CHEM F111 : General Chemistry
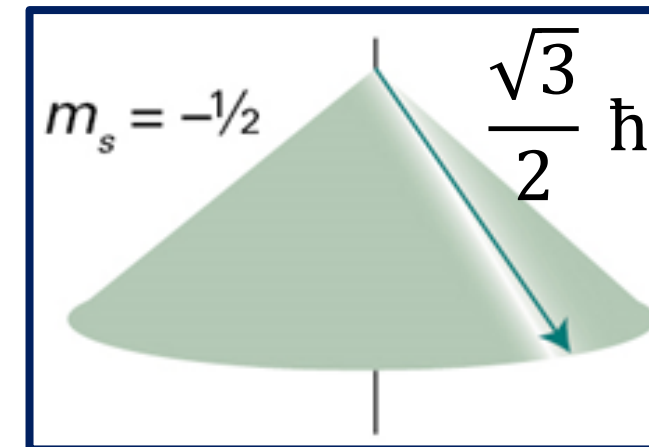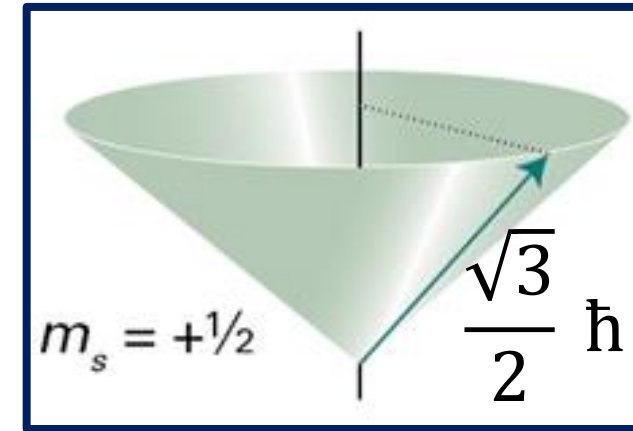## Semester II: AY 2017-18
Lecture-10 (Extra), 05/06-02-2018

Spin – one electron: Summary

- Stern-Garlach experiment: Intrinsic spin of electron

- Spin quantum number: $s = \frac{1}{2}$;

- Spin magnetic quantum number: $m_s = \pm \frac{1}{2}$

- Magnitude of spin angular momentum: $\sqrt{s(s+1)}\,\hbar$

- Z-component of spin angular momentum: $S_Z = \pm \frac{1}{2}\,\hbar$

- Possible spin states with $s = \frac{1}{2}$ is two (α, β)

- Spin multiplicity: $(2s+1)$

$m_s = +\frac{1}{2}$ $\frac{\sqrt{3}}{2}\,\hbar$

$m_s = -\frac{1}{2}$ $\frac{\sqrt{3}}{2}\,\hbar$

Antisymmetric wave function

First consider the spatial part of the wave function.

$\psi(1,2) = \phi(1)\,\phi(2) \Rightarrow$ symmetric

Pauli principle: $\psi(1,2) = -\psi(2,1)$ *(MUST FOLLOW!)*

Thus, spin part must be antisymmetric

Since each electrons has two possible spin states – four possible spin functions:

$$\boldsymbol{\alpha(1)\alpha(2), \beta(1)\beta(2), \boxed{\alpha(1)\beta(2), \alpha(2)\beta(1)}}$$

Violate the principle of indistinguishability of identical particles in quantum mechanics

Antisymmetric wave function

We can consider normalized linear combination:

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)\right]$$

Spin orbitals:

$\psi(1,2) = \phi(1)\phi(2)\ \alpha(1)\alpha(2)$

$\psi(1,2) = \phi(1)\phi(2)\ \beta(1)\beta(2)$

$\psi(1,2) = 2^{-1/2}\phi(1)\phi(2)\ \{\ \alpha(1)\beta(2) + \beta(1)\alpha(2)\ \}$

Symmetric

$\psi(1,2) = 2^{-1/2}\phi(1)\phi(2)\ \{\ \alpha(1)\beta(2) - \beta(1)\alpha(2)\ \}$

Anti-symmetric

Pauli exclusion principle

Approximate wave function for He ground state:

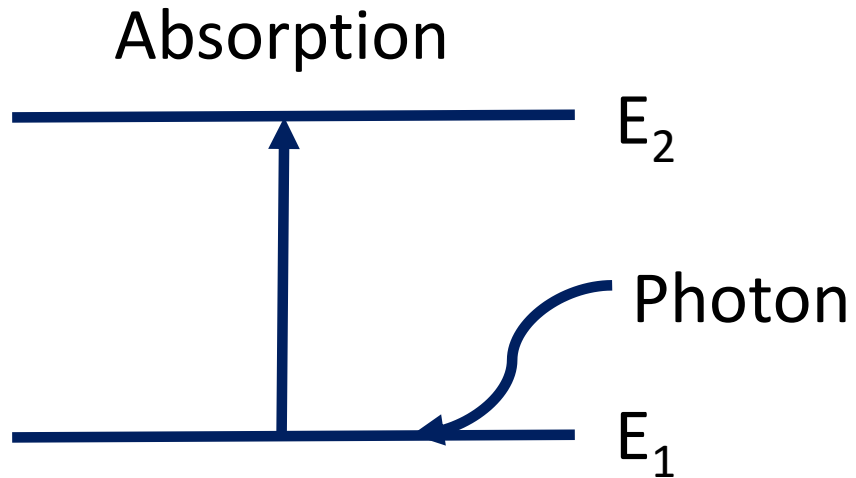$$\psi(1,2) = 2^{-1/2}\phi(1)\phi(2) \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \}$$

Spin orbitals

- Two electrons can not occupy the same spin orbital
- No two electrons in an atom can have the same values for all their quantum number: n, l, m_l, m_s

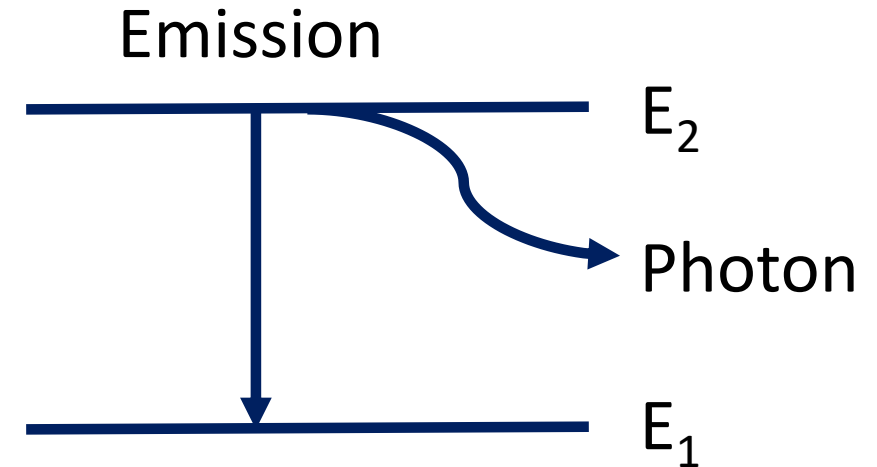Distinguishability of identical particles in classical & quantum mechanics

Spectra of complex atoms

Energy of a photon of frequency ν, $\boldsymbol{E = h\nu}$

Absorption

E_2

Photon

E_1

$$\Delta E = E_f - E_i$$
$$= E_2 - E_1$$
$$\nu = |\Delta E| h$$

Emission

E_2

Photon

E_1

$$\Delta E = E_f - E_i$$
$$= E_1 - E_2$$
$$\nu = |\Delta E| h$$

Spectra of complex atoms

Consider He atom:

$$1s^1 2s^1 \quad \underline{\hspace{5cm}} \quad E_2$$
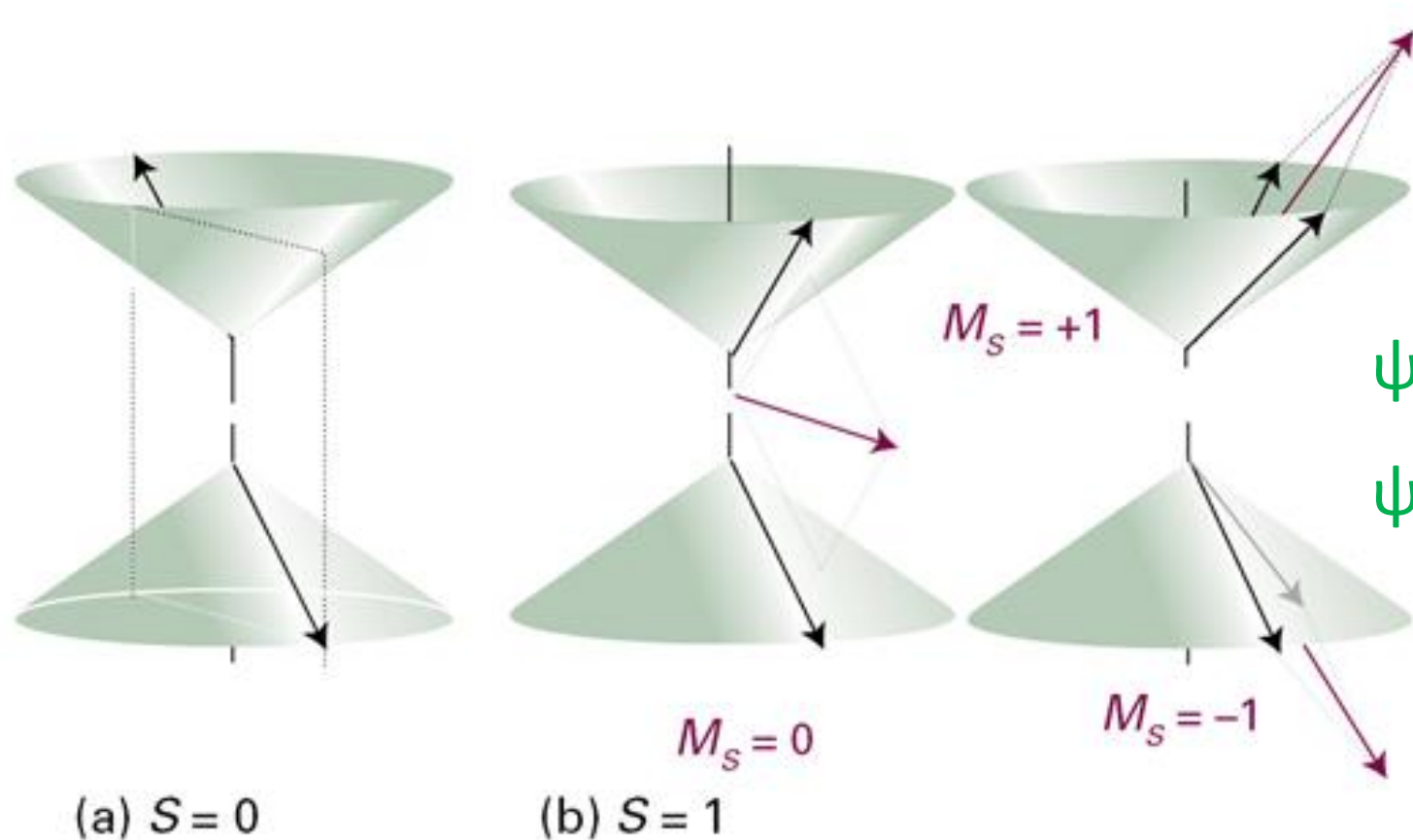
Photon

$$1s^2 \quad \underline{\hspace{5cm}} \quad E_1$$
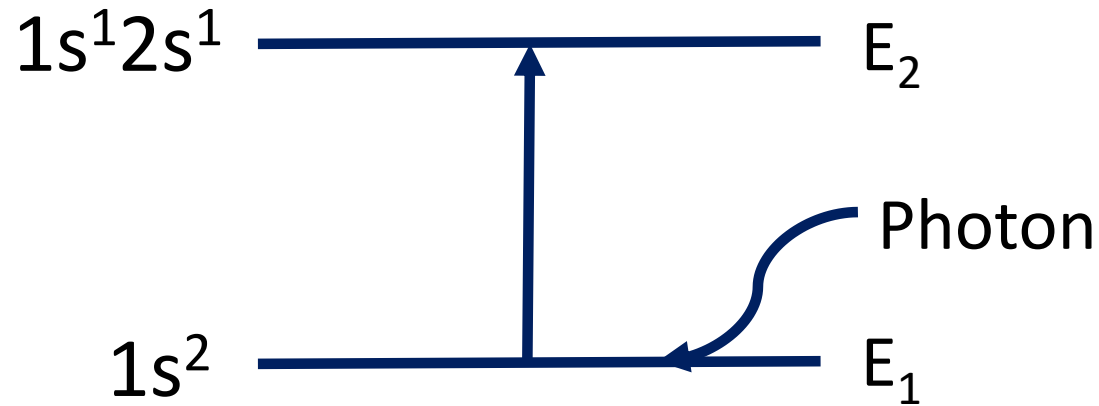
What would be the effect of spin angular momentum?

- Spins will be paired in $1s^2$ configuration
- $1s^1 2s^1$: Two electrons need not be paired
- Hund's maximum multiplicity rule

Spectra of complex atoms

(a) $S = 0$ (b) $S = 1$

Singlet state   Triplet state

Triplet spin function

$\psi(1,2) = \phi(1)\phi(2)\,\alpha(1)\alpha(2),\ S \neq 0$

$\psi(1,2) = \phi(1)\phi(2)\,\beta(1)\beta(2),\ S \neq 0$

$\psi(1,2) = 2^{-1/2}\phi(1)\phi(2)\,\{\,\alpha(1)\beta(2) + \beta(1)\alpha(2)\,\},\ S \neq 0$

Singlet spin function $\psi(1,2) = 2^{-1/2}\phi(1)\phi(2)\,\{\,\alpha(1)\beta(2) - \beta(1)\alpha(2)\,\},\ S = 0$

Spectra of complex atoms

He atom

$1s^1 2s^1 (\alpha\beta)$

$1s^1 2s^1 (\alpha\alpha / \beta\beta)$

E_S

0.80 eV

E_T

E_T: Energy of triplet state
E_s: Energy of singlet state

$1s^2$

E_1
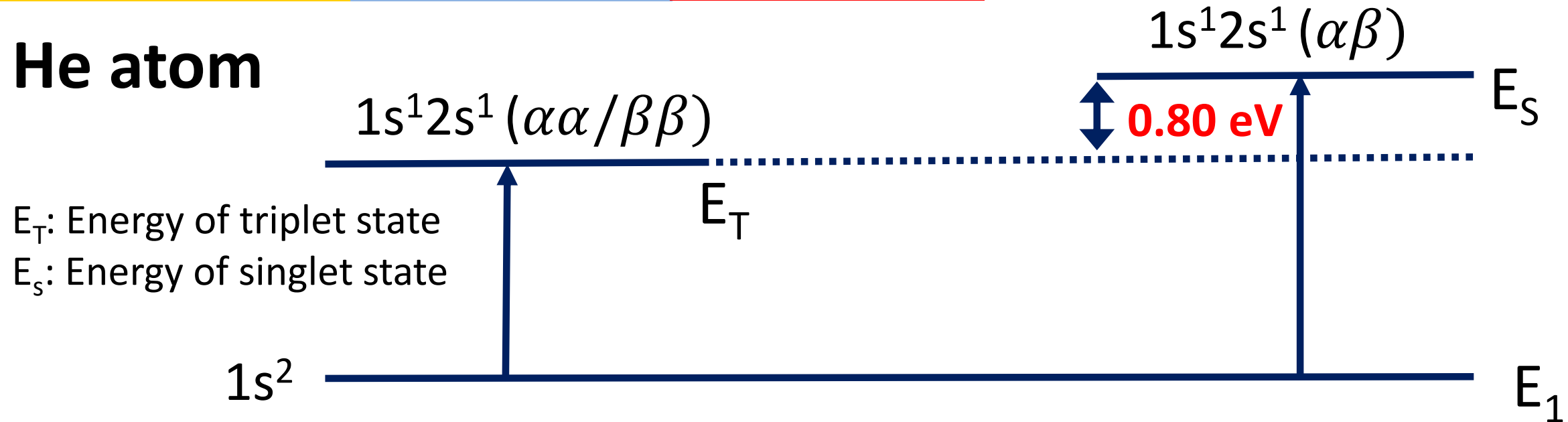
- States arising from same configuration, the triplet state generally lies lower in energy than the singlet state.
- The two states of He atom differ by 0.80 eV/6421 cm^{-1}.
- Only one electron is excited – as that requires minimum energy.
- No radiative transition takes place between the singlet and triplet states.

Orbital and spin angular momenta

Are they independent?

Magnetic moment from spin

Electron has spin angular momentum

Moving charges generate magnetic fields

Magnetic field generated from spin

Magnetic moment from orbital angular momentum

**Electron has orbital angular momentum ($l>0$)**

In effect a circulating current

Magnetic field generated from orbital momentum

Spin orbit coupling/interaction

- Spin-orbit coupling is a magnetic interaction between spin and orbital magnetic moments.

- Total angular momentum of an electron - quantum number j.
- Z-component of total angular momentum – quantum number m_j.

$$j = l + s$$

High j

Low j $$j = l - s$$

High energy

Low energy
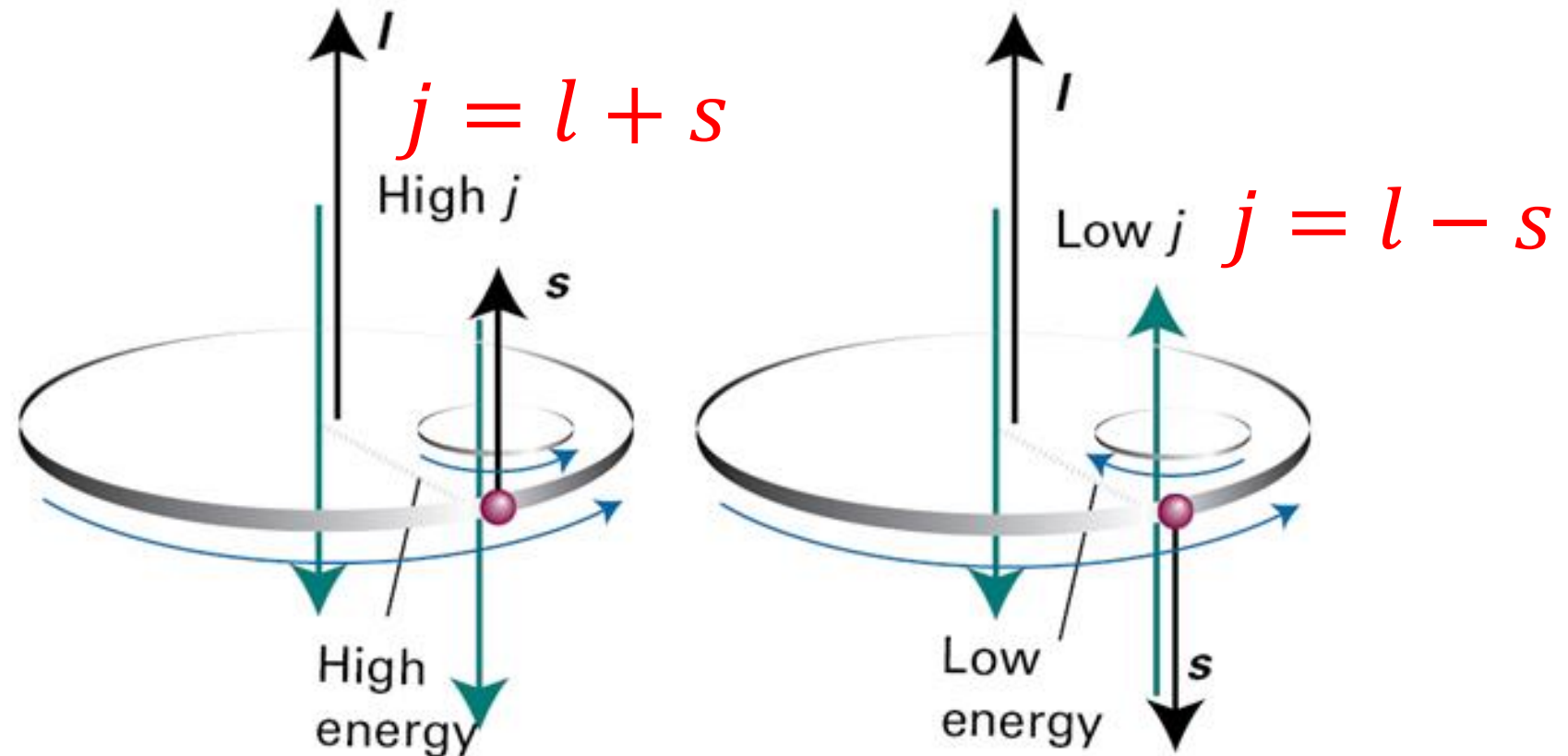
Spin-orbit coupling energy

Energy of the spin-orbit coupling depends on

$E \propto \{j(j+1) - l(l+1) - s(s+1)\}$

For electron, s= ½; $E \propto \{j(j+1) - l(l+1) - ½(½+1)\}$

If orbital ang. momentum is zero $l = 0$, $j = s = ½$

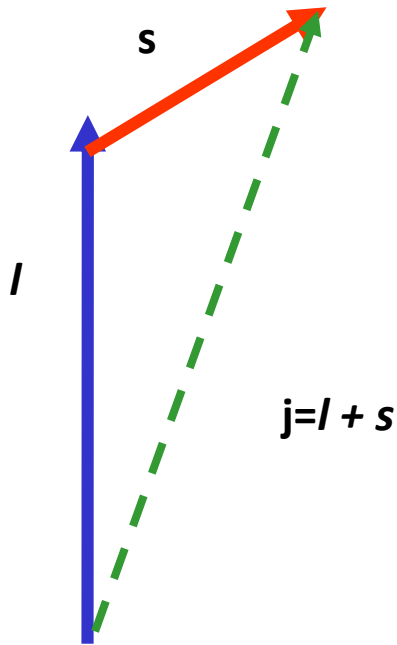$E \propto \{j(j+1) - l(l+1) - s(s+1)\} = \{½(½+1) - 0 - ½(½+1)\}=0$

No spin orbit coupling.

In other cases, coupling can happen : energy will vary: different levels

Spin orbit interaction – one electron
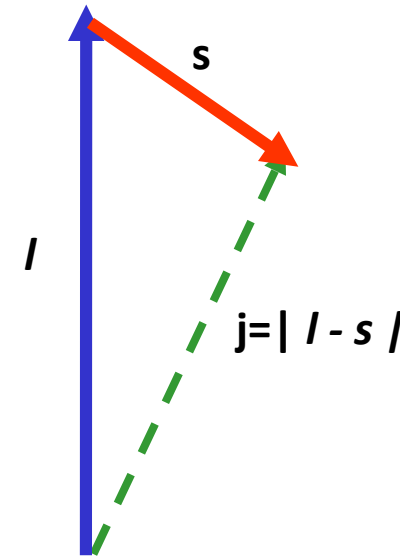
Two angular momenta adding

s

l

j=*l* + s

Total angular momenta

j = |*l* ± s*|

Two angular momenta opposing

s

l

j=| *l* - s |

For an *s*-electron: *l* = 0, s = 1/2; j = 1/2 only
For a *p*-electron: *l* = 1, s = 1/2; j = 3/2 or 1/2
For a *d*-electron: *l* = 2, s = 1/2; j = 5/2 or 3/2

Term symbols

A term represents the energy level of an atom.

The notation used to specify a term is called term symbol.

A term symbol tells us about the angular momentum of the electrons in the atom and it looks like

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

Here, S = Total spin angular momentum quantum number.

L = Total orbital angular momentum quantum number.

J = Total angular momentum quantum number.

Can we explain the formation of Na D lines?

Many electron system

Total orbital angular momentum

$$L = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, ..., |l_1 - l_2|.$$

Clebsch Gordan series

Two orbital ang. momenta are in same direction

Two orbital ang. momenta are in opposite direction

Magnitude of angular momentum = $\sqrt{L(L+1)}\,\hbar$

It has $2L+1$ orientation – distinguished by quantum number M_L

Letter code: $L = 0(S), 1(P), 2(D), 3(F), 4(G), 5(H), 6(I), ...$

Filled shells have no overall angular momentum and need to consider only unfilled shell.

Example – two p electrons

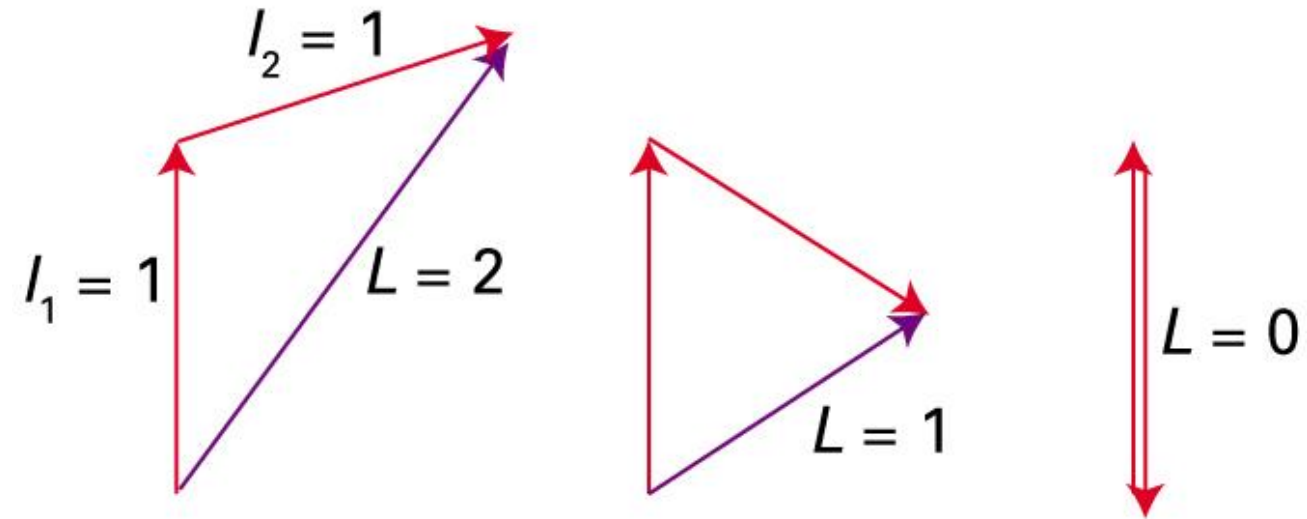Excited state configuration of C is $[He]2s^2 2p^1 3p^1$ $l_1 = 1, l_2 = 1$

$L = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, .., \left| l_1 - l_2 \right|.$

$L = (1+1=2), (1+1-1=1), \left| 1-1=0 \right|.$

$L = 2, 1, 0$

When L value for $2p^1 3p^1$ is converted into letter:
$L = S, P, D$

Significance of such different values of L: Different possible RELATIVE ORIENTATIONS OF THE TWO MOMENTA

Total spin angular momentum

Total spin angular momenta could be half integer or integer

$$S = s_1 + s_2, s_1 + s_2 - 1, s_1 + s_2 - 2, ..., |s_1 - s_2|.$$

Each electron has s = ½

S = 1,0

Multiplicity: 2S + 1

S = 0 (Singlet); S = 1 (Triplet); S = ½ (doublet)

Total angular momentum

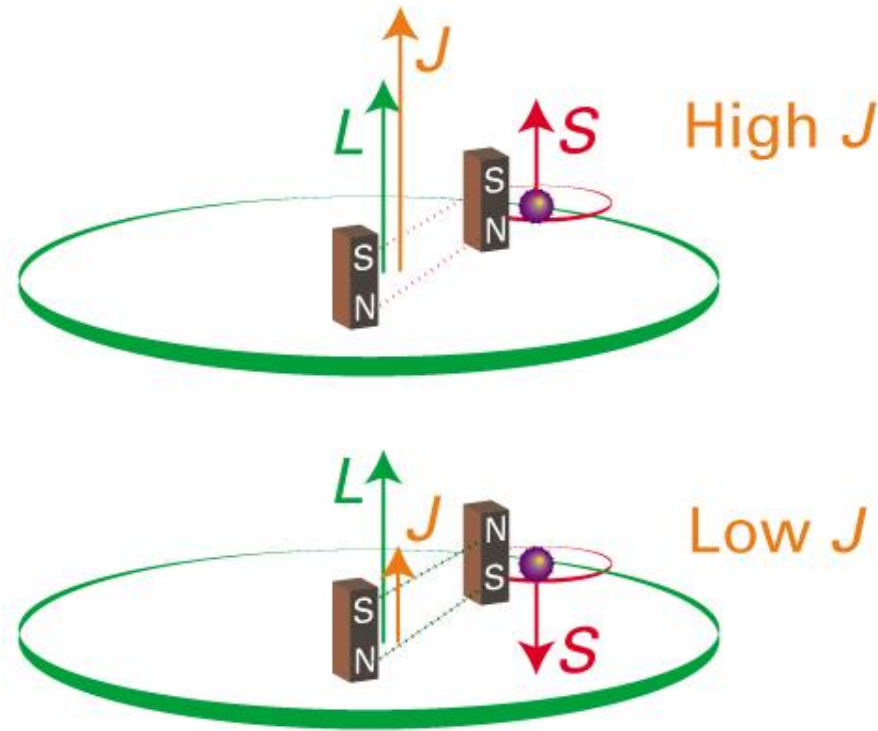We have seen that j gives relative orientation of spin and orbital angular momentum of single electron

Total angular momentum quantum number J does same thing for multi-electron system

$$J = L+S, L+S-1, \ldots\ldots\ldots, |L-S|$$
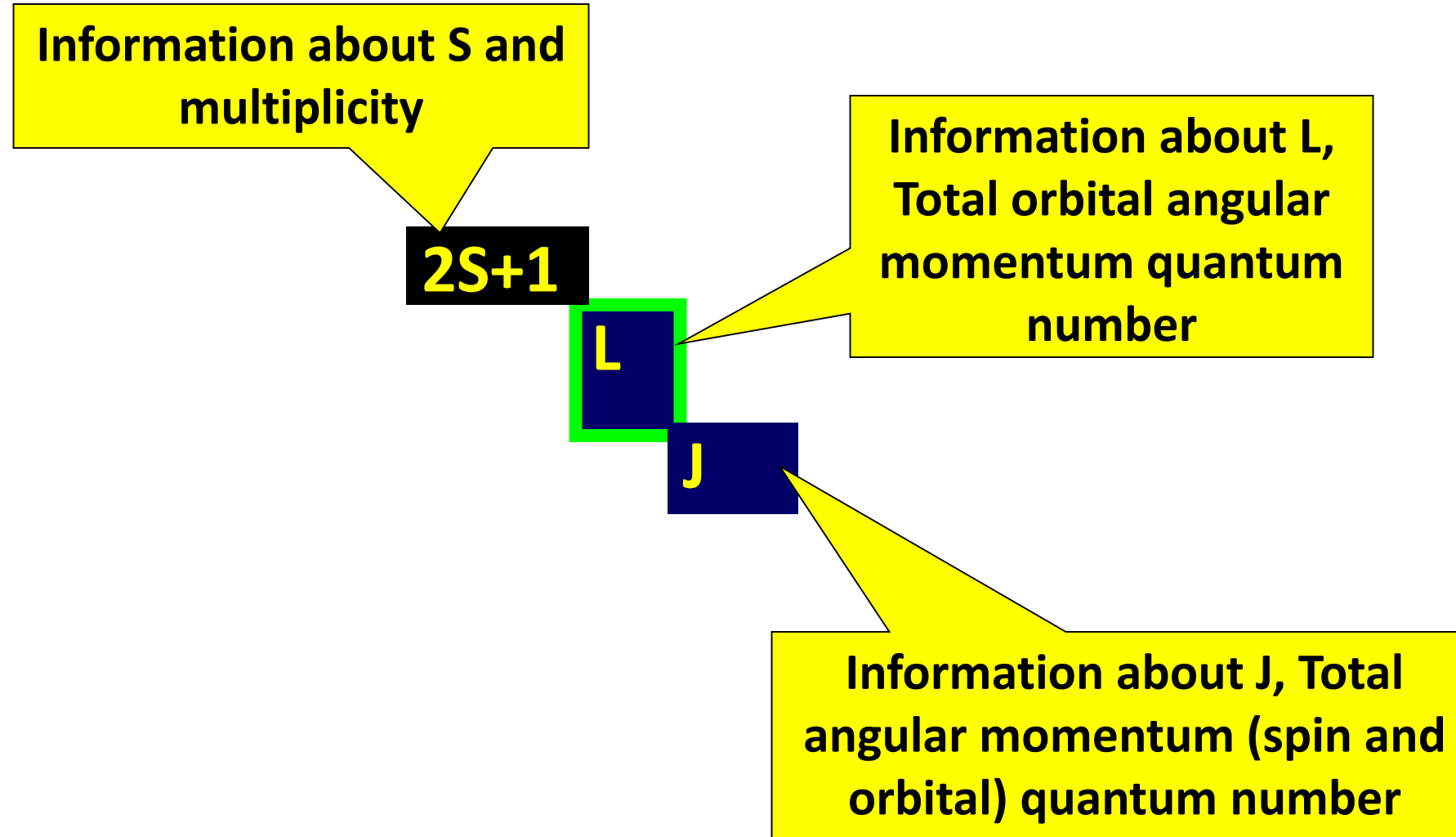
Russell-Saunders coupling

Russel-Saunders coupling fails when the spin-orbit coupling is large – for heavy atoms

Spin-orbit coupling for multi-electron system

- A term with different J values represent different levels.
- Each level with quantum number J consists of 2J+1 individual states distinguished by the M_J quantum number.
- Each state with quantum number J is 2J+1 fold degenerate.

# Information from Term Symbol

Information about S and multiplicity

2S+1

L

Information about L, Total orbital angular momentum quantum number

J

Information about J, Total angular momentum (spin and orbital) quantum number
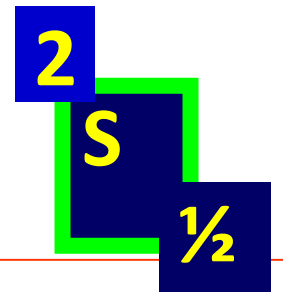
General Scheme to derive Term Symbol

- Begin writing configurations but ignore inner closed shells

- Couple all orbital momenta to find L

- Couple all spin momenta to find S

- Next couple L and S to find J

2S+1

L

J
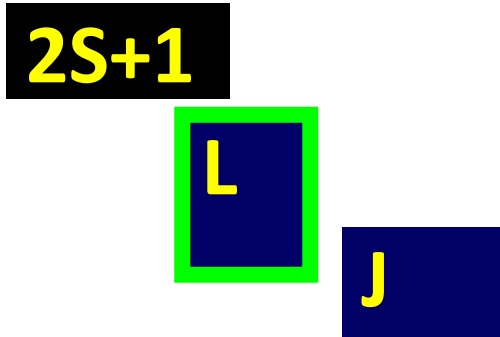
Na: [Ne] $3s^1$

- Consider single 3s electron

- L = l = 0

- S = s = ½

- J = j = ½

2

S

½

Electronic structure of atoms

Now consider the configuration $2p^1 3p^1$ (in-equivalent electrons).

- What are the possible values of L?

- The maximum value is $l_1 + l_2 = 2$, the next is $l_1 + l_2 - 1 = 1$, and the last is $|l_1 - l_2| = 0$

- L = 0, 1, 2;   L = S, P, D

- What are the possible values of S?

- $S = s_1 + s_2 = 1/2 + ½ = 1$, the next is $| s_1 - s_2 | = 1/2 - ½ = 0$

- Multiplicity = 3, 1

- Triplet terms: ^3D, ^3P, ^3S Singlet terms: ^1D, ^1P, ^1S

Electronic structure of atoms

Triplet terms: ^3D, ^3P, ^3S Singlet terms: ^1D, ^1P, ^1S

For ^3D term: L = 2 and S = 1, So J = 3,2,1.

Levels are $^3D_3$, $^3D_2$, $^3D_1$

For ^3P term, L = 1 and S = 1, So, J = 2,1,0. Levels are : $^3P_2$, $^3P_1$, $^3P_0$

Similarly for ^3S, Levels are $^3S_1$

^1D term: Level is : $^1D_2$

^1P term: Level is: $^1P_1$

^1S term: Level is: $^1S_0$

All levels exist for configuration $2p^1 3p^1$

Electronic structure of atoms

If a set of states is characterized by the values L and S for the total orbital and spin angular momentum quantum numbers respectively, how many states are there?

$(2L + 1)(2S + 1)$

For ^3D term, No. of states = $(2\times2+1)(2\times1+1)$ = 15

No. of states corresponding to other terms:

^3P term: 9

^3S term: 3

^1D term: 5

^1P term: 3

^1S term: 1

- Defined by Z-component of total angular momentum
- Will be defined by a new quantum number M_J
- Degeneracy will be $(2J+1)$

Total no. of states: 36

All 36 states exist for configuration $2p^13p^1$

Ground state term: Hund's rule

- The term with the greatest multiplicity lies lowest in energy.
The ground state therefore possesses the most unpaired spins because this gives the minimum electrostatic repulsion.
So one of the terms ^3D, ^3P, ^3S arising from [He]$2s^2 2p^1 3p^1$ configuration lies lowest.

- The term with the greatest orbital angular momentum lies lowest in energy.
So ^3D term mentioned above will lie lowest of all the terms.

- The level with lowest J lies lowest in energy if the subshell is less than half filled. The level with highest J lies lowest in energy if the subshell is more than half filled. This rule is not applicable for excited configurations.

Fine structure for np n'p configuration

All the transitions are allowed?

Selection Rules
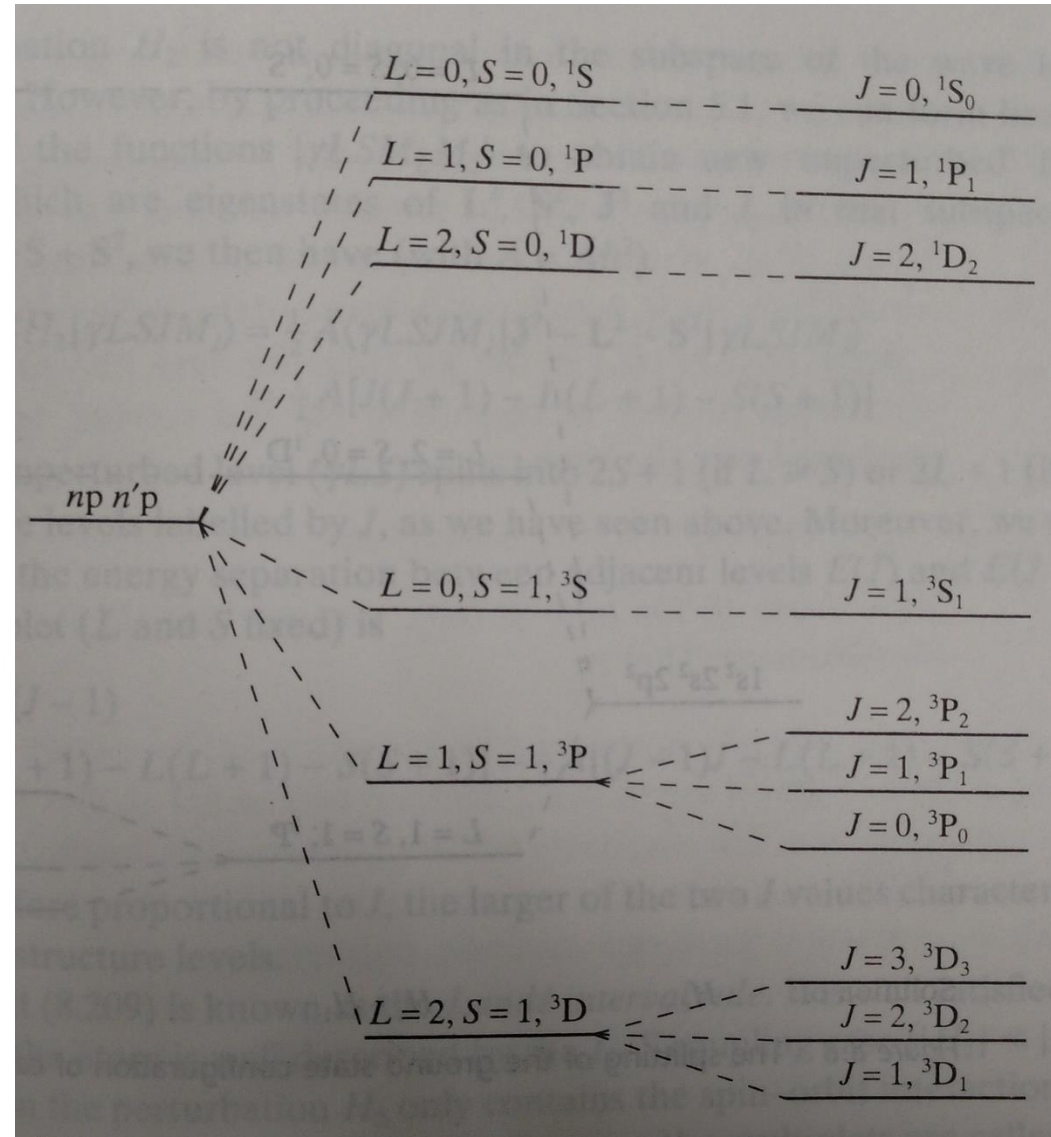
For spectroscopic transitions in many-electron atoms:
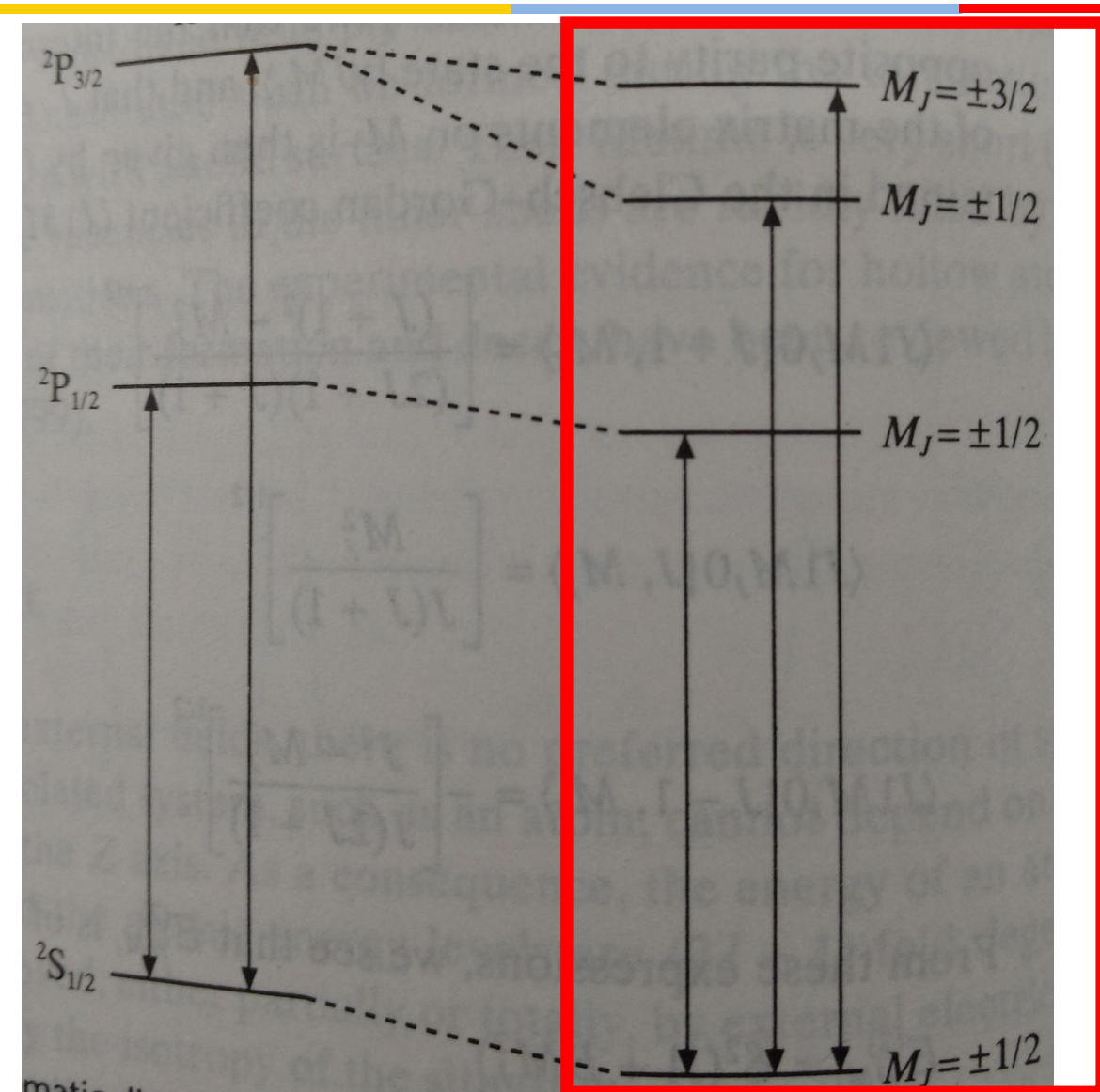
$$\Delta L = 0, \pm 1$$

$$(\Delta l = \pm 1)$$

$$\Delta S = 0$$

$$\Delta J = 0, \pm 1 \text{ (but } J = 0 <-> J = 0 \text{ is forbidden)}$$

Sodium D-lines in presence of electric field

In presence of electric field

$$\Delta L = 0, \pm 1$$

$$\Delta S = 0$$

$$\Delta J = 0, \pm 1$$

What happen in many electron atom??

Bransden & Jochain