5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

Lecture #14: Definition of Angular Momenta and $|A\ \alpha\ M_A\rangle$. Evaluation of $\widehat{H}^{ROT}$

We want to be able to set up effective Hamiltonian models for rotation-vibration-electronic structure of diatomic molecules with non-zero electronic angular momenta.

The important terms in $\widehat{H}$ are

$$\widehat{H}^{ROT} = B(R)\widehat{R}^2$$

$$\widehat{H}^{SO} = \sum_{\substack{i \\ \text{electrons}}} a(r_i)\hat{\ell}_i\cdot\hat{s}_i$$

* a convenient basis set for evaluating matrix elements of $\widehat{H}^{ROT}$ and $\widehat{H}^{SO}$ — **HUND'S CASE A**
* $\widehat{A}_z$, $\widehat{A}_{\pm}$, and $\widehat{A}_Z$, $\widehat{A}^{\pm}$ and $\widehat{A}^2$ operators and $|A\ \alpha\ M_A\rangle$ basis functions
* $\mathbf{H}^{eff}$ and van Vleck Corrections to $\mathbf{H}^{eff}$
* Limiting cases where $\mathbf{H}^{eff}$ is approximately diagonal and energy levels are expressed in terms of a pattern-forming rotational quantum number like J(J + 1), N(N + 1), R(R + 1). (Example in next lecture for $^2\Pi$ and $^2\Sigma^+$ states.)
* effects of accidental degeneracies — perturbations.

Angular Momenta

$\widehat{\mathbf{R}}$	nuclear rotation	
$\widehat{\mathbf{L}}$	e^- orbital angular momentum	
$\widehat{\mathbf{S}}$	e^- spin	
$\widehat{\mathbf{J}}$	total angular momentum	$\vec{\widehat{\mathbf{R}}}+\vec{\widehat{\mathbf{L}}}+\vec{\widehat{\mathbf{S}}}$
$\widehat{\mathbf{N}}$	angular momentum. exclusive of spin	$\hat{\mathbf{J}}-\hat{\mathbf{S}}=\widehat{\mathbf{R}}+\widehat{\mathbf{L}}$
$\hat{\mathbf{J}}_a$	total electron angular momentum	$=\widehat{\mathbf{L}}+\widehat{\mathbf{S}}$

See H. Lefebvre-Brion/R. W. Field, pages 72-81.

All angular momenta can be defined by their commutation rules.

$$\left[\hat{A}_i, \hat{A}_j\right] = +i\hbar \sum_k \varepsilon_{ijk} \hat{A}_k$$

ε_{ijk}	+1	for	x, y, z in cyclic order
	–1	for	non-cyclic
	0		repeated coordinator

Above is a "normal" Commutation Rule which is applicable for all SPACE components of $\hat{J}$, $\hat{L}$, $\hat{S}$, $\hat{R}$, $\hat{N}$, $\hat{J}_a$ and all body components of $\hat{L}$, $\hat{S}$ (but **not** $\underbrace{\hat{J}, \hat{R}, \hat{N}}_{\text{involve rotation of body}}$).

Trivial matter to derive properties of eigenbasis $|A\ \alpha\ M_A\rangle$ under operation by $\hat{A}^2$, $\hat{A}_i$, $\hat{A}_\pm$ from commutation rule.

$$\hat{A}^2 \left|A\alpha M_A\right\rangle = \hbar^2 A(A+1) \left|A\alpha M_A\right\rangle$$

$$\hat{A}_z \left|A\alpha M_A\right\rangle = \hbar\alpha \left|A\alpha M_A\right\rangle$$

$$\hat{A}_Z \left|A\alpha M_A\right\rangle = \hbar M_A \left|A\alpha M_A\right\rangle$$

$$\hat{A}_\pm \equiv \hat{A}_x \pm i\hat{A}_y \text{ and } \hat{A}^\pm \equiv \hat{A}_X \pm i\hat{A}_Y \text{ (up for upper case)}$$

$$\hat{A}_\pm \left|A\alpha M_A\right\rangle = \hbar\left[A(A+1) - \alpha(\alpha \pm 1)\right]^{1/2} \left|A\alpha \pm 1 M_A\right\rangle$$

$\hat{A}_+$ "raises" α $\hat{A}_-$ "lowers" α

$$\hat{A}^\pm \left|A\alpha M_A\right\rangle = \hbar\left[A(A+1) - M_A(M_A \pm 1)\right]^{1/2} \left|A\alpha M_A \pm 1\right\rangle$$

$\hat{A}^+$ "raises" M_A

This is all you need to know for rotation of diatomic molecules

EXCEPT

Anomalous commutation rule $\left[\hat{A}_i, \hat{A}_j\right] = -i\hbar \sum_k \varepsilon_{ijk} \hat{A}_k$ applies only to BODY components of $\hat{J}$, $\hat{R}$, $\hat{N}$.

The only difference is

$$\hat{A}_\pm \left| A \alpha M_A \right\rangle = +\hbar \left[A(A+1) - \alpha(\alpha \mp 1) \right]^{1/2} \left| A \ \alpha \mp 1 \ M_A \right\rangle$$

$\hat{A}_+$ acts as a "lowering" operator rather than as raising operator.

Now, suppose we want to evaluate what other angular momenta than $\hat{A}$ do to $|A\ \alpha\ M_A\rangle$ basis functions.

We classify these other operators as vectors or scalars with respect to $\hat{A}$ by similar commutation rules. The Wigner-Eckart Theorem will eventually tell us how to evaluate the effect of $\hat{B}$ (some other operator classified by its commutation rule with respect to $\hat{A}$) on $|A\ \alpha\ M_A\rangle$.

A scalar is defined as $\left[\hat{S}, \hat{A}_i\right] = \left[\hat{S}, \hat{A}_\pm\right] = 0$ all i, I and $\hat{S} |A\ \alpha\ M_A\rangle = s_A |A\ \alpha\ M_A\rangle$.

A normal vector (with respect to $\hat{A}$) is defined as

$$\left[\hat{A}_i, \hat{V}_j\right] = +i\hbar \sum_k \varepsilon_{ijk} V_k$$

It happens that

$\left[\hat{L}_i, \hat{S}_j\right] = \left[\hat{L}_I, \hat{S}_J\right] = 0$ — $\hat{L}$, $\hat{S}$ operate on different coordinates and are scalar operators with respect to each other

and **all** angular momenta obey normal vector operator commutation rules with respect to $\hat{J}$ for **space fixed** components.

$\left[\hat{J}_I, \hat{A}_J\right] = i\hbar \sum_k \varepsilon_{IJK} A_K$ — $\hat{J}$ generates rotations in lab frame

and **all** angular momenta obey anomalous vector operator commutation rules with respect to $\hat{R}$ for **body fixed** components.

$\left[\hat{R}_i, \hat{A}_j\right] = -i\hbar \sum_k \varepsilon_{ijk} A_k$ — $\hat{R}$ generates rotations in body frame.

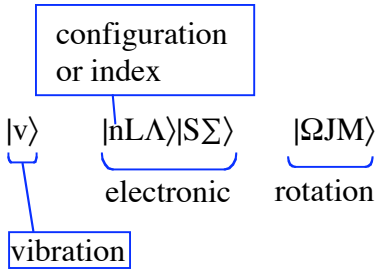
This has convenient effect that $\left[\hat{J}_i, \hat{L}_j\right] = \left[\hat{J}_i, \hat{S}_j\right] = 0$ because $\hat{J} = \hat{R} + \hat{L} + \hat{S}$. See this in example.

$$\text{E.g. } \left[\hat{J}_i,\hat{L}_j\right]=\left[\hat{R}_i,\hat{L}_j\right]+\left[\hat{L}_i,\hat{L}_j\right]+\left[\hat{S}_i,\hat{L}_j\right]$$

$$-i\hbar\varepsilon_{ijk}L_k \qquad +i\hbar\varepsilon_{ijk}L_k \qquad = 0$$

which means that $\hat{J}$ acts as a scalar operator with respect to $|n\ L\ \Lambda\ S\ \Sigma\rangle$ so we can factor ψ into electronic ⊗ vibration ⊗ rotation factors!

So we can write a convenient basis set.



Case (a)
fully "uncoupled" basis set in body

very convenient for body fixed matrix elements

Now we can work out matrix elements of $B(R)\,\hat{R}^2$ in this case(a) basis set.

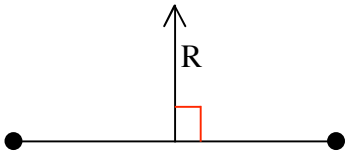
$$\left\langle v\left|B(R)\right|v\right\rangle \equiv B_v/\hbar^2$$

to cancel the $\hbar^2$ from all angular momentum matrix elements

(Note $\langle v|B(R)|v'\rangle = B_{vv'} \neq 0$)
We will see these again when we use J = 0 potential energy curve to derive centrifugal distortion effects.

$$\vec{R} = \vec{J} - \vec{L} - \vec{S}$$

Evidently



So $\hat{R}_z \equiv 0$

$$\hat{R}^2 = \hat{R}\cdot\hat{R} = \hat{R}_x^2 + \hat{R}_y^2 = \left(\hat{J}_x - \hat{L}_x - \hat{S}_x\right)^2 + \left(\hat{J}_y - \hat{L}_y - \hat{S}_y\right)^2$$

$$= \left(J_x^2 + J_y^2\right) + \left(L_x^2 + L_y^2\right) + \left(S_x^2 + S_y^2\right)$$

$$\left.\begin{array}{l} -2(J_xL_x + J_yL_y) \\ -2(J_xS_x + J_yS_y) \\ +2(L_xS_x + L_yS_y) \end{array}\right\}$$

No need to be careful of order of operators because body components of $\hat{L}$ and $\hat{S}$ commute with each other and with those of $\hat{J}$.

Now for some convenient simplifications.

$A_x^2 + A_y^2 = A^2 - A_z^2$

$2\left(A_xB_x + A_yB_y\right) = \left(A_+B_- + A_-B_+\right)$ confirm for yourself

Thus $\hat{R}^2 = \left(J^2 - J_z^2\right) + \left(L^2 - L_z^2\right) + \left(S^2 - S_z^2\right)$ diagonal part

plus off-diagonal terms below.

		selection rules
L–uncoupling term	$-(J_+L_- + J_-L_+)$	$\Delta\Omega = \Delta\Lambda = \pm 1$
S–uncoupling term	$-(J_+S_- + J_-S_+)$	$\Delta\Omega = \Delta\Sigma = \pm 1$
Rotation-electronic term	$+(L_+S_- + L_-S_+)$	$\Delta\Lambda = -\Delta\Sigma = \pm 1$ $(\Delta\Omega = 0)$

So we are almost ready to set up $\mathbf{H}^{\text{eff}}$. However L is not a well defined quantity.

Non-Lecture: Stark effect in atoms

$$\Delta\ell = \pm 1$$

$$+ \leftrightarrow -$$

$$\Delta M_L = \Delta\lambda = 0$$

Electric field (axially symmetric) of atom B mixes L's in atom A

$$\psi^A = \sum_{nL} a_{nL} \left| nL^A M_L^A \right\rangle \qquad a_{nL} \sim \frac{\overbrace{\left\langle nL \left| \hat{\mathbf{H}} \right| n'L' \right\rangle}^{\text{typically } 10^5 \text{ cm}^{-1} \text{ for } 1e^- \text{ at } 1\text{Å}}}{\underbrace{E^o_{nL} - E^o_{n'L'}}_{\text{typically } 10^4 \text{ cm}^{-1} \text{ for different nL states of atom}}}$$

- L^A destroyed
- M_L^A preserved
- L^2 and $L_\pm$ matrix elements not explicitly defined (become perturbation parameter)
- L^2 and $L_\pm$ and L_z selection rules on Λ are preserved!
- $\left(L^2 - L_z^2\right) \equiv L_\perp^2$ treated as a constant
- $\left\langle v, n\ \Lambda\ S\ \Sigma \left| B\hat{L}_+ \right| v', n'\ \Lambda - 1\ S\ \Sigma \right\rangle \equiv B_{v'v}\beta$ or $\beta_{vv'}$ perturbation parameter.

Matrix elements of $\hat{\mathbf{H}}^{ROT} = B(R)\hat{R}^2$

1. Diagonal part (in v, n, Λ, S, Σ, J, Ω, M)

$$B(R)\left[\left(J^2 - J_z^2\right) + \left(L_\perp^2\right) + \left(S^2 - S_z^2\right)\right]$$
$$B_v\left[J(J+1) - \Omega^2 + L_\perp^2 + S(S+1) - \Sigma^2\right]$$

include $B_v L_\perp^2$ in $T_e + G(v)$

2. Within a $^{2S+1}\Lambda$ multiplet state.

The splitting of Ω-components within an $S \neq 0$ state is due to $\hat{\mathbf{H}}^{SO}$ and is usually small relative to splittings between different nΛ states. $\mathbf{H}^{SO}$ gives "fine structure".

discussed later

Spin-uncoupling term — will destroy Σ, Ω provided that $E^o_\Omega - E^o_{\Omega\pm1}$ is small.

$$-B(R)\left[J_+S_- + J_-S_+\right]$$

$$-\left(B_V/\hbar^2\right)\left\langle \Sigma \pm 1\ \Omega \pm 1\ J\ S\left|\widehat{\mathbf{H}}^{ROT}\right|\Sigma\Omega JS\right\rangle = -B_v\left[J(J+1)-(\Omega\pm1)\Omega\right]^{1/2}\left[S(S+1)-(\Sigma\pm1)\Sigma\right]^{1/2}$$

notice $\Omega'\Omega$, $\Sigma'\Sigma$

Above matrix element is ≈ proportional to J, so at high J $\widehat{\mathbf{H}}^{ROT}$ will always overwhelm $\Delta E^{o}_{\Omega,\Omega\pm1}$ Σ and Ω are destroyed, thus spin "uncouples from body frame".

3. Between two electronic states $\Delta S = 0, \Delta\Sigma = 0, \Delta\Lambda = \Delta\Omega = \pm1$

"L-Uncoupling" (even though L is already destroyed) destroys Λ and Ω.

$$-\left(B(R)/\hbar^2\right)\left[\hat{J}_+\hat{L}_- + \hat{J}_-\hat{L}_+\right]$$

$$-\left[\left\langle v_{\Lambda\pm1}\left|B(R)\right|v_\Lambda\right\rangle/\hbar^2\right]\left\langle n'\ \Lambda\pm1\ S\ \Sigma\ J\ \Omega\pm1\left|\left(\hat{J}_+\hat{L}_- + \hat{J}_-\hat{L}_+\right)\right|n\ \Lambda\ S\ \Sigma\ J\ \Omega\right\rangle$$

$$-B_{v_{\Lambda\pm1}v_\Lambda}\left[J(J+1)-(\Omega\pm1)\Omega\right]^{1/2}\underbrace{\left\langle n'\Lambda\pm1\left|L_\pm\right|n\Lambda\right\rangle/\hbar}_{\beta(n'\Lambda',n\Lambda)}$$

$$-B_{v_{\Lambda\pm1}v_\Lambda}\beta(n'\Lambda',n\Lambda)\equiv\beta$$

an unknown perturbation parameter to be determined directly from spectrum

4. Between two electronic states $\Delta\Omega = 0$ $\Delta\Lambda = -\Delta\Sigma = \pm1$

$$+\beta\left[S(S+1)-\Sigma(\Sigma\pm1)\right]^{1/2}$$

same β as above in #3 for L-uncoupling