

Adding Angular Momenta

CHEM 2430

Adding Angular Momenta

$$\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2, \quad L_x = L_{1x} + L_{2x} \text{ etc.}$$

$$\hat{L}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$(\hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2) \cdot (\hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2) = \hat{L}_1^2 + \hat{L}_2^2 + \hat{\mathbf{L}}_1 \hat{\mathbf{L}}_2 + \hat{\mathbf{L}}_2 \hat{\mathbf{L}}_1$$

$$\hat{L}^2 = \hat{L}_1^2 + \hat{L}_2^2 + 2(L_{1x}L_{2x} + L_{1y}L_{2y} + L_{1z}L_{2z})$$

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \text{ etc.}$$

$$[\hat{L}^2, \hat{L}_x] = 0, \text{ etc.}$$

We can have simultaneous eigenfunctions of $\hat{L}^2, \hat{L}_z, \hat{L}_1^2, \hat{L}_2^2$

Note that for the coupled systems we don't have eigenfunctions of \hat{L}_{1z} and \hat{L}_{2z} since these operators do not commute with \hat{L}^2

As noted above we can have simultaneous eigenfunctions of

$$\hat{L}^2, \hat{L}_z, \hat{L}_1^2, \hat{L}_2^2$$

The resulting basis functions can be written as $|\ell_1 \ell_2 LM_L\rangle$
which are linear combinations of $|\ell_1 m_1\rangle$ and $|\ell_2 m_2\rangle$

Clebsch-Gordon coefficients

$$|\ell_1 \ell_2 LM_L\rangle = \sum C(\ell_1, \ell_2, L, M_L, m_1, m_2) |\ell_1 m_1\rangle |\ell_2 m_2\rangle$$

Couple L_1 and L_2

$$L = \ell_1 + \ell_2, \ell_1 + \ell_2 - 1 \dots |\ell_1 - \ell_2|$$

We already used this when we concluded that $p^2 \rightarrow S, P, D$ states

Suppose we have three angular moments of $l_1 = 1, l_2 = 2, l_3 = 3$

First couple $l_1, l_2 \rightarrow 3, 2, 1$

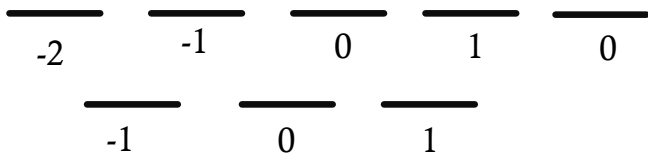
Now couple in $l_3 \rightarrow 6, 5, 4, 3, 2, 1, 0; 5, 4, 3, 2, 1; 4, 3, 2$

If one has two or more electrons, the individual \hat{L}_i^2 operators do not commute with H although \hat{L}^2 does, if we neglect spin-orbit coupling.

C atom: $1s^2 2s^2 2p^2 d$

Terms symbols $l_1 = 1, l_2 = 2 \Rightarrow L = 3, 2, 1 \Rightarrow P, D, F$ states.

There is a total of $6 \times 10 = 60$ arrangements



3F	21	}	28
1F	7		
3D	15	}	20
1D	5		
3P	9	}	12
1P	3		

Equivalent electrons

$$s^2, p^6, d^{10} \rightarrow {}^1S$$

$$p, p^5 \rightarrow {}^2P$$

$$p^2, p^4 \rightarrow {}^3P, {}^1D, {}^1S$$

$$p^3 \rightarrow 4s, {}^2D, {}^2P$$

$$d, d^9 \rightarrow {}^2D$$

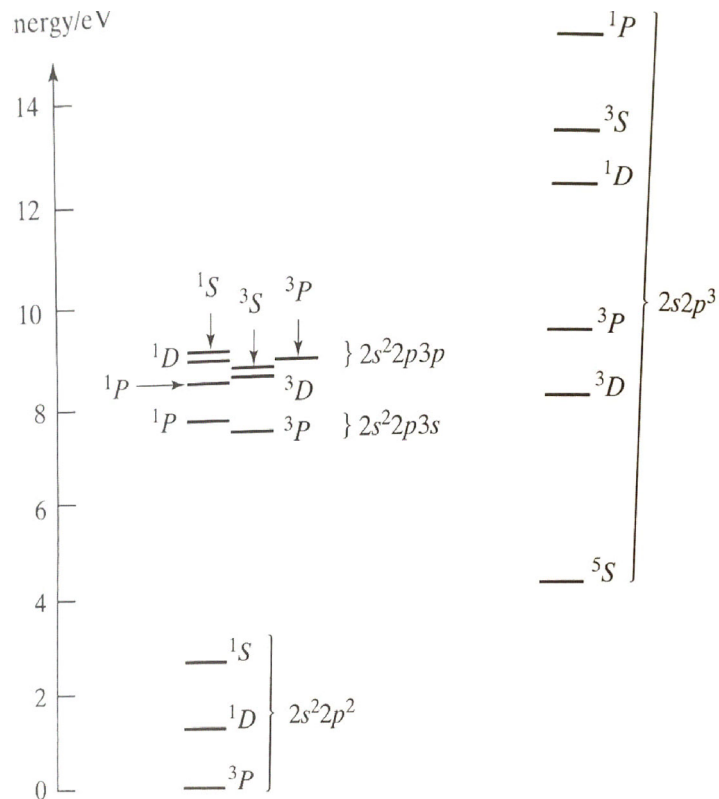
$$d^2, d^8 \rightarrow {}^3F, {}^3P, {}^1G, {}^1D, {}^1S$$

$$d^5 \rightarrow {}^6S, {}^4G, {}^4F, {}^4D, {}^4P, {}^2I, {}^2H, {}^2G(2), {}^2F(2), {}^2D(3), {}^2P, {}^2S$$

Hund's rules

States from the same electronic configuration

- The state with the highest value of S is lowest in energy.
- If there is more than one state with highest S that with the highest L is lowest in energy.



Some energy levels of the carbon atom from Levine

total spin $\mathbf{S} = \sum_{i=1}^n \mathbf{S}_i$

\hat{S}^2 has to commute with both \hat{H} and \hat{P}_{ik}

to have simultaneous eigenfunctions of three operators

$$\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$$

$$\hat{S}_z \alpha\alpha = \hbar \alpha\alpha$$

$$\hat{S}_z \beta\beta = -\hbar \beta\beta$$

$$\hat{S}_z [\alpha\beta + \beta\alpha] = 0[\alpha\beta + \beta\alpha]$$

$$\hat{S}^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2[\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z}]$$

$$\hat{S}^2 \alpha\alpha = 2\hbar \alpha\alpha$$

$$\hat{S}^2 [\alpha\beta + \beta\alpha] = 2\hbar [\alpha\beta + \beta\alpha]$$

$$\hat{S}^2 [\alpha\beta - \beta\alpha] = 0$$

Total angular momentum

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

$$J = L + S, L + S - 1, \dots, |L - S|$$

$$\hat{J}^2 \psi = J(J + 1) \hbar^2 \psi$$

Without S.O. coupling the different J components have the same energy.

However, they are split by S.O. coupling

M_J gives the z-component associated with J

$$L = 0, S = 1 \Rightarrow J = 1 \quad \Rightarrow \quad {}^3S_1$$

$$L = 1, S = 0 \Rightarrow J = 1, \Rightarrow \quad {}^1P_1$$

H atom

$$1s \rightarrow {}^2S \rightarrow {}^2S_{1/2} \left(M_J = \pm \frac{1}{2} \right)$$

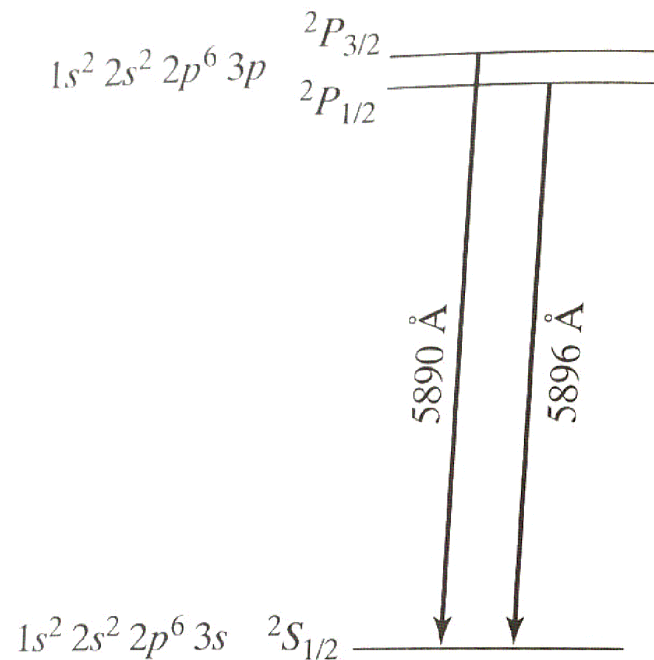
$$2p \rightarrow {}^2P \rightarrow {}^2P_{3/2}, {}^2P_{1/2}$$

He atom

$$1s2p ({}^3P): S = 2, L = 1$$

$$\longrightarrow {}^3P_0, {}^3P_1, {}^3P_2$$

$$1s2p ({}^1P) \rightarrow {}^1P_1$$



Na D line doublet
(Figure from Levine)

Spin-orbit interaction (relativistic effect)

For a one electron atom

$$\hat{H}_{so} = \frac{1}{2m_e c^2} \frac{1}{r} \frac{dV}{dr} \hat{L} \cdot \hat{S}$$

Many electron atoms

$$\begin{aligned} \hat{H}_{so} &\approx \frac{1}{2m_e c^2} \sum_i \frac{1}{r_i} \frac{dV_i(r_i)}{dr_i} \hat{L}_i \cdot \hat{S}_i \\ &= \sum_i \zeta_i(r_i) \hat{L}_i \cdot \hat{S}_i \end{aligned}$$

$$\mathbf{J} \cdot \mathbf{J} = (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S})$$

$$= L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S}$$

$$\text{So } \mathbf{L} \cdot \mathbf{S} = \frac{1}{2} [J^2 - L^2 - S^2]$$

$$\begin{aligned}\hat{L} \cdot \hat{S} \psi &= \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2) \psi \\ &= \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)] \hbar^2 \psi \\ E_{so} &\approx \frac{1}{2} \langle \zeta \rangle \hbar^2 [J(J+1) - L(L+1) - S(S+1)] \\ &= \frac{A}{2} \hbar^2 [J(J+1) - L(L+1) - S(S+1)]\end{aligned}$$

If A is +, the state with the highest J is lowest in E

If A is -, the state with the lowest J is lowest in E

Now consider the effect of an external B field

$$\hat{H}^\circ + \hat{H}_{\text{rep}} + \hat{H}_{SO} + \hat{H}_B$$

$$\hat{H}_B = -\mathbf{m} \cdot \mathbf{B} = -(\hat{\mathbf{m}}_L + \hat{\mathbf{m}}_S) \cdot \mathbf{B}$$

If the field is in the z direction

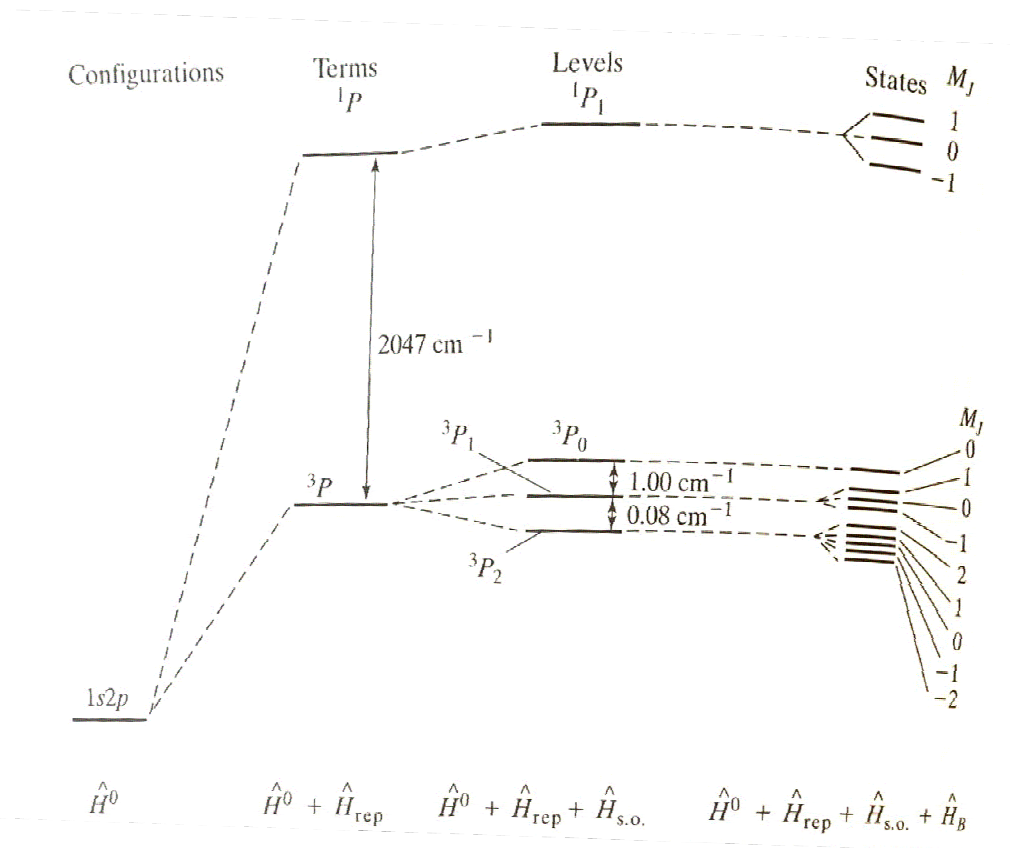
$$\hat{H}_B = \mu_B B \hbar^{-1} (\hat{J}_z + \hat{S}_z), \quad \mu_B = \frac{e\hbar}{2m_e}$$

$$E_B = \langle \psi | \hat{H}_B | \psi \rangle = \mu_B B M_J + \mu_B B \hbar^{-1} \langle S_z \rangle$$

$$E_B = \mu_B g B M_J$$

$$\text{Lande's g factor} = g_J = \frac{g_L (J(J+1) + L(L+1) - S(S+1)) + g_S (J(J+1) - L(L+1) + S(S+1))}{2J(J+1)}$$

$$= 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$



Spin-orbit and magnetic field couplings for the He atom (from Levine)

So far we have been considering L-S (Russell-Saunders) coupling

First couple the L_i and the S_i and then couple these together to get J

The other limit is j - j coupling (further down the periodic table where spin-orbit interactions are larger)

Couple l_i , s_i of individual electrons, to get j_i , and then couple these to get J

The intermediate case is especially challenging.

There is still a further coupling:

Nuclear spin I couples with electrons J to give F

Condon-Slater rules

$$\mu_i = \theta_i \sigma_i \quad \left| \begin{array}{l} \text{(spatial orbital times spin} \\ \text{function)} \end{array} \right.$$

$$\hat{B} = \sum_i \hat{f}_i + \sum_i \sum_{j>i} \hat{g}_{ij}$$

Assume \hat{f}_i and \hat{g}_{ij} do not depend on spin

$$\left\langle D \left| \sum_{i=1}^N f_i \right| D \right\rangle = \sum_{i=1}^N \left\langle \theta_i(1) \left| \hat{f}_i \right| \theta_i(1) \right\rangle$$

$$\left\langle D \left| \sum_i \sum_{j>i} g_{ij} \right| D \right\rangle = \sum_i \sum_{j>i} \left[\left\langle \theta_i(1) \theta_j(2) \left| \hat{g}_{12} \right| \theta_i(1) \theta_j(2) \right\rangle - \delta_{m_{s_i}, m_{s_j}} \left\langle \theta_i(1) \theta_j(2) \left| \hat{g}_{12} \right| \theta_j(1) \theta_i(2) \right\rangle \right]$$

$$\delta_{m_{s_i}, m_{s_j}} = 1 \quad \text{if } m_{s_i} = m_{s_j} \quad \text{and 0 otherwise}$$

$$\langle D | H | D \rangle = \sum_i \left\langle \theta_i(1) \left| \hat{f}_i \right| \theta_i(1) \right\rangle + \sum_i \sum_{j>i} \left(J_{ij} - \delta_{m_{s_i}, m_{s_j}} K_{ij} \right)$$

here f_1 is the standard 1-electron Hamiltonian not the Fock Hamiltonian.

If all orbitals are doubly occupied:

i.e. $\phi_1 = \theta_1 = \theta_2$, $\phi_2 = \theta_3 = \theta_4$, etc.

$$E = \langle D | H | D \rangle = 2 \sum_{i=1}^{n/2} \langle \phi_i(1) | \hat{f}_1 | \phi_i(1) \rangle \\ + \sum_{i,j}^{n/2} (2J_{ij} - K_{ij})$$

Be: Coulomb and exchange

$$J_{1s1s} + J_{2s2s} + 4J_{1s2s} - 2K_{1s2s}$$

Slater-Gordon rules also give us values of the integrals

$$\langle D' | \hat{B} | D \rangle \text{ when } D' \neq D$$

If D' and D differ by one spin orbital $u_n' \neq u_n$

$$\longrightarrow \langle u_n'(1) | \hat{f}_1 | u_n(1) \rangle$$

$$\text{and } \left\langle D' \left| \sum_{j>i} \hat{g}_{ij} \right| D \right\rangle = \sum_j \left[\left\langle u_n' u_j \left| \hat{g}_{12} \right| u_n u_j \right\rangle - \left\langle u_n' u_j \left| \hat{g}_{12} \right| u_j u_n \right\rangle \right]$$

What if D' and D differ by two spin orbitals $u_n' \neq u_n$ and $u_{n-1}' \neq u_{n-1}$

$$\left\langle D' \left| \sum \hat{f}_i \right| D \right\rangle = 0$$

$$\left\langle D' \left| \sum_{j>i} \hat{g}_{ij} \right| D \right\rangle = \left\langle u_n' u_{n-1}' \left| \hat{g}_{12} \right| u_n u_{n-1} \right\rangle - \left\langle u_n' u_{n-1}' \left| \hat{g}_{12} \right| u_{n-1} u_n \right\rangle$$