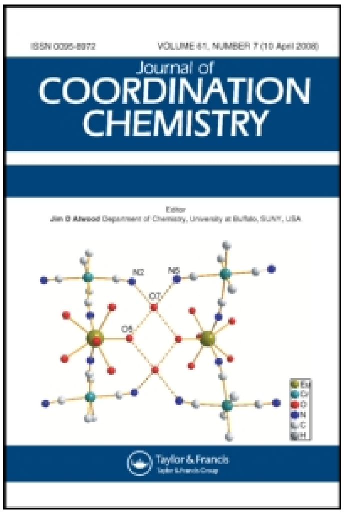

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYMMETRY ADAPTED LIGAND GROUP ORBITALS AND ANALYTICAL COMPOSITIONS OF HYBRID ORBITALS IN AB_n TYPE MOLECULES

S. K. Dhar[a]
[a] Chemistry Department, DePaul University, Chicago, Illinois, USA

To cite this Article Dhar, S. K.(1993) 'SYMMETRY ADAPTED LIGAND GROUP ORBITALS AND ANALYTICAL COMPOSITIONS OF HYBRID ORBITALS IN AB_n TYPE MOLECULES', Journal of Coordination Chemistry, 29: 1, 17 — 26
To link to this Article: DOI: 10.1080/00958979308037121
URL: http://dx.doi.org/10.1080/00958979308037121

J. Coord. Chem. 1993, Vol. 29, pp. 17–26
Reprints available directly from the publisher
Photocopying permitted by license only

SYMMETRY ADAPTED LIGAND GROUP ORBITALS AND ANALYTICAL COMPOSITIONS OF HYBRID ORBITALS IN AB_n TYPE MOLECULES

S. K. DHAR

Chemistry Department, DePaul University, Chicago, Illinois 60614, USA

(Received April 13, 1992)

A non-rigorous method of construction of SALC's for AB_n type molecules, based on the sum of the projections of the AB axes on the reference axes of the valence orbitals of the central atom, is presented. The method may be adapted to structures such as TBP where the inequivalence of the equatorial and axial ligands make the existing methods difficult to apply. A convenient method for deriving the analytical compositions of hybrid orbitals is also described.

KEY WORDS: Coordination compounds, SALC, hybrid orbitals

Determination of symmetry-adapted ligand group orbitals (SALC's) are of central interest to coordination chemists. These are determined by several ways,[1–4] including the projection operator method, and deduction from direct observation for structures of high symmetry. The analytical composition of the hybrid orbitals may be constructed from the SALC's by matrix inversion,[2] as well as several other methods described in the references. Determination of SALC of d_{z^2} symmetry for structures such as TBP however can not be easily accomplished by the existing methods in view of the inequivalence of the axial and equatorial positions and approximation has been made, neglecting any contribution from the equatorial ligands.[2] A procedure is proposed here which is mathematically simple and yields results in agreement with those from established procedures. In addition, when applied to the TBP structure it produces a SALC of d_{z^2} symmetry, which after an empirical adjustment yields an expression which appears to be a satisfactory solution embodying contributions from all the ligands. Further, in the proposed method, analytical compositions of hybrid orbitals are obtained from the SALC's through a one-step exchange of coefficients, which appears to be simpler than the existing methods. The validity of the derived SALC's and the hybrid orbitals are confirmed through their fulfillment of the orthogonality requirement, as well as an additional test for the hybrid composition.

The method will be illustrated with planer AB_3, tetrahedral AB_4, and octahedral AB_6 structures. It will then be applied to trigonal bipyramid, trigonal prismatic structures in both eclipsed and staggered forms, the square antiprism structure, and to an AB_3C molecule having C_{3v} symmetry.

It will be assumed that the ligand, B, uses its p_z orbital, ϕ_i, directed towards the central atom for sigma bonding, and this orbital transforms in the same way as the

AB_i bond under the symmetry operations. The valence orbitals of the central atom will be designated by a set of reference axes as follows. The three cartesian axes passing through A will be the reference axes for the three p orbitals, as well as for the d_{z^2} and $d_{x^2-y^2}$ orbitals since they have components in the XY plane and the Z axis. The d_{xy} orbital will be represented by the X and the Y axes rotated by 45° in the XY plane; similarly the other two d orbitals in terms of their reference cartesian axis rotated by 45° in their respective planes.

The SALC, corresponding to a valence orbital of the central atom, will be given in terms of the sum of the projection of ϕ_i on the reference axes of the valence orbital, with proper adjustment of the mathematical signs of the orbital. the projection will be given by $\phi_i \cos \theta_i$ where θ_i is the angle between AB_i and the reference axis. Since the method depends on the sum of the individual projections and does not require interchange of the axial and equatorial bonds, it may be applied to a structure with inequivalent bonds without having to resolve it into two sets.

AB_3, D_3h, (s, p_x, p_y)

The SALC of p_x symmetry, ψp_x, will be given by the sum of the projections of the three AB axes on the X axis with appropriate adjustment for the signs of the p_x orbital along this axis.

$$\psi p_x = AB_2 - AB_1 \cos 60 - AB_3 \cos 60$$

$$\equiv \phi_2 - 1/2\phi_1 - 1/2\phi_3.$$

After normalization,

$$\psi p_x = \sqrt{1/6}(2\phi_2 - \phi_1 - \phi_3) \tag{1}$$

Similarly,

$$\psi p_y = AB_1 \cos 30 - AB_3 \cos 30$$

$$\equiv \sqrt{1/2}(\phi_1 - \phi_3). \tag{2}$$

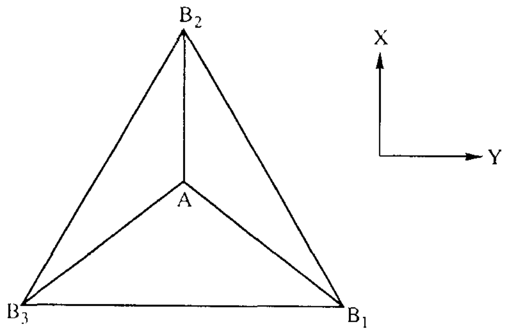

Figure 1.

ψ_s will be simply given by

$$\psi_s = \sqrt{1/3}(\phi_1 + \phi_2 + \phi_3). \tag{3}$$

The above results are identical to those obtained by the projection operator and other methods given in the literature. The analytical compositions of the hybrid orbitals of A, expressed as σ_i, may be given as linear combinations of its valence orbitals, with their coefficients in the combination derived as follows. The coefficient of ϕ_1 in the normalized SALC's of the s, p_x and p_y symmetries (1–3), become the coefficients of the s, p_x and the p_y terms, respectively, in σ_1.

$$\sigma_1 = \sqrt{1/3}s - \sqrt{1/6}p_x + \sqrt{1/2}p_y$$

Similarly, the coefficients of the valence orbitals in σ_2 and σ_3 are obtained from those of ϕ_2 and ϕ_3, respectively, in the above three SALC's as follows.

$$\sigma_2 = \sqrt{\frac{1}{3}}s + 2/\sqrt{6}p_x$$

$$\sigma_3 = \sqrt{\frac{1}{3}}s - \sqrt{1/6}p_x - \sqrt{1/2}p_y$$

The results are again found to be identical to those given in the references.

AB_4, T_d

It is easily seen that the AB_i bond axes make equal angle of 54.75° with each of the three cartesian coordinates passing through A. Thus

$$\psi p_x = \cos 54.75\ (AB_2 + AB_4 - AB_2 - AB_3)$$

On normalization,

$$\psi p_x = 1/2(\phi_1 + \phi_4 - \phi_2 - \phi_3).$$

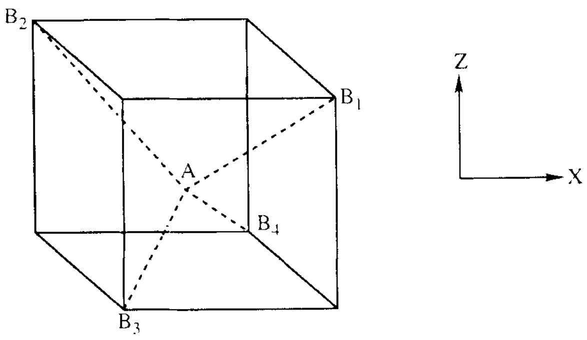

Figure 2.

Similarly, the other three SALC's are constructed, incorporating the signs of the matching orbitals in each case.

$$\psi p_y = 1/2(\phi_1 - \phi_2 + \phi_3 - \phi_4)$$

$$\psi p_z = 1/2(\phi_1 + \phi_2 - \phi_3 - \phi_4)$$

$$\psi_s = 1/2(\phi_1 + \phi_2 + \phi_3 + \phi_4)$$

The compositions of the four hybrids may be readily obtained from the above four SALC's, through the coefficient transfer method as outlined for AB_3.

AB_6, O_h

The SALC's for the p symmetries are easily obtained since only two of the bond axes coincide with any one of the cartesian coordinates at one time, with the others being at right angles and thus eliminated through coefficients of zero. The SALC of $d_{x^2-y^2}$ symmetry is obtained by taking the sum of the projections of AB_i on the X axis and subtracting from it the sum of the projections of AB_i on the Y axis. The SALC of d_{z^2} symmetry is obtained by taking the sum of the projections of AB_i twice on the Z axis and subtracting from it the sum of the projections on the X axis and Y axis. The results are shown below, along with the compositions of the six hybrid orbitals of A in the O_h symmetry derived by the one step method illustrated previously.

SALC

$$\psi_s = \sqrt{1/6}\sum_i \phi_i$$

$$\psi p_x = \sqrt{1/2}(\phi_4 - \phi_2)$$

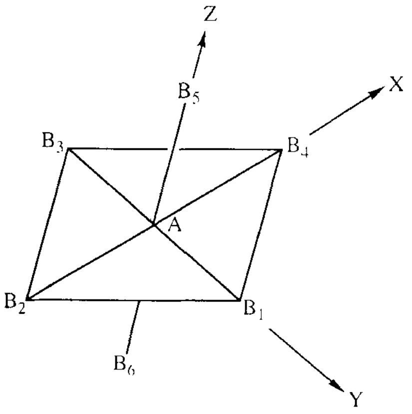

Figure 3.

$$\psi p_y=\sqrt{1/2}(\phi_1-\phi_3)$$

$$\psi p_z=\sqrt{1/2}(\phi_5-\phi_6)$$

$$\psi d_{x^2-y^2}=1/2(\phi_2+\phi_4-\phi_1-\phi_3)$$

$$\psi d_z^2=\sqrt{1/12}(2\phi_5+2\phi_6-\phi_1-\phi_2-\phi_3-\phi_4)$$

Hybrids

$$\sigma_1=\sqrt{1/6}s+\sqrt{1/2}p_y-\sqrt{1/12}d_{z^2}-1/2d_{x^2-y^2}$$

$$\sigma_2=\sqrt{1/6}s-\sqrt{1/2}p_x-\sqrt{1/12}d_{z^2}+1/2d_{x^2-y^2}$$

$$\sigma_3=\sqrt{1/6}s-\sqrt{1/2}p_y-\sqrt{1/12}d_{z^2}-1/2d_{x^2-y^2}$$

$$\sigma_4=\sqrt{1/6}s+\sqrt{1/2}p_x-\sqrt{1/12}d_{z^2}+1/2d_{x^2-y^2}$$

$$\sigma_5=\sqrt{1/6}s+\sqrt{1/2}p_z+2/\sqrt{12}d_{z^2}$$

$$\sigma_6=\sqrt{1/6}s-\sqrt{1/2}p_z+2/\sqrt{12}d_{z^2}$$

AB_5, D_{3h}

The SALC's matching the equatorial p orbitals are similar to those for planer AB_3, and those matching the p_z, d_{z^2} and $d_{x^2-y^2}$ orbitals are obtained from the projections of the AB bonds on the cartesian axes as before. The SALC of d_{xy} symmetry is obtained from the projections of the AB axes on the X and Y axes rotated by 45°. The SALC of d_{z^2} symmetry was approximated by expressing the latter as in cubic symmetry ($d_{2z^2-x^2-y^2}$) and deriving it on such a basis as was done in O_h symmetry.

It may be seen below that the SALC of d_{z^2} symmetry, thus derived, yields unequal coefficients for the three equatorial ligands, which is inconsistant with the symmetry

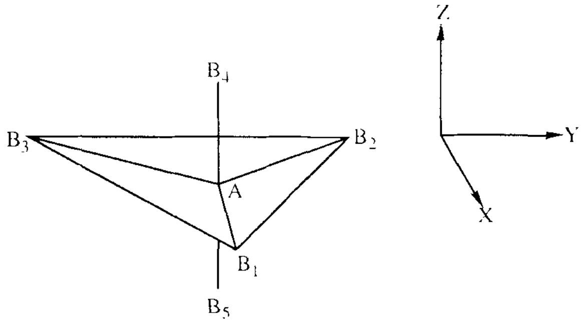

Figure 4.

of this orbital. This was empirically corrected to give equal weight as shown below to yield a set of SALC's which fulfill the criterion of orthogonality by the usual standard. The corresponding $d_{z^2}sp^3$ hybrid orbitals shown are found to be orthogonal to each other as expected, which further confirms the validity of the SALC's from which the hybrids were derived. The hybrid orbitals further satisfy the requirement given by $\sum_i c_i^2 = 1$, where c_i represent the coefficient of a given orbital in the set of hybrid orbitals.

SALC

$$\psi_s = \sqrt{1/5}\sum_i \phi_i$$

$$\psi p_x = \sqrt{1/6}(2\phi_1 - \phi_2 - \phi_3)$$

$$\psi p_y = \sqrt{1/2}(\phi_2 - \phi_3)$$

$$\psi p_z = \sqrt{1/2}(\phi_4 - \phi_5)$$

$$\psi d_{x^2-y^2} = 1/1.13(\phi_1 - 0.37\phi_2 - 0.37\phi_3)$$

$$\psi d_{xy} = \sqrt{1/2}(\phi_2 - \phi_3)$$

$$\psi d_{z^2} = 1/3.57(2\phi_4 + 2\phi_5 - \phi_1 - 1.37\phi_2 - 1.37\phi_3)$$

After empirical correction:

$$\psi d_{z^2} = \sqrt{1/13.3}[2\phi_4 + 2\phi_5 - 1.33(\phi_1 + \phi_2 + \phi_3)]$$

Hybrids $d_{z^2}sp^3$

$$\sigma_1 = \sqrt{1/5}s + \sqrt{2/6}p_x - 1.33/\sqrt{13.3}d_{z^2}$$

$$\sigma_2 = \sqrt{1/5}s + \sqrt{1/2}p_y - \sqrt{1/6}p_x - 1.33/\sqrt{13.3}d_{z^2}$$

$$\sigma_3 = \sqrt{1/5}s - \sqrt{1/2}p_y - \sqrt{1/6}p_x - 1.33/\sqrt{13.3}d_{z^2}$$

$$\sigma_4 = \sqrt{1/5}s + \sqrt{1/2}p_z + 2/\sqrt{13.3}d_{z^2}$$

$$\sigma_5 = \sqrt{1/5}s - \sqrt{1/2}p_z + 2/\sqrt{13.3}d_{z^2}$$

AB_6, TRIGONAL PRISM

In Figure 5 all the bond axes bear an equal angle to the Z axis. AB_2 and AB_4 are on the XZ plane and the rest bear an angle of 60° to this plane and an angle of 30° to the YZ plane. All the bond axes also bear an equal angle to the XY plane. The

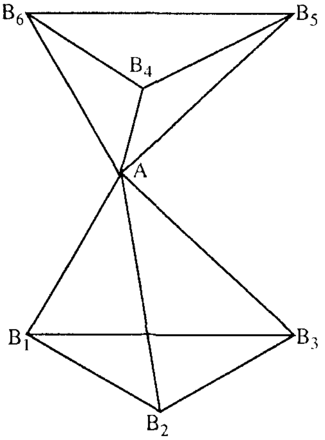

Figure 5.

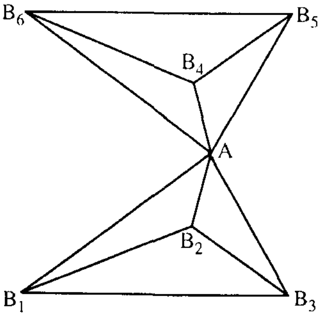

Figure 6.

angular dependence on the Z axis or the XY plane are thus factored out in the normalization step. The results shown below were derived as before. The results are in agreement with those given in the literature.[1] The SALC's corresponding to the s, d_{z^2}, $d_{x^2-y^2}$, and p_z orbitals are identical for both the eclipsed and staggered structures.

AB$_6$, D_{3h} SALC

$$\psi_{1s}=\sqrt{1/6}\sum_i \phi_i$$

$$\psi p_x=\sqrt{1/3}[\phi_2+\phi_4-1/2(\phi_1+\phi_3+\phi_5+\phi_6)]$$

$$\psi p_y=1/2(\phi_3+\phi_5-\phi_1-\phi_6)$$

$$\psi p_z=\sqrt{1/6}(\phi_4+\phi_5+\phi_6-\phi_1-\phi_2-\phi_3)$$

$$\psi d_{x^2-y^2} = 1/\sqrt{2.54}[\phi_2+\phi_4-0.37(\phi_1+\phi_3+\phi_5+\phi_6)]$$

$$\psi d_{xz} = \sqrt{1/3}(\phi_4-\phi_2+1/2\phi_1+1/2\phi_3-1/2\phi_5-1/2\phi_6)$$

$$\psi d_{yz} = 1/2(\phi_1+\phi_5-\phi_3-\phi_6)$$

$$\psi d_{xy} = 1/2(\phi_3+\phi_5-\phi_1-\phi_6)$$

AB_6, D_{3d}

$$\psi p_x = \sqrt{1/3}[\phi_4-\phi_2+1/2(\phi_1+\phi_3-\phi_5-\phi_6)]$$

$$\psi p_y = 1/2(\phi_5+\phi_3-\phi_1-\phi_6)$$

$$\psi d_{xz} = \sqrt{1/3}[\phi_2+\phi_4-1/2(\phi_1+\phi_3+\phi_5+\phi_6)]$$

$$\psi d_{yz} = 1/2(\phi_5+\phi_1-\phi_3-\phi_6)$$

$$\psi d_{xy} = 1/2(\phi_3+\phi_6-\phi_1-\phi_5)$$

AB_3C, C_{3v}

In Figure 7, C lies along the Z axis, B_3 on the XZ plane, and the other two ligands are projected at 60° from both sides of the plane. C thus is in the nodal plane of both the p_x and the p_y orbitals. The three basal ligands are symmetrically aligned at an angle of 70.5° from the Z axis. The resulting SALC's and the hybrid orbitals are shown below.

SALC

$$\psi p_x = \sqrt{1/6}(2\phi_3-\phi_1-\phi_2)$$

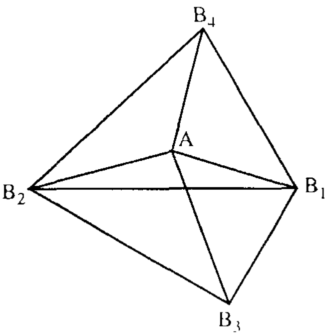

Figure 7.

$$\psi p_y = \sqrt{1/2}(\phi_1 - \phi_2)$$

$$\psi p_z = \sqrt{1/2}(3\phi_4 - \phi_1 - \phi_2 - \phi_3)$$

$$\psi_s = 1/2(\phi_1 + \phi_2 + \phi_3 + \phi_4)$$

Hybrid Composition

$$\sigma_1 = 1/2s - \sqrt{1/6}p_x + \sqrt{1/2}p_y - \sqrt{1/12}p_z$$

$$\sigma_2 = 1/2s - \sqrt{1/6}p_x - \sqrt{1/2}p_y - \sqrt{1/12}p_z$$

$$\sigma_3 = 1/2s + 2/\sqrt{6}p_x - \sqrt{1/12}p_z$$

$$\sigma_4 = 1/2s + 3/\sqrt{12}p_z$$

AB$_8$, SQUARE ANTIPRISM, D_{4d}

In this structure the two prisms are staggered by 45° with respect to each other, which results in a coefficient of cos 45 (0.707) on $\phi_5 - \phi_8$, Figure 8, in the SALC's of p_x, p_y, d_{xz}, and d_{yz} symmetries, as shown below. The results agree with those given in the literature.[2]

$$\psi_s = \sqrt{1/8}\left(\sum_i \phi_i\right)$$

$$\psi p_z = \sqrt{1/8}(\phi_1 + \phi_2 + \phi_3 + \phi_4 - \phi_5 - \phi_6 - \phi_7 - \phi_8)$$

$$\psi p_x = \tfrac{1}{2}[\phi_4 + 0.71(\phi_7 + \phi_8) - \phi_2 - 0.71(\phi_5 + \phi_6)]$$

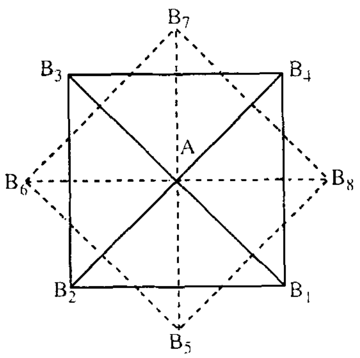

Figure 8.

$$\psi p_y = \tfrac{1}{2}[\phi_1 + 0.71(\phi_5 + \phi_8) - \phi_3 - 0.71(\phi_6 + \phi_7)]$$

$$\psi d_{xz} = \tfrac{1}{2}[\phi_4 + 0.71(\phi_5 + \phi_6) - \phi_2 - 0.71(\phi_7 + \phi_8)]$$

$$\psi d_{yz} = \tfrac{1}{2}[\phi_1 + 0.71(\phi_6 + \phi_7) - \phi_3 - 0.71(\phi_5 + \phi_8)]$$

$$\psi d_{x^2-y^2} = 1/2(\phi_2 + \phi_4 - \phi_1 - \phi_3)$$

$$\psi d_{xy} = 1/2(\phi_5 + \phi_6 - \phi_7 - \phi_8)$$

References

1. F.A. Cotton, *Chemical Applications of Group Theory*, 3rd Ed., (Wiley Interscience, New York, 1990), Chapter 8.
2. S.F. Kettle, *Symmetry and Structure*, (John Wiley and Sons, New York, 1985), Appendix 4.
3. W.E. Hatfield and W.E. Parker, *Symmetry in Chemical Bonding and Structure*, (Charles E. Merrill, New York, 1974).
4. H. Eyring, J. Walter and G.E. Kimball, *Quantum Chemistry*, (John Wiley, New York, 1944).