5.04 Principles of Inorganic Chemistry II
Fall 2008

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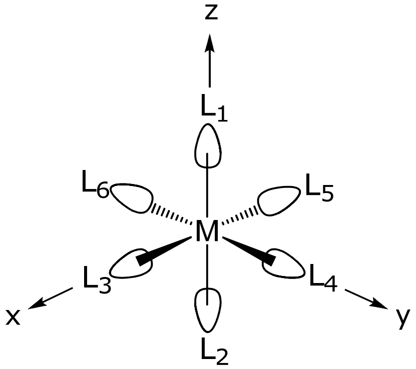
Lecture 12: Octahedral ML_6 Sigma Complexes

An octahedral complex comprises a central metal ion and six terminal ligands. If the ligands are exclusively σ-donors, then the basis set for the ligands is defined as follows,



Ligands that move upon the application of an operation, R, cannot contribute to the diagonal matrix element of the representation. Since the σ bond is along the internuclear axis that connects the ligand and metal, the transformation properties of the ligand are correspondent with that of the M–L σ bond. Moreover, a σ bond has no phase change within the internuclear axis, hence the bond can only transform into itself (+1) or into another ligand (0).

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma_{L\sigma}$	6	0	0	2	2	0	0	0	4	2

$$\Gamma_{L\sigma} = a_{1g} + t_{1u} + e_g$$

Need now to determine the SALCs of the Lσ basis set. Three different methods will deliver the SALCs.

Method 1

As we have done previously, the SALCs of Lσ may be determined using the projection operator. Note that the ligand mixing in O_h is retained in the pure rotational subgroup, O. Can thus drop from O_h → O, thereby saving 24 operations.

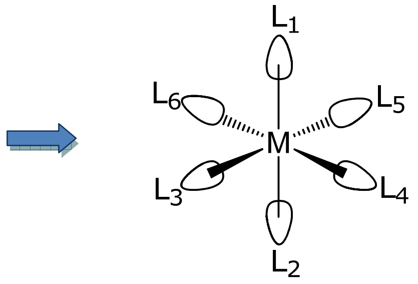
O	E	C_3	C_3	C_3	C_3	C_3	C_3	C_3	C_3	C_2	C_2	C_2	C_2	C_2	C_2	C_4	C_4	C_4	C_4	C_4	C_4	C_2	C_2	C_2
$L_1 \rightarrow$	L_1	L_3	L_4	L_4	L_5	L_6	L_5	L_6	L_3	L_2	L_2	L_6	L_5	L_4	L_3	L_1	L_1	L_5	L_3	L_4	L_6	L_1	L_2	L_2

The A_1 irreducible representation is totally symmetric. Hence the projection is simply the sum of the above ligand transformations.

$P^{A_1}(L_1) \sim 4(L_1 + L_2 + L_3 + L_4 + L_5 + L_6)$

and normalizing yields,

$$\psi_{a_{1g}} = \frac{1}{\sqrt{6}}\left(L_1 + L_2 + L_3 + L_4 + L_5 + L_6\right)$$



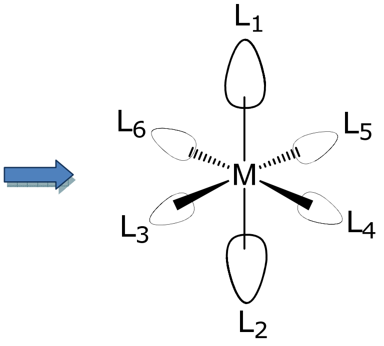
The application of the projection operator for the E irreducible representation furnishes the E_g SALCs.

$P^E(L_1) \rightarrow (2L_1 - L_3 - L_4 - L_4 - L_5 - L_6 - L_5 - L_6 - L_3 + 2L_1 + 2L_2 + 2L_2)$

$\rightarrow (4L_1 + 4L_2 - 2L_3 - 2L_4 - 2L_5 - 2L_6)$

and normalizing yields,

$$\psi_{e_g}^{(1)} = \frac{1}{\sqrt{12}}\left(2L_1 + 2L_2 - L_3 - L_4 - L_5 - L_6\right)$$



But E_g is a doubly degenerate representation, and therefore there is a another SALC. As is obvious from above, the projection operator only yields one of the two SALCs. How do we obtain the other?

Method 2

The **Schmidt orthogonalization** procedure can extract SALCs from a non-orthogonal linear combination of an appropriate basis. Suppose we have a SALC, $\mathbf{v_1}$, then there exists a $\mathbf{v_2}$ that meets the following condition,

$$\mathbf{v_2} = a\mathbf{v_1} + \mathbf{u}$$

where $\mathbf{u}$ is the non-orthogonal linear combination. Multiplying the above equation by $\mathbf{v_1}$ gives,

$$\overset{0}{\cancel{\mathbf{v_2 v_1}}} = a\overset{1}{\cancel{\mathbf{v_1 v_1}}} + \mathbf{u v_1}$$

$$\therefore a = -\mathbf{u v_1}$$

What is the nature of $\mathbf{u}$? Consider using the projection operator on L_3 instead of L_1,

$$P^{e_g}(L_3) = \frac{1}{\sqrt{12}}\left(2L_3 + 2L_5 - L_1 - L_2 - L_4 - L_6\right)$$

Note, this does not yield any new information, i.e., the atomic orbitals on one axis are twice that and out-of-phase from the atomic orbitals in the equatorial plane. However, this new wavefunction is not $\psi_{e_g}^{(2)}$ because it is not orthogonal to $\psi_{e_g}^{(1)}$.

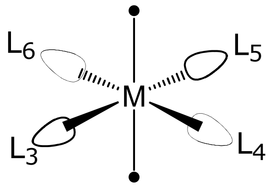
Thus the projection must yield a wavefunction that is a linear combination of $\psi_{e_g}^{(1)}$ and $\psi_{e_g}^{(2)}$, i.e., the wavefunction obtained from the projection is a viable **u**. Applying the Schmidt orthogonalization procedure,

$$a = -\mathbf{uv}_1 = -\left\langle \frac{1}{\sqrt{12}}(2L_3 + 2L_5 - L_1 - L_2 - L_4 - L_6) \middle| \frac{1}{\sqrt{12}}(2L_1 + 2L_2 - L_3 - L_4 - L_5 - L_6) \right\rangle$$
$$= -\frac{1}{12}\left[-6\right] = +\frac{1}{2}$$

so,

$$\mathbf{v}_2 = \frac{1}{2}\frac{1}{\sqrt{12}}\left(2L_1 + 2L_2 - L_3 - L_4 - L_5 - L_6\right) + \frac{1}{\sqrt{12}}\left(2L_3 + 2L_5 - L_1 - L_2 - L_4 - L_6\right)$$
$$= \frac{1}{\sqrt{12}}\left[\left(\frac{3}{2}L_3 + \frac{3}{2}L_5\right) - \left(\frac{3}{2}L_4 + \frac{3}{2}L_6\right)\right] \approx \left(L_3 + L_5\right) - \left(L_4 + L_6\right)$$

$$\therefore\ \psi_{e_g}^{(2)} = \frac{1}{2}\left(L_3 - L_4 + L_5 - L_6\right)$$ ➡



$\psi_{e_g}^{(2)}$ is orthogonal to $\psi_{e_g}^{(1)}$, thus it is the other SALC.

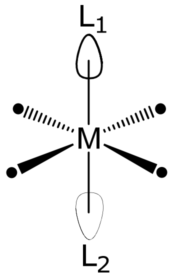
The T_{1g} SALCs must now be determined. The projection operator yields,

$P^{T_1}(L_1) \rightarrow (3L_1 - L_2 - L_2 - L_6 - L_5 - L_4 - L_3 + L_1 + L_1 + L_5 + L_3 + L_4 + L_6 - L_1 - L_1 - L_2)$

$P^{T_1}(L_1) \sim 3(L_1 - L_2)$

and normalizing yields,

$\psi_{t_{1u}}^{(1)} = \frac{1}{\sqrt{2}}\left(L_1 - L_2\right)$ ➡



Applying the Schmidt orthogonalization method,

$$P^{T_1}(L_3) \sim 3(L_3 - L_5) \rightarrow \psi_{t_{1u}} = \frac{1}{\sqrt{2}}\left(L_3 - L_5\right)$$

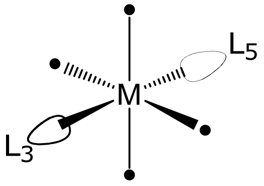
This wavefunction is orthogonal to $\psi_{t_{1u}}^{(1)}$, hence it is likely a SALC. Can prove this by applying the Schmidt orthogonalization process and setting this to be **u**. Solving for a,

$$\begin{aligned} a = -\mathbf{u}\mathbf{v}_1 &= -\left\langle \frac{1}{\sqrt{2}}(L_1 - L_2) \middle| \frac{1}{\sqrt{2}}(L_3 - L_5) \right\rangle \\ &= -\frac{1}{2}(0) = 0 \end{aligned}$$

and

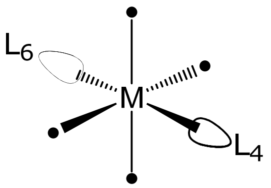
$$v_2 = av_1 + u = 0 \bullet \frac{1}{\sqrt{2}}\left(L_1 - L_2\right) + \frac{1}{\sqrt{2}}\left(L_3 - L_5\right)$$

$\psi_{t_{1u}}^{(2)} = \frac{1}{\sqrt{2}}\left(L_3 - L_5\right)$ ➡



so, as suspected, this is a SALC. And the third SALC of T_{1u} symmetry is the (L4,L6) pair.

$\psi_{t_{1u}}^{(3)} = \frac{1}{\sqrt{2}}\left(L_4 - L_6\right)$ ➡



Method 3

For those SALCs with symmetries that are the same as s, p or d orbitals, may adapt the symmetry of the ligand set to the symmetry of the metal orbitals.

Consider the d_{z^2} orbital, which is more accurately defined as $2z^2 - x^2 - y^2$. Thus the coefficient of the z axis is twice that of x and y and out of phase with x and y. The ligands on the z-axis, L_1 and L_2, should therefore be twice that and of opposite sign to the equatorial ligands, L_3,L_4,L_5,L_6. This leads naturally to,

$$\psi_{e_g}^{(1)} \approx 2L_1 + 2L_2 - L_3 - L_4 - L_5 - L_6$$

$$\psi_{e_g}^{(1)} = \frac{1}{\sqrt{12}}\left(2L_1 + 2L_2 - L_3 - L_4 - L_5 - L_6 \right)$$

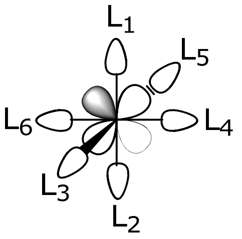
The other SALC of this degenerate set is given by $d_{x^2-y^2}$, which has no coefficient on z, and x and y coefficients that are equal but of opposite sign. By symmetry matching to the orbital,

$$\psi_{e_g}^{(2)} \approx L_3 - L_4 + L_5 - L_6$$

$$\psi_{e_g}^{(2)} = \frac{1}{2}\left(L_3 - L_4 + L_5 - L_6 \right)$$

The other SALCs follow suit.

The t_{2g} d-orbital set (i.e. d_{xy}, d_{xz}, d_{yz}) is of incorrect symmetry to interact with the Lσ ligand set and thus is non-bonding. This can be seen from the orbital picture. The Lσ orbitals are directed between the lobes of the t_{2g} d-orbitals,

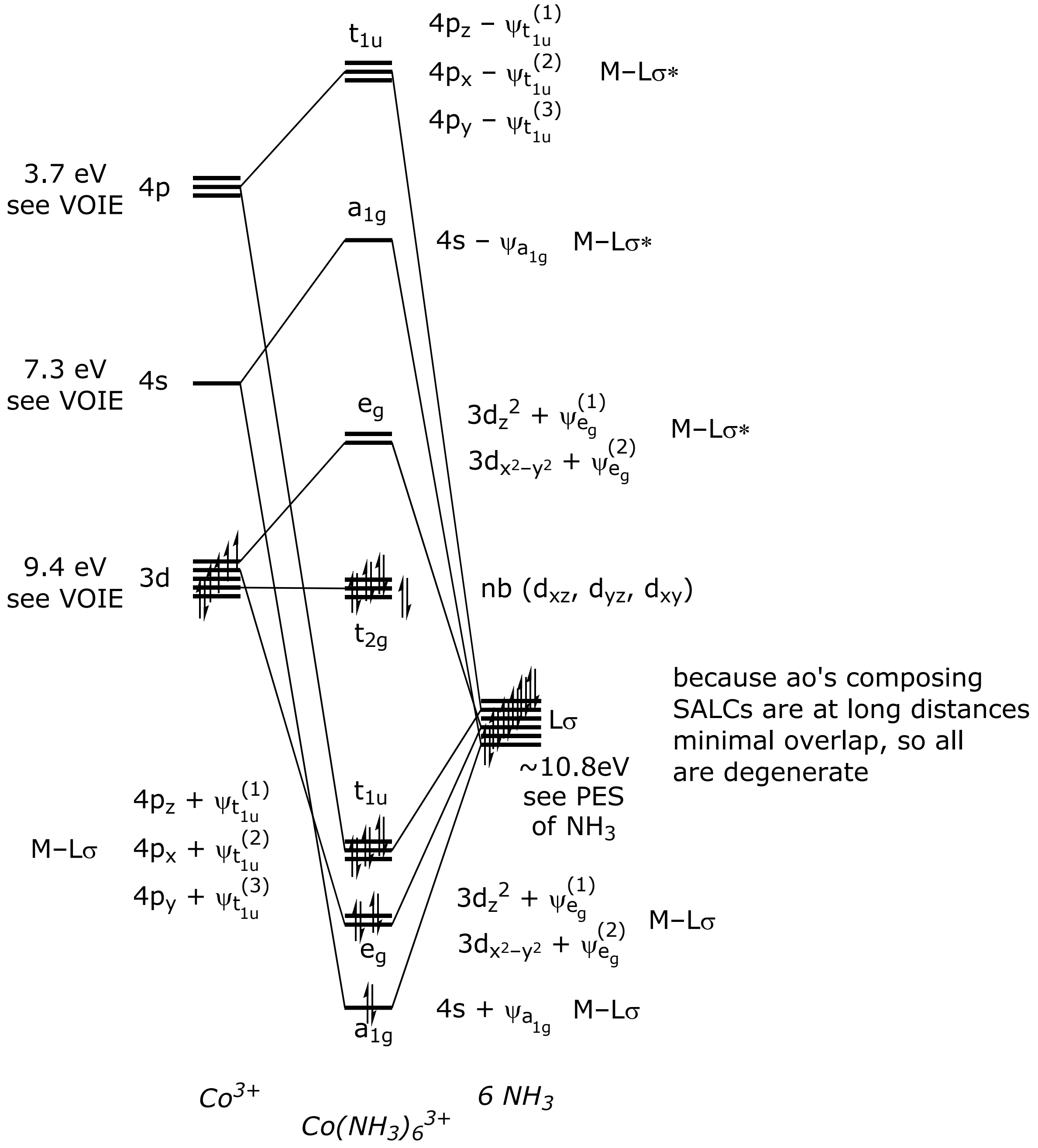


Only metal orbitals and SALCs of the same symmetry can overlap. In the case of the octahedral ML_6 σ-complex,

metal	*SALC*	*metal*	*SALC*
s	$\psi_{a_{1g}}$	p_z	$\psi_{t_{1u}}^{(1)}$
p_x	$\psi_{t_{1u}}^{(1)}$	$d_{x^2-y^2}$	$\psi_{e_g}^{(2)}$
p_y	$\psi_{t_{1u}}^{(1)}$	d_{z^2}	$\psi_{e_g}^{(1)}$

and (d_{xz}, d_{yz}, d_{xy}) are non-bonding

With above considerations of ΔE_{ML} and S_{ML} in mind, the MO diagram for $M(L\sigma)_6$ is constructed with $Co(NH_3)_6^{3+}$ as the exemplar,



Interaction energies ε_σ and ε_σ* (i.e., the off-diagonal matrix elements, H_{ML}) are smaller than the difference in energies of the metal and ligand atomic orbitals (i.e., the diagonal matrix elements, H_{MM} and H_{LL}), so molecular orbitals stay within their energy "zones".