The Atomic states

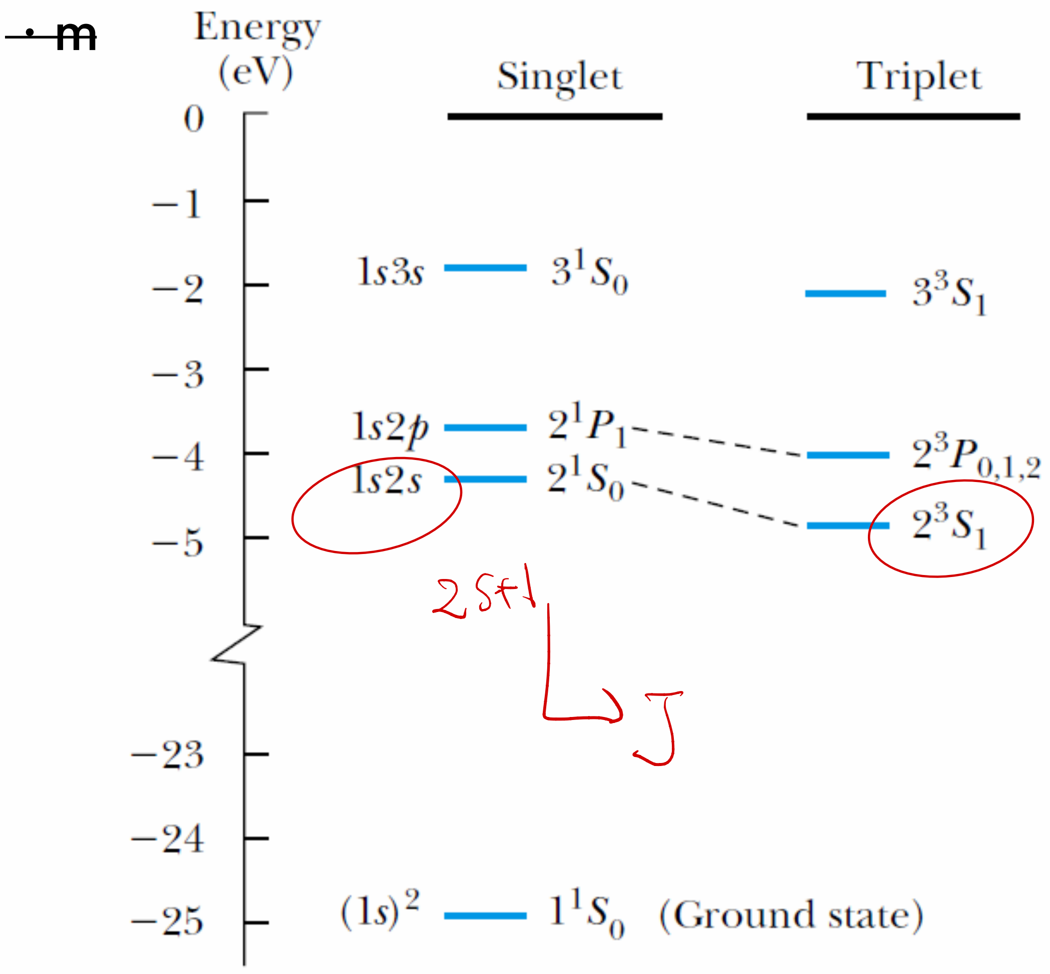


Figure 8.13 The low-lying atomic states of helium are shown. The ground state ($^1S_0$) is some 20 eV below the grouping of the lowest excited states. The level indicated by $^3P_{0,1,2}$ is actually three states ($^3P_0$, $^3P_1$, $^3P_2$), but the separations are too small to be indicated.

2^3S_1 is allowed because 1s and 2S are in different n shells, so that they are distinguishable states.

Two electrons 1S2S

① $l_1 = 0$, $s_1 = \frac{1}{2}$

② $l_2 = 0$, $s_2 = \frac{1}{2}$

⇒ $\vec{L} = \vec{L}_1 + \vec{L}_2$; $\vec{S} = \vec{S}_1 + \vec{S}_2$

($l = 0$) ($S = 0, 1$)

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

($J = 0, 1$)

⇒ 2^1S_0 & 2^3S_1

The Atomic states

Spectroscopic Notation

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

Hydrogen energy levels

Less than thermal energy → $4.5x10^{-5}\,eV = \frac{3}{2}kT$ at $0.35\ K$

$\Delta E = 4.5x10^{-5}\,eV$

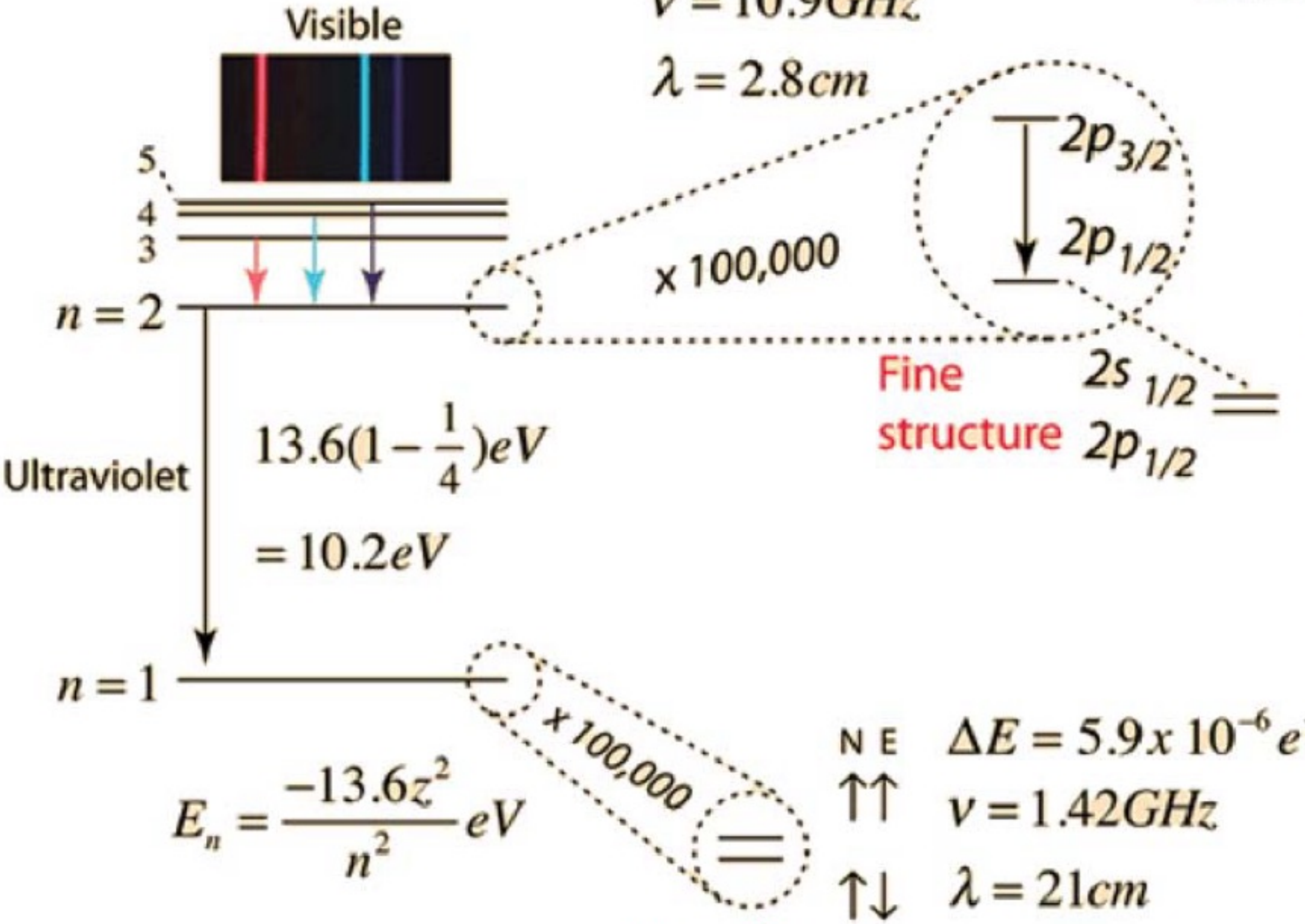
$\nu = 10.9\,GHz$

$\lambda = 2.8\,cm$

Barely resolvable since the Doppler broadening is about 4 GHz

$^{2}P_{3/2}$ (for $s=\frac{1}{2}$, $l=1$)

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



Fine structure

$2s_{1/2}$

$2p_{1/2}$

$\Delta E = 4.372x10^{-6}\,eV$

$\nu = 1.0576\,GHz$

$\lambda = 28.37\,cm$

Lamb shift

$13.6(1-\frac{1}{4})eV$

$= 10.2\,eV$

$$E_n = \frac{-13.6z^2}{n^2}eV$$

Hyperfine structure

$\Delta E = 5.9x\,10^{-6}\,eV$

$\nu = 1.42\,GHz$

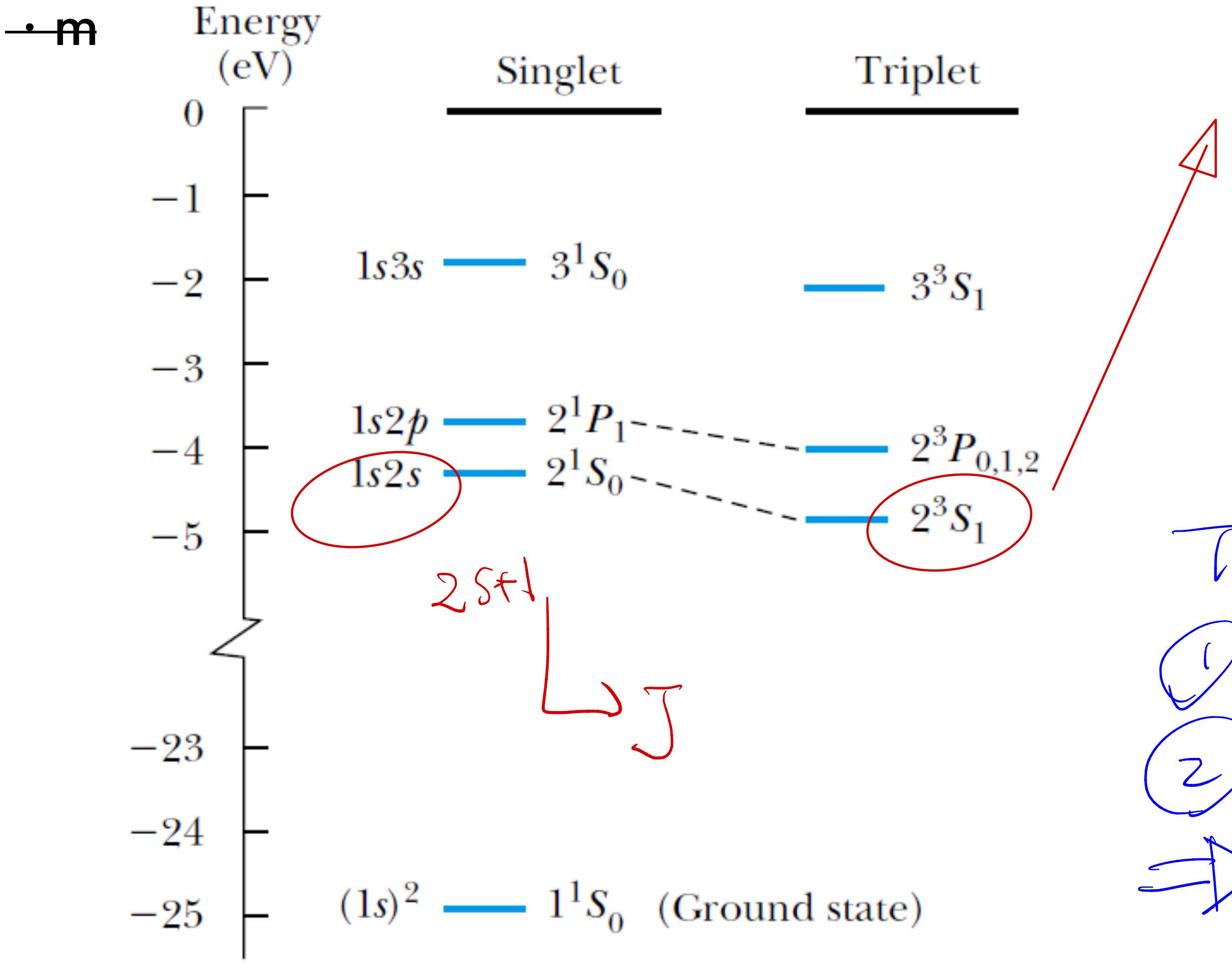
$\lambda = 21\,cm$

N = nuclear spin

E = electron spin

$^{2S+1}L_J$

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



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Two electrons 1s2s

① $l_1=0$, $s_1=\frac{1}{2}$

② $l_2=0$, $s_2=\frac{1}{2}$

$\Rightarrow$ $\vec{L}=\vec{L}_1+\vec{L}_2$; $\vec{S}=\vec{S}_1+\vec{S}_2$

($l=0$) ($s=0,1$)

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

($J=0,1$)

$\Rightarrow$ 2^1S_0 & 2^3S_1

What are the possible energy states for atomic carbon?

Strategy The element carbon has two $2p$ subshell electrons outside the closed $2s^2$ subshell. Both electrons have $\ell = 1$, so we have $L = 0, 1,$ or 2 using the LS coupling scheme. The spin angular momentum is $S = 0$ or 1.

$S=0$ (antisymmetric) $\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

$S=1$ (symmetric) $\uparrow\downarrow$, $\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$, $\downarrow\downarrow$

spin wave function

$\vec{L} = \vec{L}_1 + \vec{L}_2$

$^{2S+1}L_J$

S	L	J	Spectroscopic Notation	
0	0	0	$^1S_0$	
	1	1	$^1P_1$	$S=0,\ L=1$ Not allowed
	2	2	$^1D_2$	
1	0	1	$^3S_1$	$S=1,\ L=0$ Not allowed
	1	0, 1, 2	$^3P_{0,1,2}$	
	2	1, 2, 3	$^3D_{1,2,3}$	$S=1,\ L=2$ Not allowed

Spatial (orbital) wave function

$$(-1)^L = \begin{cases} -1, & \text{antisymmetric} \\ 1, & \text{symmetric} \end{cases}$$

For fermions (such as electrons),

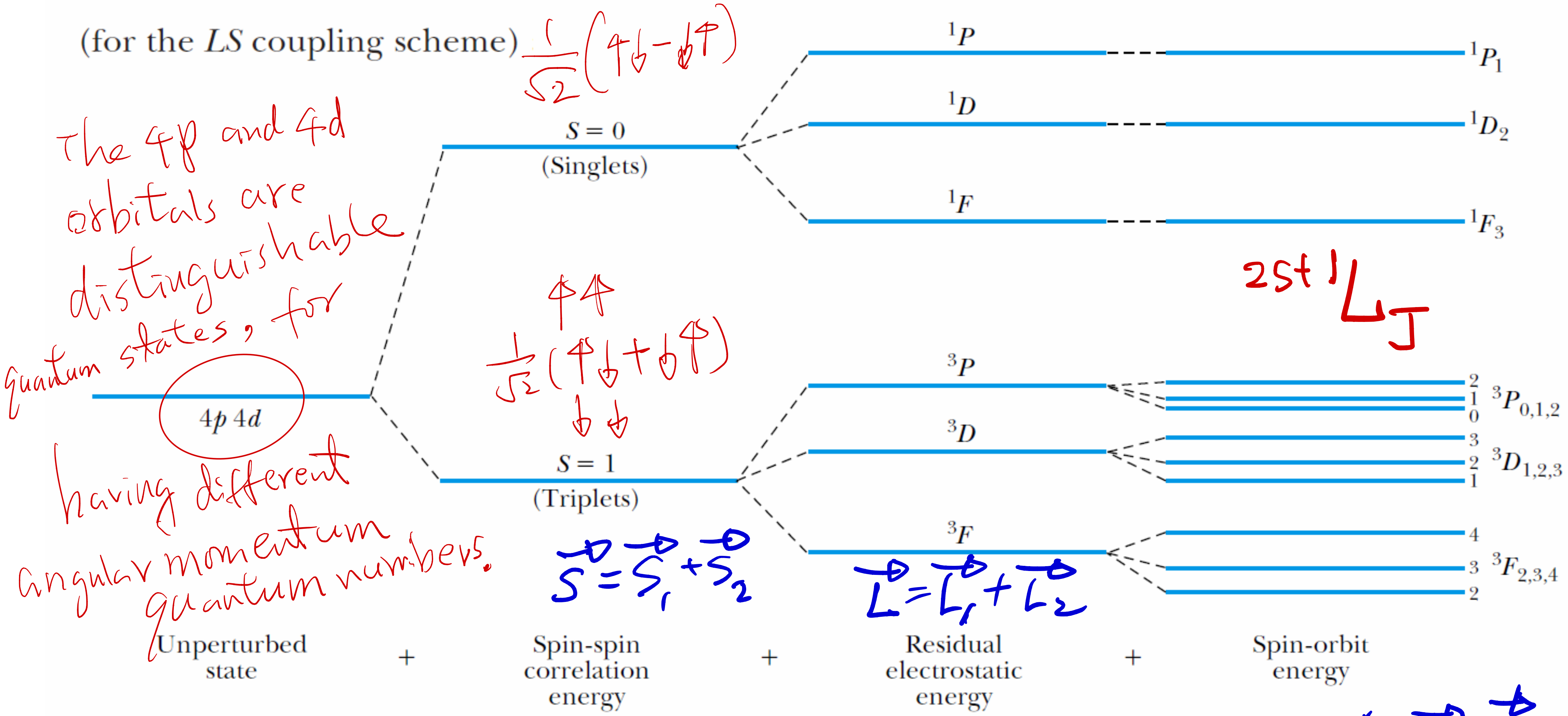
Total wave function

$\equiv$ (spin wave func.) $*$ (spatial, orbital wave func.)

$=$ anti-symmetric

(Pauli Exclusion Principle)

$\Rightarrow$ Require $\boxed{(-1)^{S+1} \cdot (-1)^L = -1}$



$\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

The 4p and 4d orbitals are distinguishable quantum states, for having different angular momentum quantum numbers.

$\uparrow\uparrow$

$\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$

$\downarrow\downarrow$

$^{2S+1}L_J$

$\vec{S} = \vec{S}_1 + \vec{S}_2$

$\vec{L} = \vec{L}_1 + \vec{L}_2$

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

Figure 8.9 Schematic diagram indicating the increasing fine-structure splitting due to different effects. This case is for an atom having two valence electrons, one in the 4*p* and the other in the 4*d* state. The energy is not to scale. *From R. B. Leighton,* Principles of Modern Physics, *New York: McGraw-Hill (1959), p. 261. Used with permission.*

Transition Matrix element

$$\langle f | H_{int} | i \rangle$$

$$= \langle f | (-e\vec{r}\cdot\vec{E}) | i \rangle$$

for the electric dipole interaction

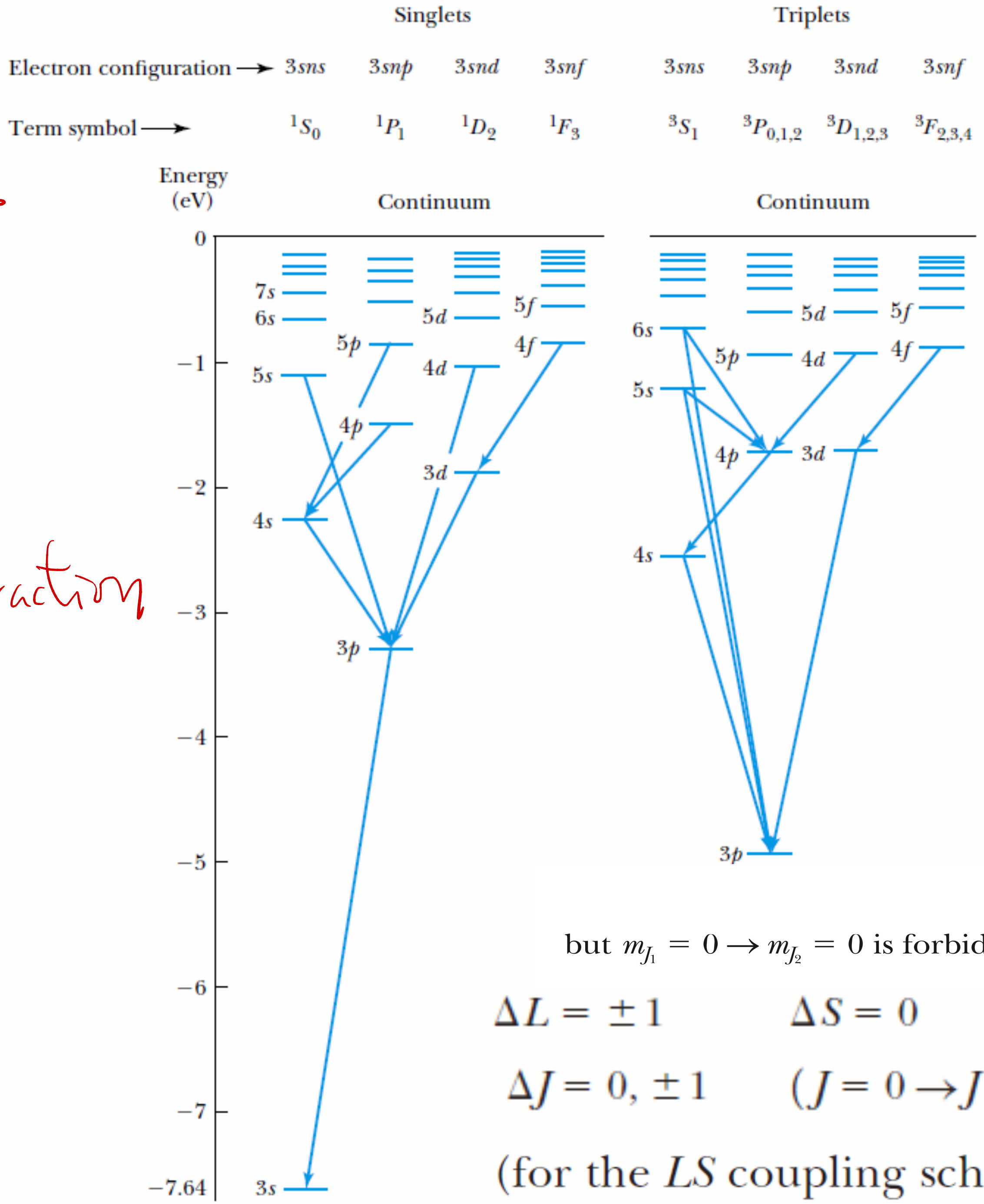


Figure 8.10 Energy-level diagram for magnesium (two-electron atom) with one electron in the 3*s* subshell and the other electron excited into the *nℓ* subshell indicated. The singlet and triplet states are separated, because transitions between them are not allowed by the $\Delta S = 0$ selection rule. Several allowed transitions are indicated.

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

but $m_{J_1} = 0 \rightarrow m_{J_2} = 0$ is forbidden when $\Delta J = 0$.

$\Delta L = \pm 1$ $\quad\quad$ $\Delta S = 0$

$\Delta J = 0, \pm 1$ $\quad\quad$ ($J = 0 \rightarrow J = 0$ is forbidden)

(for the *LS* coupling scheme)

What are the possible energy states for atomic carbon?

Strategy The element carbon has two 2*p* subshell electrons outside the closed $2s^2$ subshell. Both electrons have $\ell = 1$, so we have $L = 0, 1,$ or 2 using the *LS* coupling scheme. The spin angular momentum is $S = 0$ or 1.

$^{2S+1}L_J$

$\vec{L} = \vec{L}_1 + \vec{L}_2$

$S=0$ (antisymmetric) $\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

$S=1$ (symmetric) $\uparrow\uparrow$, $\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$, $\downarrow\downarrow$

spin wave function

Spatial (orbital) wave function

$(-1)^L = \begin{cases} -1, & \text{antisymmetric} \\ 1, & \text{symmetric} \end{cases}$

S	*L*	*J*	Spectroscopic Notation	
0	0	0	$^1S_0$	
	1	1	$^1P_1$	Not allowed
	2	2	$^1D_2$	
1	0	1	$^3S_1$	Not allowed
	1	0, 1, 2	$^3P_{0,1,2}$	
	2	1, 2, 3	$^3D_{1,2,3}$	Not allowed

$S=0,\ L=1$

$S=1,\ L=0$

$S=1,\ L=2$

For fermions (such as electrons),

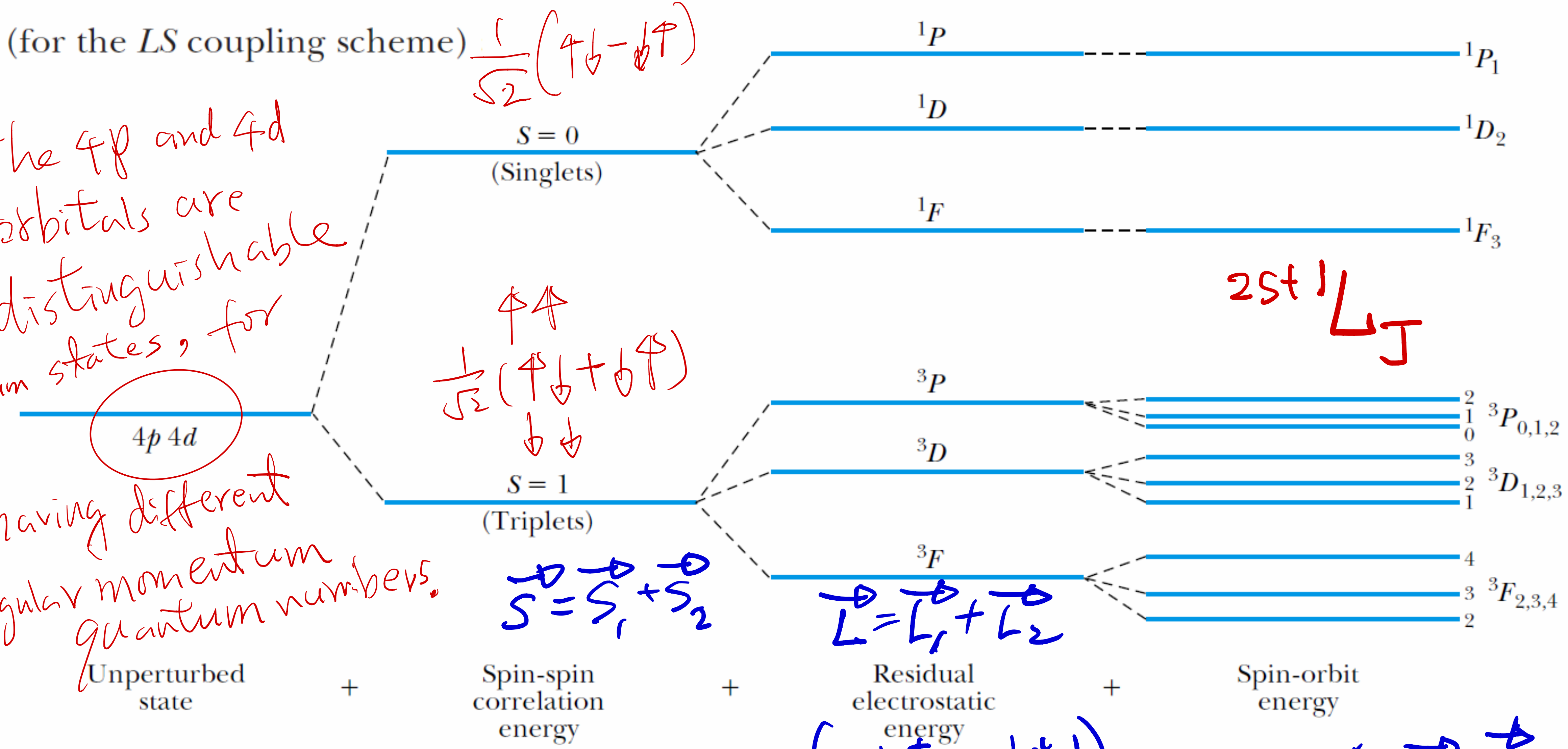
Total wave function

$\equiv$ (spin wave func.) * (spatial, orbital wave func.)

= anti-symmetric

(Pauli Exclusion Principle)

$\Rightarrow$ Require $\boxed{(-1)^{S+1} \cdot (-1)^L = -1}$



$\frac{1}{\sqrt{2}}(\uparrow\downarrow-\downarrow\uparrow)$

The 4p and 4d orbitals are distinguishable quantum states, for having different angular momentum quantum numbers.

$\uparrow\uparrow$

$\frac{1}{\sqrt{2}}(\uparrow\downarrow+\downarrow\uparrow)$

$\downarrow\downarrow$

$^{2S+1}L_J$

$\vec{S}=\vec{S}_1+\vec{S}_2$

$\vec{L}=\vec{L}_1+\vec{L}_2$

(orbital-orbital)

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

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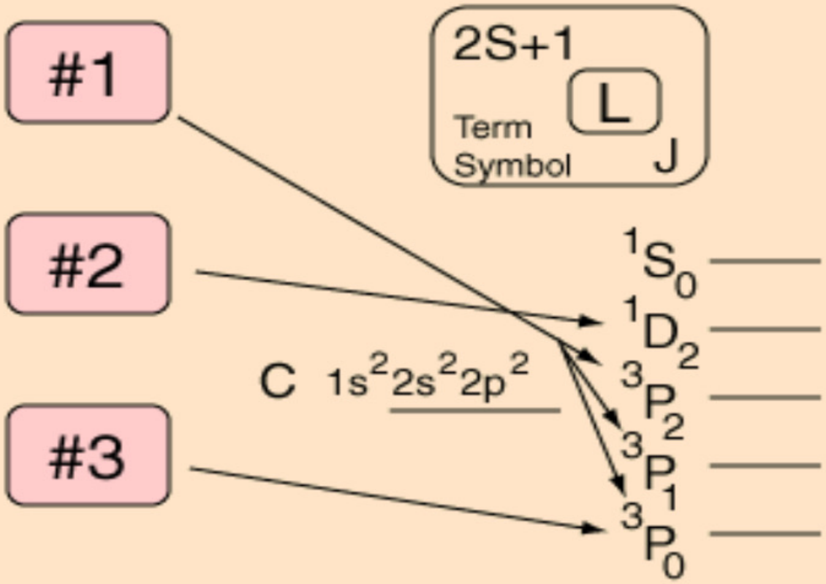
Hund's Rules

1. The term with maximum multiplicity lies lowest in energy.

2. For a given multiplicity, the term with the largest value of L lies lowest in energy.

3. For atoms with less than half-filled shells, the level with the lowest value of J lies lowest in energy.

Click on the indicated buttons for more detail.



Hund's rules assume combination to form S and L, or imply L-S (Russell-Saunders) coupling.

Note: Some references, such as Haken & Wolf, use Hund's Rule #1 to apply to the nature of full shells and subshells. Full shells and subshells contribute nothing to the total angular momenta L and S. If you call this Hund'e Rule #1, then the above rules will be bumped up one in number. I don't know which is the more common practice.

Exceptions to Hund's Rules

Index

Atomic structure concepts

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$$= \langle f | (-e\vec{r}\cdot\vec{E}) | i \rangle$$

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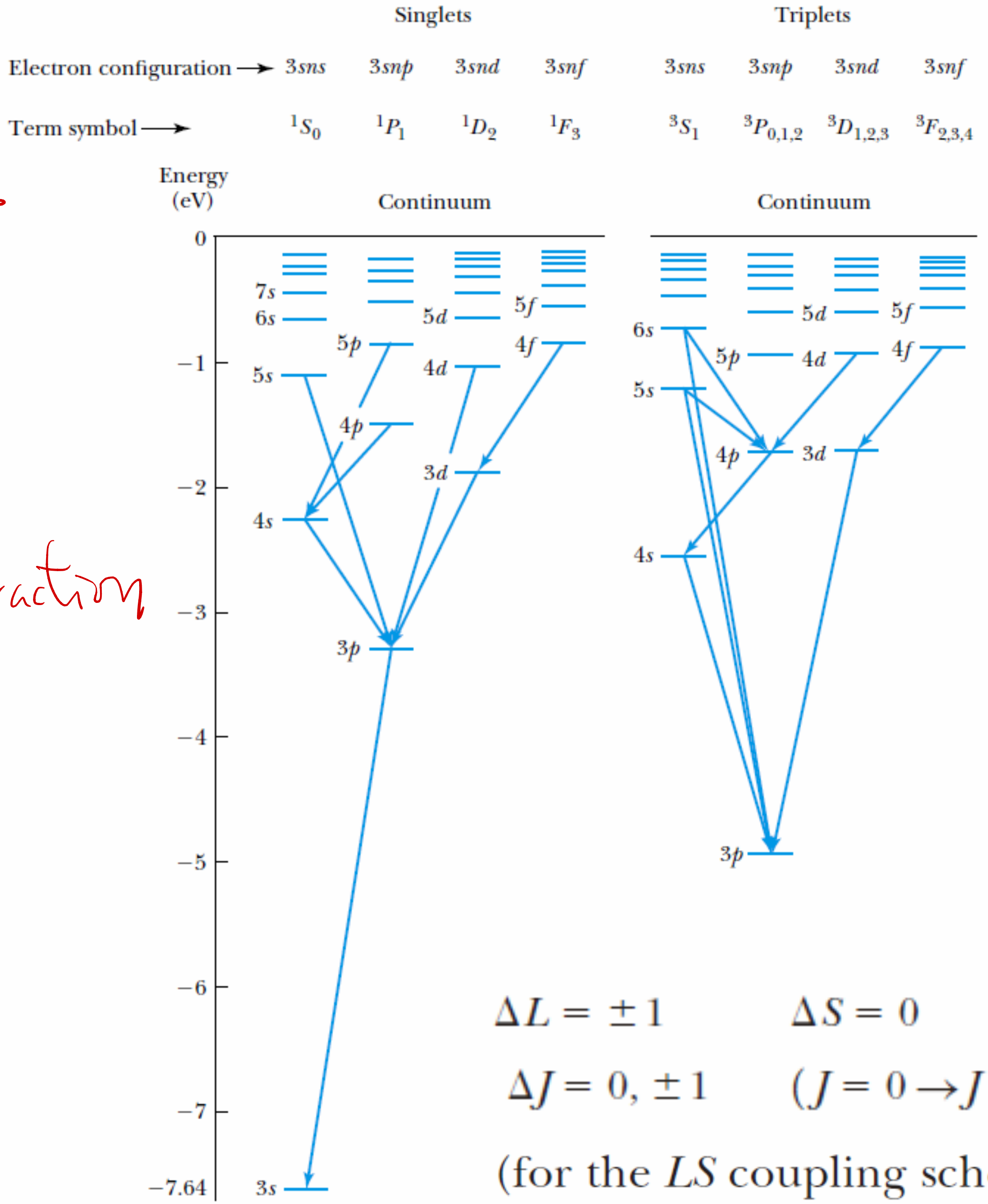

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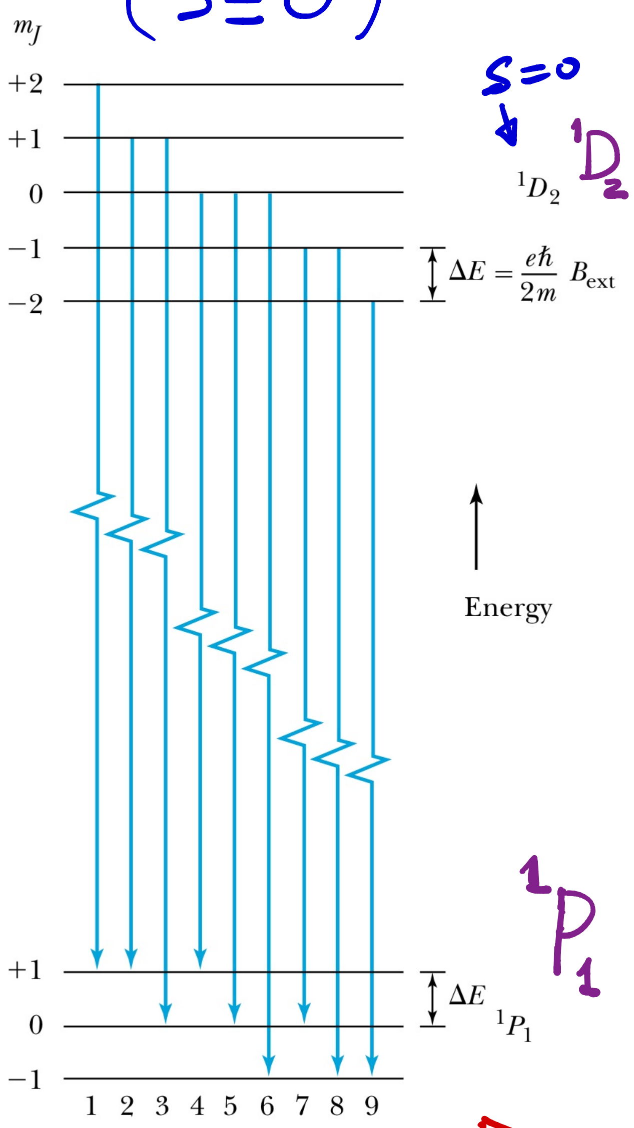
$\Delta L = \pm 1 \qquad \Delta S = 0$

$\Delta J = 0, \pm 1 \qquad (J = 0 \rightarrow J = 0 \text{ is forbidden})$

(for the *LS* coupling scheme)

normal
Zeeman Effect
$(s=0)$



with $\overrightarrow{B}_{\text{ext}}$

$^{2S+1}L_J$

anomalous
Zeeman Effect
$(s\neq 0)$