The Need for Hybrid Orbitals in VB Theory

- Valence Bond (VB) theory constructs trial wave functions as products of the individual atomic orbitals (AOs) on bonding atoms.

$$\Psi_{VB} = \psi_A\psi_B$$

- Standard AOs for isolated atoms (*s*, *p*, *d*, etc.) generally do not have the correct orientations to account for the geometrical aspects of bonding.

- Pauling proposed making new hybrid orbitals from linear combinations of the standard orbitals to better describe bonding.

- Hybrid orbitals are simply alternate solutions to the Schrödinger equation.

☞ Techniques of group theory can be used to identify those AOs that must be combined and how they must be combined to construct a set of hybrid orbitals with the desired geometry to account for known shapes of molecules.

Outline of the Approach for Constructing Hybrids

- A set of vectors radiating from a central atom and having the desired orientation for bonding is taken as the basis for a representation in the point group of the desired hybrid set.

- The vector set is subjected to the operations of the group, and a reducible representation, Γ_{hybrid}, is constructed on the basis of the effects of the operations on the vectors.

- Γ_{hybrid} is reduced into its component irreducible representations.

- The species into which Γ_{hybrid} reduces are matched with the species by which conventional AOs transform in the point group.

- Those AOs that transform by the same species as the components of Γ_{hybrid} have the appropriate symmetry to be used in constructing hybrid orbitals.

- Wave functions are constructed by taking positive and negative combinations of the appropriate AOs,

- All hybrid wave functions are normalized with appropriate factors such that $N^2 \int \Psi\Psi^* d\tau = 1$

- The number of hybrid wave functions is the same as the number of AOs used in their construction.

Transformation Properties of AOs

☞ Transformation properties for the standard AOs in any point group can be deduced from listings of vector transformations in the character table for the group.

s – transforms as the totally symmetric representation in any group

p – transform as x, y, and z, as listed in the second-to-last column of the character table

d – transform as xy, xz, yz, $x^2 - y^2$, and $z^2 \equiv 2z^2 - x^2 - y^2$ (e.g., in T_d and O_h), as listed in the last column of the character table

Example Problem

☞ Which AOs can be combined to form a hybrid set of four orbitals with tetrahedral orientation relative to one another?

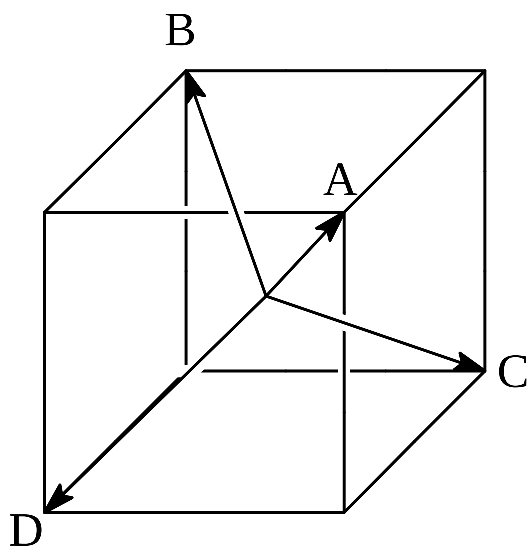
✔ We already know one such set, the four sp^3 hybrids, whose specific functions are

$$\Psi_1 = \tfrac{1}{2}(s + p_x + p_y + p_z)$$
$$\Psi_2 = \tfrac{1}{2}(s + p_x - p_y - p_z)$$
$$\Psi_3 = \tfrac{1}{2}(s - p_x + p_y - p_z)$$
$$\Psi_4 = \tfrac{1}{2}(s - p_x - p_y + p_z)$$

✔ The group theory approach to this problem should identify this set, but it may also identify other possible sets.

✔ The wave functions for any alternative sets will have the same general form as the wave functions for the sp^3 set, including the normalization factor $N = \tfrac{1}{2}$.

Vector Basis for Γ_t in T_d



- ✔ All operations of T_d simply interchange vectors, so we may follow the effects of each operation by noting the transformations of the vector tips, A, B, C, and D.

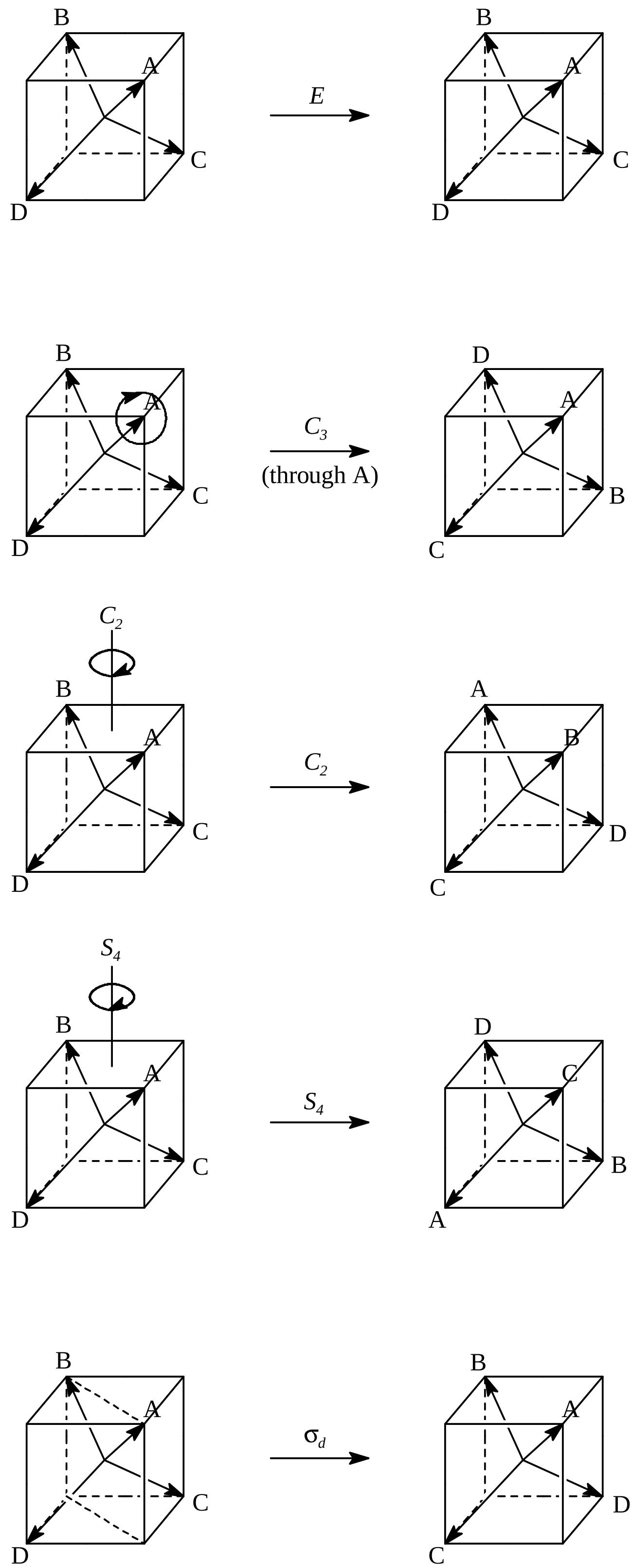
- ✔ The character generated by any operation of a class is the same as all other members of the class.

- ✔ We do not need to subject the set to all h = 24 operations of the group T_d, just one operation from each of the five classes of operations: E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$.

- ✔ We can describe the effect of each representative operation by a 4x4 transformation matrix that shows how A, B, C, and D are interchanged.

- ✔ The traces of the matrices will give us the characters of Γ_t.

Effects of Representative Operations of T_d



Generating the Reducible Representation

$$E: \quad \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix}$$

$$C_3: \quad \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} A \\ D \\ B \\ C \end{bmatrix}$$

$$C_2: \quad \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} B \\ A \\ D \\ C \end{bmatrix}$$

Generating the Reducible Representation - Cont.

$$S_4: \quad \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} C \\ D \\ B \\ A \end{bmatrix}$$

$$\sigma_d: \quad \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} A \\ B \\ D \\ C \end{bmatrix}$$

Gathering all characters:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_t	4	1	0	0	2

☞ The character for each class of operations is the number of nonshifted vectors in each case.

☺ **We really don't have to construct matrices; just count nonshifted vectors!**

Reduction of Γ_t

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
Γ_t	4	1	0	0	2	Σ	$\Sigma/24$
A_1	4	8	0	0	12	24	1
A_2	4	8	0	0	-12	0	0
E	8	-8	0	0	0	0	0
T_1	12	0	0	0	-12	0	0
T_2	12	0	0	0	12	24	1

$$\Rightarrow \Gamma = A_1 + T_2$$

AOs with the correct symmetry:

$A_1 = s$

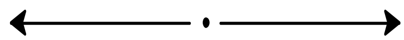
$T_2 = (p_x, p_y, p_z)$ & (d_{xy}, d_{xz}, d_{yz})

$\Rightarrow$ Possible hybrids: sp^3 & sd^3

General Method for Identifying AO Combinations for Hybrid Orbitals

1. Use a vector model of the desired hybrid set as a basis for a representation in the appropriate point group.
2. Consider the effect of one operation in each class on the vector set.
3. Count the number of vectors not shifted by the representative operations in all classes. A nonshifted vector contributes +1 to the character of the reducible representation. Shifted vectors contribute 0.
4. Reduce the representation into its component species.
5. Identify appropriate AOs with the same symmetries as the species in the reducible representation.
6. Make hybrids by combining the indicated number of AOs of each species.
    a. The total number of AOs used matches the number of hybrids formed.
    b. More than one set may be possible.

Linear Hybrids



$D_{\infty h}$	E	$2C_\infty^{\phi}$	…	$\infty\sigma_v$	i	$2S_\infty^{\phi}$	…	∞C_2
Γ_l	2	2	…	2	0	0	…	0

$D_{\infty h}$	E	$2C_\infty^{\phi}$	…	$\infty\sigma_v$	i	$2S_\infty^{\phi}$	…	∞C_2
Σ_g^+	1	1	…	1	1	1	…	1
Σ_u^+	1	1	…	1	-1	-1	…	-1
Γ_l	2	2	…	2	0	0	…	0

$$\Rightarrow \Gamma_l = \Sigma_g^+ + \Sigma_u^+$$

AOs with the correct symmetry:

$$\Sigma_g^+ = s \ \& \ d_{z^2} \qquad \Sigma_u^+ = p_z$$

Possible hybrid sets: sp_z & $d_{z^2}p_z$