PH 585
AMO

Lecture #19

L-S and j-j coupling

L-S : $H = H_c + \underbrace{H_1} = \sum_{i<j=1}^{N} \frac{1}{r_{ij}} - \sum_i \left(\frac{Z}{r_i} + \bar{V}(r_i) \right)$

$\uparrow$ $H_1 \gg |H_2|$

$[H, \vec{L}^2] = 0$ $\nearrow$

$[H, \vec{S}^2] = 0$ ← recall properties of central potentials

- $E_c \leftarrow \underset{\overset{\uparrow}{M_L}}{(2L+1)} \underset{\overset{\uparrow}{M_s}}{(2S+1)}$ - degenerate

- $H_1 \rightarrow$ partially removes degeneracy
- work in $|\gamma L S M_L M_s\rangle$ basis
- energy levels corresponding to definite L & S; terms ^{2S+1}L

• addition of angular momenta ⇐

• Pauli exclusion principle

multiplicity $\swarrow$ $\nearrow$ $\qquad$ $\uparrow$

$S, P, D, F, ..$
$0, 1, 2, 3$

S: 0 $\frac{1}{2}$ 1

$2S+1$: 1 2 3 ...

$\uparrow$ singlet $\uparrow$ doublet $\uparrow$ triplet

1) Closed sub-shell ⇒ 2(2l+1) equivalent electrons

specified n & l

$$\Downarrow$$

$$\underset{S}{M_L} = \sum_i \underset{s}{m_{l_i}} = 0 \Rightarrow L = S =$$

all closed sub-shells are ^1S

degeneracy = $2 \cdot 2(2l_1+1) \cdot (2l_2+1)$

2) Non-equivalent electrons → say, $np \; \& \; n'p$

$L = l_1 + l_2, \ldots |l_1 - l_2|$; $S = s_1 + s_2, \ldots |s_1 - s_2|$

addition of $\vec{L}_1$ & $\vec{L}_2$

↑ Pauli principle already satisfi
since $n \neq n'$

$l_1 = l_2 = 1$, $s_1 = s_2 = \frac{1}{2}$

$L = 0, 1, 2 \quad S = 0, 1 \Rightarrow {}^1S, {}^3S, {}^1P, {}^3P, {}^1D, {}^3$

If more than 2 electrons ⇒ first add two ⇒ $\vec{L}_{12} = \vec{L}_1 + \vec{L}_2$ and then $\vec{L} = \vec{L}_{12} + \vec{L}_3$

3) Equivalent electrons ⇒ watch out for Pauli principle.

$np^2 \Rightarrow$ degeneracy $\frac{6!}{2!\,4!} = 15 \leftarrow \sum_{\text{all allowed terms}} (2L+1)(2S+1)$

Exclude terms with $\underset{s_1}{m_{l_1}} \underset{\&}{=} \underset{s_2}{m_{l_2}}$

as well as count $m_{l_1} = 1$, $m_{l_2} = 0$, $m_{s_{1,2}} = \pm\frac{1}{2}$
$m_{l_1} = 0$, $m_{l_2} = 1$, $m_{s_{1,2}} = \mp\frac{1}{2}$ as 1 stat

degeneracy:

$$\binom{2(2l+1)}{2} = (2l+1)(4l+1)$$

So, can't have $\underset{M_S=1}{\uparrow}\,{}^3D \nwarrow$ e.s. $M_L=2$, but $\underset{M_S=0}{\uparrow}\,{}^1D \underset{M_L=2}{\uparrow}$ is OK

${}^3S \Leftarrow$ forbidden $\Rightarrow m_{l_1}=m_{l_2}=0 \Leftarrow M_L=0$

$m_{s_1}=m_{s_2}=1/2 \Leftrightarrow M_s=1$

${}^1P \Leftarrow$ excluded (equivalency of $m_{l_{\substack{1\\2}}}=1,\ m_{l_{\substack{2\\1}}}=0$ & $m_{s_{\substack{1\\2}}}=\frac{1}{2},\ m_{s_{\substack{2\\1}}}=-\frac{1}{2}$ configurations)

Over all, only ${}^1S$, ${}^1D$, ${}^3P$ survive

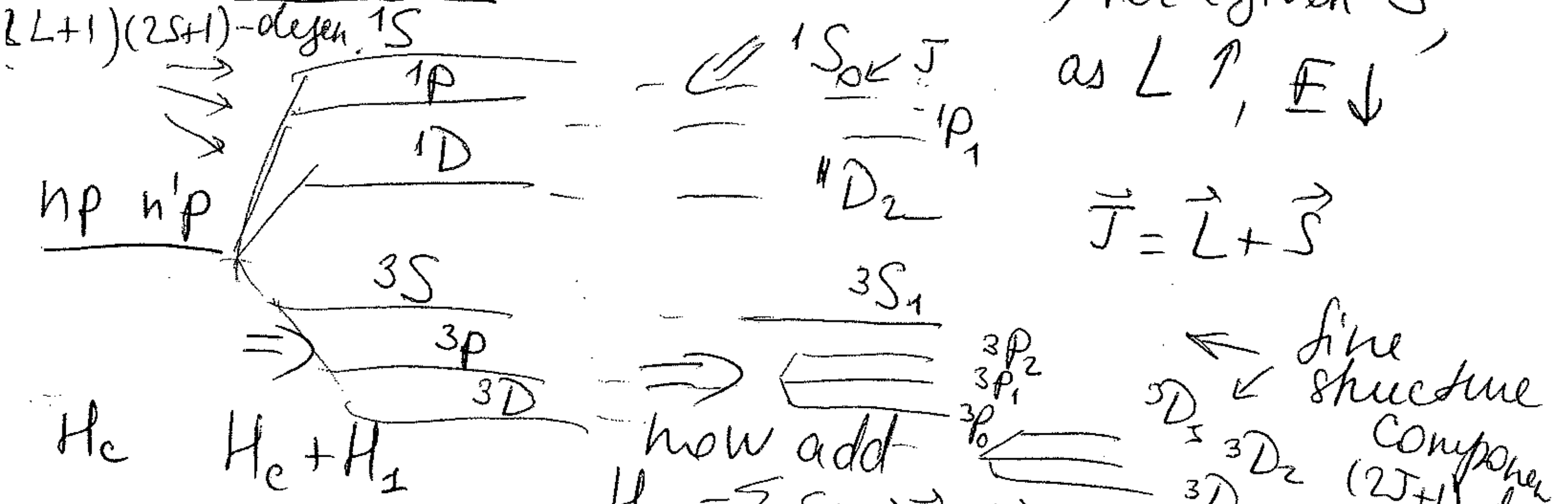
$$\underset{2L+1\nearrow}{1}\cdot\underset{\uparrow\,2S+1}{1} + 5\cdot 1 + 3\cdot 3 = 1+5+9 = 15 \checkmark$$

So, how are these ${}^{2S+1}L$ terms related to energy?

Hund's rules ⇒ for ground state and for equiv. electrons

1) As $S\uparrow$, $E\downarrow$

2) For a given S, as $L\uparrow$, $E\downarrow$



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

now add $H_2=\sum_i \xi(r_i)\vec{L}_i\cdot\vec{S}_i$ as a perturbation.

Note: $$\sum_{J=|L-S|} (2J+1) = (2L+1)(2S+1)$$

To evaluate correction due to $H_2 \Rightarrow$ need $\xrightarrow{}$ fine structure

$$\langle \gamma L S M_L M_S | H_2 | \gamma L S M_L' M_S' \rangle = \bar{A} \langle L S M_L M_S | \underbrace{\vec{L}\cdot\vec{S}}_{\frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)} | L S M_L' M_S' \rangle$$

$$|L S M_L M_S\rangle \Rightarrow |L S J M_J\rangle$$
basis change

$$\Downarrow$$

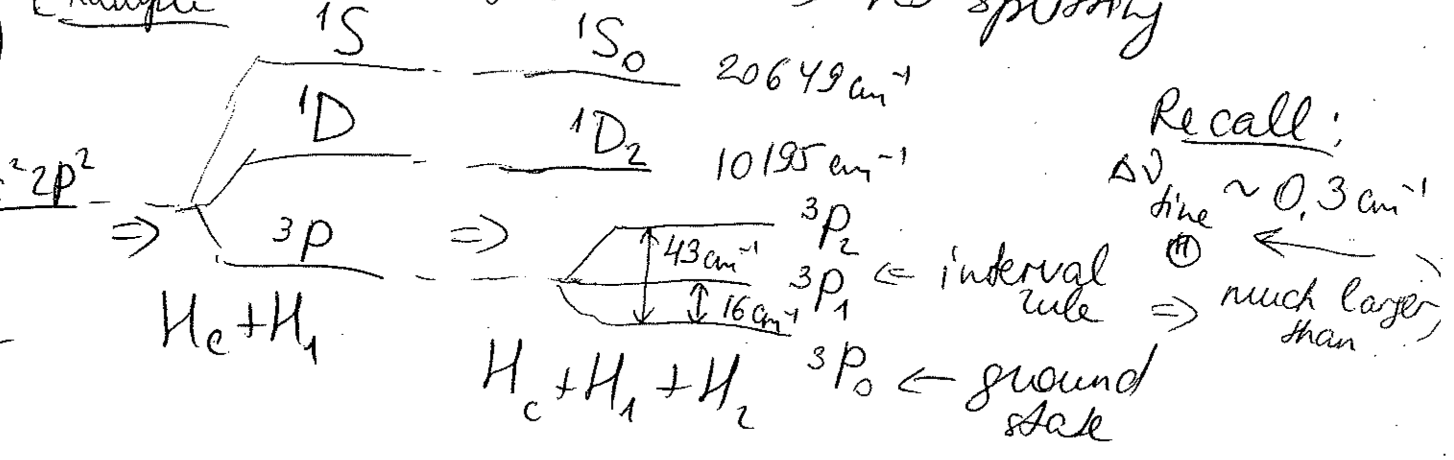
$$\langle L S J M_J | H_2 | L S J M_J \rangle = \frac{\bar{A}}{2}\hbar^2 \left[J(J+1) - L(L+1) - S(S+1) \right]$$ ← splitting ⇒ regular multiplets (if no other perturbation)

$$E(J) - E(J-1) = \underset{\substack{\uparrow \\ \text{fixed} \\ L,S}}{A} J$$ ← Landé interval rule

If $A > 0 \Rightarrow$ normal multiplet ⇒ observed in < half-filled sub-shells
$ < \Rightarrow$ inverted — · · — ⇒ > half-filled sub-shells

If sub-shell is half-filled ⇒ no splitting

Ⓒ Example



2) $\hat{j}-\hat{j}$ coupling $\Leftarrow |H_2| \gg |H_1| \Rightarrow H_2$ important for atoms (ions) with large Z

↑ e.g. Pb (Z=82)

Recall: $\Delta E_{\vec{L}\cdot\vec{S}} \underset{\uparrow}{\sim} Z^4$ p. 242 $\qquad \left\langle \frac{1}{r_{12}} \right\rangle \underset{\uparrow}{\sim} Z$ p. 328

So, consider
$$\hat{H} = H_c + H_2 \underset{\substack{\uparrow \\ \text{in a.u.}}}{=} \sum_{i=1}^{N}\Big[\underbrace{-\frac{1}{2}\vec{\nabla}_{r_i}^2 + V(r_i)}_{\Downarrow\; E_{nl}} + \underbrace{\xi(r_i)\,\vec{L}_i\cdot\vec{S}_i}\Big]$$

but: (2j+1)-degenerate

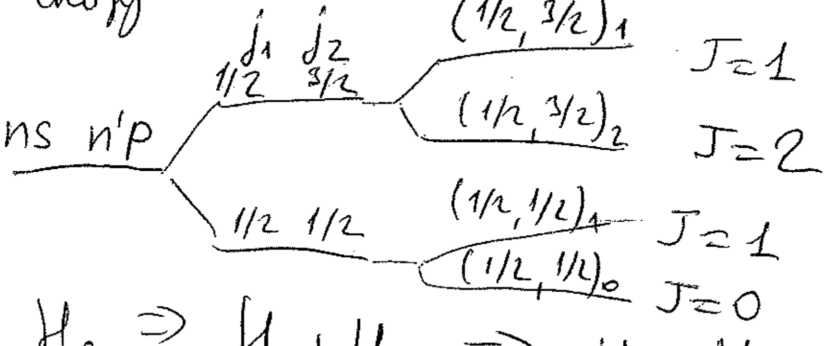
$\Rightarrow E_{nlj}$ ← energy level splitting according to $j = l \pm \frac{1}{2}$

⇓

end up in $|nljm_j\rangle$ basis with u_{nljm_j} ← single-electron functions

$$\underset{\substack{\uparrow \\ \text{total energy}}}{E} = \sum_{i=1}^{N} E_{n_i l_i j_i}$$

, wave function ⟹ Slater determinant of u_{nljm_j}



$J = j_1 + j_2, \ldots, |j_1 - j_2|$

← (2J+1)-degenerate

$$H_c \Rightarrow \underset{\substack{\uparrow \\ \text{doesn't couple diff. } e^-}}{H_c + H_2} \Rightarrow H_c + H_2 + H_1$$

↑ add as perturbation