Most molecular spectroscopies result from the application of the Hamiltonian operator

\[ H \psi_n = E_n \psi_n \]

The spectroscopy measures the eigenvalue, \( E_n \). Thus we will need to address the solution of the above equation.

\[ H = -\frac{\hbar^2}{2m} \nabla^2 + \frac{1}{2} Kq^2 \]

VIBRATIONAL SPECTROSCOPY

\[ H = -\frac{\hbar^2}{2m} \nabla^2 \]

where \( \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \)

free particle

\( E_n = KE = \frac{p^2}{2m} \)

\[ H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \]

hydrogen atom

(1e\(^{-}\) problem)

\[ \sum_{i=1}^{N} \left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze_i^2}{r_i} \right] + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} \frac{P(R)}{|R - r_i|} \frac{d\tau_r}{r} + \frac{e^2}{2mc^2} \frac{1}{r} \frac{\partial V(r)}{\partial r} \hat{\ell} \cdot \hat{s} \]

- free ion or atom
- ligand field
- spin-orbit coupling

ELECTRONIC SPECTROSCOPY

MAGNETISM
Electronic spectroscopy

We will begin by considering the electronic spectroscopy of transition metal complexes. To date we have considered the electronic configurations that result from the occupation of the molecular orbitals. In an electronic transition, the promotion of an electron over the energy gap, separating the orbitals, is only part of the problem... there is also an energy contribution resulting from 2e⁻ contributions to the Hamiltonian, i.e. \( \langle \phi_i | H | \phi_j \rangle \) and \( \langle \phi_i | H | \phi_j \phi_i \rangle \) and \( \langle \phi_i | H | \phi_i \phi_j \rangle \). For instance, consider the 2e⁻ bond of H₂ ... four different electronic configurations or “states” arise from the electron occupation of the orbital manifold:

\[
\begin{align*}
\phi_i & \quad \Delta E & \quad \phi_j \\
1s & \quad \sigma & \quad 1s
\end{align*}
\]

Based on “1e⁻” energies, one would predict that the energies of the transitions between these states would be \( \Delta E \) for \( ^1\sigma^* \rightarrow ^3\sigma^* \) and \( ^1\sigma^* \rightarrow ^1\sigma^* \) and \( 2\Delta E \) for \( ^1\sigma^* \rightarrow ^1\sigma^* \) and \( ^3\sigma^* \). But this ignores the 2e⁻ contributions. The transition energy may or may not track the orbital splitting energy, depending on the relative magnitudes of 1e⁻ vs 2e⁻ contributions to the Hamiltonian. This can be demonstrated with the \( M^\pm M \) MO diagram of the past lecture. Consider the \( \delta \rightarrow \delta^* \) transition of a \( M^\pm M \) complex and its oxidized and reduced counterparts:

\[
\begin{align*}
\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4^n & \quad n = 0 & \quad n = +1 & \quad n = -1 \\
17090 \text{ cm}^{-1} & \quad 6350 \text{ cm}^{-1} & \quad 7970 \text{ cm}^{-1}
\end{align*}
\]

Crystal structures of the three complexes reveal that the M-M separation changes by less than 0.05 Å. In this case, the \( \delta/\delta^* \) splitting should be the same for all three complexes, and it is. Then why aren’t the transition energies for the \( \delta \rightarrow \delta^* \) transition the same?
The energy diagram for the two electron bond contains 1e\(^-\) and 2e\(^-\) contributions:

\[ \varphi = \frac{1}{\sqrt{2+2s}} \left[ d_{xy}(A) - d_{xy}(B) \right] \]

where \( S = \langle d_{xy}(A) | d_{xy}(B) \rangle \)

\[ \phi = \frac{1}{\sqrt{2+2s}} \left[ d_{xy}(A) + [d_{xy}(B)] \right] \]

Under \( D_{4\text{h}} \), \( \phi \to b_{2g} \) and \( \varphi \to b_{1u} \) ... under \( D_{2d} \), \( \phi \to b_1 \) and \( \varphi \to a_2 \)

Two electrons in two orbitals give rise to 4 strong field configurations (3 singlets and 1 triplet, composed of three sub-states):

\[ ^1\delta\delta = \Phi_1 = \begin{vmatrix} \phi \phi \end{vmatrix} \rightarrow ^1A_{1g} \]

\[ ^3\delta\delta^* = \Phi_2 = \frac{1}{\sqrt{2}} \left[ \begin{vmatrix} \phi \varphi \end{vmatrix} - \begin{vmatrix} \varphi \phi \end{vmatrix} \right] \]

\[ \Phi_2' = \begin{vmatrix} \phi \varphi \end{vmatrix} \]

\[ \Phi_2'' = \begin{vmatrix} \varphi \phi \end{vmatrix} \]

\[ ^1\delta\delta^* = \Phi_3 = \frac{1}{\sqrt{2}} \left[ \begin{vmatrix} \phi \varphi \end{vmatrix} - \begin{vmatrix} \varphi \phi \end{vmatrix} \right] \rightarrow ^1A_{2u} \]

\[ ^1\delta^*\delta^* = \Phi_4 = \begin{vmatrix} \varphi \varphi \end{vmatrix} \rightarrow ^1A_{1g} \]

Note \( \Phi_2 \) and \( \Phi_3 \) are unique single Slater determinantal wave functions... thus the energies of these states may be solved directly:

\[ \Delta E[\Phi_2 \left( ^3A_{2u}, ^3\delta\delta^* \right)] = \langle \phi \varphi | \hat{H} | \phi \varphi \rangle \]

where this is our typical Hamiltonian \( \hat{H} = \mu_q + Q_{ij} \)

\[ \therefore \Delta E[\Phi_2 \left( ^2A_{2u} \right)] = \langle \phi \varphi | \mu_q + Q_{ij} | \phi \varphi \rangle = \langle \phi \varphi | \mu_q + Q_{ij} | \varphi \phi \rangle \]

\[ = \langle \phi | \mu_q | \varphi \rangle + \langle \varphi | \mu_q | \phi \rangle + J_{\varphi \phi} - K_{\varphi \phi} \]

\[ = f_q + f_q + J_{\varphi \phi} - K_{\varphi \phi} \]
Similarly $\Delta E[\Phi_3(^1A_{2u})] = f_v + f_q + J_{qv} + J_{qy}$

Unlike $\Phi_2$ and $\Phi_3$ ... $\Phi_1$ and $\Phi_4$ can configurationally interact:

$\Psi(^1A_{1g}) = c_1\Phi_1 + c_4\Phi_4$

leading to the secular determinant

$$
\begin{vmatrix}
\langle \Phi_1|H|\Phi_1 \rangle - \Delta E(^1A_{1g}) & \langle \Phi_1|H|\Phi_4 \rangle \\
\langle \Phi_4|H|\Phi_1 \rangle & \langle \Phi_4|H|\Phi_4 \rangle - \Delta E(^1A_{1g})
\end{vmatrix} = [D]
$$

thus need to calculate diagonal and off-diagonal elements... we find

$$
\begin{vmatrix}
2f_q + J_{qq} - \Delta E(^1A_{1g}) & K_{qq} \\
K_{qy} & 2f_q + J_{qy} - \Delta E(^1A_{1g})
\end{vmatrix} = [D]
$$

Solving for $\Delta E(^1A_{1g})$

$$
\Delta E(^1A_{1g}) = \frac{E_y + E_q}{2} \pm \sqrt{\left(\frac{E_y + E_q}{2}\right)^2 + K_{qq}}
$$

defining the following relations,

$$
\frac{E_y + E_q}{2} = f_y + f_q + \frac{J_{qq} + J_{qy}}{2}
$$

$$
\Delta J = J_{qq} - \frac{J_{qq} + J_{qy}}{2}
$$

$$
\Delta W = \frac{E_q - E_y}{2} = f_q - f_y + \frac{J_{qy} - J_{qq}}{2}
$$

permits the energies of the four states to be reformulated as:

$$
\Delta E_{1,4}(-1A_{1g}) = \frac{E_y + E_q}{2} \pm \sqrt{(-\Delta W)^2 + [K_{qq}]} \\
\Delta E_{2}(-1A_{2u}) = \frac{E_y + E_q}{2} + [\Delta J - K_{qy}] \\
\Delta E_{3}(-1A_{2u}) = \frac{E_y + E_q}{2} + [\Delta J + K_{qy}]
$$

all energies referenced to the same value:

$$
\frac{E_y + E_q}{2}
$$
Can make one further approximation, 

\[
J_{\phi\phi} = J_{\psi\psi} = J_{\phi\psi}
\]

This is called the zero-differential overlap (ZDO) approximation. Hence \( \Delta J = 0 \) and \( \Delta W = f_\phi - f_\psi \) (i.e. energy difference between the \( \delta (= \phi) \) and \( \delta^* (= \psi) \) orbitals). The reformulated energies, summarized on the diagram below becomes...

\[
\sqrt{\Delta W^2 + K_{\phi\psi}^2}
\]

\[
\begin{align*}
\text{Energy} & \\
K_{\phi\psi} & = \frac{E_\phi + E_\psi}{2} \\
\text{1A_1g (1}\delta\delta^*)
\end{align*}
\]

\[
\begin{align*}
\text{1A_2u (1}\delta\delta^*)
\end{align*}
\]

\[
\begin{align*}
\text{3A_2u (3}\delta\delta^*)
\end{align*}
\]

\[
\begin{align*}
\text{1A_1g (1}\delta\delta)
\end{align*}
\]

If \( 1e^- \) energy, i.e. the \( \delta/\delta^* \) splitting (\( = \Delta W \)) is much greater than the \( 2e^- \) exchange energy, \( K_{\phi\psi} \) ... then we get the expected result from the MO diagram. However if \( 2e^- \) energy is much greater than \( 1e^- \) energy, then get the non-intuitive result:

\[
\begin{align*}
\Delta W & >> K \\
\end{align*}
\]

\[
\begin{align*}
+\Delta W & \quad 1\delta\delta^* \\
0 & \quad 3\delta\delta^* \\
-\Delta W & \quad 1\delta\delta \\
\end{align*}
\]

\[
\begin{align*}
+K & \quad 1\delta\delta^* \\
2\Delta W & \quad 2K \\
-K & \quad 3\delta\delta^* \\
\end{align*}
\]

\[
\begin{align*}
\Delta W >> K \\
K >> \Delta W
\end{align*}
\]