Atomic Terms,Hund's Rules, Atomic Spectroscopy

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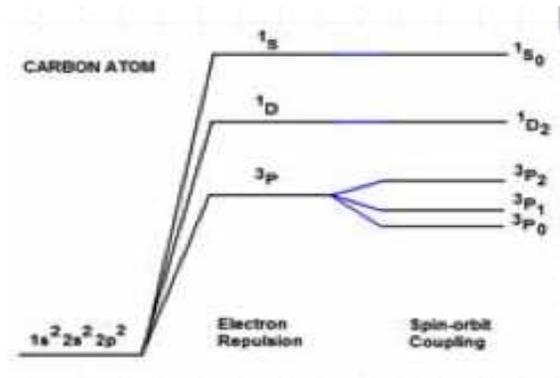### I. Atomic Terms, Hund's Rules, Atomic Spectroscopy

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

CARBON ATOM

^1S $^1S_0$

^1D $^1D_2$

^3P $^3P_2$
            $^3P_1$
            $^3P_0$

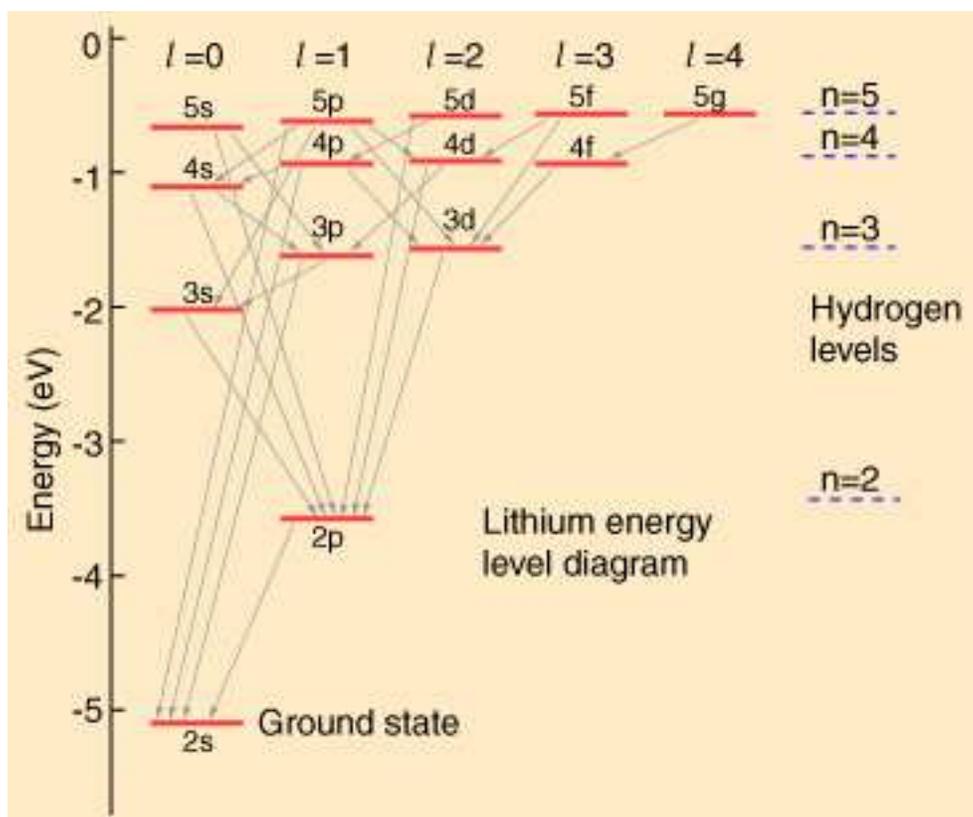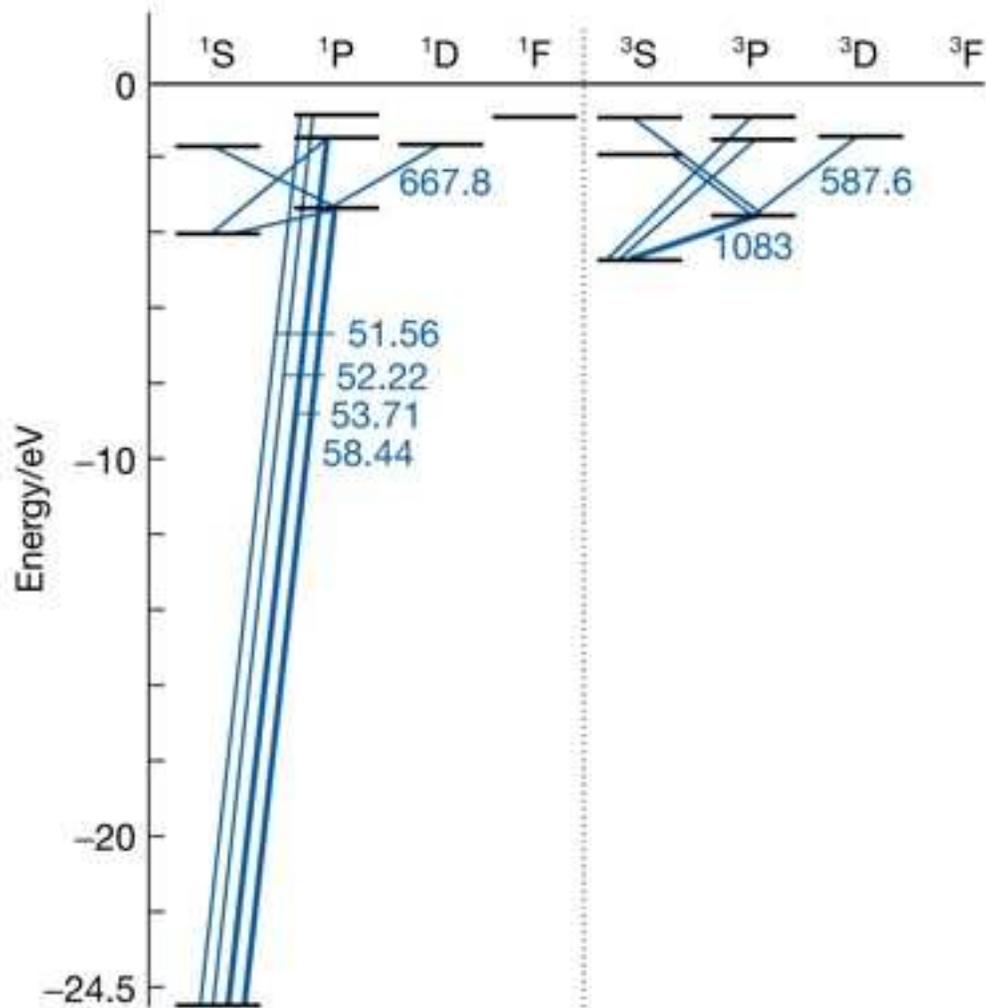$1s^2 2s^2 2p^2$ Electron Repulsion   Spin-orbit Coupling

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 wwho 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.

Lithium energy level diagram

Energy/eV

^{1}S ^{1}P ^{1}D ^{1}F ^{3}S ^{3}P ^{3}D ^{3}F

0

667.8

587.6

1083

51.56
52.22
53.71
58.44

−10

−20

−24.5

Spectroscopic Selection Rules 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 transtions based on the dipole approximation are:

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

- $J = 0$ **to** $J^{'} = 0$ **not allowed**

- $\Delta S = 0$

- Laporte's Rule: For transitions involving more than one electron, the parity of the total orbital angular momentum $L = \sum l_i$ must change by ± 1; $\Delta L = Transitions\,among\,terms\,derived\,from\,the\,same\,configuration\,are\,forbidden\,(i.e.,{}^3P$ to ${}^1S$ for np^2 configuration not allowed)

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.