

Atomic Terms, Hund's Rules, Atomic Spectroscopy

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I. Atomic Terms, Hund's Rules, Atomic Spectroscopy and Spectroscopic Selection Rules

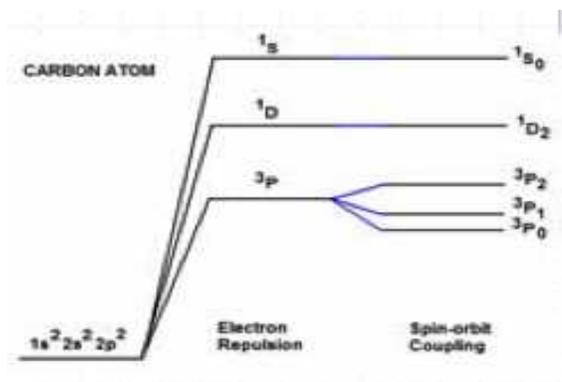
Having defined ways to determine atomic terms (which group various quantum microstates of similar energy) we need to specify a protocol to allow us to determine qualitatively the **relative energetics** of the terms.

Up till now, apart from the example of the carbon atom ground state, we have not considered too deeply the idea of spin-orbit coupling. This is important for nuclei starting with $Z=30$ and moving to higher charge. For these atoms, the various terms arising from L-S (Russel-Saunders) coupling of orbital and spin angular momenta are further split based on the spin multiplicity, effectively.

Hund's Rules:

- The **lowest energy** term is that which has the **greatest spin multiplicity**.
- For terms that have the same spin multiplicity, the term with the highest orbital angular momentum lies lowest in energy.
- spin-orbit coupling (more pronounced for heavier nuclei) splits terms into levels.
 - If the unfilled subshell is exactly or more than half full, the level with the highest J value has the lowest energy
 - If the unfilled subshell is less than half full, the level with the lowest J value has the lowest energy.

Splitting of Carbon Atom energy levels in Many-Electron Atoms



Spectroscopy and General Selection Rules in the Dipole Approximation Molecular and atomic spectroscopy afford information on various properties of atoms and molecules:

- Bond lengths (rotational spectroscopy)
- Vibrational frequencies for characteristic dynamical modes in molecules (vibrational spectroscopy)
- Allowed electronic states (atomic spectroscopy)

Spectroscopy attempts to connect the **discrete** quantum energy (and angular momentum) states to atomic/molecular properties. Since the states are quantized, one realizes that the differences in energy between states are discrete. Moreover, the energy differences can be related to frequencies of EM radiation (as we have seen before):

$$h\nu = |E_2 - E_1|$$

We see that the *energy spacing* between levels is central to spectroscopy. In fact, the spacing between levels defines the EM radiation required to probe the transitions. The following table (adopted from Engel and Reid) shows the major spectroscopic techniques and the radiation involved.

Table 1. Spectroscopies and Associated EM Radiation

<i>Spectral Range</i>	$\lambda(\text{nm})$	$\nu (10^{14} \text{ Hz})$	$\tilde{\nu} (\text{cm}^{-1})$	Energy (kJ/mol)	Spectroscopy
Radio	10^9	1×10^{-6}	0.01	10^{-8}	NMR
Microwave	100,000	0.01			
Infrared	1000	3.0			
Visible (red)	700	4			
Visible (blue)	450	6			
Ultraviolet	< 300	10			

- NMR has smallest energy spacing
- Electronic transitions have largest energy spacings
- Rotational and vibrational energy levels have intermediate energy spacings
- Each type of transition (and thus, spectroscopy) dictates a specific set of selection rules for "allowed" transitions.

"Allowed" Transitions: Spectroscopic Selection Rules Within the Dipole Approximation

Qualitative Discussion:

Spectroscopy involves the *interaction of electromagnetic radiation* with atoms and molecules. For certain types of interactions, the dynamical molecule can be considered (and in fact is) an oscillating electric dipole, possessing a static and dynamic dipole moment. It is this dipole moment that interacts with the *electric field* of EM radiation. If the mode of oscillation and the electric field have the same frequency and phase, there can be transfer of energy to the quantum mode of the chemical species, and a spectroscopic transition can occur. It turns out that the dynamical dipole moment dictates whether the transition occurs.

Selection rules tell us which transitions (among the many available) will be experimentally observable.

The Dipole Approximation

It can be shown that a non-zero probability for a transition from a state n to m is realized if the **transition dipole moment**, μ_x^{mn} is non-zero, giving the requirement:

$$\mu_x^{mn} = \int \psi_m^*(x) \mu_x(x) \psi_n(x) d\tau \neq 0$$

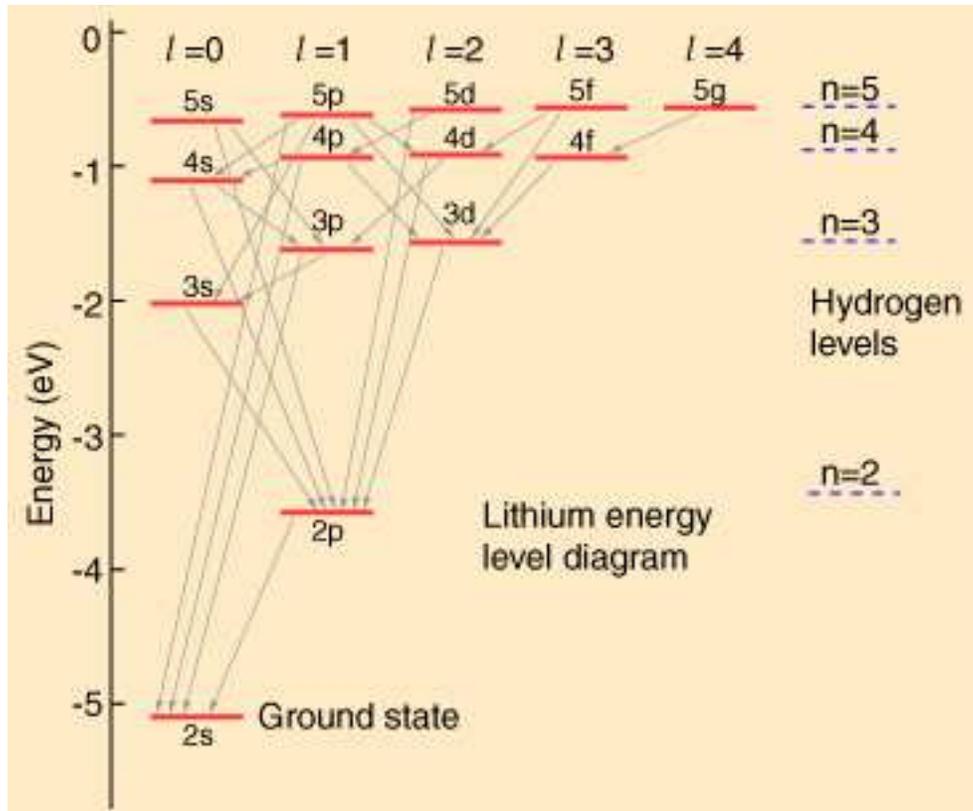
where μ_x is the dipole moment along the electric field direction, in this case the x – *direction*. As discussed in Engel and Reid for the case of a quantum harmonic oscillator, the integral vanishes for all vibrational transitions except in which the principal quantum number (for H.O.) changes by ± 1 . More generally, selection rules are different for different spectroscopies. Within the dipole approximation, however, selection rules are determined using the transition dipole and the appropriate total energy eigenfunctions for any spectroscopy.

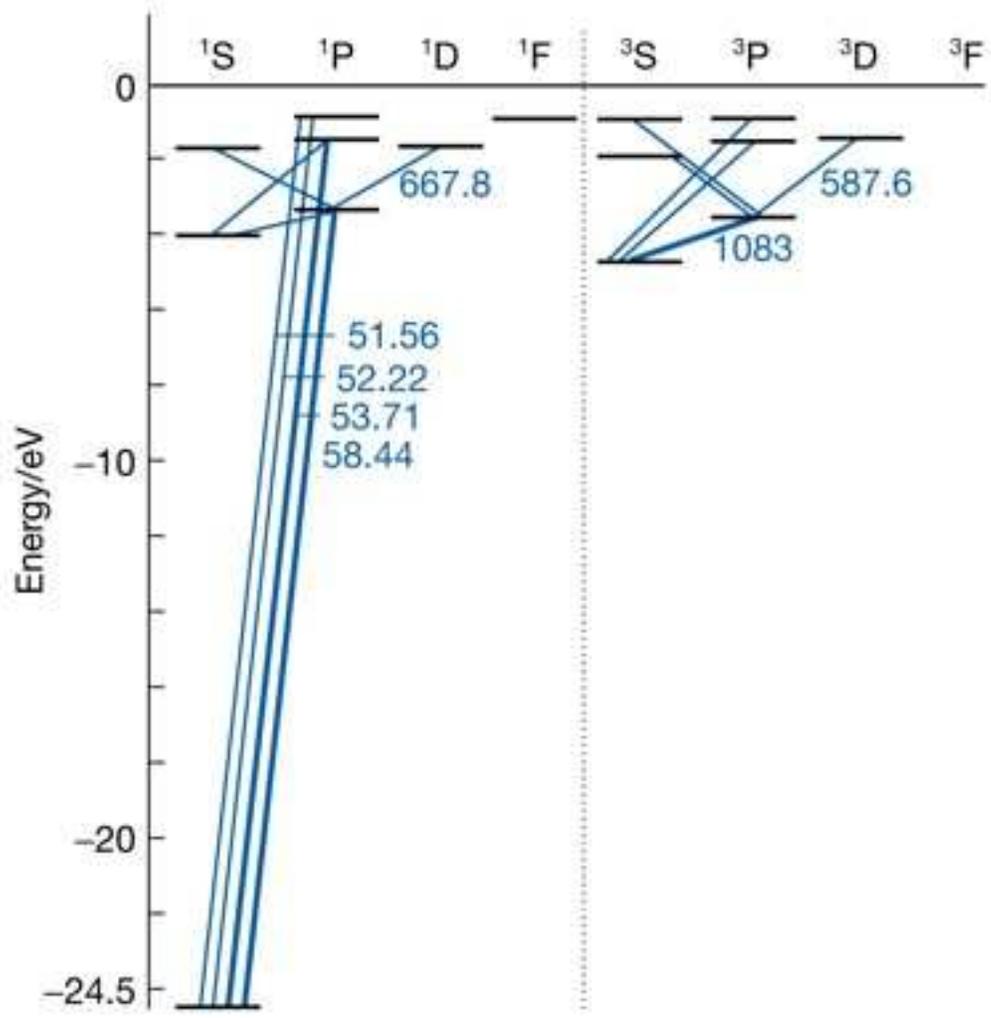
Atomic Spectroscopy The practicality of the previous discussions of atomic terms comes from the association of the formalism to atomic spectroscopy. We have already seen for the hydrogen atom that for absorption and emission spectroscopy (based on transitions between principle quantum states) the relation of the energetics of the transitions to quantum states is determined by a relation of the form:

$$\tilde{\nu} = R_H \left(\frac{1}{n_{initial}^2} - \frac{1}{n_{final}^2} \right)$$

where R_H is the Rydberg constant. We also discussed that the values of $n_{initial}$ determine specific spectroscopic series of lines in the EM spectrum. The series of spectral lines associated with $n_{initial} = 1$ is the Lyman series, and those coupled with the $n_{initial} = 2, 3, 4, 5$ are the Balmer, Paschen, Brackett, and Pfund series, respectively (named for the spectroscopists who discovered them)

Many-Electron Atom Transitions **Grotrian Diagrams** map the various energy states of many-electron systems so as to allow a view of the possible transitions between states. The following is an example for the Lithium and Helium atoms.





Spectroscopic Selection Rules: Electronic Transitions in Many-Electron Atoms In atomic absorption and emission processes, only certain transitions are allowed. This makes intuitive sense since the transitions have to maintain states that comply with the commutativity relation between angular momenta and the system Hamiltonian. Thus, the spectroscopic selection rules for atomic transitions based on the dipole approximation are:

- $\Delta l = \pm 1$
- $\Delta L = 0, \pm 1$
- $\Delta J = 0, \pm 1$

- $\Delta S = 0$ (no transition between singlet and triplet states in Helium)

NOTE: The first selection rule refers to the angular momentum of a single electron; the other rules pertain to the vector sum of all electrons in the atom. J refers to the total electron angular momentum.

Magnetic Field Effects on Spin States

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:

$$\begin{aligned}\mu_s &= -\frac{e}{2m_e}g\vec{S} \\ |\mu_s| &= -\frac{e\hbar}{2m_e}g\sqrt{s(s+1)} = -\beta_o g\sqrt{s(s+1)} \\ \mu_{s_z} &= -\frac{e}{2m_e}gS_z = -\frac{e\hbar}{2m_e}gm_s = -\beta_o gm_s = \pm\beta_o \\ g &\equiv \text{"electronic } g \text{ factor"} = 2.0023\end{aligned}$$

Energetics of Magnetic Field Effects

Potential energy in magnetic field \vec{B} :

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

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

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

Thus, the 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:

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

Electron Spin Resonance: ESR Low-frequency radiation stimulates transitions between electron spin sublevels.

- Selection rule: $\delta m_s = \pm 1$.
- $\delta E = g\beta_o B \left(\frac{1}{2} - \frac{-1}{2} \right) = g\beta_o B = h\nu$
- Radiation frequency in microwave (GHz) region
- ESR: applicable to **unpaired** electron spins.
- ESR: information on electronic orbital structure (line positions and splittings depend on coupling between unpaired electron spin and other (including nuclear) spins.
- Which nuclei does the electron interact with "most"

Nuclear Spin and Magnetic Field Effects: Nuclear Magnetic Resonance Spectroscopy

- Electrons (fermions) have intrinsic spin magnetic moment (spin 1/2)
- Some nuclei possess intrinsic nuclear magnetic moment

- Nuclear magnetic moments give rise to transitions exploited by NMR
- Nucleus with non-zero magnetic moment is sensitive probe of local electron distribution in a molecule
- Uses: structure determination, electron distribution, chemical kinetics, organ imaging(MRI)

Energy of Spin Active Nuclei in Magnetic Field

The **nuclear** magnetic moment is related to the nuclear angular momentum via:

$$\vec{\mu} = g_N \frac{e}{2m_{proton}} \vec{I} = g_N \beta_N \frac{\vec{I}}{\hbar} = \gamma \frac{\vec{I}}{\hbar}$$

- γ is the magnetogyric ratio: $g_N \beta_N$
- β_N is the nuclear magneton, $\beta_N = \frac{e\hbar}{2m_{proton}}$ (see above for the analogue for the electron)
- The nuclear g-factor, g_N , is specific to a particular nucleus, and is a dimensionless number.
- Most abundantly occurring nuclei are not spin-active (have no nuclear magnetic moment) and are thus not suitable for use in NMR. Thus, one encounters NMR with isotopes of common elements, such as 1H and ^{13}C .

NOTE: The operators and commutation relations for nuclear spin are the same as for electron spin.

The energies associated "up" and "down" nuclear spins in a magnetic field aligned in the z-direction are determined as:

$$E = -\vec{\mu} \cdot \vec{B}_o = -\gamma B_o m_z \hbar$$

With the z-component of the nuclear spin taking on values of $\pm 1/2$, there are two energies for the "up" and "down" spins in a z-oriented magnetic field:

$$E = -\left(\pm\frac{1}{2}\right)g_N\beta_N B_o = -\left(\pm\frac{1}{2}\right)\gamma B_o$$

NOTE: There are 2 distinct energy levels; however, the separation is a *continuous* function of the **magnetic field!**

Note on precession of individual nuclei

The discussion so far has considered only magnetic moments parallel to an applied external magnetic field. If the nuclear magnetic moment is not parallel to the external field, then it experiences a torque (much like a spinning top as it wobbles in a gravitational field). The torque leads to a **precessive** motion of the nuclear magnetic moment that can be described as motion on a cone about the z-direction (magnetic field direction). The frequency of this precession is called the **Larmor frequency** given by:

$$\nu = \frac{1}{2\pi}\gamma_o$$

We see that the Larmor frequency scales linearly with the applied magnetic field. It has characteristic values for particular nuclei. Finally, we note that in a given "macroscopic" sample, there are Avogadro's number of nuclear magnetic moments precessing. Individually, the moments have different transverse components, but collectively, they cancel one another to leave only the z-component. Thus, in a practical sense, we consider the total magnetization, \vec{M} defined as the sum of the individual magnetic moments.

Since NMR, as any spectroscopy, requires transitions between states, let's consider the populations of states at normal conditions to get an idea of one practical aspect of the NMR technique. First, let's consider the energy separation for a magnetic field of 5.5 Tesla:

$$\begin{aligned} E &= \pm\frac{1}{2}g_N\beta_N B_o \\ E &= \pm 7.76 \times 10^{-26} J \\ \Delta E &= 2(7.76 \times 10^{-26} J) = 1.55 \times 10^{-25} J \end{aligned}$$

The frequency associated with this transition is in the radiofrequency range (you may hear NMR spectroscopists talk about RF frequencies associated with inducing transitions via "pulse sequences"). The **relative populations** of the "up" and "down" spin states are:

$$\frac{n_{\beta}}{n_{\alpha}} = \exp^{-\frac{\epsilon_{\beta}-\epsilon_{\alpha}}{k_B T}} = 0.999962$$

This shows us that at 300K, with a 5.5 T magnet, the rate of upward and downward transitions will be roughly the same, and so a relatively weak NMR signal is obtained. In general, the energy absorbed is proportional to the product of the energy difference and populations of the two spin states, both of which depend on the magnetic field. Thus, NMR measurements are invariably performed at *high magnetic fields* employing superconducting magnets.

Practical Application: Chemical Shifts

Up to now, we have implicitly considered the effects of a "bare" nucleus in a magnetic field. In reality:

- Electron density surrounds nucleus and contributes to an induced magnetic dipole at the nucleus
- Other nuclei and electrons neighboring the nucleus of interest also contribute to modulating the local magnetic field at the nucleus of interest.

These effects must be explicitly included in the theoretical framework in order to connect to actual measurement. With respect to the effects of local electron density associated with the atom of interest, we need to consider the response of the electron density to the nuclear magnetic moment. This response is in the form of an **induced magnetic field** that **opposes** the external field at the nucleus. The induced field is proportional to the external field: $\vec{B}_{induced} = -\sigma\vec{B}_o$. The proportionality constant is the **shielding constant**. Thus, the total field at the nucleus is the sum of applied external and induced fields, $B_{total} = (1 - \sigma)\vec{B}_o$. The resonance frequency (the frequency of the RF radiation required to induce transitions) is also modulated by the shielding constant:

$$\nu = \frac{\gamma B_o(1 - \sigma)}{2\pi}$$

This modulation of the resonance frequency of the nuclear spin is the basis of **chemical shift** in NMR spectroscopy. Keep in mind that the shift is due to the response of the *electron density* in the neighborhood of the nucleus; the shielding is a *local* effect.

In a molecule, the presence of other atoms and chemical functionalities gives rise to chemical shifts based on the influences of electronic density surrounding other nuclei, and the interaction with magnetic fields generated by other nuclei. Groups that tend to draw electron density away from nucleus decrease the shielding for that nucleus, and reduce the chemical shift. Electron donating groups have the opposite effect.

Finally, NMR signals from nuclei in different chemical environments can "split" due to effects of spin-spin interactions. For the non-interacting spin case (no **explicit** coupling in the Hamiltonian), the Hamiltonian can be written as:

$$\hat{H} = -\gamma B_o(1 - \sigma_1)\hat{I}_{z_1} - \gamma B_o(1 - \sigma_2)\hat{I}_{z_2}$$

The eigenfunctions of this Hamiltonian are products of the eigenfunctions of the individual operators \hat{I}_{z_1} and \hat{I}_{z_2} :

$$\begin{aligned}\psi_1 &= \alpha(1)\alpha(2) \\ \psi_2 &= \beta(1)\alpha(2) \\ \psi_3 &= \alpha(1)\beta(2) \\ \psi_4 &= \beta(1)\beta(2)\end{aligned}$$

Four energy eigenvalues are obtained after solving the Schrodinger equation for this system, and these lead to two unique transition frequencies; thus, the NMR spectrum simulated for this case would give two peaks. Introducing a spin-spin coupling term into the Hamiltonian:

$$\hat{H} = -\gamma B_o(1 - \sigma_1)\hat{I}_{z_1} - \gamma B_o(1 - \sigma_2)\hat{I}_{z_2} + \frac{hJ_{12}}{\hbar^2}\hat{I}_1\hat{I}_2$$

gives rise to a quartet (4 unique transition frequencies). Thus, though we do not show explicitly here, more detailed calculations demonstrate that

spin interactions and shielding effects are important and at the heart of extracting meaningful information from NMR methods.