7.9: Spin–orbit coupling:

$$\vec{L} = \sum_i \vec{\ell}_i \qquad \vec{S} = \sum_i \vec{s}_i \qquad \vec{J} = \vec{L} + \vec{S}$$

Russell–Saunders coupling assumes that coupling interactions between the electrons are stronger than between individual spin angular momenta and orbital angular momenta.

Otherwise: $\qquad \vec{J} = \sum_i \vec{j}_i = \sum_i \left(\vec{\ell}_i + \vec{s}_i \right) \quad$ = j-j coupling

Russell–Saunders Term Symbols: used to designate electron energy states in multielectron atoms

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

> The degeneracy of ^{2S+1}L energy level
> $$g_{LS} = (2S+1)(2L+1)$$

a) **Total Orbital Angular Momentum**

$$L = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \dots$$
$$= S \quad P \quad D \quad F \quad G \quad H \quad I \quad J \quad K \dots$$

Compare with H-atom:

$$\ell = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \dots$$
$$= s \quad p \quad d \quad f \quad g \quad h \quad i \quad j \quad k \dots$$

Similar: In H-atom these are states which correspond to a unique one–electron configuration. In multielectron atoms one electron configuration can give rise to many terms.

b.) Total Spin Angular Momentum

Gives rise to (2S+1) multiplicity of states.

$$S \quad = 0 \quad \frac{1}{2} \quad 1 \quad \frac{3}{2} \quad 2 \quad \ldots$$

$$2S+1 = 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad \ldots$$

singlet $\quad$ triplet $\quad$ quintet

doublet $\quad$ quartet
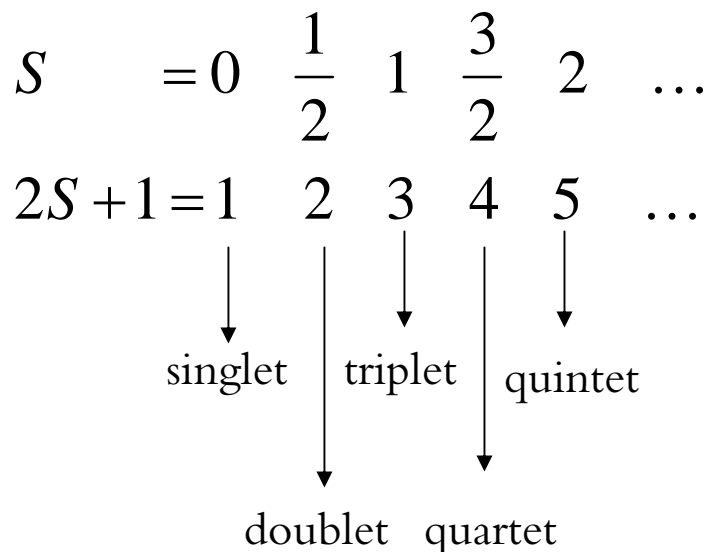
c.) Atomic states with common L and S values are said to belong to the same term

For example:

$$^2S \qquad ^2P \qquad ^2D$$

$$L = 0 \quad L = 1 \quad L = 2$$

$$S = \frac{1}{2} \quad S = \frac{1}{2} \quad S = \frac{1}{2}$$

d.) Total angular momentum determines level

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

States belonging to the same term and same level have approximately the same energy, although spin–orbit interactions cause small but measurable shifts.

e.) Pauli Exclusion Principle (PEP)

Equivalent electrons have same n, ℓ

Particles with half–integer spins are **FERMIONS**
Particles with integer spins are **BOSONS**

Wave functions describing a system of fermions must be **antisymmetric** with respect to interchange of ay pair of fermions.
The implication of this is that no two wave functions can have the same set of quantum numbers.

Wave functions describing a system of bosons must be **symmetric** with respect to interchange of any pair of bosons.
The implication of this is that any and all wave functions can have the same set of quantum numbers.

Consider **two non-equivalent p electrons**: configuration = $(np^1)(n'p^1)$. Since n $\neq$ n', the Pauli principle is not a factor here. Therefore we can use what we've learnt from the Clebsch–Gordon series to derive terms and levels.

$$\ell_1 = 1, s_1 = \frac{1}{2}; \ell_2 = 1, s_2 = \frac{1}{2}$$

$$L = (\ell_1 + \ell_2) \to |\ell_1 - \ell_2| = (1 + 1) \to |1 - 1| = 2,1,0$$

$$S = (s_1 + s_2) \to |s_1 - s_2| = \left(\frac{1}{2} + \frac{1}{2}\right) \to \left|\frac{1}{2} - \frac{1}{2}\right| = 1,0$$

$$(2S + 1) = 3,1$$

$$J = (L + S) \to |L - S| = (2 + 1) \to |2 - 1| = 3,2,1$$

$$= (2 + 0) \to |2 - 0| = 2$$

$$= (1 + 1) \to |1 - 1| = 2,1,0$$

$$= (1 + 0) \to |1 - 0| = 1$$

$$= (0 + 1) \to |0 - 1| = 1$$

$$= (0 + 0) \to |0 - 0| = 0$$

Terms and levels are:

$$^3D_{3,2,1} \quad ^3P_{2,1,0} \quad ^3S_1$$

$$^1D_2 \quad\quad ^1P_1 \quad\quad ^1S_0$$

Six terms, 10 levels for one electron configuration.

Now consider two equivalent p electrons: electron configuration is $(np)^2$

Here the Pauli Exclusion Principle is important. To see why set up a table as shown:

$m_\ell(1)$	$m_\ell(2)$	$m_s(1)$	$m_s(2)$	M_L	M_S	Comment
1	1	$\frac{1}{2}$	$\frac{1}{2}$	2	1	× PEP
1	1	$\frac{1}{2}$	$-\frac{1}{2}$	2	0	
1	1	$-\frac{1}{2}$	$\frac{1}{2}$	2	0	× same as line above
1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	2	−1	× PEP
1	0	$\frac{1}{2}$	$\frac{1}{2}$	1	1	
1	0	$\frac{1}{2}$	$-\frac{1}{2}$	1	0	
1	0	$-\frac{1}{2}$	$\frac{1}{2}$	1	0	
1	0	$-\frac{1}{2}$	$-\frac{1}{2}$	1	−1	
1	−1	$\frac{1}{2}$	$\frac{1}{2}$	0	1	
1	−1	$\frac{1}{2}$	$-\frac{1}{2}$	0	0	
1	−1	$-\frac{1}{2}$	$\frac{1}{2}$	0	0	
1	−1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	−1	
0	−1	$\frac{1}{2}$	$\frac{1}{2}$	−1	1	
0	−1	$-\frac{1}{2}$	$\frac{1}{2}$	−1	0	
0	−1	$\frac{1}{2}$	$-\frac{1}{2}$	−1	0	
0	−1	$-\frac{1}{2}$	$-\frac{1}{2}$	−1	−1	
0	1					× same as 1 0
−1	1					× same as 1 −1
0	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	0	
0	0	$-\frac{1}{2}$	$\frac{1}{2}$	0	0	× same as above
−1	−1	$\frac{1}{2}$	$-\frac{1}{2}$	−2	0	
−1	−1	$-\frac{1}{2}$	$\frac{1}{2}$	−2	0	× same as above
0	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$			× PEP
−1	−1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$			× PEP

Construct a **Slater Diagram**

$$\frac{M_L \mid M_S}{\downarrow} \rightarrow \qquad \underline{-1} \qquad \underline{0} \qquad \underline{+1}$$

M_L	$M_S \rightarrow$	-1	0	$+1$
$+2$				
$+1$		$\mid$	$\parallel$	$\mid$
0		$\mid$	$\parallel\mid$	$\mid$
-1		$\mid$	$\parallel$	$\mid$
-2			$\mid$	

$$= \begin{pmatrix} \mid \\ \mid \\ \mid \\ \mid \\ \mid \end{pmatrix} + \begin{pmatrix} \mid & \mid & \mid \\ \mid & \mid & \mid \\ \mid & \mid & \mid \end{pmatrix} + \left(\mid \right)$$

$$= {}^1D \;+\; {}^3P \;+\; {}^1S$$

$$\Rightarrow \; L = 2 \qquad\quad 1 \qquad\quad 0$$
$$S = 0 \qquad\quad 1 \qquad\quad 0$$
$$J = 2 \qquad\quad 2,1,0 \qquad 0$$

Parity $= \;\; (-1)^{\sum\limits_{i=1}^{2}\ell_i} = (-1)^{\ell_1 + \ell_2} = (-1)^{1+1} = (-1)^2 = +1$

All states are gerade (even)
regardless of L.

Given that we can determine terms from a configuration, how do we order them by energy?

Two options:

1.) Do a high level quantum mechanical calculation: involved

2.) Make an intelligent guess. We can do this by invoking **Hund's Rules**

Warning:
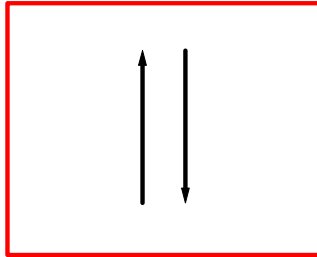
Very approximate and only valid for ground state configurations. Also presumes L-S coupling is valid

Hund's Rule #1: States of highest spin multiplicity (2S+1) lies lowest in energy.
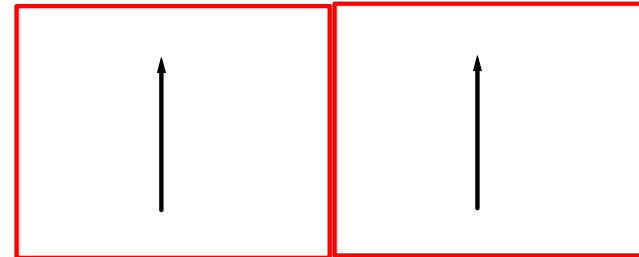
The explanation of the rule lies in the effects of the **spin–spin interaction**.

S = 0   **S = 1**

versus

-same orbital   -different spatially oriented orbitals
-electrons closer together   -electrons are farther apart
-more e^- – e^- repulsion   -less e^- – e^- repulsion

Hund's Rule #2: For a given S (or 2S+1) the state of highest L lies lowest in energy.

e⁻   e⁻

e⁻   +Ze   versus   e⁻   +Ze

e⁻   e⁻

e⁻   e⁻
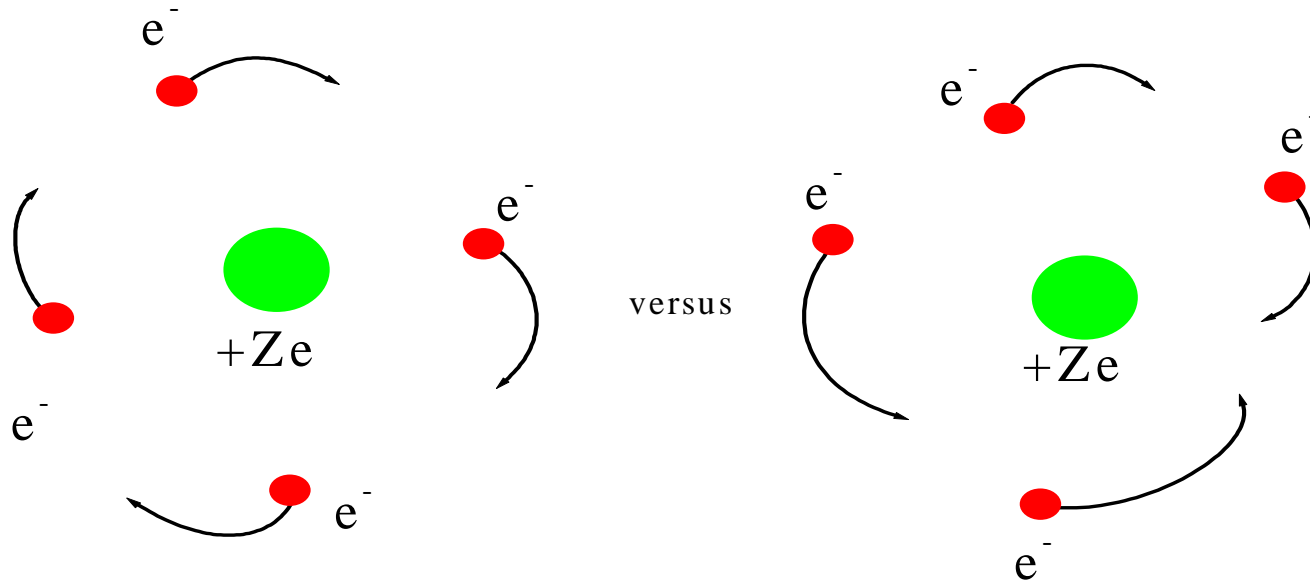
–higher L; that is electrons "orbit"
 in same direction and keep out
of each other's way.
–minimizes e⁻ –e⁻ repulsions.

–lower L; that is, some electrons
"orbit" in the opposite direction to
others and therefore can not avoid
each other
–increased e⁻ – e⁻ repulsions.