Angular Momentum Review – Chem 347

Classical: $\underset{\sim}{L} = \underset{\sim}{r} \times \underset{\sim}{p}$ — "axial vector", even with respect to inversion

Q. M. representation:

$$\underset{\sim}{\hat{L}} = -i\hbar(\underset{\sim}{r} \times \underset{\sim}{\nabla})$$ — note: vector operator

$$\left.\begin{aligned}
\hat{L}_x &= -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\\
\hat{L}_y &= -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\\
\hat{L}_z &= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)
\end{aligned}\right\}$$ scalar operators components of $\underset{\sim}{\hat{L}}$

$$\underset{\sim}{\hat{L}} = \hat{L}_x \underset{\sim}{i} + \hat{L}_y \underset{\sim}{j} + \hat{L}_z \underset{\sim}{k}$$

where $\underset{\sim}{i}\ \underset{\sim}{j}\ \underset{\sim}{k}$ are unit vectors.

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$ — scalar (dot) product

Q.M. definition of angular momentum:

$$[\hat{J}_i, \hat{J}_j] = i\hbar\hat{J}_k$$ i, j, k indicate relative ordering of x, y, z

$$[\hat{J}_i, \hat{J}^2] = 0$$

this is more general than transformation of classical representation, this also covers spin

Orbital $\hat{L}$:

$$L_z Y_{lm} = m\hbar Y_{lm}$$

$$L^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$$

$$L_\pm Y_{lm} = \hbar\sqrt{l(l+1) - m(m\pm1)}\, Y_{l\,m\pm1}$$

these results can be worked out from L_z, L^2 formulations (eg. $L_z = -i\hbar \, \partial/\partial\phi$) but more generally:

Eigenfunctions of Angular Momentum: (general)

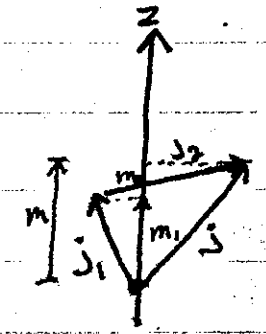
$$\hat{J}_z \, |j\, m\rangle = m\hbar \, |j\, m\rangle$$
$$\hat{J}^2 \, |j\, m\rangle = \hbar^2 j(j+1) \, |j\, m\rangle$$
$$\hat{J}_\pm \, |j\, m\rangle = \hbar \sqrt{j(j+1) - m(m\pm 1)} \; |j \;\; m\pm 1\rangle$$

where $|j\,m\rangle \Rightarrow \Psi_{jm}$ that's an eigenfct of angular momentum, J

Combine angular momenta: vector picture

$$\underset{\sim}{j} = \underset{\sim}{j_1} + \underset{\sim}{j_2} = (j_1 + j_2),\ (j_1 + j_2 - 1),\ \cdots,\ (j_1 - j_2)$$

idea: combine 2 vectors at a time
must account for direction
- angular momentum limited in magnitude and direction (i.e. m)
- but m is a scalar:



$\underset{\sim}{j} = \underset{\sim}{j_1} + \underset{\sim}{j_2}$

$$m = m_1 + m_2 \; ; \quad -j \le m \le +j$$

eg. for an electron: $\underset{\sim}{j} = \underset{\sim}{l} + \underset{\sim}{s} = (l + \tfrac{1}{2}),\ (l - \tfrac{1}{2})$

$\underset{\sim}{m} = m_l + m_s = m_l - \tfrac{1}{2},\ m_l + \tfrac{1}{2}$

eg. 2: 2 electrons – $\underset{\sim}{L} = \underset{\sim}{l_1} + \underset{\sim}{l_2}$

$\underset{\sim}{S} = \underset{\sim}{s_1} + \underset{\sim}{s_2}$

p^2: $L = 1+1,\ 1+1-1,\ 1+1-2 = 2, 1, 0$

$S = \frac{1}{2}+\frac{1}{2},\ \frac{1}{2}+\frac{1}{2}-1 = 1, 0$

note: $M_L = 0, \pm 1, \pm 2$ $L=2$; $M_L = \pm 1, 0$ $L=1$; $M_L = 0$ $L=0$ et

combine into term symbols: (affected by Pauli)

$p'p''$: $^3S, {}^3P, {}^3D$; $^1S, {}^1P, {}^1D$ eg: $(2p)^1(3p)^1$

p^2: $^1S, {}^3P, {}^1D$ – alternate eg: $(2p)^2$

Can also combine L & S: $\underset{\sim}{J} = \underset{\sim}{L} + \underset{\sim}{S}$

$\underset{\sim}{M} = \underset{\sim}{M_L} + \underset{\sim}{M_S}$

^1S : $J = 0 + 0 = 0$, $M = 0$

^3P : $J = 1+1,\ 1+1-1,\ 1+1-2 = 0, 1, 2$

$J = 0$ – $M = 0$

$J = 1$ – $M = 0, \pm 1$

$J = 2$ – $M = 0, \pm 1, \pm 2$

^1D: $J = 2 + 0 = 2$; $M = 0, \pm 1, \pm 2$

Multi electrons: a) – closed shell – $L=0, S=0, J=0$

b) – open shells – combine 2, add 3rd, then 4th etc.

Pauli Principle makes determination of possible terms difficult.

handout

The following properties of angular momentum for multi electron atoms (open) shells are important and can be proven by example. You should do this for yourself to better illuminate the material covered in lecture: (note methods for L, S usually same)

$\underset{\sim}{L} = \sum_{i=1}^{n} \underset{\sim}{l}_i \quad , \quad M = \sum_{i=1}^{n} m_i$ — n electrons

$\underset{\sim}{S} = \sum_i \underset{\sim}{s}_i \quad , \quad M_S = \sum_i m_{s_i}$ in <u>open</u> shell

a) $[L, \mathcal{H}] = 0 \quad , \quad [S, \mathcal{H}] = 0$ where $\mathcal{H}$ is the complete hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$

b) $[\underset{\sim}{L}_i, \underset{\sim}{L}_j] = i\hbar \underset{\sim}{L}_k \quad , \quad [S_i, S_k] = i\hbar S_k$

$[L_i, L^2] = 0 \quad , \quad [S_i, S^2] = 0$

c) $L_z \Psi_{LM} = M\hbar \Psi_{LM}$

$L^2 \Psi_{LM} = L(L+1)\hbar^2 \Psi_{LM}$

Ψ_{LM} – product wave fct of n - one-electron orbitals characterized by <u>total</u> ang. mom. L

$S_z \Psi_{SM_s} = M_s \hbar \Psi_{SM_s}$

$S^2 \Psi_{SM_s} = S(S+1)\hbar^2$

Ψ_{SM_s} – same, tot. spin S

d) $[\underset{\sim}{J}, \mathcal{H}_{SO}] = 0 \qquad \underset{\sim}{J} = \underset{\sim}{L} + \underset{\sim}{S} \qquad \mathcal{H}_{SO} = \sum_i \xi_i \underset{\sim}{l}_i \cdot \underset{\sim}{s}_i$