & \dots & u_N(\mathbf{r}_2,\sigma_2) \\ \vdots & \vdots & & \vdots \\ u_1(\mathbf{r}_N,\sigma_N) & u_2(\mathbf{r}_N,\sigma_N) & \dots & u_N(\mathbf{r}_N,\sigma_N) \end{vmatrix}$$

For **closed shell** systems each spatial orbital is occupied by 2 electrons (of opposite spin). Thus we require a single Slater determinant:

$$\Psi(\mathbf{r}_1,\sigma_1,\mathbf{r}_2,\sigma_2,...,\mathbf{r}_{2N},\sigma_{2N}) =$$

$$\frac{1}{\sqrt{(2N)!}}\begin{vmatrix} \phi_1(\mathbf{r}_1)\alpha(\sigma_1) & \phi_2(\mathbf{r}_1)\beta(\sigma_1) & \dots & \phi_N(\mathbf{r}_1)\alpha(\sigma_1) & \phi_N(\mathbf{r}_1)\beta(\sigma_1) \\ \phi_1(\mathbf{r}_2)\alpha(\sigma_2) & \phi_2(\mathbf{r}_2)\beta(\sigma_2) & \dots & \phi_N(\mathbf{r}_2)\alpha(\sigma_2) & \phi_N(\mathbf{r}_2)\beta(\sigma_2) \\ \vdots & \vdots & & \vdots & \vdots \\ \phi_1(\mathbf{r}_{2N})\alpha(\sigma_{2N}) & \phi_2(\mathbf{r}_{2N})\beta(\sigma_{2N}) & \dots & \phi_N(\mathbf{r}_{2N})\alpha(\sigma_{2N}) & \phi_N(\mathbf{r}_{2N})\beta(\sigma_{2N}) \end{vmatrix}$$

The Hamiltonian **operating only on spatial coordinates** in atomic units is:

$$\hat{H} = -\frac{1}{2}\sum_{j=1}^{2N} \nabla_j^2 - \sum_{j=1}^{2N} \frac{Z}{r_j} + \sum_{i=1}^{2N}\sum_{j>i}^{2N} \frac{1}{r_{ij}}$$

The Hartree-Fock total energies,**for this closed-shell configuration** much like we have seen earlier are:

$$E \quad = \quad 2\sum_{j=1}^{N} I_j + \sum_{i=1}^{N}\sum_{j=1}^{N} (2J_{ij} - K_{ij})$$

The various terms in the energy expression are:

$$\begin{aligned}
I_j &= \int \phi_j^*(\mathbf{r}_j)\left[-\frac{\nabla_j^2}{2} - \frac{Z}{r_j}\right]\phi_j(\mathbf{r}_j)d\mathbf{r}_j \\
J_{ij} &= \int\int \phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi_i(\mathbf{r}_1)\phi_j(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \quad \textit{Coulomb Integral} \\
K_{ij} &= \int\int \phi_i^*(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi_i(\mathbf{r}_2)\phi_j(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_2 \quad \textit{Exchange Integral } i \neq j
\end{aligned}$$

NOTE:

In the definitions of the various one- and two-electron integrals listed immediately above, the summations are effectively over *orbitals*. These can be written in terms of summations over electrons with minor modifications in the leading multiplicative factors (see Szabo and Ostlund for further details).

Let's consider the meaning of the Coulomb and Exchange terms we have discussed just now. The coulomb integral can be rearranged as:

$$\int\int \phi_i^2(\mathbf{r}_1)\frac{1}{r_1 2}\phi_j^2(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$

The square of the wavefunction is the probability of finding an electron at a given point in space. So this term is the energy of the Coulombic interaction between an electron in orbital i with an electron in orbital j. For this reason, this integral is called the Coulomb Integral. Because the Coulomb potential is always positive for like charges, and the square of the wavefunction is always positive, this term contributes a *positive* energy to the toatl energy. This is a destabilizing energy contribution (arising from unfavorable repulsion).

The Exchange integral has no immediate classical interpretation. The name arises from the fact that the 2 electrons exchange their positions from the left to the right of the integrand, and in this sense the integral is connected to the Pauli principle.

The probability density for two electrons is significantly different in the case of an antisymmetrized Slater Determinant than in the simple Hartree product. The total density is not a simple product of each orbital density. The Coulomb integral expression suggests that the total probability is of a product-like nature. But since we have incorporated the antisymmetric nature of electronic wavefunctions via the Slater Determinantal form, the effect is apparane tin the form of the exchange integrals which arise naturally The total density is not a simple product of each orbital density. The Coulomb integral expression suggests that the total probability is of a product-like nature. But since we have incorporated the antisymmetric nature of electronic wavefunctions via the Slater Determinantal form, the effect is apparanet in the form of the exchange integrals which arise naturally. The exchange integrals "correct" the Coulomb integrals to take into account the antisymmetry of the wavefunction. It is easy to show that electrons of the same spin are more "correlated" in the Slater Determinantal form than in the Hartree Product form, so the Coulomb integrals should exaggerate the Coulomb repulsion of the electrons since the purely Coulomb integrals represent a probability that is of the form of a Hartree product wavefunction. Keep in mind that the "correlation" we introduce here is still not the total correlation between electrons, as the effect fundamentally arises from the indistinguishablity of electrons (as embodied in the antisymetrized wavefunctions) and has nothing to do with electron correlation. This is a subtle matter of semantics one should bear in mind.

The Hartree-Fock Method with Antisymmetric Wavefunctions
The variational principle yields the Hartree-Fock equation for each orbital:

$$\begin{aligned} \hat{F}_i\phi_i &= \epsilon_i\phi_i \\ \hat{F}_i &= \hat{f}_i + \sum_{j=1}^{N}\left(2\hat{J}_j - \hat{K}_j\right) \qquad \textit{Fock Operator} \end{aligned}$$

The various secondary operators embedded in the Fock operator are defined as:

$$
\begin{aligned}
\hat{f}_i &= -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \\
\hat{J}_j(\mathbf{r}_1)\phi_i(\mathbf{r}_1) &= \phi_i(\mathbf{r}_1)\int \phi_j^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi_j(\mathbf{r}_2)d\mathbf{r}_2 \\
\hat{K}_j(\mathbf{r}_1)\phi_i(\mathbf{r}_1) &= \phi_j(\mathbf{r}_1)\int \phi_j^*(\mathbf{r}_2)\frac{1}{r_{12}}\phi_i(\mathbf{r}_2)d\mathbf{r}_2
\end{aligned}
$$

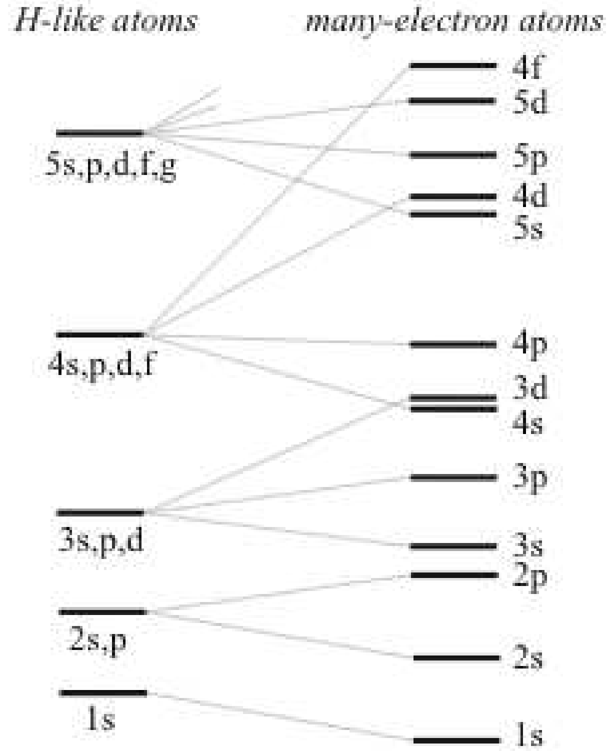
With these operators defined, one follows the protocol introduced earlier to solve the individual orbital Fock equations to obtain self-consistently the orbitals and orbital energies.

To summarize:

- Coulomb integrals describe repulsions between pairs of electrons. Always positive: integrands are positive everywhere (repulsion!)
- Exchange integrals arise through exchange of indistinguishable electrons. Positive, but have positive and negative intgrand contributions.
- Orbital energies are generally associated with ionization potentials (Koopman's Theorem).

Splitting of Hydrogen atom orbital energies due to many-electron shielding effects.

Splitting of Hydrogen Atom energy levels in Many-Electron Atoms



- Orbital energies are non-degenerate
- Relative orbital energetics for many-electron atoms are determined through interplay of one-electron kinetic and nuclear-electron interactions, electron-electron repulsions, and exchange effects. Thus, relative stabilities of many-electron atom orbitals are defined in a non-intuitive manner
- Afbau principle guides filling of orbitals

Angular Momentum of Many-Electron Atoms

Energies for various orbitals of many-electron atoms are dependent on **spin** and **orbital** angular momentum. Unlike the case for a single electron atom such as Hydrogen, the quantum numbers n, l, m_l, and m_s are no longer valid (or good) quantum numbers to define the system. This is intuitively so since we now have a plethora of combinations of orbital angular momentum and spin that can give rise to a multitude of atomic electronic states.

The implication of the last statement is that for a given electronic configuration, there are numerous states that exist. These states can be grouped together based on the equivalence of their energies. These groupings are called Atomic Terms. We now turn to a discussion of how these terms are obtained given a configuration.

For many-electron atoms, the total orbital angular momentum and total spin vectors are determined by simple vectorial addition of the orbital and spin momenta of the indificual electrons:

$$\begin{aligned} \vec{L} &= \sum_i \vec{l}_i \\ \vec{S} &= \sum_i \vec{s}_i \end{aligned}$$

The magnitude of the vectors is related to the quantum numbers for many-electron atoms, L and S, as:

$$\begin{aligned} \left|\vec{L}\right| &= \sqrt{L(L+1)}\hbar \qquad L = 0, 1, 2, 3, ... \\ \left|\vec{L}_z\right| &= M_L\hbar \qquad M_L = 0, \pm 1, \pm 2, \pm 3, ... \\ \left|\vec{S}\right| &= \sqrt{S(S+1)}\hbar \qquad S = 0, \frac{1}{2}, 1, \frac{3}{2}, ... \\ \left|\vec{S}_z\right| &= M_S\hbar \qquad M_S = 0, \frac{\pm 1}{2}, \pm 1, \frac{\pm 3}{2}, ... \end{aligned}$$

Furthermore, since the vectors add vectorially, we can easily obtain M_L and M_S as:

$$\begin{aligned} M_L &= \sum_i m_{l,i} \\ M_S &= \sum_i m_{s,i} \end{aligned}$$

We can define operators for the total angular momentum and spin vectors as we did for the one-electron case as follows:

$$\hat{S}_z = \sum_i \hat{s}_{z,i}$$

$$\hat{L}_z = \sum_i \hat{l}_{z,i}$$

$$\hat{S}^2 = \hat{S}\hat{S} = \left(\sum_i \hat{s}_i\right)^2$$

$$\hat{L}^2 = \hat{L}\hat{L} = \left(\sum_i \hat{l}_i\right)^2$$

Energy of a Configuration depends on $\left|\vec{S}\right|$ and $\left|\vec{L}\right|$ (L and S quantum numbers for many-electron systems)

Consider the first excited state of Helium with configuration: $1s^1\ 2s^1$. For this configuration (recalling the above definitions), $L = 0$ (s-orbitals have no angular momentum). Thus, we are left with spin to consider. What possibilities can we think of that will accommodate 2 electrons in two different s-orbitals. The following shows an enumeration:

- $\uparrow\uparrow$ $\quad \mathrm{M}_S = \sum_i m_{s,i} = +\frac{1}{2} + \frac{1}{2} = 1$
- $\uparrow\downarrow$ $\quad \mathrm{M}_S = \sum_i m_{s,i} = +\frac{1}{2} - \frac{1}{2} = 0$
- $\downarrow\uparrow$ $\quad \mathrm{M}_S = \sum_i m_{s,i} = -\frac{1}{2} + \frac{1}{2} = 0$
- $\downarrow\downarrow$ $\quad \mathrm{M}_S = \sum_i m_{s,i} = -\frac{1}{2} - \frac{1}{2} = -1$

Now, to analyze the results of the above enumeration. We see that the maximum value of M_S is 1. If we consider the analogy to orbital angular momentum for the hydrogen atom case, we recall the relation between m_l and l as:

$$|m_l| \le l$$

By analogy,

$$|M_S| \le S$$

Thus, the $M_S = 1$ value indicates that there is a group of states for which $S = 1$; it also requires that there be 3 states for this S value to correspond to the 3 values that M_S can take, namely $M_S = 1, 0, -1$. This takes care of 3 of the 4 states we enumerated above. The last state corresponds to a M_S value of zero. Thus, for this single state, $S = 0$ as well (by necessity). Thus, we see the following:

- There are two groups of states that emerge because of the various combinations of spin states of multiple electrons
- One group is comprised of 3 states; this is a triplet (and because L=0, it is triplet S, ${}^3S$.)
- The second is comprised of 1 state; this is a singlet (and because L=0, it is singlet S, ${}^1S$.)

- For reasons that we will not consider here, the triplet state is lower in energy than the singlet state. See Supplemental section 21.10 in Engel and Reid)

Dependence of energies of configurations on L

We have seen that S affects the energies of configurations. Since the values of m_l and m_s of individual electrons are related by the Pauli exclusion principle, we have to ask **under what conditions does the choice of particular values of m_l and m_s for a given configuration lead to different spatial distributions of electrons and therefore to a different electron-electron repulsion**.

The answer is that we are concerned with systems with 2 unpaired electrons in valence (outermost) subshells; equivalently, we would like to know the multiple states that arise as combinations of the multiple choices possible for m_l and m_s consistent with the Pauli exclusion principle.

Atomic Terms

We define an atomic term as a group of states with the same L and S value, but different M_L and M_S values. These states are of equal energy if there is no spin-orbit coupling (to be discussed further below).

Once we know L and S, we can determine the number of states that belong to this term; this is the **degeneracy** of the term. Again, in the absence of spin-orbit coupling, we see that the degeneracy is:

$$degeneracy = (2L+1)(2S+1)$$

Another quantity associated with terms is the **spin multiplicity** calculated as $2S+1$.

The convention for specifying an atomic term is the term symbol:

$$^{2S+1}L$$

don't confuse the L in the last equation with the orbital angular momentum quantum number!!!!!.

The following table lists the letter of the atomic term symbol associated with a specific numerical quantity for L Table 2. Letter conversions for atomic term symbols.

L	Letter
0	S
1	P
2	D
3	F
4	G
5	H

1 Determining Atomic Terms in the Russel-Saunders Scheme (R-S Scheme)

1.1 Filled Subshells

For filled subshells, $L = 0$ and $S = 0$. The atomic term is ^1S, a singlet S term. This is known as **Unsold's Theorem**. (make sure you understand why the filled subshell has no orbital or spin moment).
Filled subshells within a configuration do not contribute to L and S.
If a configuration has only a single electron outside of a filled subshell, then the L and S values are: $L = l_1$ and $S = \frac{1}{2}$. Thus the term symbol is $^2l_1$.

1.2 Two unpaired electrons in different subshells

This case has a heuristic for determining L and S; it is called the Clebsch-Gordan series. For configurations such as np^1d^1 or ns^1p^1 or ns^1d^1, where unpaired electrons reside in **different** subshells, the values of L and S can be determined as:

$$L = |l_1 - l_2|, |l_1 - l_2| + 1, |l_1 - l_2| + 2, ..., l_1 + l_2$$
$$S = |s_1 - s_2|, |s_1 - s_2| + 1, |s_1 - s_2| + 2, ..., l_1 + l_2$$

NOTE: in the Clebsch-Gordan series, take care to use s and l rather than m_s and m_l!

For the example of np^1d^1, the possible L values are $1, 2, 3$ and the possible S values are $0, 1$. Thus the terms are:

$$^3P,\ ^1P,\ ^3D,\ ^1D,\ ^3F,\ ^1F$$

1.3 Configurations with partially filled subshells; multiple electrons in unfilled subshells

For the general case of multiple electrons in a partially filled subshell, there is no simple heuristic to determine L and S. But we can make use of the relation between M_S and M_L to obtain information on L and S from maxmimum values of M_L and M_S. First consider the case of an np^2 configuration, such as for the carbon atom.

We can enumerate the states by first determining the maximum values that M_L and M_S can take. For the np^2 configuration, these are 2 and 1 respectively. Thus, we can construct a table of the possible states as follows

Table. Microstates for Ground State Carbon $1s^12s^22p^2$.

M_L	M_S		
	1	0	-1
2		$(1^+, 1^-)$	
1	$(0^+, 1^+)$	$(1^+, 0^-)$,$(0^+, 1^-)$	$(0^-, 1^-)$
0	$(1^+, -1^+)$	$(1^+, -1^-)$,$(-1^+, 1^-)$, $(0^+, 0^-)$	$(1^-, -1^-)$
-1	$(0^+, -1^+)$	$(-1^+, 0^-)$,$(0^+, -1^-)$	$(0^-, -1^-)$
-2		$(-1^+, -1^-)$	

Now we see how to analyze the data.

- For $|M_L|$ to be 2, $|M_S|$ can only be 0; thus, L=2 and S=0 (5 states) ^1D
- For $|M_L|$ to be 1, $|M_S|$ is 1; thus L = 1 and S=1 (9 states) ^3P
- For $|M_L|$ to be 0, $|M_S|$ is 0; thus L = 0 and S = 0 (1 state) ^1S
- These terms correspond to Table 21.5 for p^2
- **NOTE: p^2 and p^4 configurations are equivalent; convince yourself of this**

The relative energy of different **terms** is determined by applying **Hund's Rules**. These are empirically determined heuristics one can use to determine the characteristics of a given configuration. These rules are:

- **Rule 1** The lowest energy term is that which has the greatest spin multiplicity. Thus, as we have seen before, triplet states are lower in energy than singlet states.
- **Rule 2**. For states with same spin multiplicity, the term with higher orbital angular momentum lies lower in energy.

Given a configuration with partially filled subshells, the lowest energy term can be found by determining the maximum value of M_L and M_S (maximize spin and orbital angular momentum).

2 Spin - Orbit Coupling

So far, for light nuclei, we have considered the spin of the electron and the orbital angular momentum to be independent; as such the vectors representing these quantities add simply.

Spin-orbit coupling is about magnetic dipole moments (magnet dipoles) interacting with one another. In this case, the dipoles are generated by electron spin angular momentum and orbital angular momentum.
The spin of the electron establishes an **intrinsic magnetic dipole moment** as:

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

where

$$\mu_b = \frac{e\hbar}{2mc}$$

is the Bohr magneton (a fundamental unit of magnetic dipole moment). the g_s is the spin gyromagnetic ratio of the electron. It is predicted by Dirac theory to be 2 (exactly), but experimentally has been determined to be $g_s = 2.00232$.
By analogy to the spin case, the magnetic moment arising from the orbital angular momentum of the electron is:

$$\mu_l = -g_l \mu_b \frac{\vec{L}}{\hbar}$$

where $g_l = 1$ is the orbital gyromagnetic ratio of the electron. (the electron creates 2x as much dipole moment per unit spin angular momentum than it does per unit orbital angular momentum. **These magnetic dipoles interact, leading to spin-orbit coupling**.
The spin-orbit effect can be simply understood by considering the electron at rest and taking the nucleus as moving around the electron with linear speed, v. Since the nucleus with charge Z is moving around the electron, its motion generates a **magnetic field**:

$$B = \frac{Zev}{cr^2}$$

If we recall that the angular momentum of this rigid rotor-like system is $L = r(mv)$, we can rewrite the expression for the magnetic field in terms of the electron orbital angular momentum as:

$$\vec{B} = \frac{Ze}{mcr^3}\vec{L}$$

The energy of the spin magnetic dipole in the magnetic field generated by the orbital angular momentum of the nucleus-electron system is given as:

$$E_{SO} = -\mu_s\dot{\vec{B}}$$

and substituing the above relation for mu_s, we obtain:

$$E_{SO} = \frac{Ze^2}{2m^2c^2r^3}\vec{L}\dot{\vec{S}}$$

the Hamiltonian for spin-orbit coupling is thus:

$$\hat{H}_{SO} = \frac{Ze^2}{2m^2c^2r^3}\hat{L}\dot{\hat{S}}$$

Because of this additional term in the total Hamiltonian, the operators L_z and S_z do not commute with the total Hamiltonian. But the total angular momentum operator,

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

can be defined, and the operators $\hat{J}^2$ and $\hat{J}_z$ do commute with the total Hamiltonian. Though we will not go into the details, the physical meaning of this is that though $\vec{S}$ and $\vec{L}$ exert equal and opposite torques on each other, they couple together and precess about $\vec{J}$ so as to maintain a constant z-projection of $\vec{J}$

The action of the operators $\hat{J}^2$ and $\hat{J}_z$ on a wavefunction is:

$$\begin{aligned} \hat{J}^2\Psi &= J(J+1)\hbar^2\Psi \\ \hat{J}_z\Psi &= M_J\hbar\Psi \end{aligned}$$

The possible values of J are: $J = |L-S|, |L-S|+1, |L-S|+2, ..., L+S$. For the energy involving spin-orbit coupling, the equation we discussed above shows that there is a term proportional to $\vec{L}\dot{\vec{S}}$. To evaluate this, we can write as follows:

$$\begin{aligned} \vec{J}^2 &= \vec{J}\dot{\vec{J}} \\ &= (\vec{L}+\vec{S})\dot{(}\vec{L}+\vec{S}) \end{aligned}$$

$$= \vec{L}\vec{L} + \vec{S}\vec{S} + 2\vec{L}\dot{\vec{S}}$$

Thus,

$$\vec{L}\vec{S} = \frac{1}{2}\left(\vec{J}\vec{J} - \vec{L}\vec{L} - \vec{S}\vec{S}\right)$$

The spin-orbit energy is thus, (see page 11-6 in Dybowski and Teplyakov; page 12-1 also)

$$E_{SO} = \frac{hA}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

Rules for filling levels arising from spin-orbit coupling in at term:

- If unfilled subshell is half-full or more, then level with **highest J** has lowest energy
- If unfilled subshell is less than half-full, then level with **lowest J** has lowest energy

For carbon, with valence subshell $2p^2$, spin-orbit coupling breaks the degeneracy of the ^3P state to give. The J values are $J = 0, 1, 2$, thus giving for the terms, $^3P_0, ^3P_1, ^3P_2$ with the $J = 0$ state being the lowest in energy.

3 Hyperfine Coupling, Splitting, Effects

Hyperfine coupling and splitting effects lead to further splitting of the terms into states; the nomenclature “hyperfine” indicates that the energy splittings are rather small. The phenomenon is present in atoms, molecules, and ions. The energy splittings arising from hyperfine coupling are generally **orders of magnitude smaller** than those arising from fine structure splitting (such as spin-orbit coupling discussed above).

Like spin-orbit coupling, hyperfine coupling involves the coupling of **spin** angular momenta of the electron and nucleus, S and I. The energy depends on the relative orientation of the nuclear and electronic spin angular momenta. The hyperfine energy is given as:

$$E_{hyperfine} = \frac{h\epsilon}{2}\left[T(T+1) - I(I+1) - S(S+1)\right]$$

For the Hydrogen atom, the nuclear and electronic spin angular momenta numbers are $I = \frac{1}{2}$ and $S = \frac{1}{2}$. Thus, $T = 0, 1$ and the states are

$$E_0 = \frac{hA_{hf}}{4}$$
$$E_1 = \frac{3hA_{hf}}{4}$$

The energy difference is

$$\Delta E = hA \tag{1}$$

The constant "A" is the hydrogen hyperfine splitting constant and is known quite precisely; $A = 1.4204057518 GHz$. As you can tell by the units, these effects are associated with low energy (low frequency) radiation, such as radio waves. The use of these techniques in radio astronomy has allowed the characterization of celestial objects.

4 Zeeman Effect: Coupling of Atomic Magnetic Moments to External Magnetic Fields

Orbital and spin angular momenta of electronic states lead to magnetic moments that can interact with *applied external* magnetic fields.
The orbital magnetic moment is related to the orbital angular momentum by:

$$\begin{aligned}
\mu_L &= -\frac{e}{2m_e}\vec{L} \\
|\mu_l| &= -\frac{e\hbar}{2m_e}\sqrt{l(l+1)} \equiv -\beta_o\sqrt{l(l+1)} \\
|\mu_{l_z}| &= -\frac{e}{2m_e}L_z = -\frac{e\hbar}{2m_e}m = -\beta_o m
\end{aligned}$$

The electron **spin** magnetic moment is given by:

$$\mu_s = -\frac{e}{2m_e}g\vec{S}$$

$$|\mu_s| = -\frac{e\hbar}{2m_e}g\sqrt{s(s+1)} = -\beta_o g\sqrt{s(s+1)}$$

$$\mu_{s_z} = -\frac{e}{2m_e}gS_z = -\frac{e\hbar}{2m_e}gm_s = -\beta_o gm_s = \pm\beta_o$$

$$g \equiv \text{"}electronic\ g\ factor\text{"} = 2.0023$$

Energetics of Magnetic Field Effects

Potential energy in magnetic field $\vec{B}$:

$$E = -\mu\vec{B} = -\mu_z B_z = \frac{eB_z}{2m_e}\left(L_z + gS_z\right)$$

where the L_z and S_z are the orbital and spin angular momentum z-components. The total Hamiltonian operator is thus:

$$\begin{aligned}
\hat{H} &= \hat{H}_o + \frac{eB_z}{2m_e}\left(\hat{L}_z + g\hat{S}_z\right) \\
\hat{H}\Psi_{nlmm_s} &= \hat{H}_o\Psi_{nlmm_s} + \frac{eB_z}{2m_e}\left(\hat{L}_z\Psi_{nlmm_s} + g\hat{S}_z\Psi_{nlmm_s}\right) = E\Psi_{nlmm_s} \\
E &= E^o_{nlmm_s} + \beta_o B(m + gm_s)
\end{aligned}$$

Thus, the Zeeman energy in a magnetic field depends on the orbital and spin magnetic quantum numbers! Every electron orbital state is split into spin sublevels $m_x = \pm 1/2$.

Optical transitions between different electronic levels follow selection rules:

$$\delta m = \pm 1 \qquad \delta m_s = 0$$

5 Atomic Spectroscopies

- NMR, ESR (electron spin resonance). energy transfer between nuclear/electronic states and external magnetic fields
- Surface spectroscopies: Auger electron spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS) Introduce sufficient energy to extract electrons from atoms; measure kinetic energy of electrons.
- Depends on accurate assessment of inelastic mean free path (ejected electrons interact with atoms of native material, thus losing information of original atomic state (energy level)).
- Usually performed in vacuum to minimize energy losses
- Inelastic mean free path depends on energy of ejected electron

- Auger: incident electron ejects core-level (low energy) electron in surface atom. This hole is filled by a transition of higher energy electron to core-level. For energy conservation, a third electron is emitted – the Auger electron.

- XPS: simpler than Auger: only one energy level involved.

$$E_{kinetic} = h\nu - E_{binding}$$

- XPS: measure the difference in local environment for different atoms. observe chemical shift for same atom in different local environments (free atom versus bound atom in molecular systems)