Physical Chemistry II: Quantum Chemistry
Lecture 18:Many-electron Atoms & Atomic Term Symbols

Yuan-Chung Cheng
yuanchung@ntu.edu.tw
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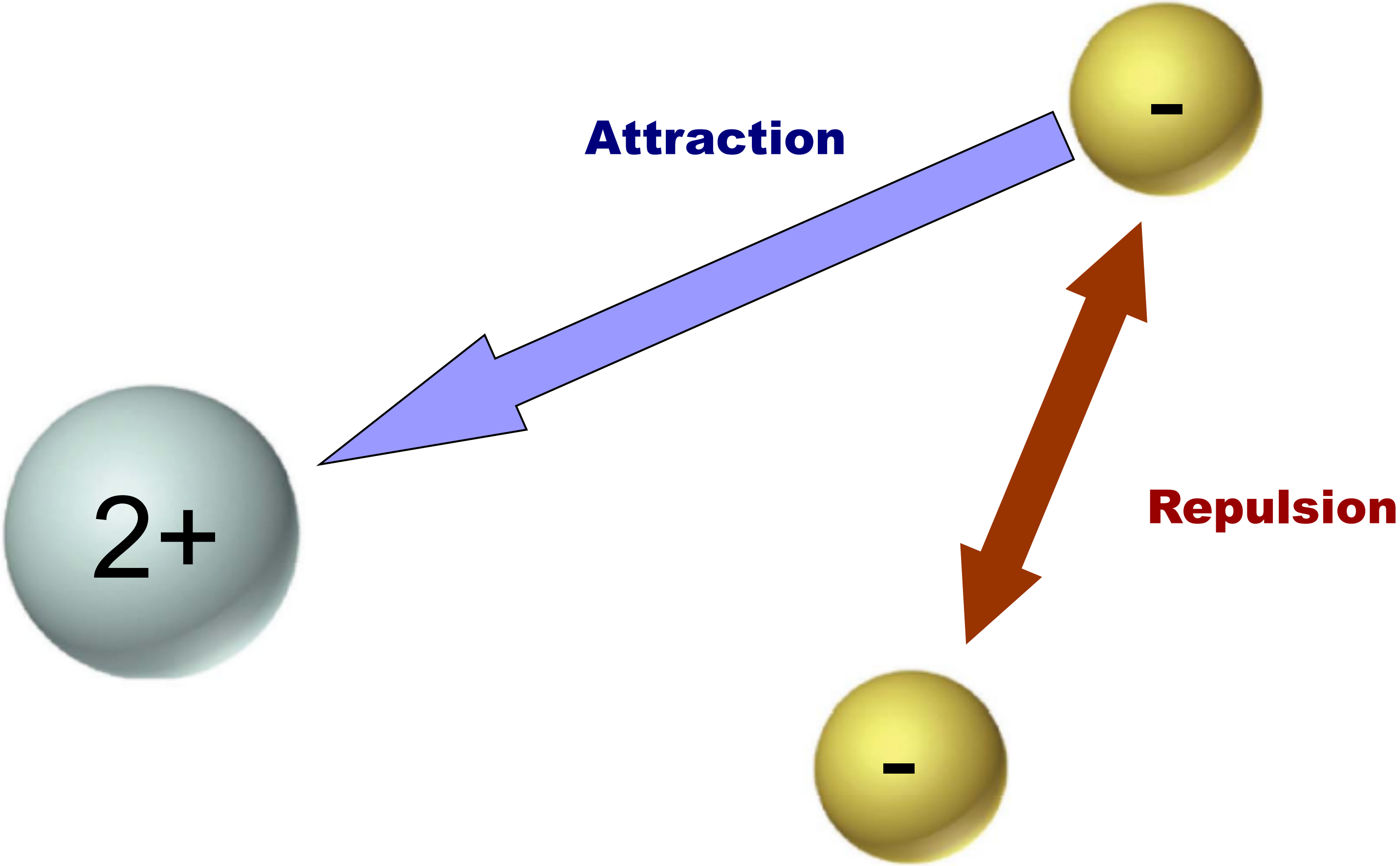
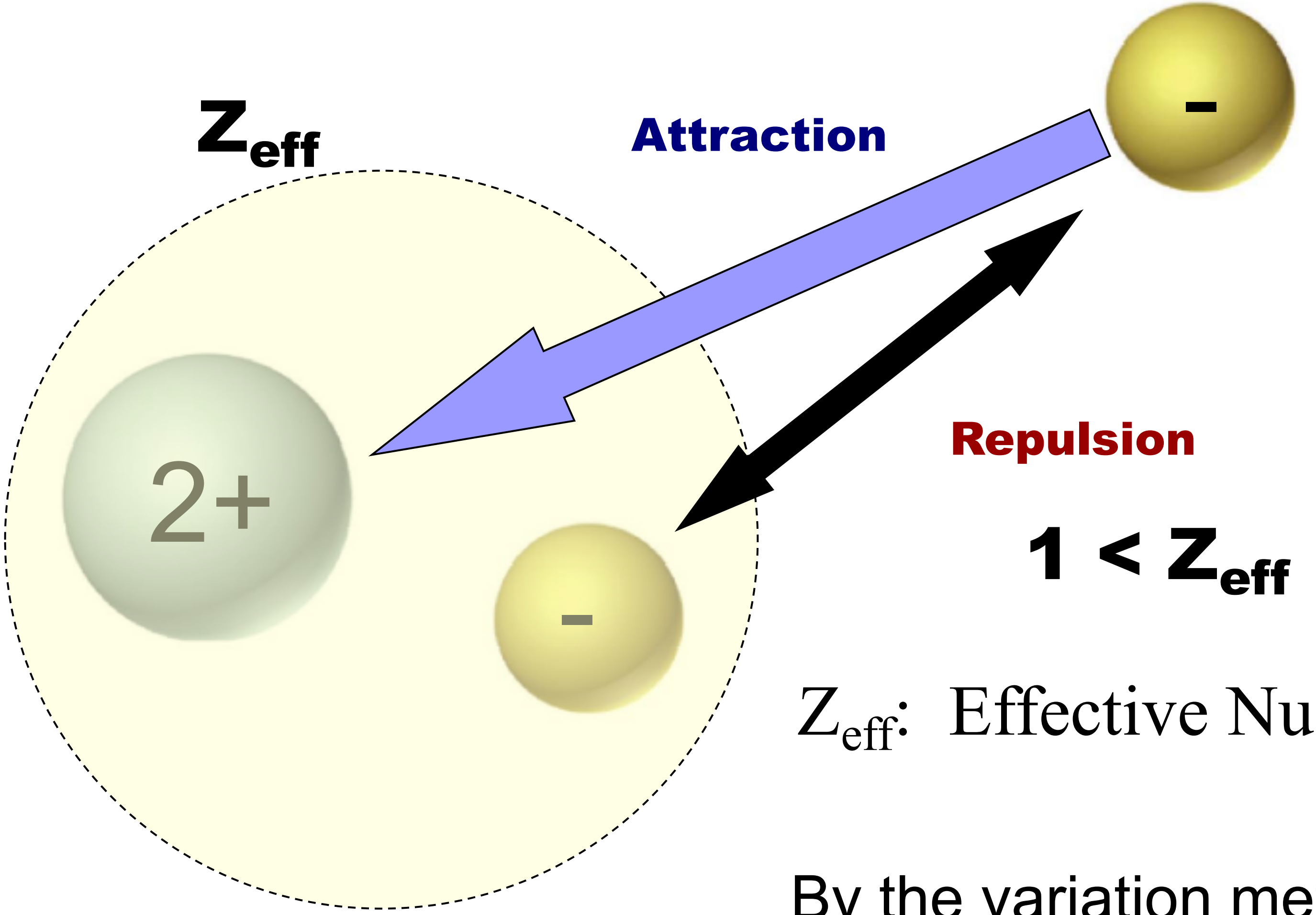
Courtesy of Prof. Jerry Chen

He: Two-Electron Atom



He: Two-Electron Atom



$1 < Z_{eff} < 2$

Z_{eff}: Effective Nuclear Charge

By the variation method, Z_{eff} is calculated as 1.69

Atomic Orbitals for Many-Electron Atoms

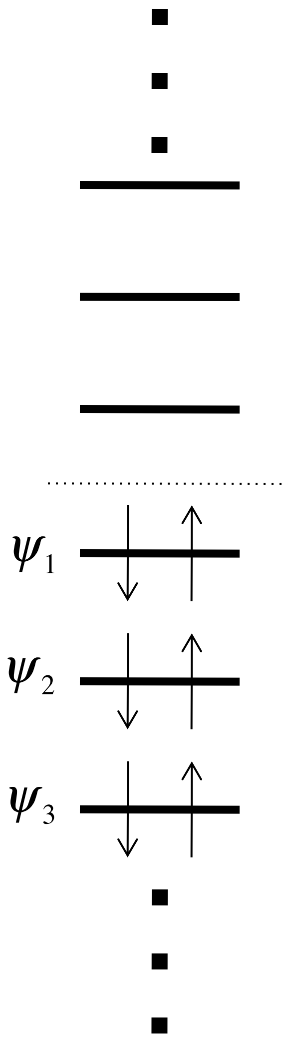
$$\hat{H}\,\Psi = E\,\Psi$$

No analytical solutions even for He because of electron repulsion

He and Li atoms can be handled by variation methods

Need more practical approach for other atoms!

Hartree-Fock Self-Consistent Field Method



Single-electron wavefunction:

$\psi_i(\mathrm{x}_1)$: atomic spin orbital

x_1 : electron variable

Example for 1*s*: $\psi_{1s}(r) = \sum_{a=1}^{m} c_a N_a e^{-Z_a r/a_0}$

linear combination of basis functions with variational parameters

N-electron wavefunction: Slater determinants

$$\Psi(\mathrm{x}_1,\ldots,\mathrm{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathrm{x}_1) & \psi_2(\mathrm{x}_1) & \cdots & \psi_N(\mathrm{x}_1) \\ \psi_1(\mathrm{x}_2) & \psi_2(\mathrm{x}_2) & \cdots & \psi_2(\mathrm{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathrm{x}_N) & \psi_2(\mathrm{x}_N) & \cdots & \psi_N(\mathrm{x}_N) \end{vmatrix}$$

Mean-Field Approximation

Many-electron Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\frac{Ze^2}{r_i} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{e^2}{r_{ij}}$$

Many-electron Integrals:

$$\left\langle \psi_1\psi_2\cdots\psi_j\cdots\left|\sum_{j=2}^{N}\frac{e^2}{r_{1j}}\right|\psi_1\psi_2\cdots\psi_j\cdots\right\rangle = \sum_{j=2}^{N}\left\langle\psi_1\psi_j\left|\frac{e^2}{r_{1j}}\right|\psi_1\psi_j\right\rangle$$

$$= \sum_{j=2}^{N}\iint |\psi_1|^2|\psi_j|^2\frac{e^2}{r_{1j}}d\tau_1 d\tau_2$$

$$= \int|\psi_1|^2\left\{\sum_{j=2}^{N}\int\frac{e^2|\psi_j|^2}{r_{1j}}d\tau_2\right\}d\tau_1$$

A Slater determinant,
product of spin orbitals

Mean-field term due to averaged distribution of all other electrons

Mean-Field Approximation

Hartree-Fock Mean-field Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\frac{Ze^2}{r_i} + \frac{1}{2}\sum_{i=1}^{N}V_i(r_i) \equiv \sum_{i=1}^{N}\hat{h}_i$$

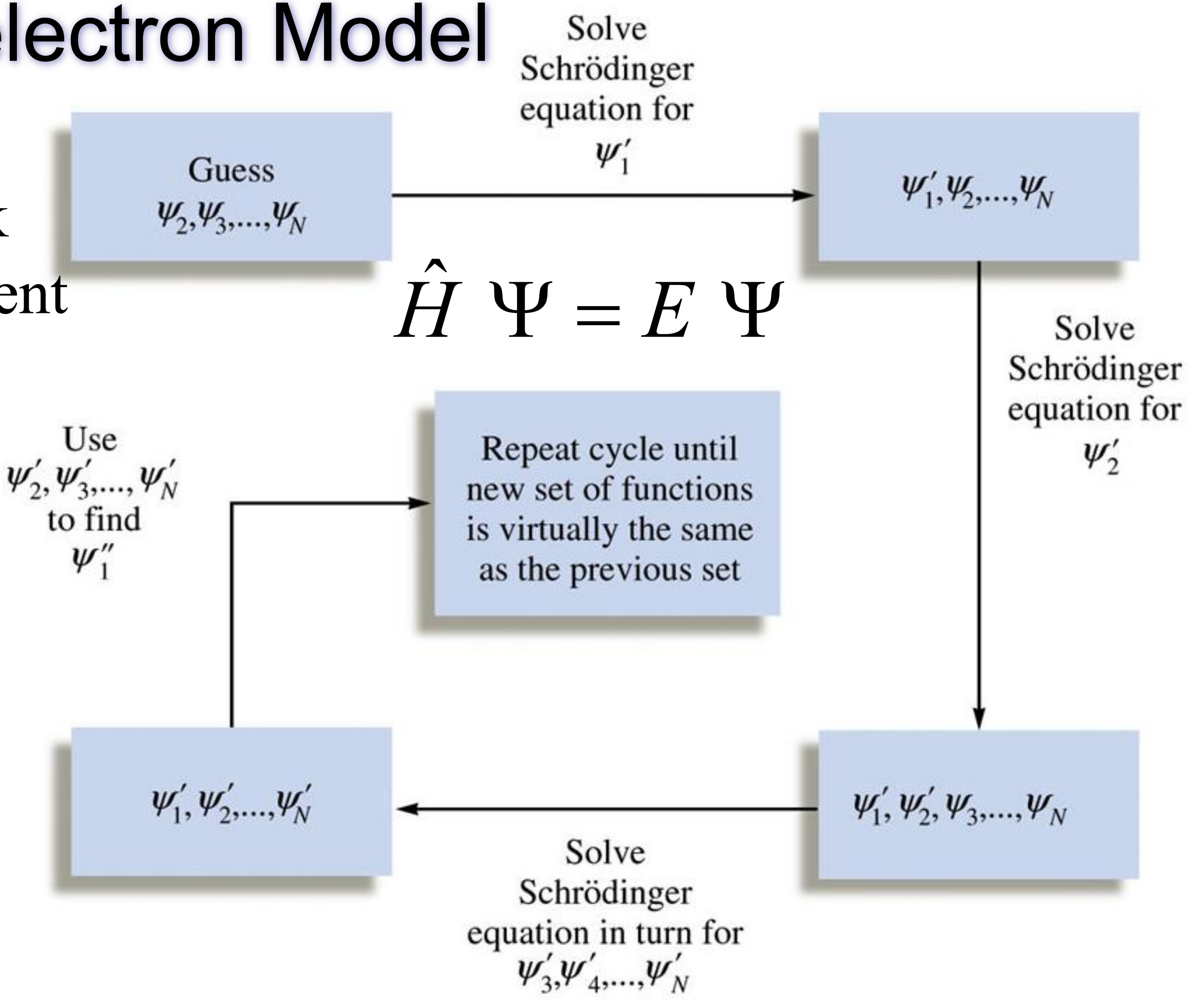
$$\text{where } V_i(r_i) = \sum_{j\neq i}^{N} e^2 \int \frac{|\psi_j|^2}{r_{ij}} d\tau_j$$

- Single determinantal wavefunction leads naturally to the mean-field approximation
- The approximation allows a factorization of the Hamiltonian into N single-electron problems
- Given a basis, the theory provides a variational groundstate & **optimal atomic orbitals within the single determinant approximation ➔** mean-field, no electron correlations
- N single-electron Schrodinger equations are interdependent ➔ requires solving self-consistently via an iterative procedure

Many-electron Model

Hartree-Fock (Self-consistent field, SCF) Method

$$\hat{H}\,\Psi = E\,\Psi$$



Guess $\psi_2, \psi_3, \ldots, \psi_N$

Solve Schrödinger equation for ψ'_1

$\psi'_1, \psi_2, \ldots, \psi_N$

Solve Schrödinger equation for ψ'_2

$\psi'_1, \psi'_2, \psi_3, \ldots, \psi_N$

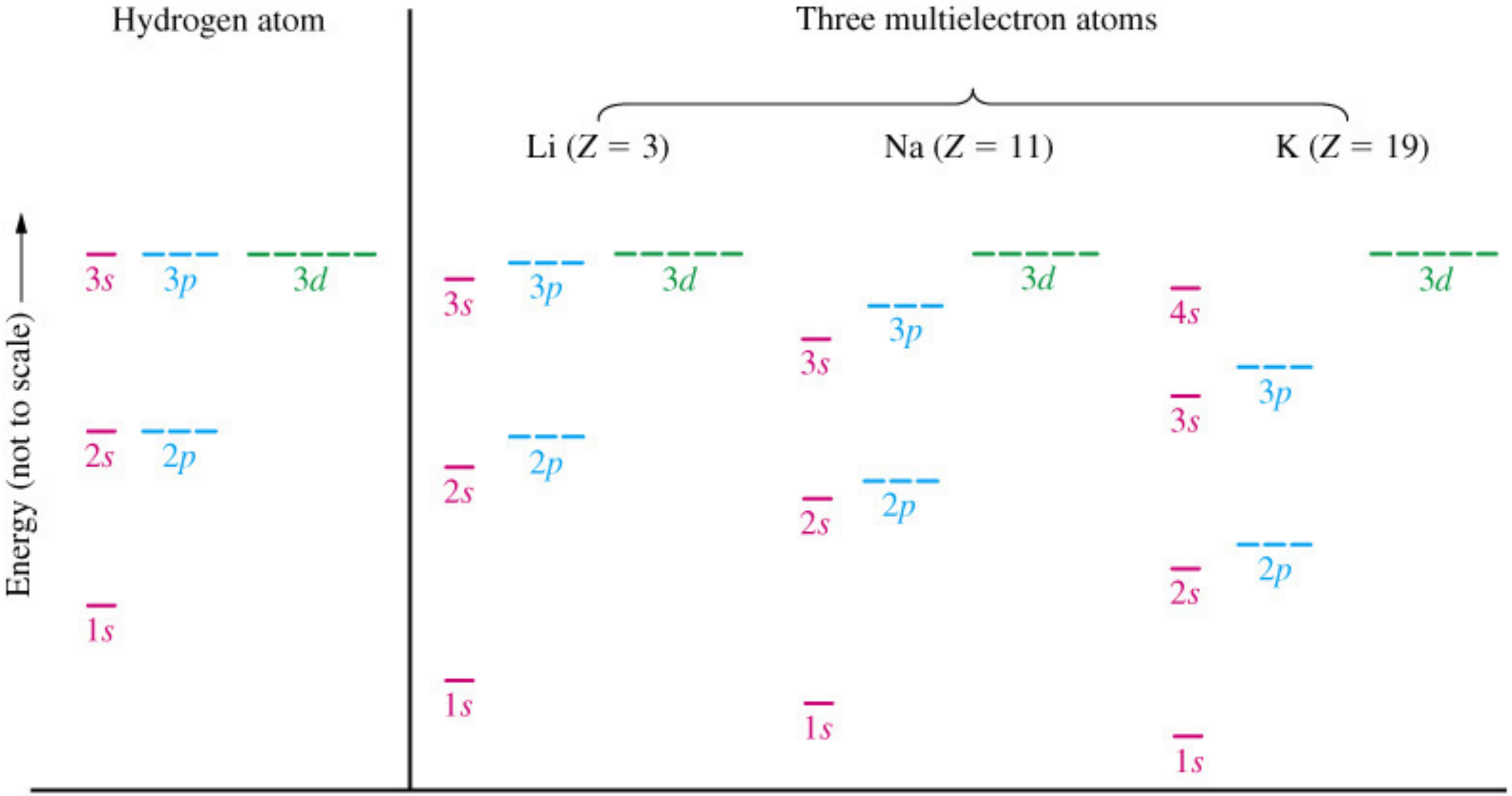
Solve Schrödinger equation in turn for $\psi'_3, \psi'_4, \ldots, \psi'_N$

$\psi'_1, \psi'_2, \ldots, \psi'_N$

Use $\psi'_2, \psi'_3, \ldots, \psi'_N$ to find ψ''_1

Repeat cycle until new set of functions is virtually the same as the previous set

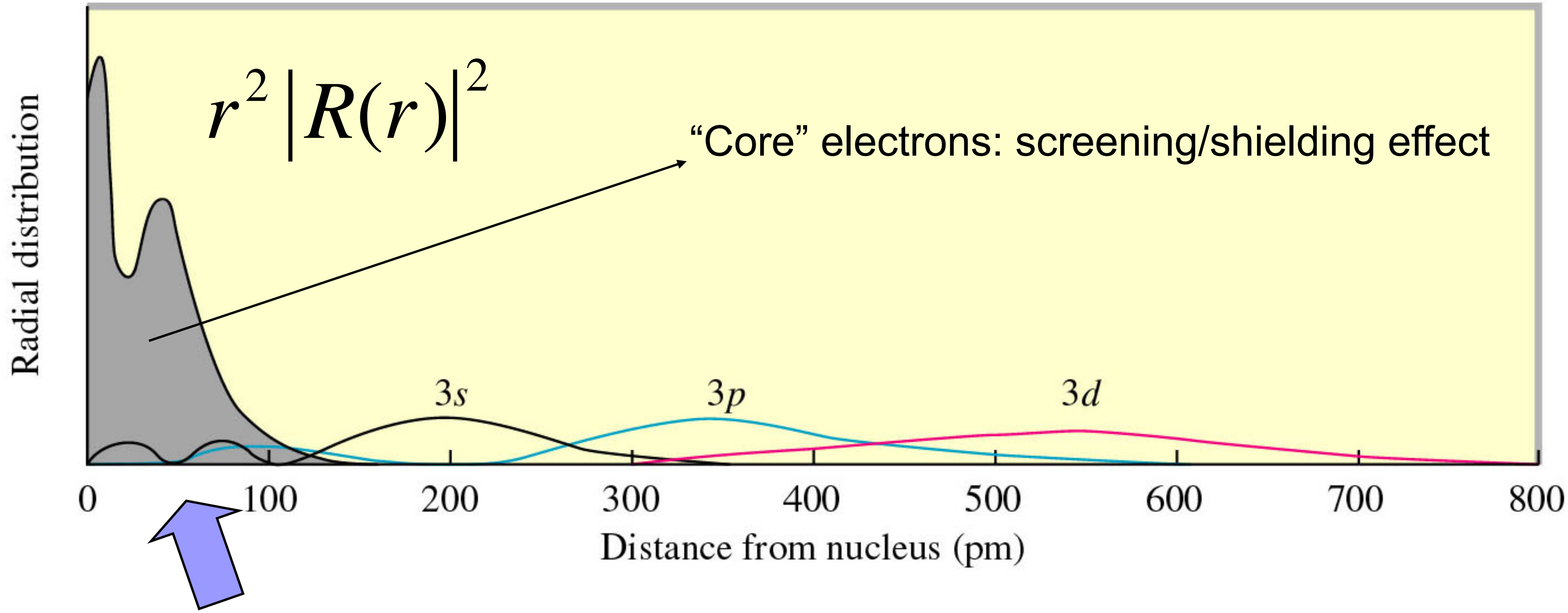
Atomic Orbitals for Many-Electron Atoms



The concept of orbital is exact

The use of “orbital” is just a good approximation

Na Radial Distribution Function for "Valance" Orbitals



$r^2|R(r)|^2$

"Core" electrons: screening/shielding effect

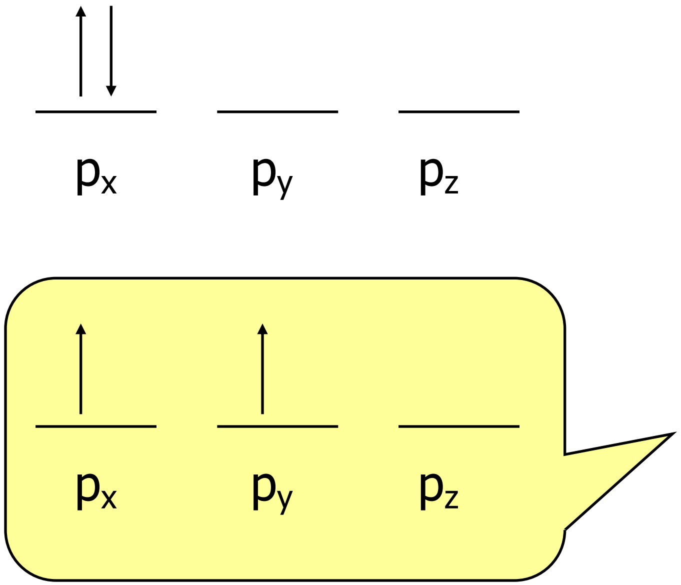
Penetration effect
of the 3s and 3p orbitals

$$E_{3s} < E_{3p} < E_{3d}$$

Increase screening

Hund’s Rule

For degenerate orbitals, electrons occupy them one at a time.



p_x p_y p_z

Less likely

p_x p_y p_z

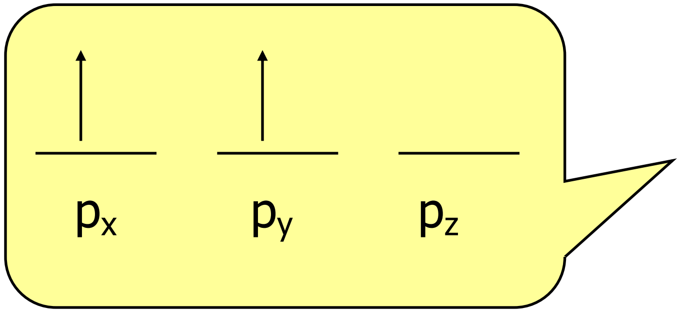
Likely

Hund’s Rule

Smaller electrostatic repulsion?

The electron-electron repulsion does not allow the two electrons getting too close to each other.

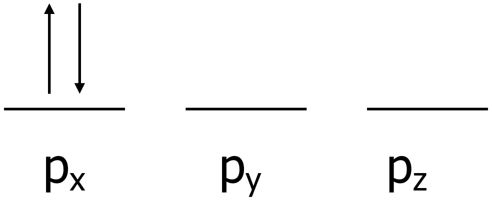
However, this explanation is now obsolete.



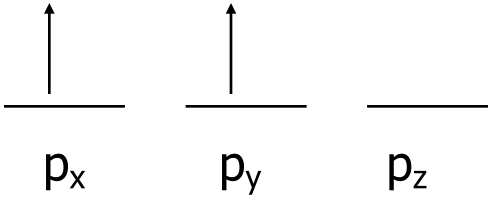
Likely

Hund’s Rule

“Exchange energy” makes the triplet configuration more stable



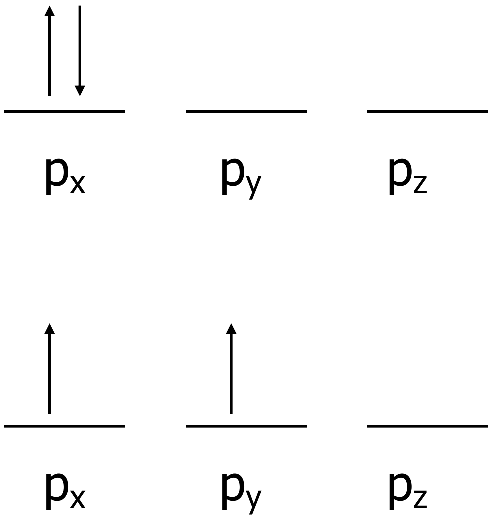
Different spins: two electrons do not exchange



Same spin: two electrons can exchange

Hund’s Rule

Larger electron-nucleus interaction due to less screening when two different orbitals are occupied!



Less likely

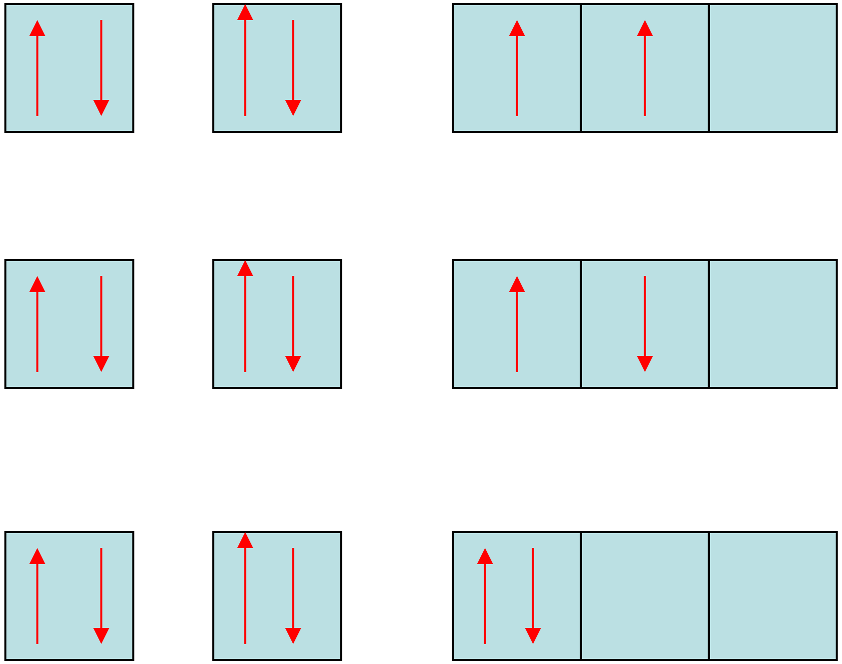
Likely

Proven by exact QM calculations, see Levine.

Atomic Energy States

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

"Electron configuration" along does not fully specify the "state" of a many-electron system.



These three arrangements (states) have different energies when electron-electron repulsions are included!

Depending on total angular momentum!

Atomic Energy States -- Terms

The energy of a many-electron state depends on the total orbital angular momentum and total spin angular momentum of the state.

$$\hat{L} = \hat{L}_1 + \hat{L}_2 + \hat{L}_3 + \ldots$$

$$\hat{S} = \hat{S}_1 + \hat{S}_2 + \hat{S}_3 + \ldots$$

Notations:

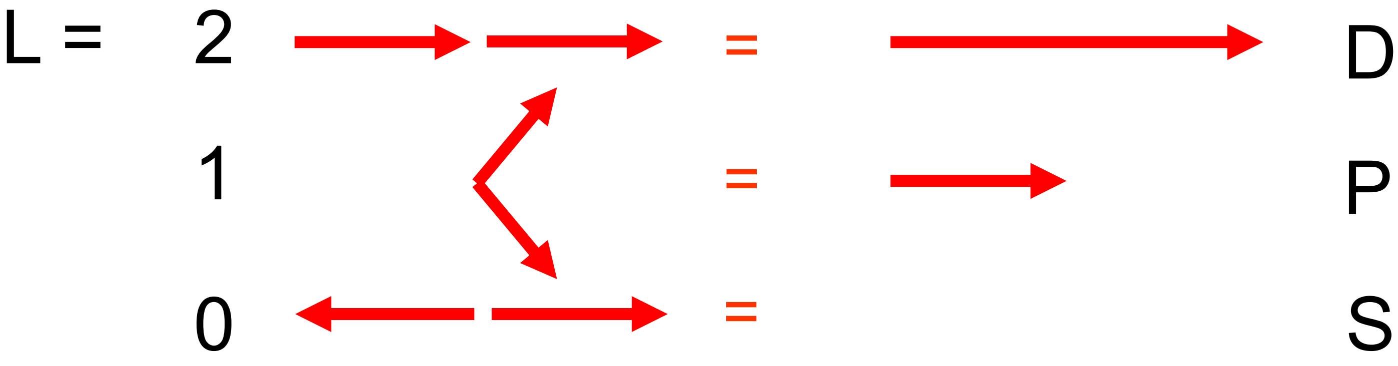
L: quantum number for total orbital angular momentum
$l_1, l_2, \ldots$: orbital angular momentum quantum numbers for each individual electrons

S: quantum number for total spin angular momentum
$s_1, s_2, \ldots$: spin angular momentum for each electrons

L & S are determined by vector addition/subtraction rules.

Example: two electrons in p

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



L = 2 = D

1 = P

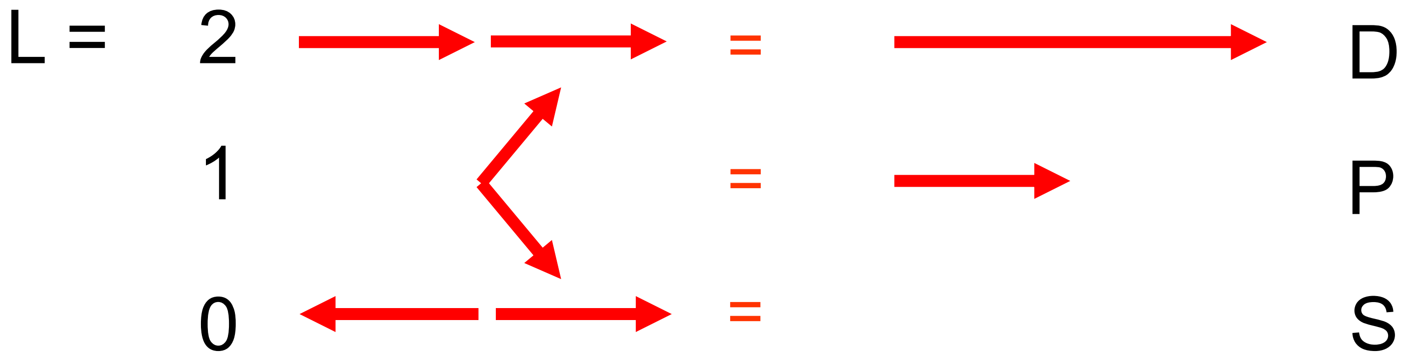
0 = S

$$L = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|$$

2 0

Example: two electrons in p

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

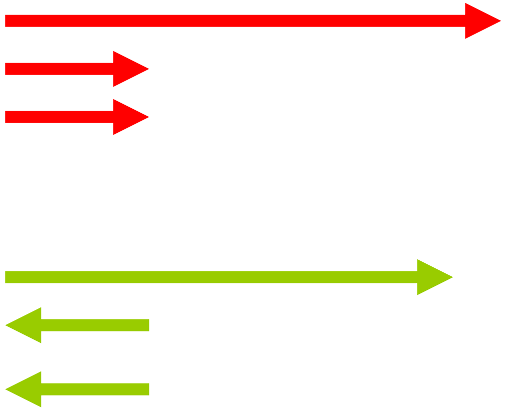


L = 2 = D

1 = P

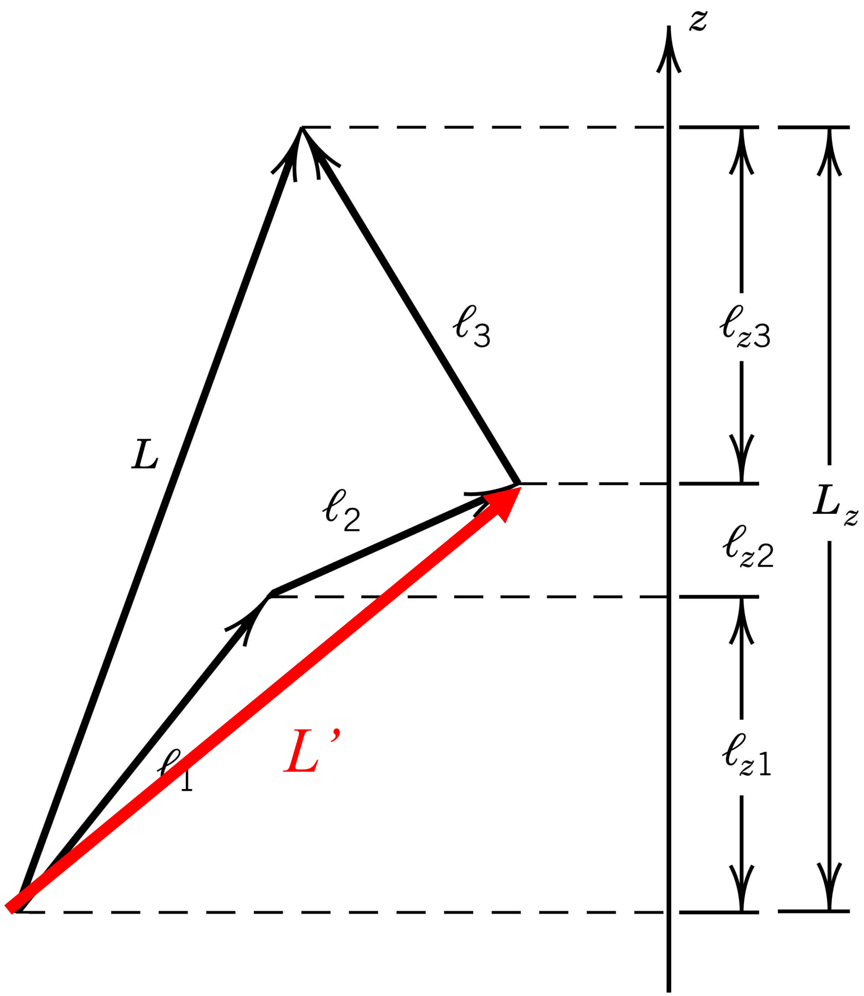
0 = S

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



L=5, 4, 3, 2, 1, …

Addition of Three Angular Momenta two at a time…



$$L' = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2|$$

$$L = L' + l_3, L' + l_3 - 1, \ldots, |L' - l_3|$$

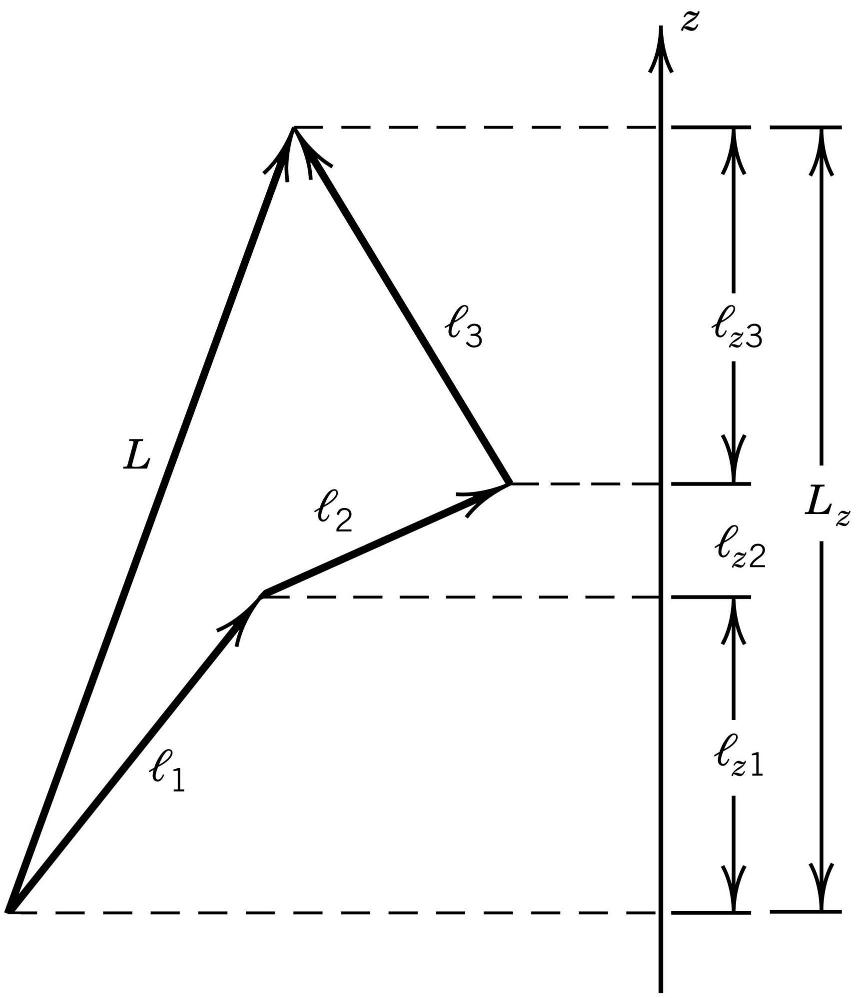
$$L_z = l_{z1} + l_{z2} + l_{z3}$$

If all *l* are equal, the minimum is zero, if one *l* is larger than the others, the minimum is that given by

$$\big||l_1 - l_2| - l_3\big|$$

(*vector sum of all vectors*).

Addition of Three Angular Momenta



p^2f^1 ($\underline{l_1 = 1, l_2 = 1}, l_3 = 3$)

$L' = 2, 1, 0$

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

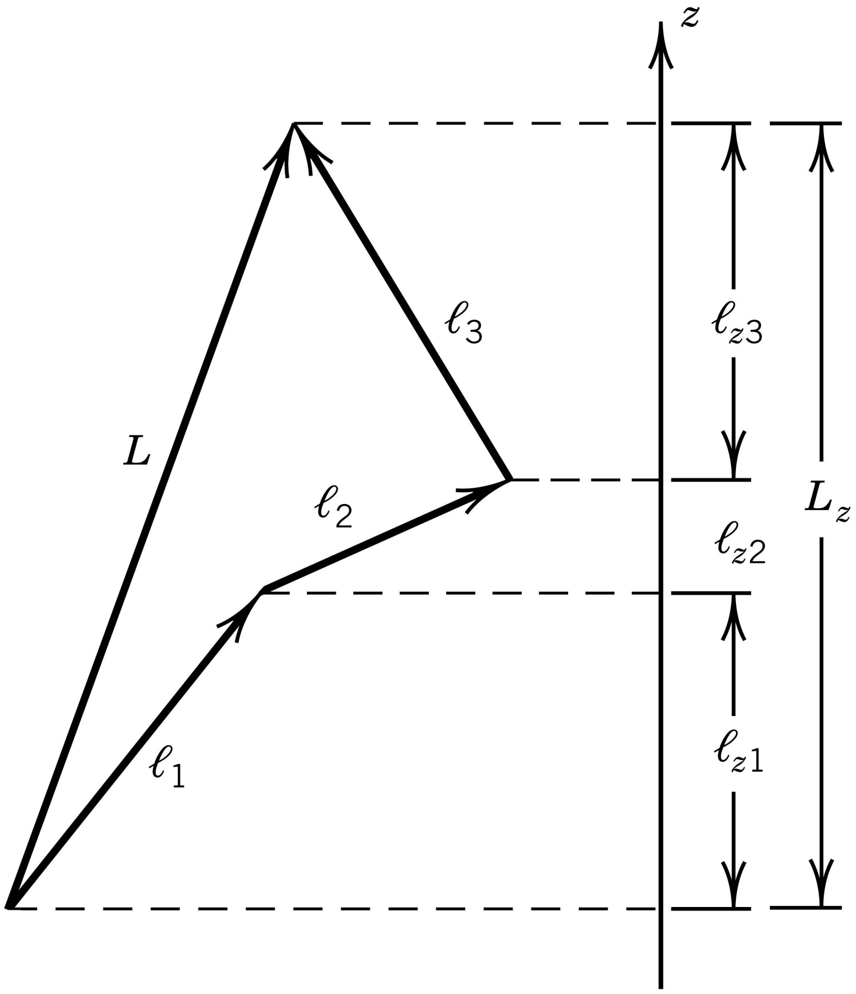
$L = 4, 3, 2$

$L = 3$

Degeneracy = 2L + 1

Addition of Three Angular Momenta

Degeneracy 2L+1



Number of microstates:

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

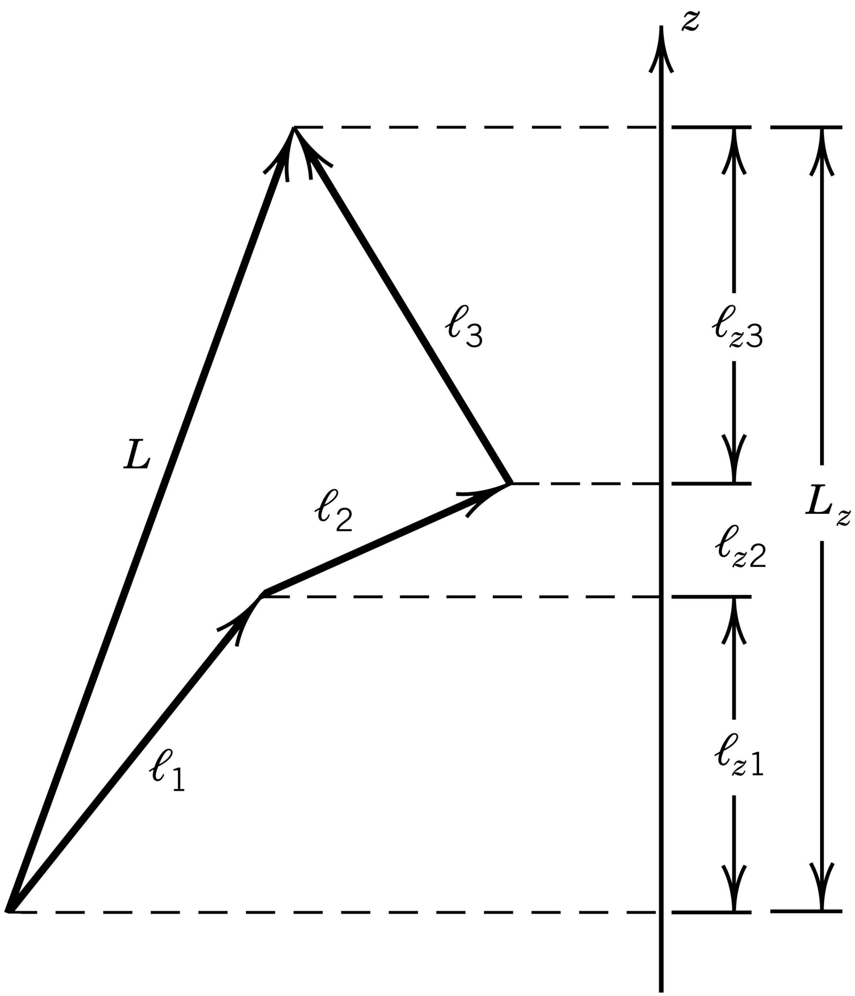
L = 5, 4, 3, 2, 1

$2\times5+1 = 11$
$2\times4+1 = 9$
$2\times3+1 = 7$
$2\times2+1 = 5$
$2\times1+1 = 3$

35

Addition of Three Angular Momenta

Degeneracy 2L+1



Number of microstates:

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

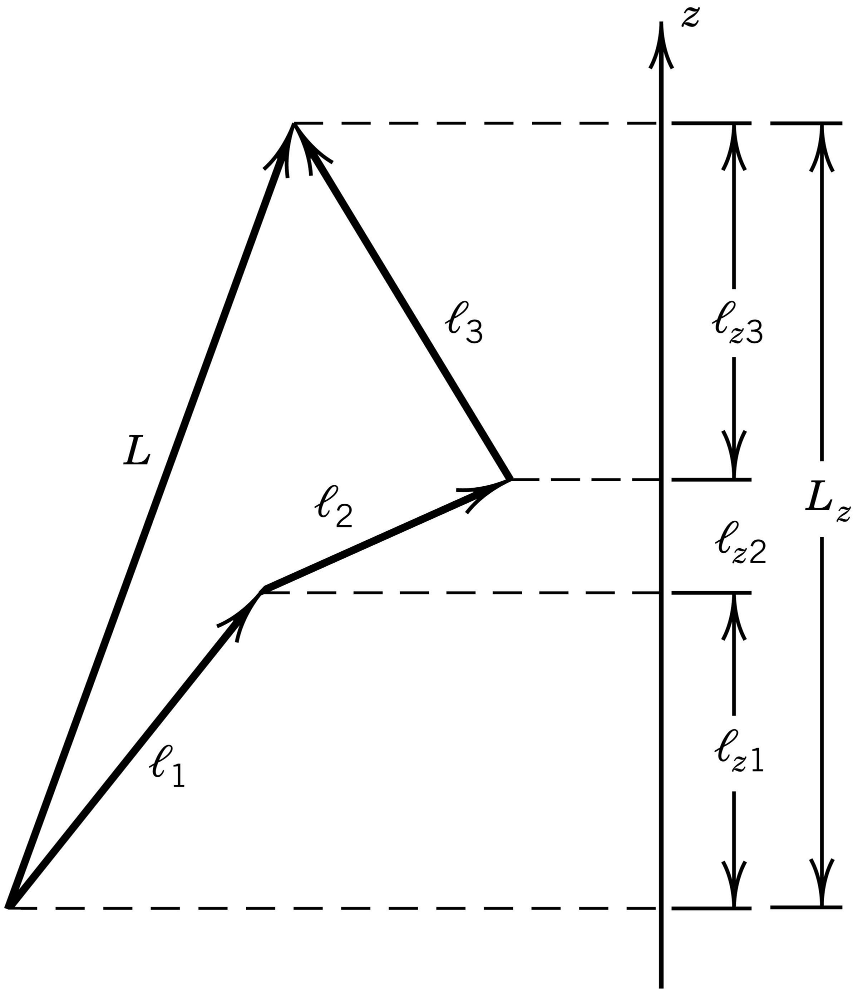
L = 4, 3, 2

2×4+1 = 9
2×3+1 = 7
2×2+1 = 5

21

Addition of Three Angular Momenta

Degeneracy 2L+1



Number of microstates:

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

$L = 5, 4, 3, 2, 1$	35
$L = 4, 3, 2$	21
$L = 3$	7
	63

$3 \times 3 \times 7$ → 63

Total spin angular momentum S for *n* electrons:

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

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

Spin multiplicity = 2S+1

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

S=1/2, 2S+1=2, doublet, $m_s = \frac{1}{2}, -\frac{1}{2}$

S=1, 2S+1=3, triplet, $m_s = 1, 0, -1$

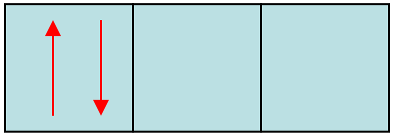
Total spin angular momentum S for n electrons:

$$S = n/2,\ n/2-1,\ n/2-2, \ldots, 0, \text{ for } n \text{ even}$$

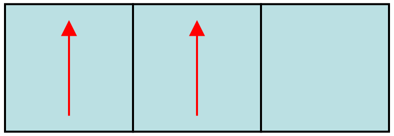
$$S = n/2,\ n/2-1,\ n/2-2, \ldots, 1/2, \text{ for } n \text{ odd}$$

$2p^2$

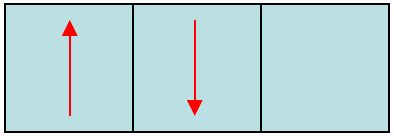
Spin **multiplicity** = 2S+1



S=0 singlet, $m_s = 0$



S=1 triplet, $m_s = 1, 0, -1$



S=0 singlet, $m_s = 0$

Hund’s Rule of Maximum Multiplicity

Hund's first rule states that the lowest energy atomic state is the one which maximizes the total multiplicity for all of the electrons in the open sub-shell.

http://en.wikipedia.org/wiki/List_of_Hund%27s_rules

Russell-Saunders/L-S Term Symbol

Total orbital angular momentum L
Total spin angular momentum S
Total angular momentum J (couple L & S)

$^{2S+1}L_J$ $J = L+S, L+S-1, \ldots |L-S|$

$^{2}S_{1/2}$ *Double* **s** *one-half*

Designation: L =0, 1, 2, 3, 4, 5….
S, P, D, F, G, H….

L-S Terms determine energy levels of atomic electronic states for atoms with small spin-orbital coupling (L-S coupling), i.e. not for heavy atoms.

Example 1: a single electron

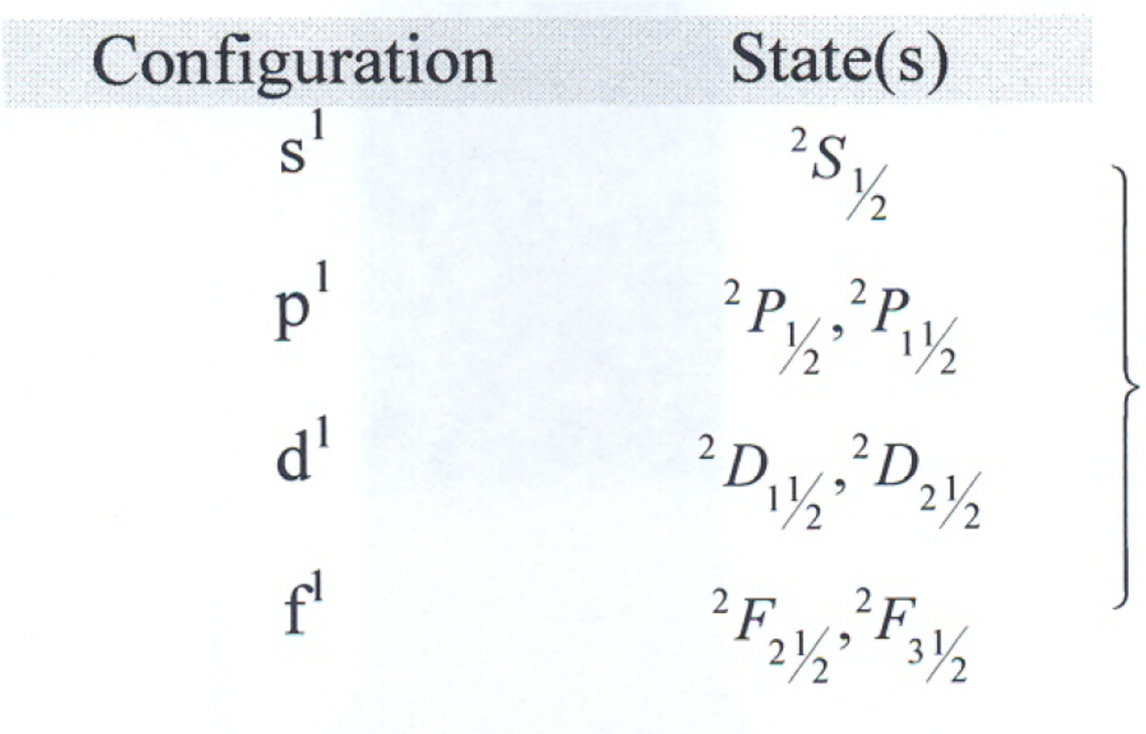
$1s^1$

$^{2S+1}L_J$

$\vec{L} = \vec{\ell}_1 = 0,$

$\vec{S} = \vec{s}_1 = \frac{1}{2}, \text{ or } 2S+1 = 2.$

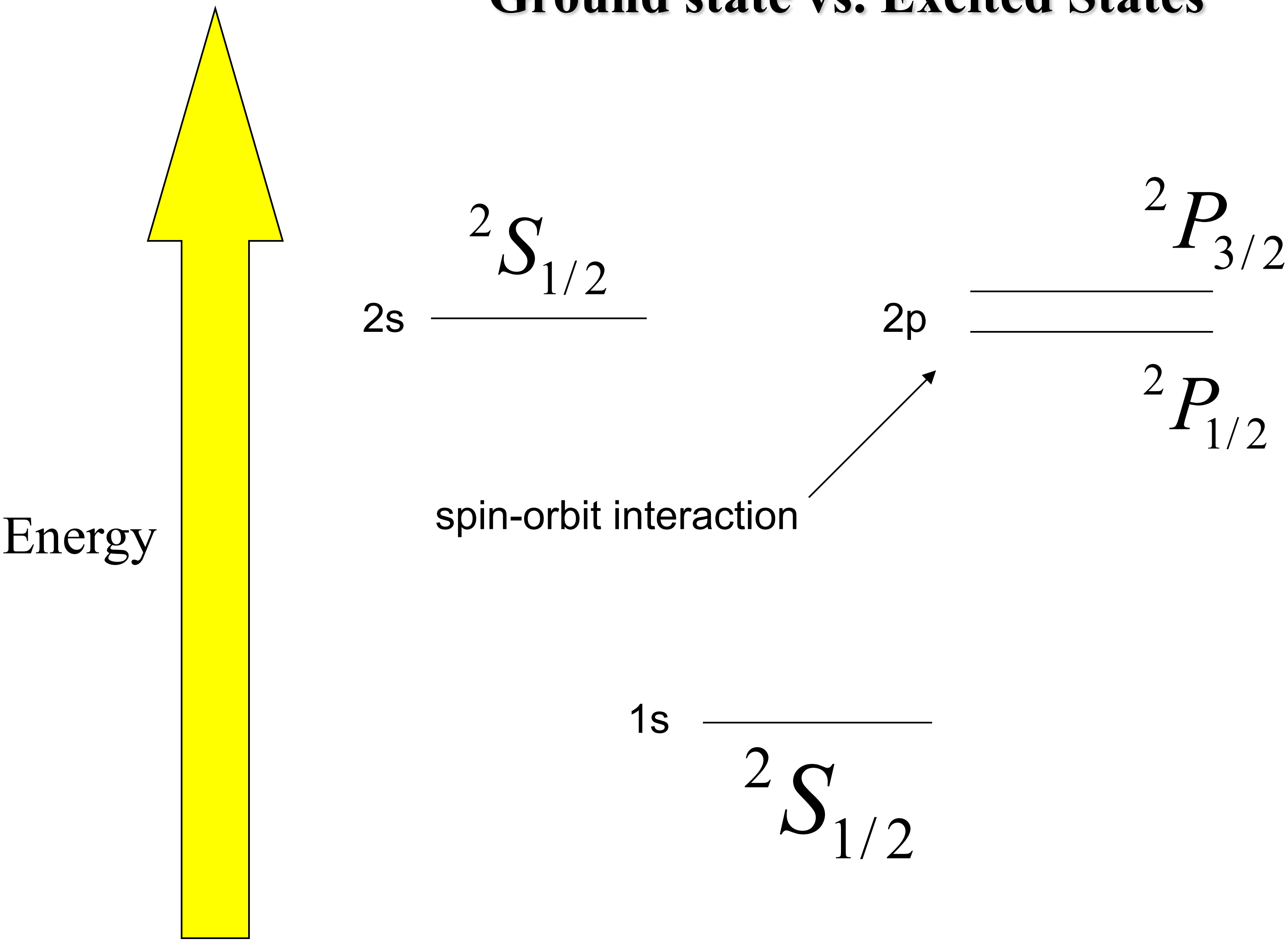
$\Rightarrow \; ^2S_{\frac{1}{2}}$



Configuration	State(s)
s^1	$^2S_{\frac{1}{2}}$
p^1	$^2P_{\frac{1}{2}}, {}^2P_{1\frac{1}{2}}$
d^1	$^2D_{1\frac{1}{2}}, {}^2D_{2\frac{1}{2}}$
f^1	$^2F_{2\frac{1}{2}}, {}^2F_{3\frac{1}{2}}$

$^{2S+1}L_J$

Hydrogen atom (single electron)
Ground state vs. Excited States



2s $^{2}S_{1/2}$

2p $^{2}P_{3/2}$ $^{2}P_{1/2}$

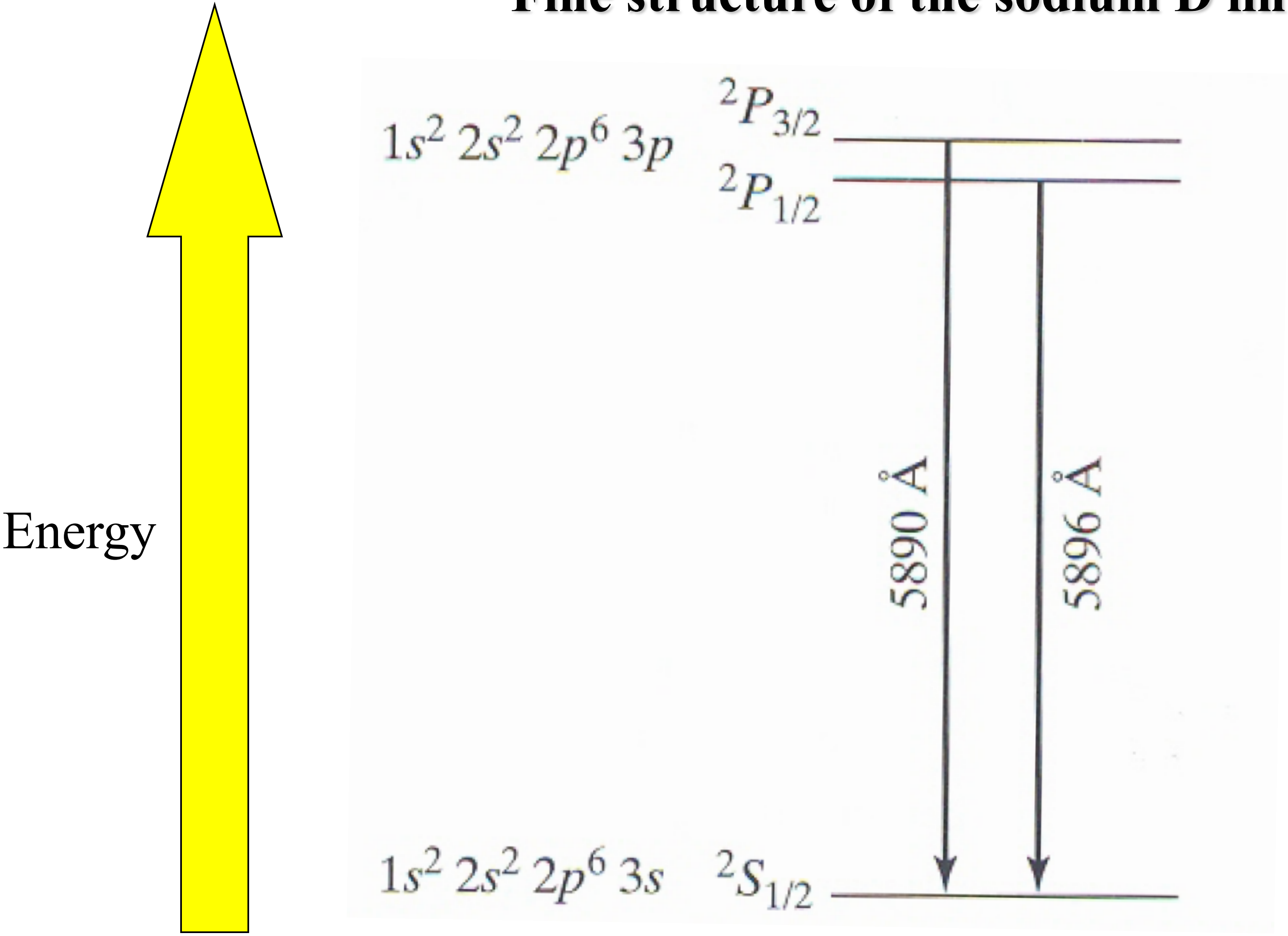
spin-orbit interaction

1s $^{2}S_{1/2}$

Energy

$^{2S+1}L_J$

Fine structure of the sodium D line



Many-electron Atoms

For many-electron system, one may derive the electronic states from the M_L, M_S, and M_J values.

$$M_L = \sum_i (m_l)_i = 0, \pm 1, \pm 2, ... \pm L$$

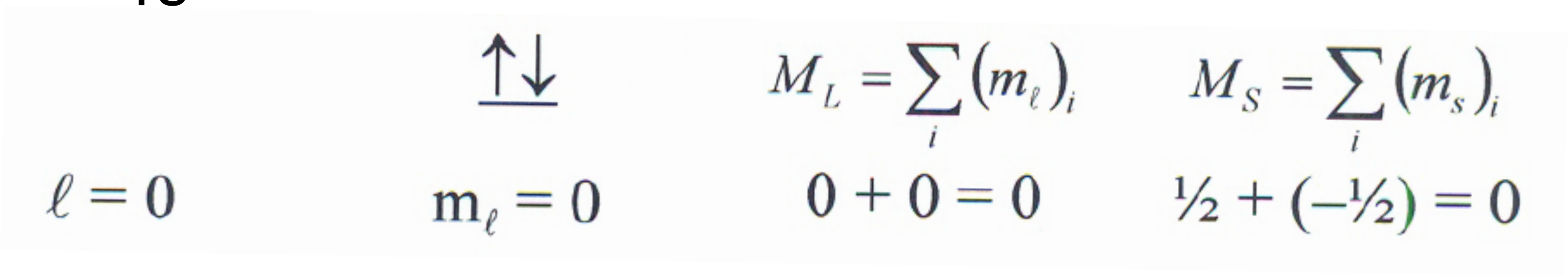
$$M_S = \sum_i (m_s)_i = 0, \pm 1, \pm 2, ... \pm S$$

$$M_J = M_L + M_S = 0, \pm 1, \pm 2, ... \pm J$$

These magnetic quantum numbers are easy to determine from electronic configurations → we can then derive (*L*, *S*, *J*) from the intervals!

Example 2

$1s^2$

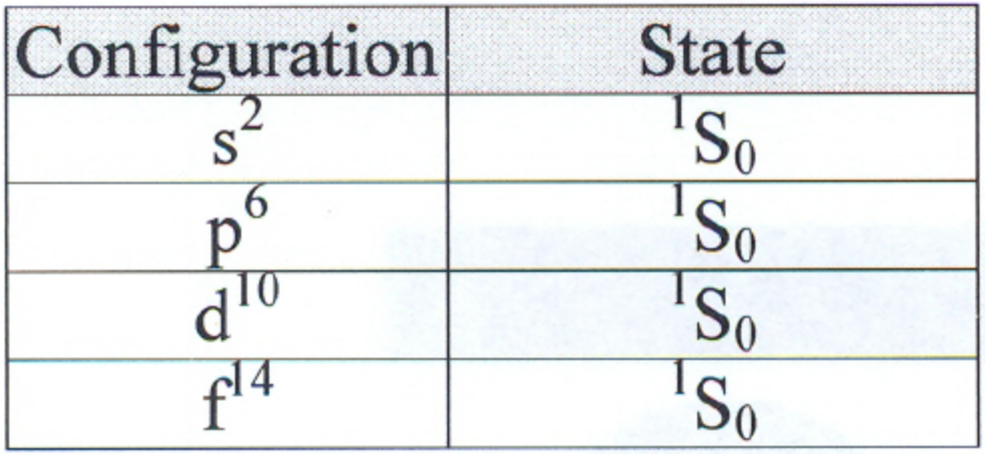


$\underline{\uparrow\downarrow}$

$$M_L = \sum_i (m_\ell)_i \qquad M_S = \sum_i (m_s)_i$$

$\ell = 0$ $\quad m_\ell = 0$ $\quad 0 + 0 = 0$ $\quad \tfrac{1}{2} + (-\tfrac{1}{2}) = 0$

For any filled shell, we just have the state $^1S_0$ with L = S = J = 0



Configuration	State
s^2	$^1S_0$
p^6	$^1S_0$
d^{10}	$^1S_0$
f^{14}	$^1S_0$

No need to consider “closed shells”

Term Symbols & Electronic Configurations

To determine all term symbols in a configuration:

1. List all electronic microstates by filling orbitals with spin specified
2. Calculate M_L and M_S, then tabulate the number of states belonging to each (M_L, M_S)
3. Divide states into separate terms based on the bounds of M_L and M_S (starting from largest L)
4. Determine term symbols

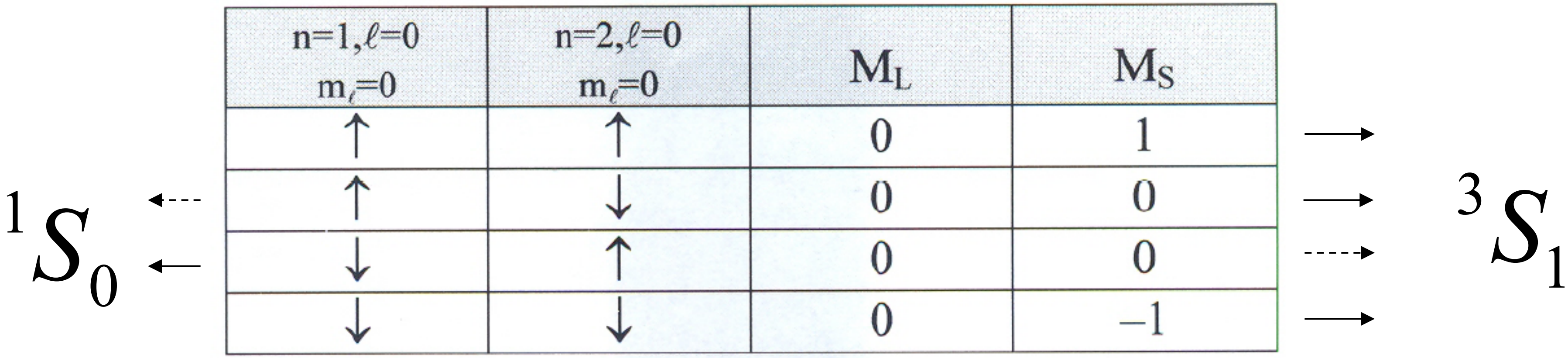
Core shells are fully occupied and do not give rise to additional states → only open shell electrons need to be considered.

$^{2S+1}L_J$

Example 3

Totally 2x2 = 4 states
4 microstates!

$1s^1 2s^1$



n=1, ℓ=0 m_ℓ=0	n=2, ℓ=0 m_ℓ=0	M_L	M_S
↑	↑	0	1
↑	↓	0	0
↓	↑	0	0
↓	↓	0	–1

$^1S_0$

$^3S_1$

	-1	0	1
$M_L = 0$	1	2	1

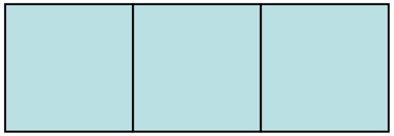
M_S

$$^1S_0 + {}^3S_1$$

Example 4

Carbon: $\underset{\text{Ignored}}{\underline{1s^2 2s^2}}\,2p^2$

$2p^2$



Number of possible arrangement is

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

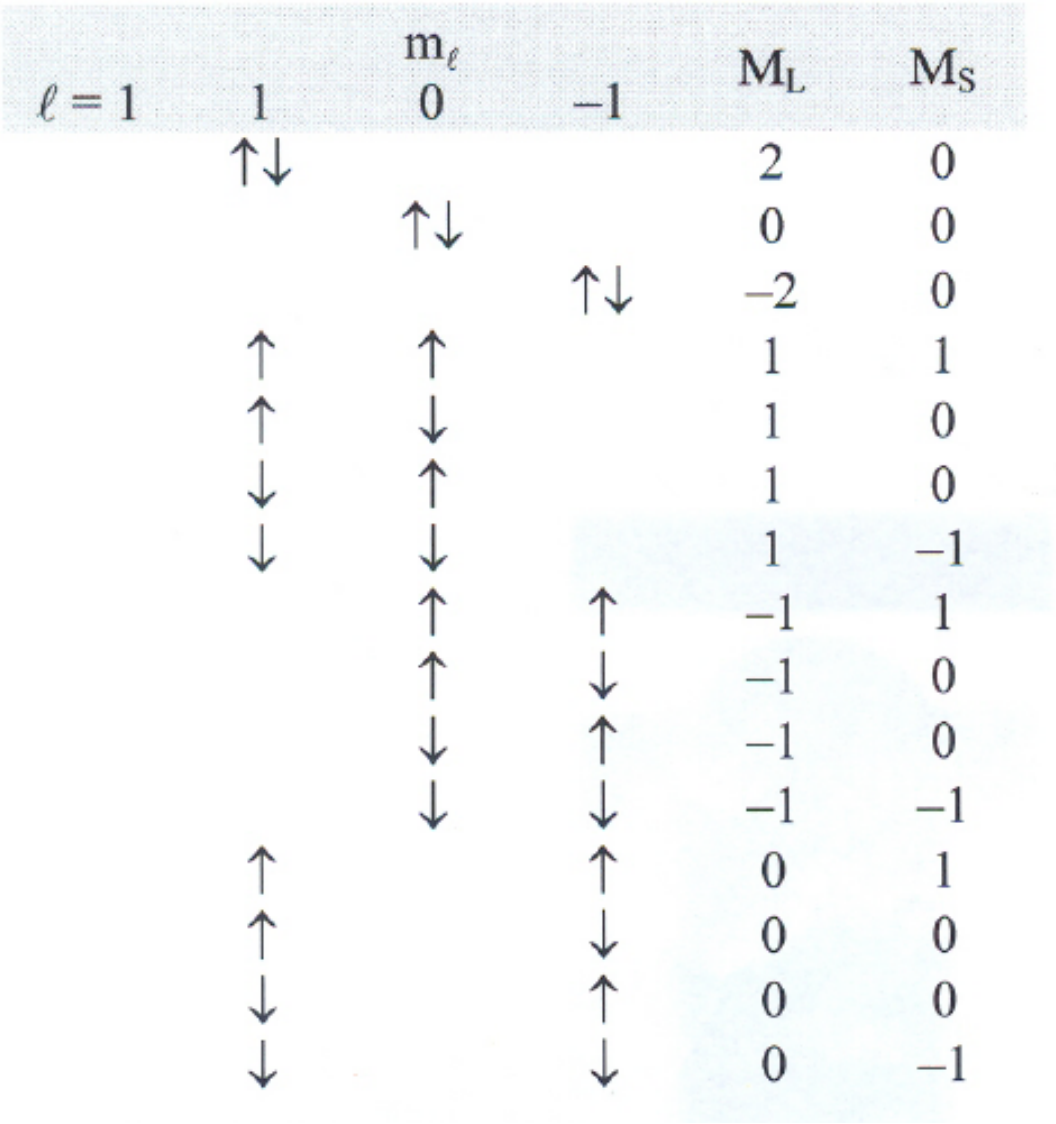
$$C^{M}_{n}$$

$M \leftarrow$ Number of spin orbitals

$n \leftarrow$ Number of electrons

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

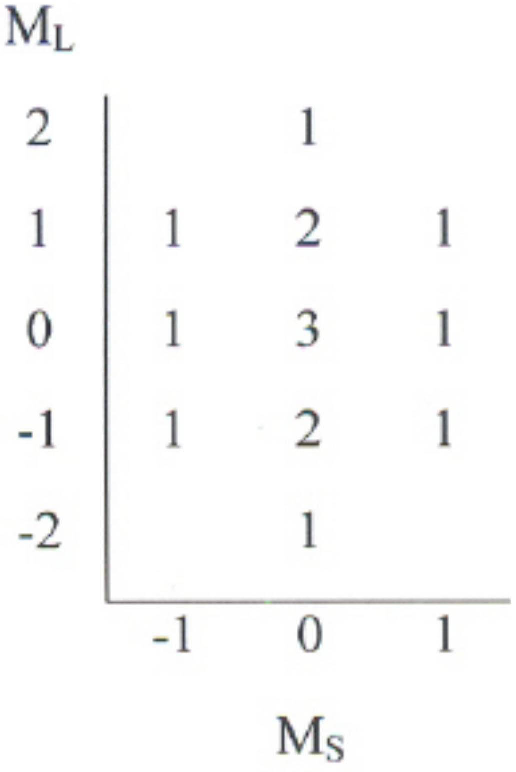
Carbon: $2p^2$



	m_ℓ				
$\ell = 1$	1	0	−1	M_L	M_S
	↑↓			2	0
		↑↓		0	0
			↑↓	−2	0
	↑	↑		1	1
	↑	↓		1	0
	↓	↑		1	0
	↓	↓		1	−1
		↑	↑	−1	1
		↑	↓	−1	0
		↓	↑	−1	0
		↓	↓	−1	−1
	↑		↑	0	1
	↑		↓	0	0
	↓		↑	0	0
	↓		↓	0	−1

M_L \ M_S	-1	0	1
2		1	
1	1	2	1
0	1	3	1
-1	1	2	1
-2		1	

Carbon: $2p^2$



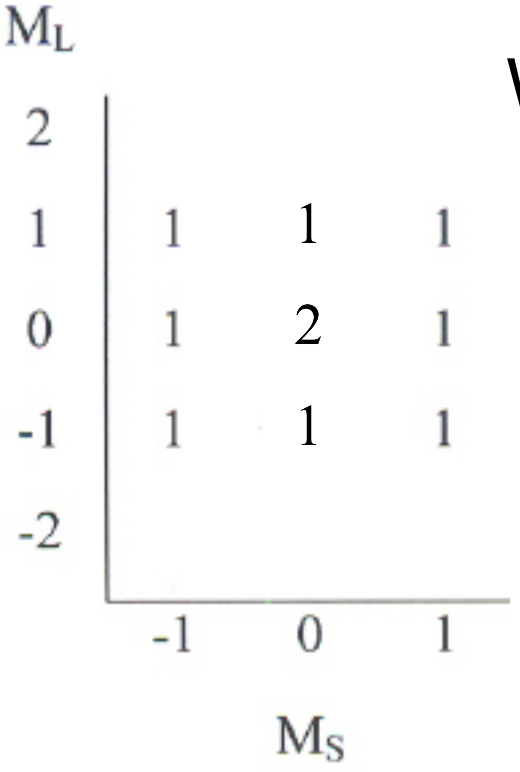
M_L			
2		1	
1	1	2	1
0	1	3	1
-1	1	2	1
-2		1	
	-1	0	1
		M_S	

While M_L= -2…2, M_S=0 → L=2, S=0

Must have a ^1D

We have identified 5 microstates, let's remove them from the table – substrate 1 from the column M_S=0.

Carbon: $2p^2$

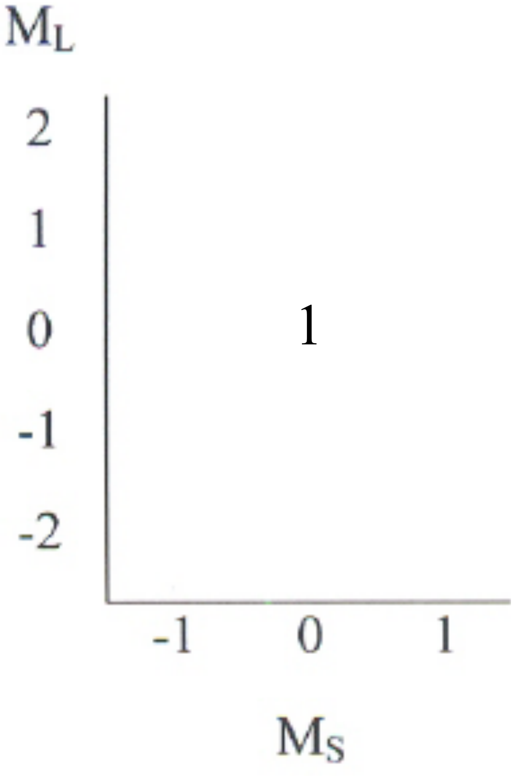


M_L \ M_S	-1	0	1
2			
1	1	1	1
0	1	2	1
-1	1	1	1
-2			

While M_L= -1…1, M_S= -1…1 → L=1, S=1

Must have a ^3P

Carbon: $2p^2$



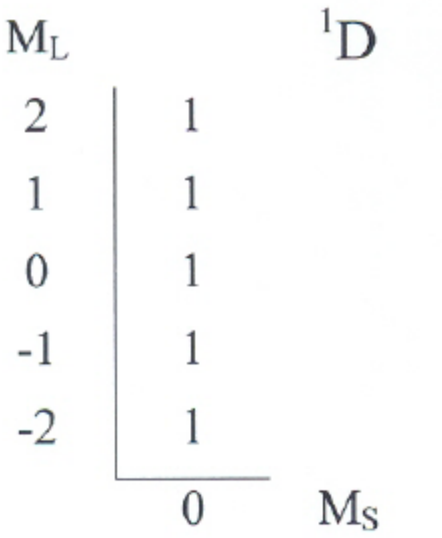
While M_L= 0, M_S= 0 → L=0, S=0

Must have a ^1S too!!

GOTCHA!!

Carbon: $2p^2$

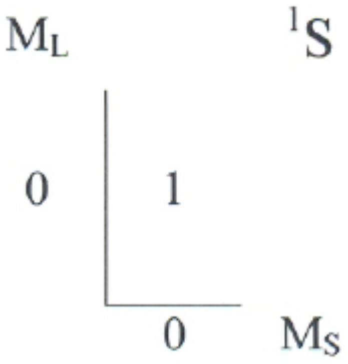
$J = 2$



^1D

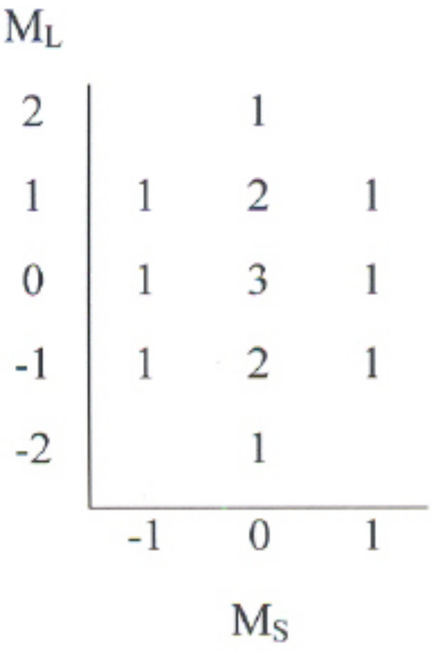
M_L	
2	1
1	1
0	1
-1	1
-2	1
	0
	M_S

$J = 0$

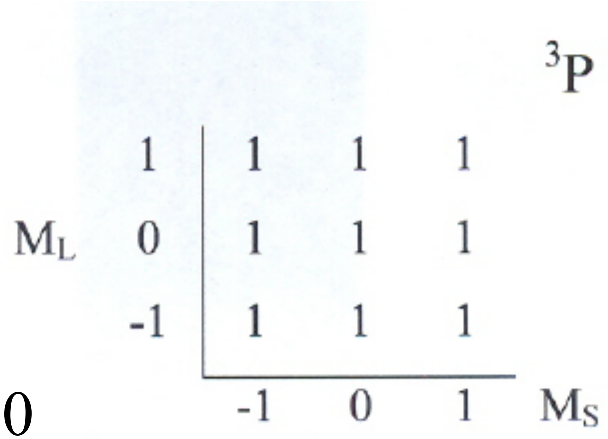


^1S

M_L	
0	1
	0
	M_S



M_L			
2		1	
1	1	2	1
0	1	3	1
-1	1	2	1
-2		1	
	-1	0	1
		M_S	



^3P

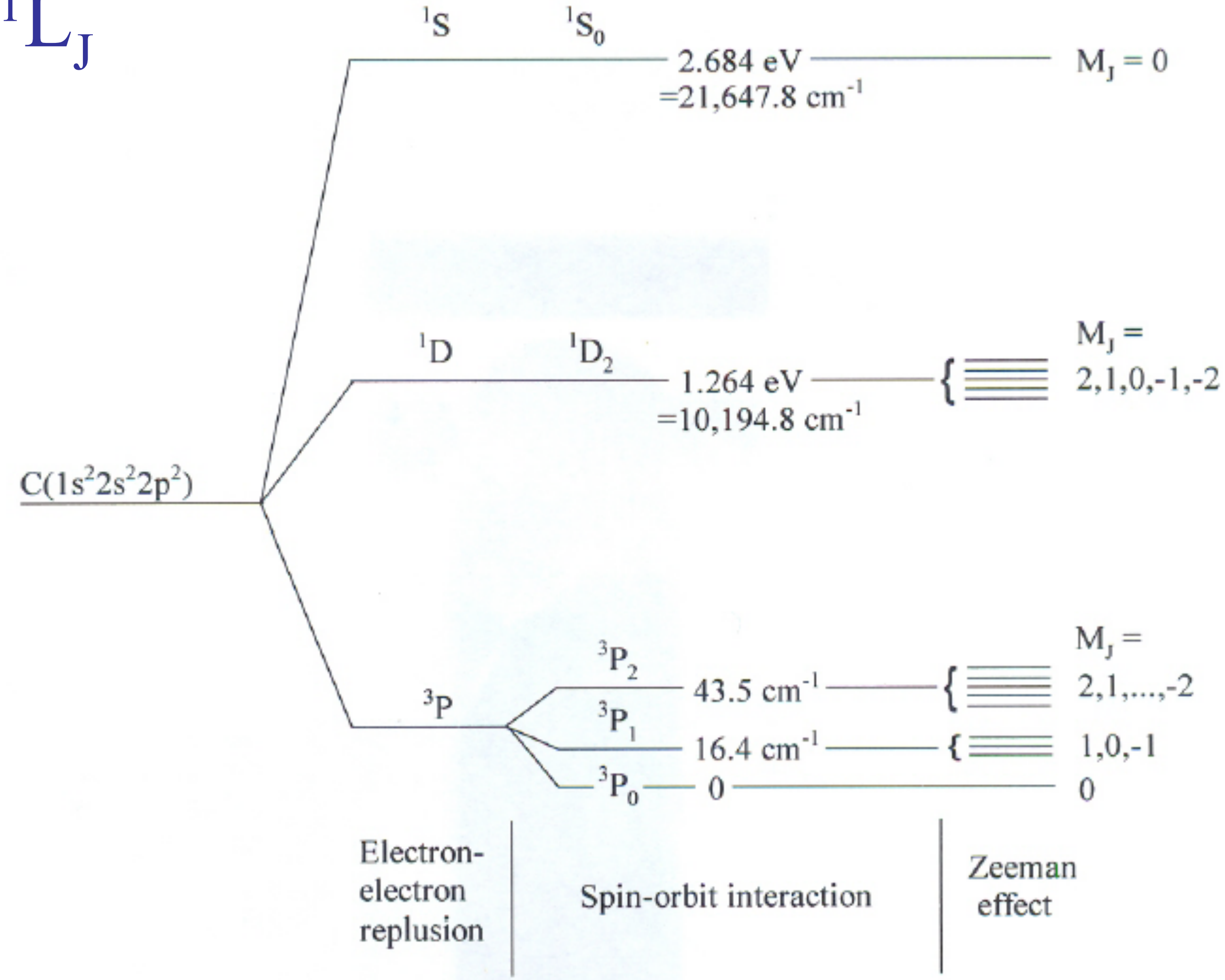
M_L			
1	1	1	1
0	1	1	1
-1	1	1	1
	-1	0	1
			M_S

$J = 2, 1, 0$

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

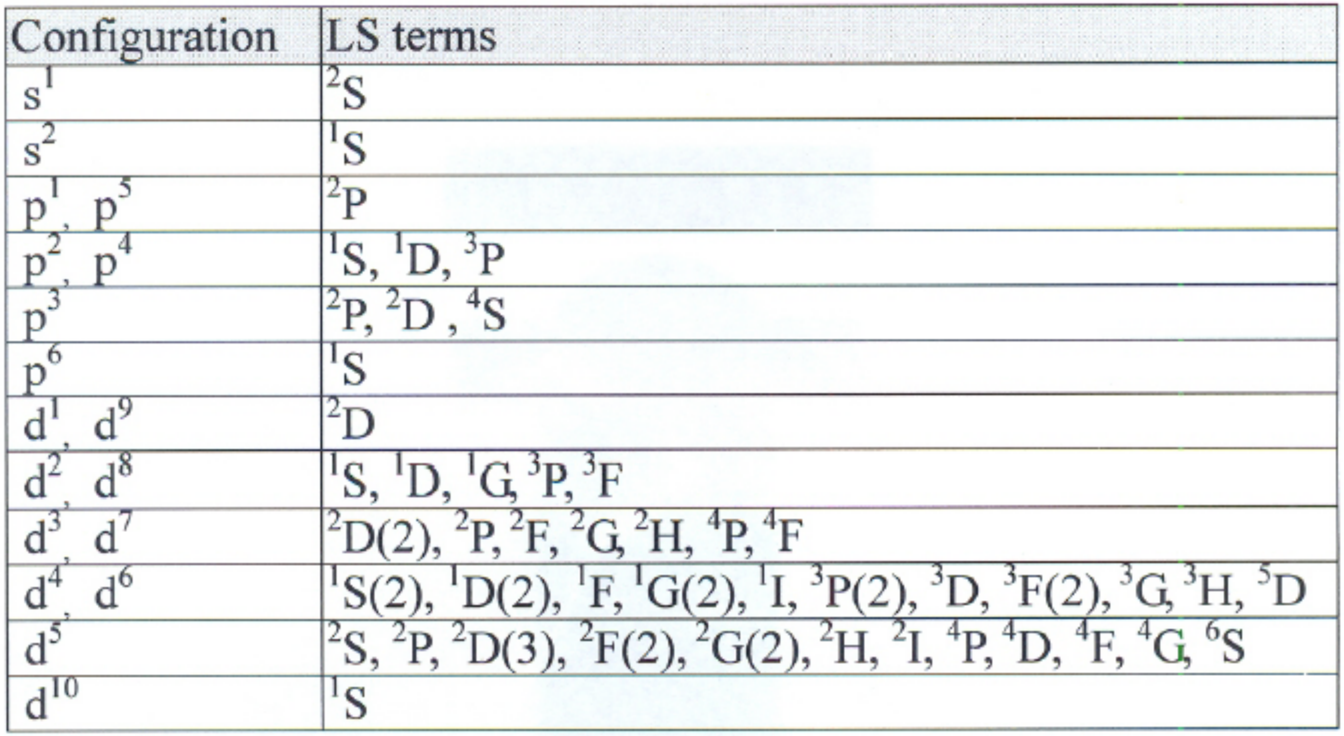
Carbon: $2p^2$

$^{2S+1}L_J$



$$\hat{H}^0 \qquad \hat{H}^0 + \hat{H}_{rep} \qquad \hat{H}^0 + \hat{H}_{rep} + \hat{H}_{s.o.} \qquad \hat{H}^0 + \hat{H}_{rep} + \hat{H}_{s.o.} + \hat{H}_Z$$

Electronic transitions may occur within the same electronic configuration!



Configuration	LS terms
s^1	^2S
s^2	^1S
p^1, p^5	^2P
p^2, p^4	^1S, ^1D, ^3P
p^3	^2P, ^2D , ^4S
p^6	^1S
d^1, d^9	^2D
d^2, d^8	^1S, ^1D, ^1G, ^3P, ^3F
d^3, d^7	$^2D(2)$, ^2P, ^2F, ^2G, ^2H, ^4P, ^4F
d^4, d^6	$^1S(2)$, $^1D(2)$, ^1F, $^1G(2)$, ^1I, $^3P(2)$, ^3D, $^3F(2)$, ^3G, ^3H, ^5D
d^5	^2S, ^2P, $^2D(3)$, $^2F(2)$, $^2G(2)$, ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S
d^{10}	^1S

If spin-orbit coupling is larger than the electron-electron repulsion, the scheme of j-j coupling is used instead of L-S coupling.

The j-j coupling scheme is more appropriate for heavy transition metal atoms: stronger core potential, faster electron, much more prominent relativistic effects.