5.04, Principles of Inorganic Chemistry II
MIT Department of Chemistry
Lecture 26: One-Electron Crystal Field Energies

d^1 ion → ^2D state (10-fold degenerate)

Degenerancy removed upon application of the ligand field. Generally,

$$\hat{C}_\alpha \Psi_{n,\ell,m_\ell} = R_{n,\ell}(r)\Theta_{\ell,m_\ell}\underbrace{(\theta)\psi_s \cdot}\hat{C}_\alpha \Phi_{\ell,m_\ell}(\phi)$$

$$\hat{C}_\alpha \Phi_{\ell,m_\ell}(\phi) = \hat{C}_\alpha \begin{bmatrix} e^{i\ell\phi} & 0 & \cdots & \cdots & & \\ 0 & e^{i(\ell-1)\phi} & & & & \\ \vdots & \vdots & \ddots & & \vdots & \vdots \\ \vdots & \vdots & & \ddots & \vdots & \vdots \\ & & & & e^{i(1-\ell)\phi} & 0 \\ & & \cdots & \cdots & 0 & e^{-i\ell\phi} \end{bmatrix}$$

$$= \begin{bmatrix} e^{i\ell(\phi+\alpha)} & 0 & \cdots & \cdots & & \\ 0 & e^{i(\ell-1)(\phi+\alpha)} & & & & \\ \vdots & \vdots & \ddots & & \vdots & \vdots \\ \vdots & \vdots & & \ddots & \vdots & \vdots \\ & & & & e^{i(1-\ell)(\phi+\alpha)} & 0 \\ & & \cdots & \cdots & 0 & e^{-i\ell(\phi+\alpha)} \end{bmatrix}$$

so...

$$\hat{C}_\alpha = \begin{bmatrix} e^{i\ell\phi} & 0 & \cdots & \cdots & & \\ 0 & e^{i(\ell-1)\phi} & & & & \\ \vdots & \vdots & \ddots & & \vdots & \vdots \\ \vdots & \vdots & & \ddots & \vdots & \vdots \\ & & & & e^{i(1-\ell)\phi} & 0 \\ & & \cdots & \cdots & 0 & e^{-i\ell\phi} \end{bmatrix}$$

The character of the operation is the trace of the matrix representation. By using L'Hôpital's rule, the trace of $\hat{C}_\alpha$ may be determined as $\alpha \to 0$

$$\lim_{\alpha \to 0} \chi(\alpha) = \frac{\left(\ell + \frac{1}{2}\right)\cos\left(\ell + \frac{1}{2}\right)\alpha}{\frac{1}{2}\cos\frac{\alpha}{2}} = 2\ell + 1$$

For $\alpha \neq 0$, the trace is simply the sum of the exponents

$$\chi(\alpha) = \frac{\sin\left(\ell + \frac{1}{2}\right)\alpha}{\sin\frac{\alpha}{2}} \quad \alpha \neq 0$$

Thus considering the pure rotational subgroup for the 1e$^-$ system

	0	E	$6C_4$	$3C_2$ ($\equiv C_4^2$)	$8C_3$	$6C_2$	
$\ell = 0$	Γ_s	1	1	1	1	1 $\rightarrow$	A_{1g}
$\ell = 1$	Γ_p	3	1	-1	0	1 $\rightarrow$	T_{1u}
$\ell = 2$	Γ_d	5	-1	1	-1	1 $\rightarrow$	$E_g + T_{2g}$

$\vdots$

$\Gamma_f = A_{2u} + T_{1u} + T_{2u}$

$\Gamma_g = A_{1g} + E_g + T_{1g} + T_{2g}$

we see, therefore, that the O_h ligand field lifts the degenerancy of the free ion state. Applying the projection operator to the real parts of the spherical harmonics (i.e. the d-orbitals)

$$E\begin{cases} \varphi_1 = \psi_{n,2,0} & = d_{z^2} \\ \varphi_2 = \dfrac{1}{\sqrt{2}}\left(\psi_{n,2,-2+} + \psi_{n,2,-2}\right) & = d_{x^2-y^2} \end{cases}$$

$$T_2\begin{cases} \varphi_3 = \dfrac{1}{\sqrt{2}}\left(\psi_{n,2,-2} - \psi_{n,2,-2}\right) & = id_{xy} \\ \varphi_4 = -\psi_{n,2,1} & d_{xz}\left(= \dfrac{1}{\sqrt{2}}\left(\psi_{n,2,1} - \psi_{n,2,-1}\right)\right) \\ \varphi_5 = \psi_{n,2,-1} \quad \Rightarrow & d_{yz}\left(= \dfrac{1}{\sqrt{2}}\left(\psi_{n,2,1} + \psi_{n,2,-1}\right)\right) \end{cases}$$

The two energy terms are obtained from the following secular determinants (which are diagonal because the φ_i's are symmetry adapted)

$$\begin{vmatrix} H_{1,1} - \Delta\varepsilon(E_g) & 0 \\ 0 & H_{2,2} - \Delta\varepsilon(E_g) \end{vmatrix} = 0$$

The SALC's for the spherical harmonics in the O_h point group are given in pg IE5.

$$\begin{vmatrix} H_{3,3} - \Delta\varepsilon(T_{2g}) & 0 & 0 \\ 0 & H_{4,4} - \Delta\varepsilon(T_{2g}) & 0 \\ 0 & 0 & H_{5,5} - \Delta\varepsilon(T_{2g}) \end{vmatrix} = 0$$

If you use these SALC's… the secular determinant will always be diagonalized as shown here.

need only calculate one energy root

$$\Delta\varepsilon(E_g) = \int_0^\infty \int_0^\pi \int_0^{2\pi} R^*_{n,2}(r) Y^*_{2,0}(\theta,\phi)\, V_{O_h}(r,\theta,\phi)\, R_{n,2} Y_{2,0}(\theta,\phi)\, r^2 dr \sin\theta d\theta d\phi$$

$$= A_{0,0} \int_0^\infty R^*_{n,2}(r) r^0 R_{n,2}(r) r^2 dr \int_0^\pi \int_0^{2\pi} Y^*_{2,0}(\theta,\phi) \left[Y_{4,0} + \sqrt{\frac{5}{14}} (Y_{4,+4} + Y_{4,-4}) \right] Y_{2,0}(\theta,\phi) \sin\theta d\theta d\phi$$

integrals $\int_0^\infty R^*_{n,2}(r) r^k\, R_{n,2}(r) r^2 dr = \bar{r}^k$ … so

$$\Delta\varepsilon(E_g) = -A_{0,0}\bar{r}^0 \int_0^\pi \int_0^{2\pi} Y^*_{2,0}(\theta,\phi) \cdot Y_{0,0} \cdot Y_{2,0}(\theta,\phi) \sin\theta d\theta d\phi -$$
$$A_{4,0}\bar{r}^4 \int_0^\pi \int_0^{2\pi} Y^*_{2,0}(\theta,\phi) \left[Y_{4,0} + \sqrt{\frac{5}{14}} (Y_{4,+4} + Y_{4,-4}) \right] Y_{2,0}(\theta,\phi) \sin\theta d\theta d\phi$$

Using the appropriate integration tables (see next page)

$$\Delta\varepsilon(E_g) = -A_{0,0}\bar{r}^0 \cdot \frac{1}{2\sqrt{\pi}} - A_{4,0}\bar{r}^4 \left[\frac{6}{14\sqrt{\pi}} + \sqrt{\frac{5}{14}} \frac{1}{2\sqrt{\pi}} (0+0) \right]$$

$$= -\frac{A_{0,0}}{2\sqrt{\pi}}\bar{r}^0 - 6\frac{A_{4,0}}{14\sqrt{\pi}}\bar{r}^4 \qquad \text{since } -A_{4,0}(O_h) = \frac{21}{4\sqrt{\pi}} a_4^{(L)}$$

$$\Downarrow$$

$$= \varepsilon_0(O_h) + 6Dq \quad \text{where } Dq = -\frac{A_{4,0}}{14\sqrt{\pi}}\bar{r}^4 \quad \text{or} \quad \frac{3}{8\sqrt{\pi}} a_4^{(L)} \bar{r}^4$$

angular independent position of potential energy (in K_h symmetry) resulting in e^- repulsion of e^- on M with e^- pairs of L… causes energy shift with no split

Values of the integrals $\int_0^{\pi}\int_0^{2\pi} Y^*_{2,m_l}(\theta,\phi)\,Y_{\lambda,n}(\theta,\phi)\,Y_{2,m_l}{}'(\theta,\phi)\sin\theta\, d\theta\, d\phi$

Table removed due to copyright considerations.

For $\Delta\varepsilon(T_{2g})$ will solve $H_{4,4}$ … only one wave function in calculation of φ_4 (this example reveals convenience of choosing spherical harmonic over real d-orbital wave functions, which are linear combinations)

$$\Delta\varepsilon(T_{2g}) = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} R^*_{n,2}(r)Y^*_{2,1}(\theta,\phi)V_{O_h}(r,\theta,\phi)R_{n,2}Y_{2,1}(\theta,\phi)r^2 dr\,\sin\theta\, d\theta\, d\phi$$

$$= -A_{0,0}\int_0^{\infty} R^*_{n,2}(r)r^0R_{n,2}(r)r^2dr\int_0^{\pi}\int_0^{2\pi} Y^*_{2,1}(\theta,\phi)Y_{0,0}Y_{2,1}(\theta,\phi)\sin\theta\, d\theta\, d\phi$$

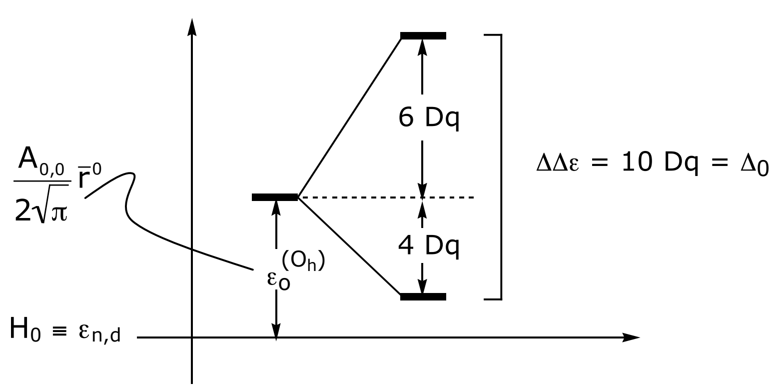
$$-A_{4,0}\int_0^{\infty} R^*_{n,2}(r)r^4R_{n,2}(r)r^2dr\int_0^{\pi}\int_0^{2\pi} Y^*_{2,1}(\theta,\phi)\left[Y_{4,0} + \sqrt{\frac{5}{14}}\left(Y_{4,+4} + Y_{4,-4}\right)\right]Y_{2,1}(\theta,\phi)\sin\theta\, d\theta\, d\phi$$

$$= -\frac{A_{0,0}}{2\sqrt{\pi}}\bar{r}^0 - \left[-\frac{4}{14\sqrt{\pi}} + \sqrt{\frac{5}{14}}\frac{1}{2\sqrt{\pi}}(0+0)\right]A_{4,0}\bar{r}^4$$

$$= -\frac{A_{0,0}}{2\sqrt{\pi}}\bar{r}^0 + 4\frac{A_{4,0}}{14\sqrt{\pi}}\bar{r}^4$$

$$= \varepsilon_0(O_h) - 4\text{ Dq} \quad \text{...where Dq} = \frac{A_{4,0}}{14\sqrt{\pi}}\bar{r}^4$$

Summarizing…



Symmetry adapted linear combinations of spherical harmonics Y_{l,m_l} *for the symmetry group O.*

Table removed due to copyright considerations.