REVIEW

- MONDAY 5-6

VALLEY LIFE SCIENCES RM 2060

Bonding in Polyatomic
- Hybridization
  (Wavefunctions are written as sum over different l states of AO's)

Ex: BH₃

$$\psi = \frac{1}{\sqrt{3}} 2s + \frac{1}{\sqrt{6}} 2p_y - \frac{1}{\sqrt{2}} 2p_x$$

- Delocalized Bonds
  - Hückel Theory

Find energies by diagonalizing the secular determinant

\[
\begin{pmatrix}
A & E & 0 & 0 & 0 \\
0 & A & -E & 0 & 0 \\
0 & 0 & A & E & 0 \\
0 & 0 & 0 & A & E \\
0 & 0 & 0 & 0 & A
\end{pmatrix} = 0
\]

\[B \rightarrow 1\]

E is energies of system (fill -1/2^ acc. to Pauli)
Eigenvectors give π structure
**Time Dependence**

\[ H = H_0 + H(t) \]

\[ \psi(t) = \sum c_n e^{-iE_n t / \hbar} \alpha_n \] where \( H_0 \alpha_n = E_n \alpha_n \)

If no time depend, have state \( \uparrow \)

\[ \psi(t) = \sum c_n e^{-iE_n t / \hbar} \alpha_n \]

Rephasing time is obtained by solving

\[ \psi(T) = e^{-i\phi} \psi(0) ; T \text{ is time it takes for } \uparrow \text{ to sample all possible states} \]

If time dep.

\[ \psi(t) = \sum c_n(t) e^{-iE_n t / \hbar} \alpha_n \]

Coefficients now depend on time because \( H(t) \) causes \( \alpha_n \) to not be an eigenfunc of \( H \).

\( |c_n(t)|^2 \) is prob. that a system is in state \( \alpha_n \) at time \( t \). Use time-dep. pert. theory to calculate.

\[ c_n(t) = \delta_{mn} - \frac{i}{\hbar} \int_0^t dt' e^{i\omega_{nm} t'} \langle m | H(t') | n \rangle \]
FROM T.D.P.T. GET SELECTION RULES.

\[ H(t) = \vec{M} \cdot \vec{E} \cos \omega t \]

SELECTION RULES COME FROM CALCULATING

\[ \langle M | \vec{M} \cdot \vec{E} \cos \omega t | n \rangle \] AND SEEING WHERE IT VANISHES AND WHERE IT IS NON-ZERO.

\[ |C_m(\vartheta)|^2 \]

PEAKS CORRESPOND TO WHEN ENERGY FROM LIGHT IS EQUAL TO THE ENERGY DIFFERENCE (OR INTEGRAL MULTIPLE)

\[ \Delta \vartheta \]

TRANSITIONS BETWEEN STATES CAUSED BY LIGHT IS CALLED SPECTROSCOPY

\[ I \quad \uparrow \quad \uparrow \quad \uparrow \]

\[ \quad + F \quad + \quad + \quad + \quad + \]

\[ \quad + i \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \]

\[ \quad + \quad + \quad + \quad + \quad + \]

EL WF H.O.WF RIGID ROTOR WF

\[ \Delta J = \pm 1 \]

a) ROTATIONAL SPECTROSCOPY

\[ + i = + e_1 + + + + + + \]

\[ + F = + e_1 + + + + + + \]

\[ \langle F | M_i | i \rangle = \langle M \rangle \Rightarrow \text{NEED A PERMANENT DIPOLE FOR ROTATIONAL SPECTRA.} \]
b) Vibrational Transitions

\[ T_i = T_e1 + T_v + T_j \rightarrow T_{e1} + T_v + T_{j,m} \]

\[ \Delta V = \pm 1 \]

\[ \Delta J = \pm 1 \]

- R Branch (\( \Delta J = +1 \))
- P Branch (\( \Delta J = -1 \))

C) Electronic Transitions

\[ T_i = T_e1 + T_v + T_j + T_{j,m} \rightarrow T_{F} = T_e1 + T_v + T_{j,m} \]

Electronic S.R. \( \Delta \Lambda = \pm 1 \)

Intensity is Dep. of FCF.

IF POSITIONS ARE SIMILAR ONLY HAVE \( V \rightarrow V \) TRANSITIONS (IF ARE ALMOST ORTHOGONAL)

IF POSITIONS OF POTENTIALS ARE DIFFERENT, HAVE A BUNCH OF TRANSITIONS.
Polyatomic Molecule Rotation

- Can have rot. about 3 axes.
Always keep center of mass constant

\[ \mathbf{X}_{\text{cm}} = \frac{\sum m_i \mathbf{X}_i}{\sum m_i} \]

Rotational Energy

\[ \text{Rotational Energy} = \frac{1}{2} \mathbf{I} \omega \]

\[ \mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \]

- Diagonalize this gives principle axes.

Principle axis always lie in positions of highest symmetry, principle axis \((\mathbf{a})\)

\([\mathbf{a}, \mathbf{b}, \mathbf{c}] \text{ are defined by} \]

\[ \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix} = \mathbf{I}_a \leq \mathbf{I}_b \leq \mathbf{I}_c \]
3 TYPES OF MOLECULES

ASYMMETRICAL TOP \( I_A \neq I_B \neq I_C \)

SYMMETRICAL TOP (2 I's ARE EQUAL) \( I_A = I_B = I_C \)

Spherical Top \( I_A = I_B = I_C \)

Rot. Const \( \tilde{A} = \frac{\hbar}{8\pi^2cI_A} \)

Energy Defined by \( = B_J(J+1) + A_J(J_A+1) + C_J(J_AJ) \)

VIBRATIONS IN POLYATOMICS

3N - 6 (S) DOE 3OF

Vibrate in Normal Coordinates (Do this to separate Hamiltonian)

For a Vibrational mode to be excited, it must have a dipole moment as it vibrates

Ex.

\[ \text{H}_2 \]: \( 0 = \text{c} = 0 \) has a dipole moment, can have Q branch (QJ = 0 now)

\[ \text{H}_2 \]: \( 0 \rightarrow \text{c} = 0 \) doesn't come from new QM flow location
Lasers

\[ \frac{dN_2}{dt} = B_{21} S_{v_2}(v_{12}) N_2(+) \quad \text{for Stim Emission} \]

\[ = B_{21} N_2(+) \quad \text{for Spont. Emission} \]

\[ = A_{12} N_1(+) \ll S_{v_1}(v_{12}) \quad \text{for Absorption to higher state} \]

Total rate accounts for all processes

Steady state approx. Rate of change of intermediate is zero

Laser Types