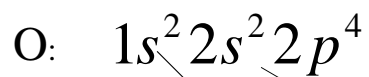


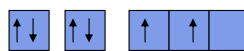
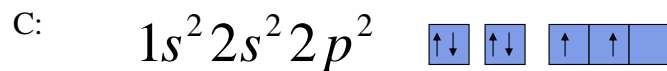
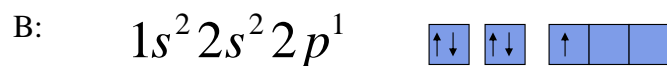
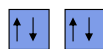
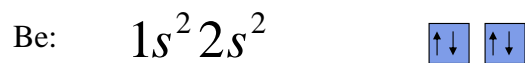


Example:



$$\sigma_{2p} = 2(0.85) + 5(0.35) = 4.55$$

$$Z_{eff} = Z - \sigma = 8 - 4.55 = 3.45$$



Hund's rule: For any set of orbitals of equal energy (degenerate orbitals), the electron configuration with the maximum number of parallel spins is the ground state.



Now 4s, 3d orbitals:



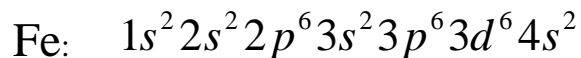
For neutral, many-electron atoms, the 4s orbital is filled before the 3d orbital.

How to write the electron configuration?

In the sequence of ionization energy from left to right, those first be removed, in the right.



Note the aufbau process gives you: ~~$[Ar]4s^2 3d^6$~~



3p $\sigma_{3p} = 7(0.35) + 8(0.85) + 2(1.00) = 11.25$

3d $\sigma_{3d} = 5(0.35) + 18(1.00) = 19.75$

4s $\sigma_{4s} = 1(0.35) + 14(0.85) + 10(1.00) = 22.25$

$$Z_{eff}(3p) = 14.75$$

$$Z_{eff}(3d) = 6.25$$

$$Z_{eff}(4s) = 3.75$$



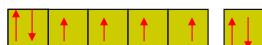
$$E(3p) < E(3d) < E(4s)$$

4s electrons will be first removed!



Question:

Since $E(3d) < E(4s)$, why not $[Ar]3d^8$??



1. Electron-electron repulsion
2. Spin-pairing energy

Compare the total energy



$$a^m b^n$$

Binding energy

$$E(A) = -mW(a) - nW(b) + \frac{m(m-1)}{2} J(a,a)$$

$$+ m \cdot n J(a,b) + \frac{n(n-1)}{2} J(b,b)$$

e-e repulsion



Example: Sc Z=21

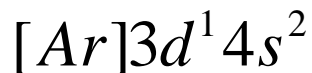
$$[Ar]3d^1 4s^2 \quad E = -W(d) - 2W(s) + 2J(ds) + J(ss)$$

$$[Ar]3d^3 \quad E = -3W(d) + 3J(dd)$$

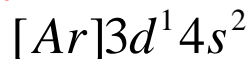
$$\begin{aligned} W(d) &= 24.75 \text{ eV} \\ W(s) &= 21.60 \text{ eV} \\ J(ds) &= 8.38 \text{ eV} \\ J(dd) &= 11.78 \text{ eV} \\ J(ss) &= 6.6 \text{ eV} \end{aligned}$$

$$\begin{aligned} E(3d^3) - E(3d^1 4s^2) \\ &= -2W(d) + 3J(dd) + 2W(s) - 2J(ds) - J(ss) \\ &= 5.68 \text{ eV} \end{aligned}$$

Ground state:



e-e repulsion in d orbital: **ground state**



Stronger shielding for 4s, smaller effective Z:

4s electron will be first removed.

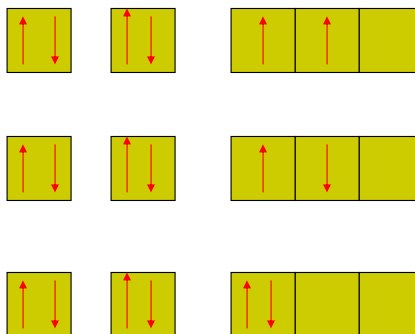
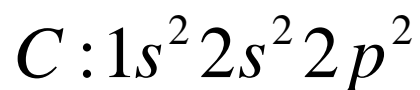
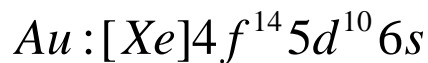
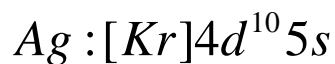
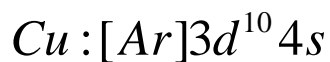
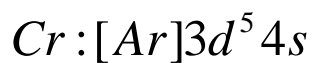
Ground state for





Exceptions:

Special stability of half-filled and filled shell:



These microstates are defined by a set of unique quantum numbers and correspond to electronic states of a specific energy.



Atomic Energy States

Term Symbol

Reading: DG 1



Atomic energy states

Total orbital angular momentum **L**

Total spin angular momentum **S**

Total angular momentum **J**

$$2S+1L_J$$

Term Symbol

$${}^2S_{1/2} \quad \text{Double S one-half}$$

n electron system

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$$L = l_1 + l_2 + \dots + l_n,$$
$$l_1 + l_2 + \dots + l_n - 1,$$
$$l_1 + l_2 + \dots + l_n - 2, \dots$$

If all l are equal, the minimum is zero, if one l is larger than the others, the minimum is that given by orienting the other angular momentum to oppose it as long as $L \geq 0$. (*vector sum of all vector l_j*).

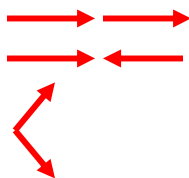
Designation: $L = 0, 1, 2, 3, 4, 5, \dots$
S, P, D, F, G, H, \dots

Example:

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$$p^2 (l_1=1, l_2=1): L=2, 1, 0$$



$$p^2 f^1 (l_1=1, l_2=1, l_3=3)$$



$$L=5, 4, 3, 2, 1$$





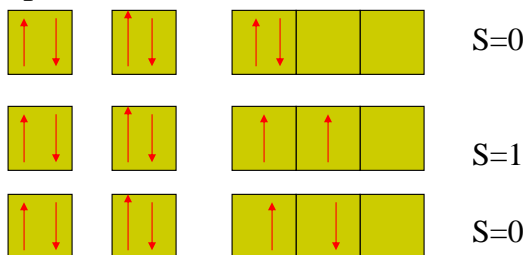
Total spin angular momentum **S**:

$S = n/2, n/2-1, n/2-2, \dots, 0$, for n even

$S = n/2, n/2-1, n/2-2, \dots, 1/2$, for n odd

Vector sum of all of the vector \vec{s}_i

$C: 1s^2 2s^2 2p^2$



Spin multiplicity = $2S+1$

$S=0$, $2S+1=1$, singlet

$S=1/2$, $2S+1=2$, Doublet

$S=1$, $2S+1=3$, Triplet.

Total angular momentum **J**:

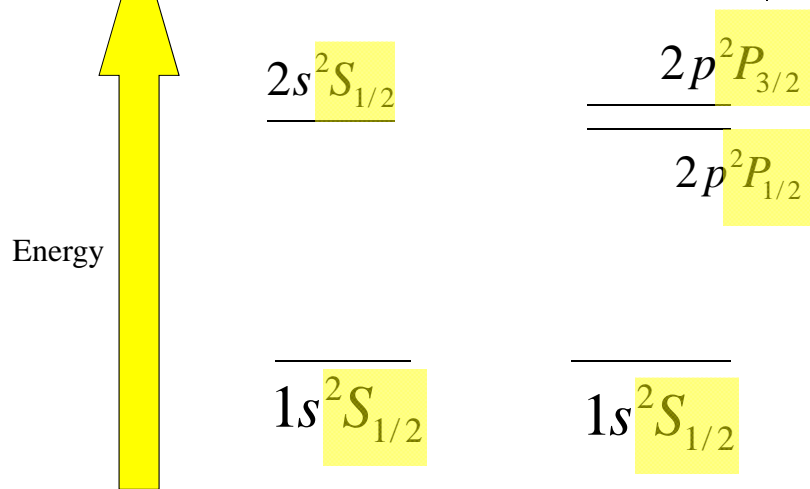
$J = L+S, L+S-1, \dots, |L-S|$

Allowed vector sum for

$\vec{L} + \vec{S}$



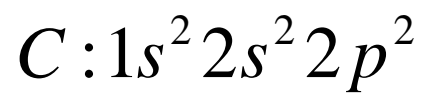
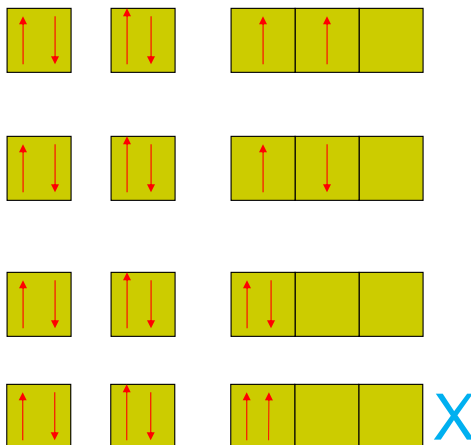
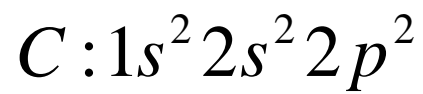
Hydrogen atom Ground state vs. Excited States



Electron configuration: $2p^1 3p^1$

Term Symbols:

		S
L	0	1
2	1D_2	$^3D_{3,2,1}$
1	1P_1	$^3P_{2,1,0}$
0	1S_0	3S_1



???

		S
L	0	1
2	1D_2	${}^3D_{3,2,1}$
1	1P_1	${}^3P_{2,1,0}$
0	1S_0	3S_1



M_L : total orbital-orientation quantum No.

$$M_L = \sum m_l = 0, \pm 1, \pm 2, \dots \pm L$$

$2L + 1$ possible values

$$L = \max(M_L)$$

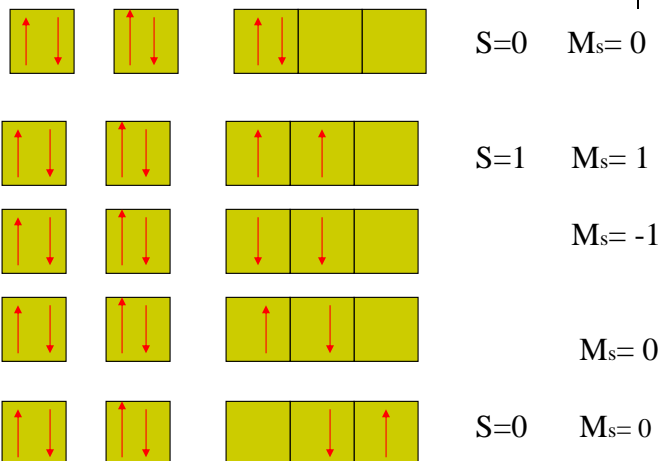
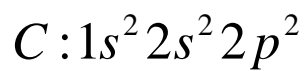


For a given value of S , there will be $2S+1$ spin states characterized by M_S .

$$M_S = \sum m_s$$

$$M_S = S, S-1, S-2, \dots, -S$$

$$S = \max(M_S)$$



Atomic energy states

Total orbital angular momentum **L**

Total spin angular momentum **S**

Total angular momentum **J**

$$2S+1L_J$$

M_L : total orbital-orientation quantum No.

$$M_L = \sum m_l = 0, \pm 1, \pm 2, \dots, \pm L$$

$$M_S = \sum m_s$$

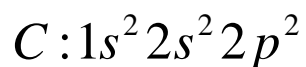
$$L = \max(M_L)$$

$$S = \max(M_S)$$



In general, the total No. of ways N that x electrons can be placed into y orbitals of equivalent energy with either spins is given by

$$N = \frac{(2y)!}{x!(2y-x)!}$$



$$\frac{6!}{2!4!} = 15 \text{ microstates}$$

$4! = \text{Factorial } 4 = 1 \times 2 \times 3 \times 4$




Step I:

Sum all m_s and m_l for each microstates,
Determine M_S , M_L for each

$$M_S = \sum m_s$$


$$M_L = \sum m_l$$

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$$M_S = \sum m_s$$

$$M_L = \sum m_l$$

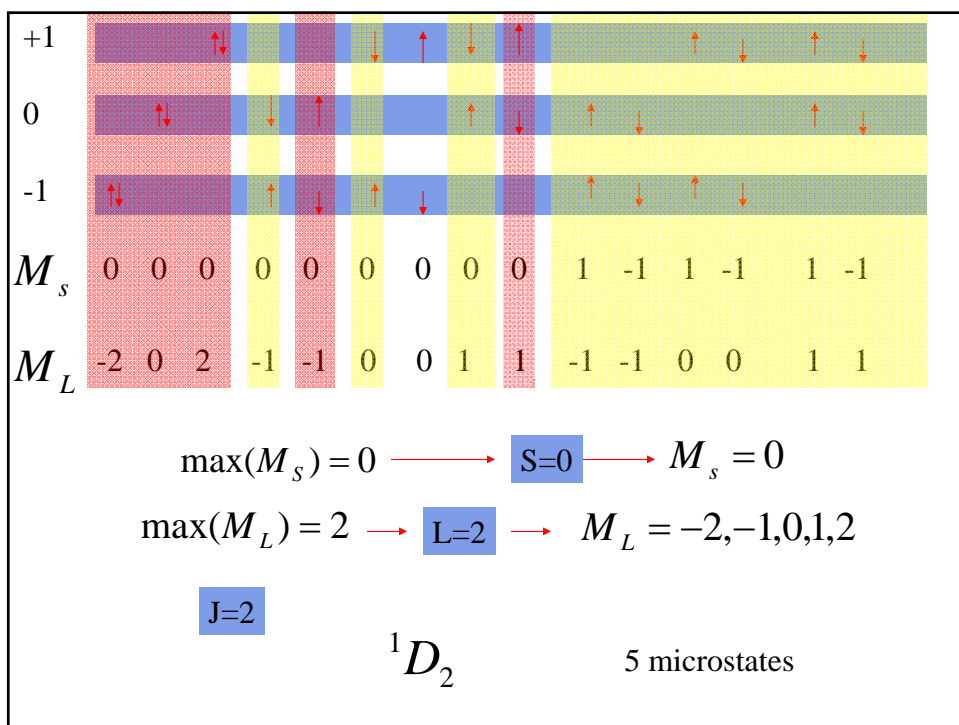
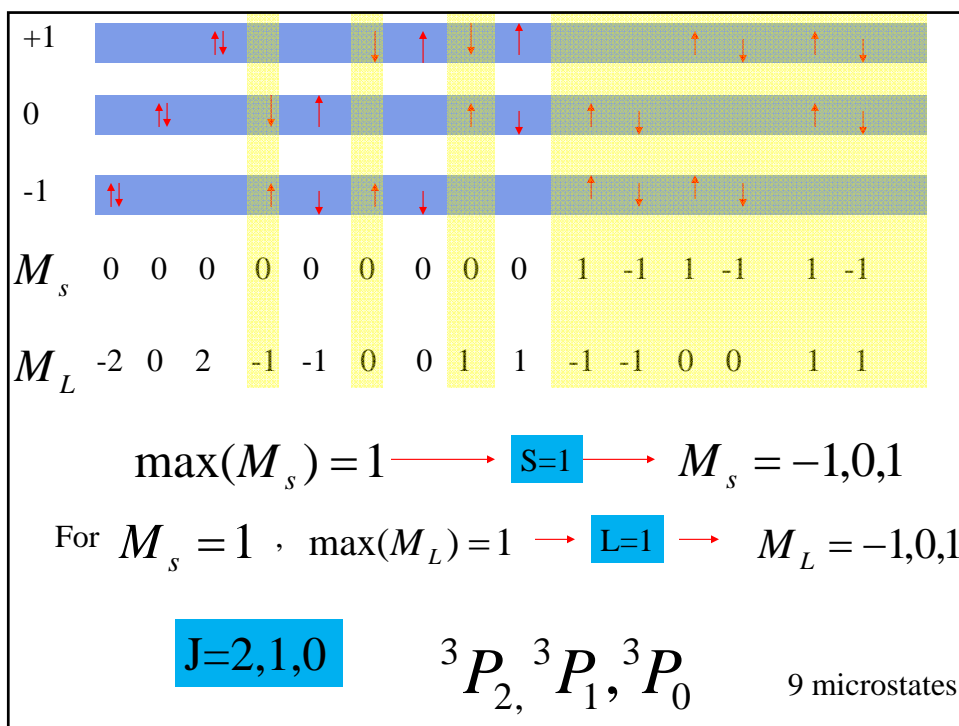
m_l														
+1	↑↓			↓	↑	↓	↑	↑	↓	↑	↓	↑	↓	↑
0	↑↓	↑↓	↑↓	↓	↑	↑	↓	↑	↓	↑	↓	↑	↓	↑
-1	↑↓	↑↓	↑↓	↑	↓	↑	↓	↑	↓	↑	↓	↑	↓	↑
M_S	0	0	0	0	0	0	0	0	0	1	-1	1	-1	1
M_L	-2	0	2	-1	-1	0	0	1	1	-1	-1	0	0	1

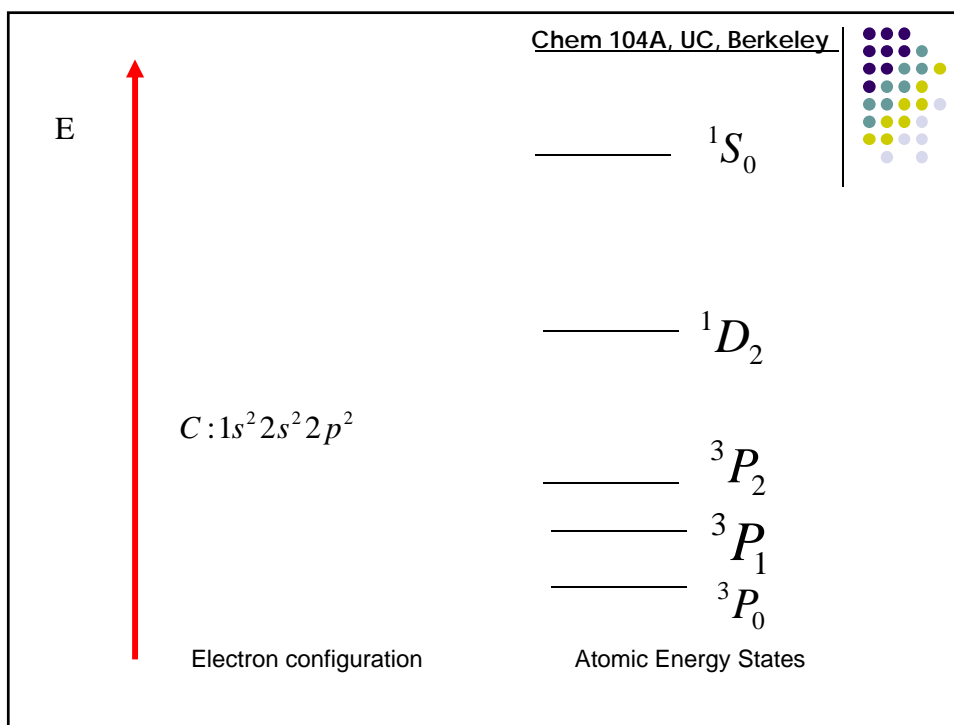
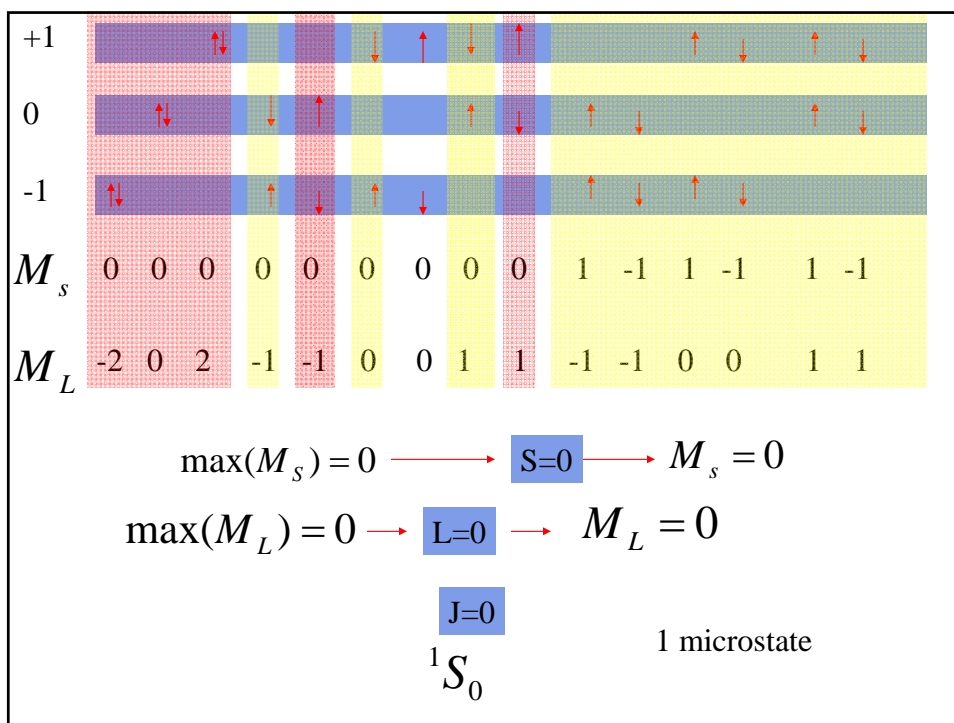
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Step II:
Starting with maximum M_S , partition microstates into sets.

Note: A term ^{2S+1}L corresponds to $(2L+1) \times (2S+1)$ microstates

$S = \max(M_S)$
 $L = \max(M_L)$







Ground State Terms for many-electron atoms:

determine which of several energy states will be lowest in energy.

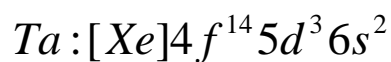
1. The ground state term always has maximum spin multiplicity. therefore, for the carbon atom, the ${}^3P_{2,1,0}$ terms will be more stable than the 1D_2 and 1S_0

2. When comparing two states of the same spin multiplicity, the state with the higher L value is usually more stable. This is the case with the 1D_2 and 1S_0 of the carbon atom.

3. For given S and L values, the minimum J value is most stable if there is a single open subshell that is **less than half-full**, and the maximum J is most stable if the subshell is **more than half-fill**. Thus for the carbon atom, the 3P_0 state is the ground state term.



Example:



Rule 1. $\rightarrow S=3/2 \rightarrow 2S+1 = 4$

Rule 2. $\rightarrow \max(M_L) \rightarrow L=3$

Rule 3. $\rightarrow J_{\min}=3/2$

${}^4F_{3/2}$ Ground state



Identifying Ground State:

$3d^5$

${}^6S_{5/2}$

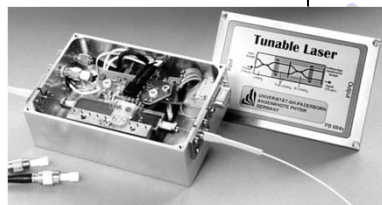
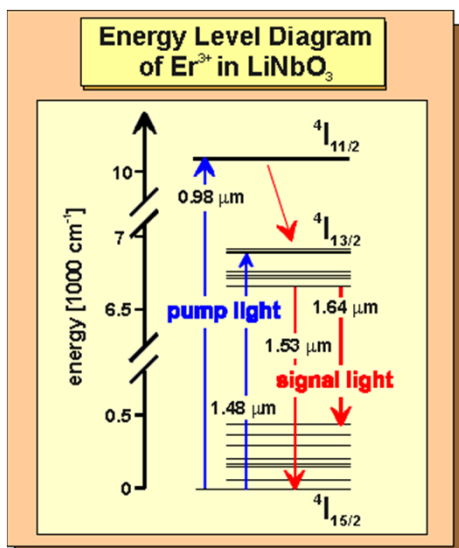
$3d^2$

3F_2

$3d^8$

3F_4

Term Symbol: example



Er^{3+}

$[Xe]4f^{11}$