Term Symbols and Many-electron Atoms

$$S = s_1 + s_2, s_1 + s_2 - 1, \cdots, |s_1 - s_2|$$
$$L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1, \cdots, |\ell_1 - \ell_2|$$
$$J = L + S, L + S - 1, \cdots, |L - S|$$

for 2 electrons

2p¹3p¹ → ^3D, ^1D, ^3P, ^1P, ^3S, ^1S
(keeping track of only *L* and *S*)

6x6=36
3x5+1x5+3x3+1x3+3x1+1x1=36

$(2p)^2$ → ^3P, ^1S, ^1D ← fewer states due to Pauli principle

$$\frac{6*5}{2} = 15 \text{ arrangements}$$
$$3x3 + 1x1 + 1x5 = 15$$

Selection rules

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

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

$2p3p(^1P) \rightarrow 2s2p(^1P)$ 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.

O atom: ^1S, ^1D, ^3P

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

$(2p)^2$: $^3P_2$, $^3P_1$, $^3P_0$

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

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

---

Stark effect

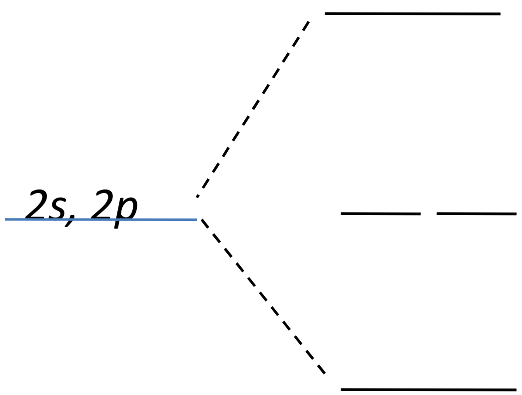
$$H^{(1)} = -\mu z \varepsilon = e z \varepsilon$$

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

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



$$\frac{1}{\sqrt{2}}(2s + 2p_z)$$

$$2p_x, 2p_y$$

$$\frac{1}{\sqrt{2}(2s - 2p_z)}$$

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

Even for large fields, the splitting is very small (~cm^{-1})

Quadratic stark effect $\propto \varepsilon^2$

e.g., *He* atom

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

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

Atoms in Magnetic Fields

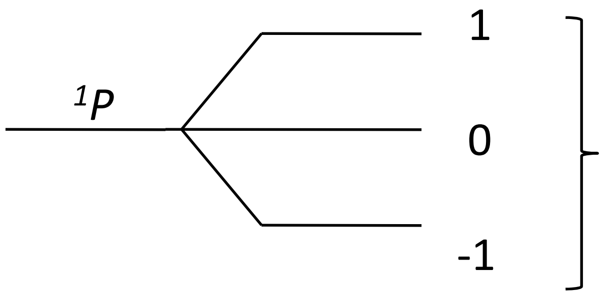
Normal Zeeman effect *(S = 0)*

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

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

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

$$= \mu_B m_L B$$



three components split by magnetic field

$$\Delta m_L = \pm 1$$ Circularly polarized *(σ)*

$$= 0$$ Linearly polarized *(π)*

Anomalous Zeeman effect *(S ≠ 0)*

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

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