

Term Symbols and Many-electron Atoms

$$\begin{aligned}
 S &= s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2| \\
 L &= \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \dots, |\ell_1 - \ell_2| \\
 J &= L + S, L + S - 1, \dots, |L - S|
 \end{aligned}
 \left. \vphantom{\begin{aligned} S \\ L \\ J \end{aligned}} \right\} \text{for 2 electrons}$$

$$2p^1 3p^1 \rightarrow {}^3D, {}^1D, {}^3P, {}^1P, {}^3S, {}^1S$$

(keeping track of only L and S)

$$6 \times 6 = 36$$

$$3 \times 5 + 1 \times 5 + 3 \times 3 + 1 \times 3 + 3 \times 1 + 1 \times 1 = 36$$

$$(2p)^2 \rightarrow {}^3P, {}^1S, {}^1D \leftarrow \text{fewer states due to Pauli principle}$$

$$\frac{6 \times 5}{2} = 15 \text{ arrangements}$$

$$3 \times 3 + 1 \times 1 + 1 \times 5 = 15$$

Selection rules

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

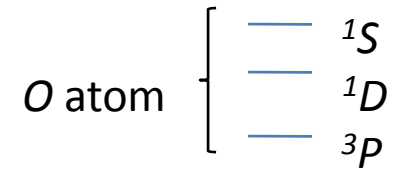
$$\Delta J = 0, \pm 1, \quad J = 0 \rightarrow J = 0$$

$$2p^2({}^1D) \rightarrow 2p3p({}^1D) \quad \text{Not allowed since } \Delta \ell = 0$$

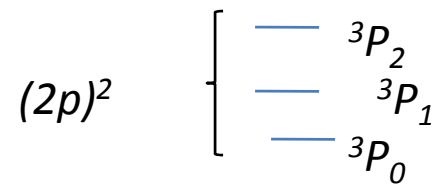
$$2p3p({}^1P) \rightarrow 2s2p({}^1P) \quad \text{Allowed since } \Delta \ell = 1$$

Hund's rules

1. term with lowest multiplicity is lowest in E .
2. for a given multiplicity, the term with the highest L is lowest in E .



3. For atoms with $<$ half-filled shells, the level with the lowest J is lowest in E .



Term symbols based on weak (LS) Russel-Saunders coupling

If spin-orbit coupling is strong, jj coupling scheme is more appropriate

Stark effect

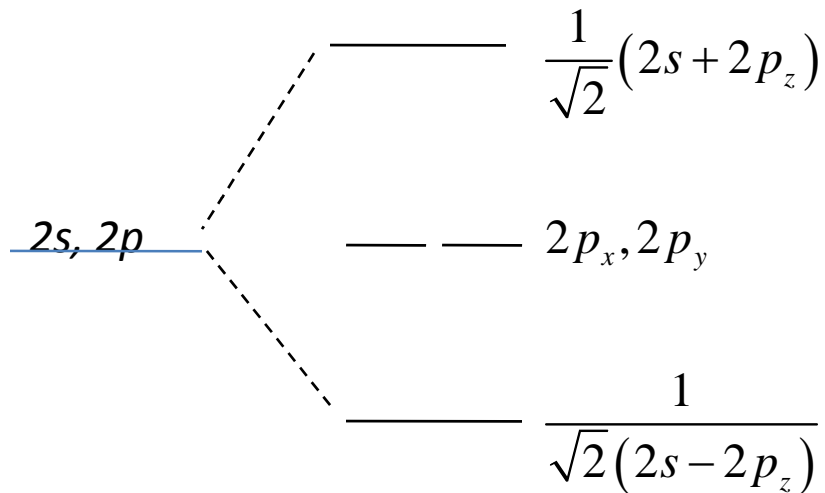
$$H^{(1)} = -\mu_z \mathcal{E} = e z \mathcal{E}$$

$$H^{(1)} = ez\varepsilon$$

Couples levels that differ in ℓ by 1 but have same m_ℓ values

Linear Stark effect between degenerate levels

e.g., between $2s$ and $2p_z$ of the H atom



$$\langle 2s | H^{(1)} | 2p_z \rangle = 3ea_0\varepsilon$$

Even for large fields, the splitting is very small ($\sim \text{cm}^{-1}$)

Quadratic stark effect $\propto \varepsilon^2$

e.g., He atom

The shifts in the $1s$ and $2p_z$ levels are proportional to

$$\frac{|\langle 1s^2 | z | 1s2p_z \rangle|^2}{E_{1s} - E_{2p_z}} e^2 \varepsilon^2$$

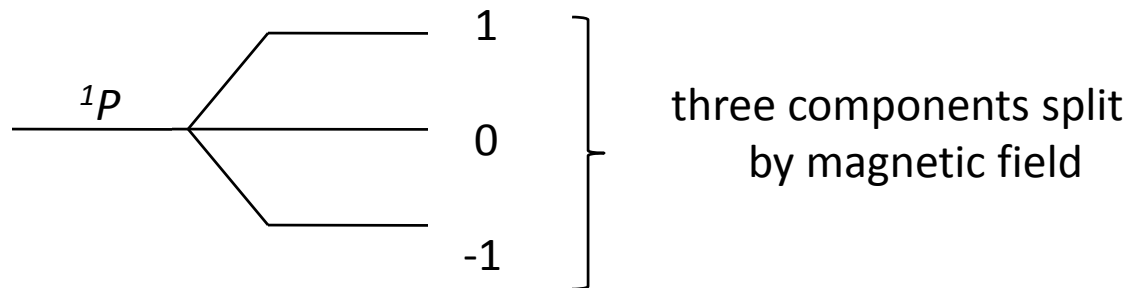
Atoms in Magnetic Fields

Normal Zeeman effect ($S = 0$)

1P Apply magnetic field (B) in the z direction

$$H^{(1)} = -m_z B = \gamma_e \ell_z B$$

$$E^{(1)} = \langle P^{m_L} | H^{(1)} | P^{m_L} \rangle = -\gamma_e m_L \hbar B \\ = \mu_B m_L B$$



$$\Delta m_L = \pm 1 \quad \text{Circularly polarized } (\sigma)$$

$$= 0 \quad \text{Linearly polarized } (\pi)$$

Anomalous Zeeman effect ($S \neq 0$)

$$H^{(1)} = -\gamma_e (L + 2S) \cdot B$$

$$= -\gamma_e \left\{ 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right\} \vec{J} \cdot \vec{B}$$

