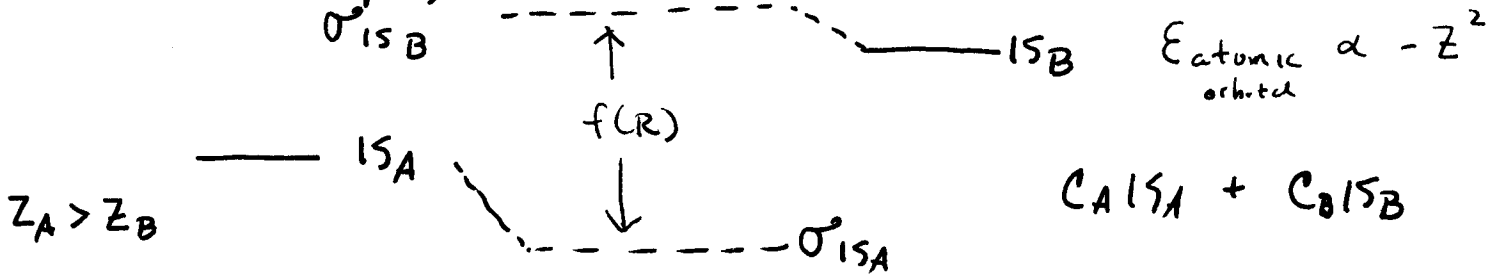


10. Heteronuclear Diatomics; Nuclear Motions

Heteronuclear Diatomics

Molecular orbitals are no longer \pm combinations of atomic orbitals, but are asymmetric combinations.

For example, consider



See 2nd hand-out sheet for correlation diagram.

Examples: CH (7 electrons) $(\sigma_{1s_C})^2 (\sigma_{1s_H})^2 (\sigma_{2s_C})^2 (\pi_{2p_C})^1 X^2 \Pi$

symm

NH (8 electrons) $(\pi_{2p_N})^2 \quad {}^3 \Sigma^- < {}^1 \Delta < {}^1 \Sigma^+ \quad \checkmark$

Dipole Selection Rules

1. $u \leftrightarrow g$ 1a. $\Sigma^+ - \Sigma^+ \quad \Sigma^- - \Sigma^-$

2. $\Delta S = 0 \quad (\Delta \Sigma = 0)$

3. $\Delta |L| = 0, \pm 1 \quad \Sigma - \Pi \quad \Pi - \Delta$

4. No strong transitions between states arising from the same MO configuration.

Fine Structure

- occurs for non $^1\Sigma$ states; must be some electronic angular momentum

(i) spin-orbit coupling $H' = \hat{A} \vec{L} \cdot \vec{S}$ L not defined

$O \cdots O \cdots z$ $H' = \hat{A} (L_x S_x + L_y S_y + L_z S_z)$ Hund's case (a)

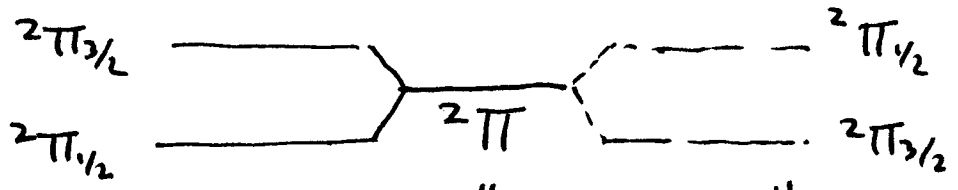
$\langle L_x \rangle = \langle L_y \rangle = \langle S_x \rangle = \langle S_y \rangle = 0$ (vector diagram)

1st order perturbation theory: $\langle \Lambda S \Sigma | L_z S_z | \Lambda S \Sigma \rangle = \Lambda \Sigma \hbar^2$

$$E_{s-o}^{(1)} = A \Lambda \Sigma$$

$^2\Pi$ state $\Lambda = \pm 1$ $S = 1/2$ $\Sigma = \pm 1/2$


Λ	Σ	E_{s-o}	$\Omega \equiv \Lambda + \Sigma$	$\Omega \leftrightarrow M_{J''}$
1	1/2	A/2	3/2	} $^2\Pi_{3/2}$
-1	-1/2	A/2	-3/2	
1	-1/2	-A/2	1/2	} $^2\Pi_{1/2}$
-1	1/2	-A/2	-1/2	



$A > 0$ "normal" $A < 0$ "inverted" $^2\Pi_i$
 outer shell $< 1/2$ full 3 $> 1/2$ full

Example: OH ($\Pi 2p_0$) $^2\Pi_i$ $A = -0.017 \text{ eV} = -140 \text{ cm}^{-1}$
 CH ($\Pi 2p_0$) normal

(ii) spin-rotation interaction (small)

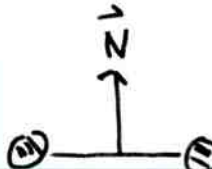
 $H' = \hat{\gamma} \vec{N} \cdot \vec{S}$ as in $^2\Sigma$ state

define $\vec{J} = \vec{N} + \vec{S}$

You choose:

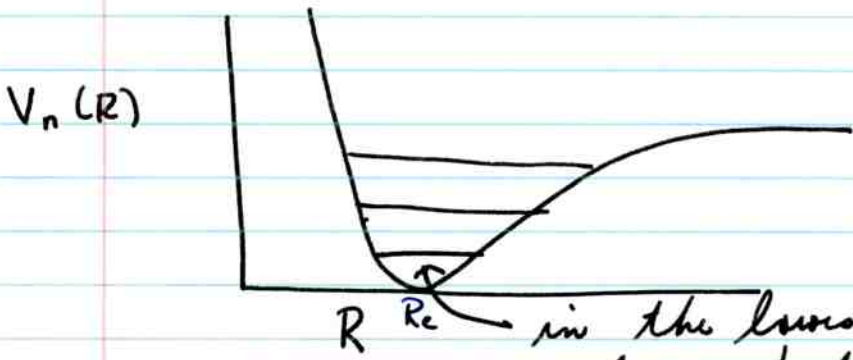
$$H' = \hat{\gamma} (N_x S_x + N_y S_y + N_z S_z) \text{ or}$$

$$\vec{N} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 - \vec{N}^2 - \vec{S}^2)$$



$$H' = \gamma \vec{N} \cdot \vec{S} \quad (\text{homework})$$

Nuclear Motions ($^1\Sigma$ states)



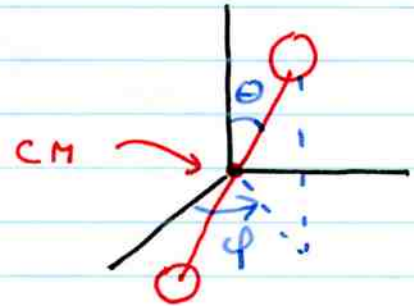
in the lowest vibrational states, the nuclei are highly localized. Let us first determine the rotational energy levels assuming no vibrations at all. $R \approx R_e$

The Rigid Rotator

$\hat{H} \Psi_{rot} = E \Psi_{rot}$

R fixed $\Psi_{rot}(\theta, \phi)$

$$\hat{H} = \hat{T} = \frac{\hat{J}^2}{2\mu R^2} = \frac{\hat{J}^2}{2I}$$



$\Psi_{rot} = \chi_N$

J: rigid body angular momentum (N sometimes)

$$\left(\hat{H} = -\frac{\hbar^2}{2\mu R^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \right)$$

J_z as well

The energy eigenfunctions are the eigenfunctions of \hat{J}^2 , which are the well known spherical harmonics $Y_{J, M_J}(\theta, \phi)$ appearing in all central force problems.

$Y_{J, M_J} = \Psi_{rot}(\theta, \phi) = \Theta_{J, M_J}(\theta) \Phi_{M_J}(\phi)$

$\Phi_{M_J}(\phi) = \frac{1}{\sqrt{2\pi}} e^{i M_J \phi}$

$\Theta_{J, M_J}(\theta) = N_{J, M_J} P_J^{|M_J|}(\cos\theta)$

$M_J = 0, \pm 1, \pm 2, \pm 3, \dots$

$J \geq |M_J|$ Legendre functions

$$\hat{J}^2 Y = J(J+1) \hbar^2 Y \Rightarrow E_J = \frac{\hbar^2}{2\mu R^2} J(J+1) \quad J=0, 1, 2, \dots$$

$g_J = 2J+1$ since M_J not in energy expression

$$E_J = \frac{\hbar^2}{2I} J(J+1) = \frac{h^2}{8\pi^2 I} J(J+1) = \underbrace{\frac{h}{8\pi^2 I}}_B h J(J+1)$$

B "rotational constant"
(Hz, MHz, GHz)

Also used

$$E_J = B h J(J+1) = \tilde{B} h c J(J+1) \quad \tilde{B} = \frac{B}{c} \quad (\text{cm}^{-1})$$

Size of B

$\text{O} \text{---} \text{O} \quad R \sim 1.5 \text{ \AA} \quad \mu = 10 \text{ amu} \quad B = 2.25 \times 10^{10} \text{ Hz} = 22.5 \text{ GHz}$

$c = 3 \times 10^{10} \text{ cm s}^{-1} \Rightarrow \tilde{B} = 0.75 \text{ cm}^{-1} \approx 0(1)$

In general $B (\text{GHz}) = \frac{5.05376 \times 10^2}{I (\text{amu} \cdot \text{\AA}^2)}$

Selection Rules

$\mathcal{H}' = -\vec{\mu} \cdot \vec{E}$ need to investigate (μ_z) only

$\mu_x = \mu \sin\theta \cos\phi \quad \mu_y = \mu \sin\theta \sin\phi \quad \mu_z = \mu \cos\theta$

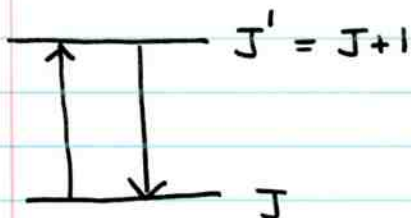
μ : permanent moment (must be non-zero)

$\langle J' M_J' | \mu_x | J M_J \rangle$
 \uparrow
 upper state $(J'' M_J'')$

The matrix elements of the spherical harmonics are well-known.

To be mm-gyro: $\Delta J = J' - J'' = 1$

$$\Delta M_J = 0 (\mu_z); \pm 1 (\mu_{x,y})$$

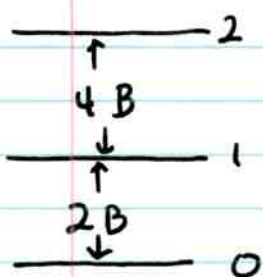


$$\frac{E(J+1) - E(J)}{h} = \nu \quad \text{Bohr Spectral Conditions}$$

$$\begin{aligned} \nu &= B [(J+1)(J+2) - J(J+1)] \\ &= 2B(J+1) = 2B, 4B, 6B \text{ etc.} \end{aligned}$$

occur in microwave

↓ millimeter-wave region of spectrum



e.g. CO B (GHz) = 57.8975 [doesn't quite obey formula]
 $R = 1.128 \text{ \AA}$
 $\mu = 6.856 \text{ amu}$

$$\nu(1-0) = 2B = 115.8 \text{ GHz} \quad \nu(2-1) = 4B = 231.6 \text{ GHz} \text{ etc.}$$

○ The rotational levels tend to be closer together than kT :

$$\frac{\Delta E}{kT} \stackrel{1-0}{=} \frac{2Bh}{kT} = \frac{2B}{(k/h)T} \quad \frac{k}{h} = 2.08 \times 10^{10} \text{ s}^{-1} \text{K}^{-1}$$

$$\begin{aligned} B &= 60 \text{ GHz} & \Delta E/kT &= \frac{2.6 \times 10^{10}}{(2.08 \times 10^{10}) 300} = 0.019 \\ T &= 300 \text{ K} \end{aligned}$$

Thus, these levels can be appreciably populated at room temperature. Microwave spectroscopists, who normally study transitions in absorption, must worry about stimulated emission corrections.

The Boltzmann equation is:

$$P(E_J) = \frac{g_J e^{-E_J/kT}}{q_{\text{rot}}} = \frac{(2J+1) e^{-hB J(J+1)/kT}}{q_{\text{rot}}}$$

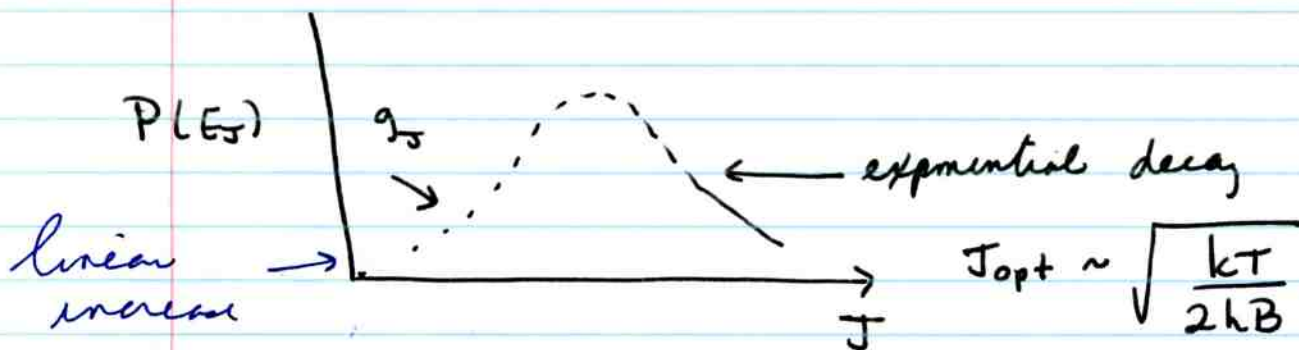
$$q_{\text{rot}} = \sum_J (2J+1) e^{-hB J(J+1)/kT}$$

The partition function can be obtained by an integral approximation since the rotational levels are so closely spaced:

$$q_{\text{rot}} \approx \int_0^{\infty} (2J+1) e^{-hB(J^2+J)/kT} dJ = kT/hB$$

$x = J^2 + J$
 $dx = (2J+1) dJ$

$$P(E_J) = \frac{(2J+1) e^{-hB J(J+1)/kT}}{kT/hB}$$



$$\text{CO } T = 300 \text{ K } J_{\text{opt}} = 7 \quad 10 \text{ K } J_{\text{opt}} = 1$$

Homonuclear Molecules: The Pauli Exclusion Principle

See next chapter.

