Constructing Hybrid Orbitals Using Group Theory

- 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.

- 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 / $2z^2$-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.
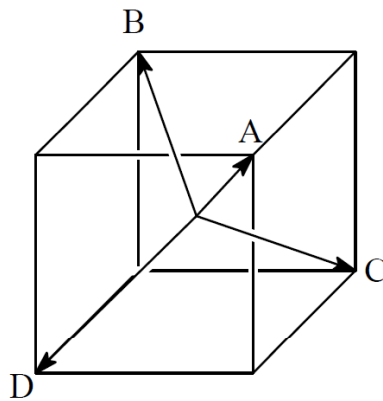
Effects of Representative Operations of T_d
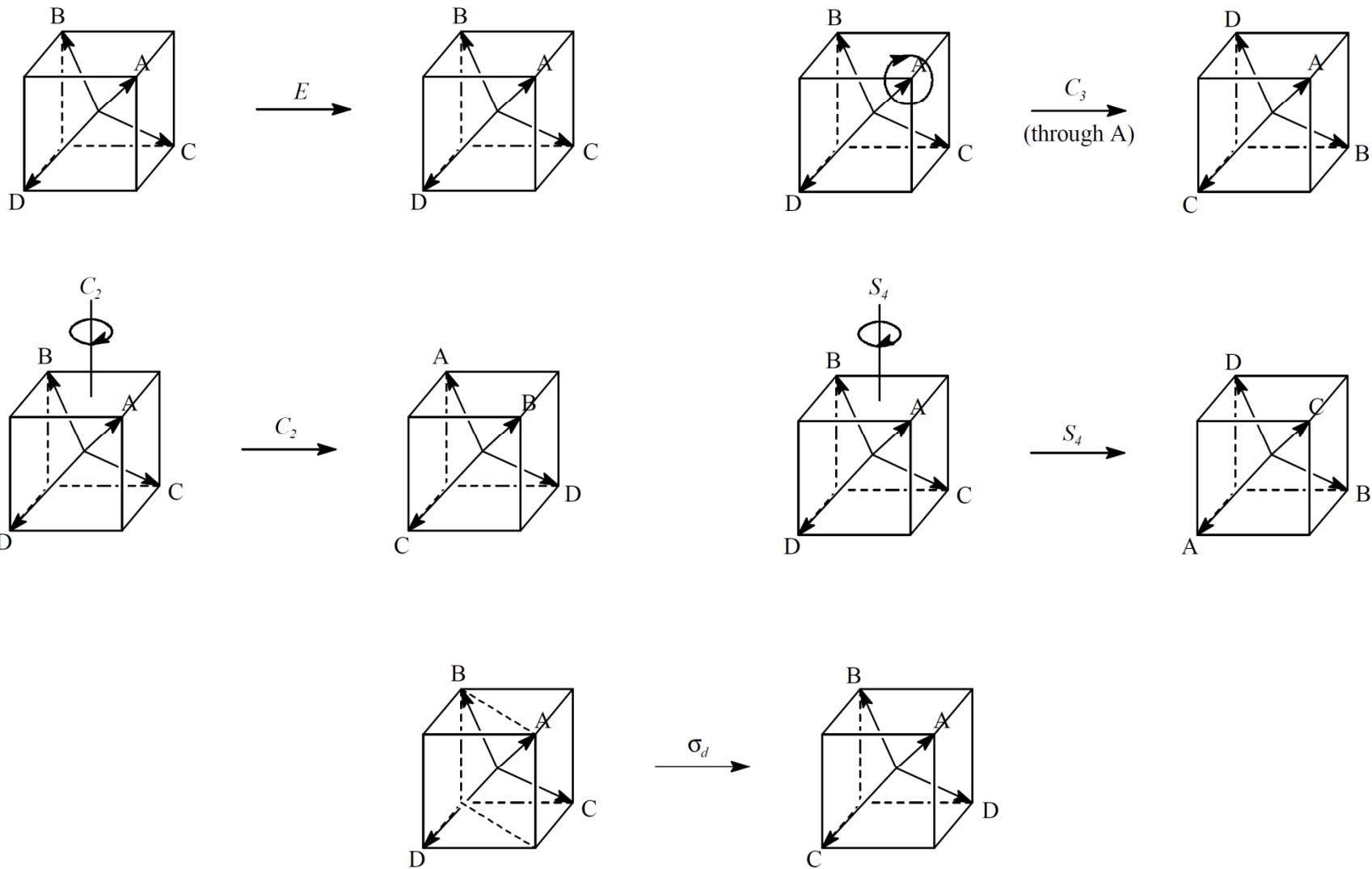
Generating the Reducible Representation Γ_t in T_d

E:

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

C_3:

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

C_2:

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

S_4:

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

σ_d:

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

- Gathering all reducible characters from the trace of each matrix we find the following:

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 non-shifted vectors in each case.

- Thus, we really don't have to construct matrices; just count non-shifted vectors!

- Systematic reduction of Γ_t will then give the component irreducible representations from which we can identify the contributing atomic orbitals.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Σ	$\Sigma/24$
Γ_t	4	1	0	0	2		
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

$\Gamma_t = A_1 + T_2$
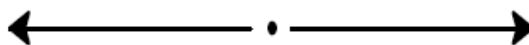
AOs with the correct symmetry:

$A_1 = s$

$T_2 = (p_x, p_y, p_z)$ & (dxy, dxz, dyz)

Γ_t possible hybrids: sp^3 & sd^3

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:

$\Sigma_g^+ = s$ & dz^2 $\qquad\qquad$ $\Sigma_u^+ = p_z$

Possible hybrid sets: sp_z & dz^2p_z

Molecular Orbitals

- The molecular orbital (MO) approach seeks to construct orbitals for the bonded system.

- Approximate wave function solutions are constructed as a Linear Combination of Atomic Orbitals (LCAO).

- For diatomic molecules, AB, these LCAO MOs have the general form

$$\Psi_1 = a\ \Psi_A + b\ \Psi_B$$

$$\Psi_2 = a\ \Psi_A - b\ \Psi_B$$

- If S > 0, a bonding MO results; if S < 0, an antibonding MO results *(Slater overlap integrals)*.

Localized MOs for BeH$_2$

- A localized MO approach takes pairs of adjacent atoms and uses matching AOs to form bonding and antibonding MOs.

- A localized MO approach is an extension of the VB model.

- Both approaches seek to partition the overall electron density into separate orbital-based regions.

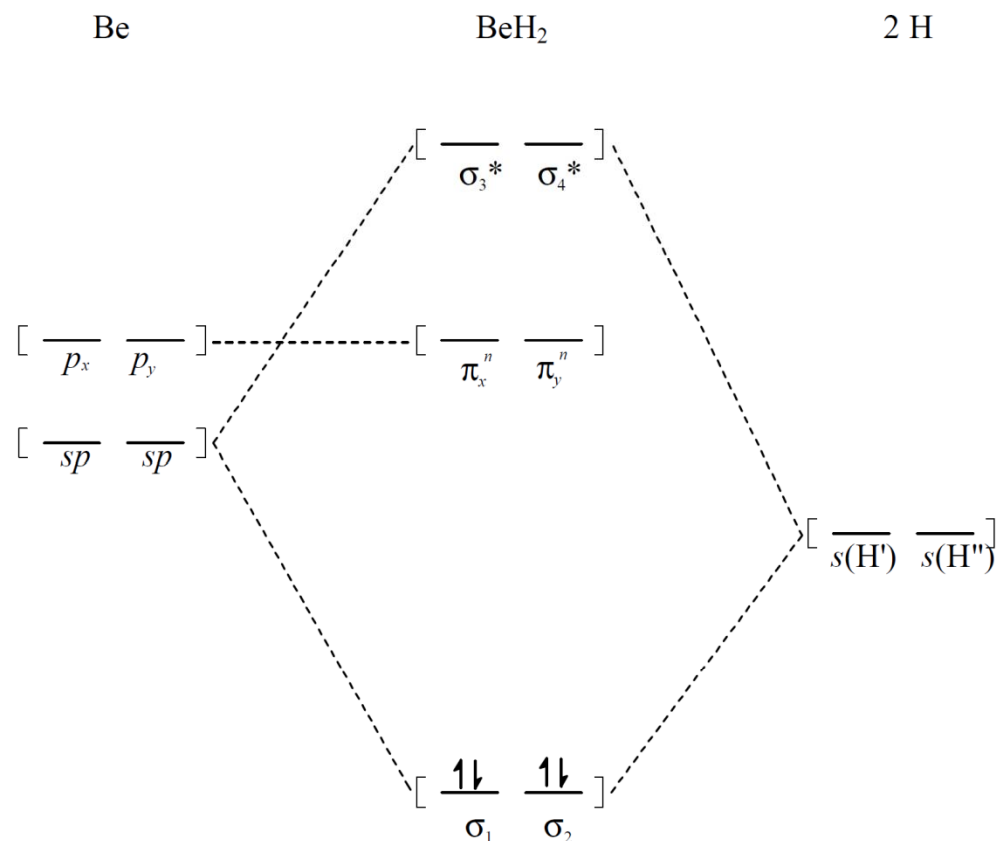- Using sp hybrids on Be and $1s$ orbitals on the two H atoms we form the following localized MOs:

$$\sigma_1 = a[sp(1)_{Be}] + b[s_{H'}]$$

$$\sigma_1^* = a[sp(1)_{Be}] - b[s_{H'}]$$

$$\sigma_2 = a[sp(2)_{Be}] + b[s_{H''}]$$

$$\sigma_2^* = a[sp(2)_{Be}] - b[s_{H''}]$$

Qualitative <u>Localized</u> MO Scheme for BeH_2

Be BeH_2 2 H

σ_3^* σ_4^*

$[\ \overline{p_x}\ \ \overline{p_y}\ ]$ - - - - - - - - - - - $[\ \overline{\pi_x^n}\ \ \overline{\pi_y^n}\ ]$

$[\ \overline{sp}\ \ \overline{sp}\ ]$

$[\ \overline{s(H')}\ \ \overline{s(H'')}\ ]$

$[\ \underline{\uparrow\downarrow}\ \ \underline{\uparrow\downarrow}\ ]$
σ_1 σ_2

- The two π^n MOs are just the unused $2p$ orbitals on Be, perturbed by the presence of the two H nuclei.

- The degenerate σ MOs in this scheme are an artifact of the way in which the problem was set up, rather than an experimentally verifiable result.

- A more realistic representation of the electron energies is obtained by taking a delocalized MO approach, in which electrons are not constrained to atom-pair bonds a priori.

General MO Approach for MX$_n$ Molecules

- To construct delocalized MOs we define a *linear combination of atomic orbitals (LCAOs)* that combine central-atom AOs with combinations of pendant-atom AOs, called SALCs:

$$\Psi_{MO} = a\,\Psi\,(\text{Metal AO}) \pm b\,\Psi\,(\text{SALC } nX)$$

(SALC = Symmetry Adapted Linear Combination)

- SALCs are constructed with the aid of group theory, and those SALCs that belong to a particular species of the group are matched with central-atom AOs with the same symmetry to make bonding and antibonding MOs.

$$\Psi_{SALC} = c_1\,\Psi_1 \pm c_2\,\Psi_2 \pm c_3\,\Psi_3 \dots \pm c_n\,\Psi_n$$

General MO Approach for MX$_n$ Molecules

1. Use the directional properties of potentially bonding orbitals on the outer atoms (shown as vectors on a model) as a basis for a representation of the SALCs in the point group of the molecule.

2. Generate a reducible representation for all possible SALCs by noting whether vectors are shifted or non-shifted by each class of operations of the group.

   ➢ Each vector shifted through space contributes 0 to the character for the class. Each non-shifted vector contributes 1 to the character for the class.

   ➢ A vector shifted into the negative of itself (base non-shifted but tip pointing in the opposite direction) contributes -1 to the character for the class.

3. Decompose the representation into its component irreducible representations to determine the symmetry species of the SALCs.

4. The number of SALCs, including members of degenerate sets, must equal the number of AOs taken as the basis for the representation.

5. Determine the symmetries of potentially bonding central-atom AOs by inspecting unit vector and direct product transformations listed in the character table of the group.

   ➢ Remember that an *s* orbital on a central atom always transforms as the totally symmetric representation of the group.

6. Central-atom AOs and pendant-atom SALCs with the same symmetry species will form both bonding and antibonding LCAO-MOs.

7. Central-atom AOs or pendant-atom SALCs with unique symmetry (no species match between AOs and SALCs) form nonbonding MOs.
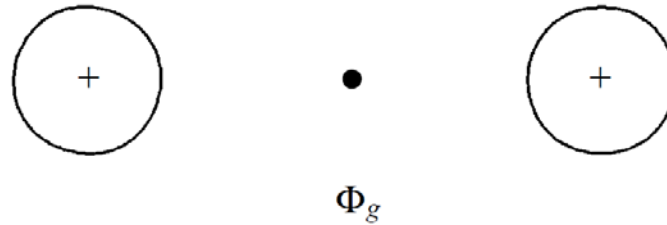
General MOs for BeH$_2$ *(delocalized)*

- Forming the Hydrogen SALCs

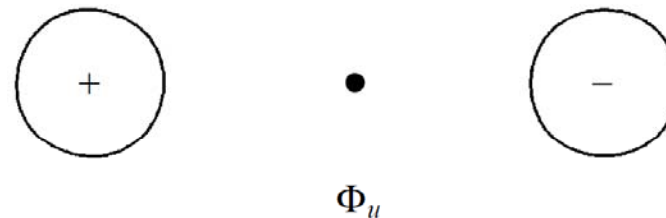| $D_{\infty h}$	E	$2C_\infty^\varphi$	...	$\infty\sigma_v$	i	$2S_\infty^\varphi$	...	∞C_2
Γ_{SALC}	2	2	...	2	0	0	...	0

$$\Rightarrow \Gamma_{SALC} = \Sigma_g^+ + \Sigma_u^+$$

- SALC equations:

$\Sigma_g^+:\quad \Phi_g = (1/\sqrt{2})\,(1s_{H'} + 1s_{H''})$

Φ_g

$\Sigma_u^+:\quad \Phi_g = (1/\sqrt{2})\,(1s_{H'} - 1s_{H''})$
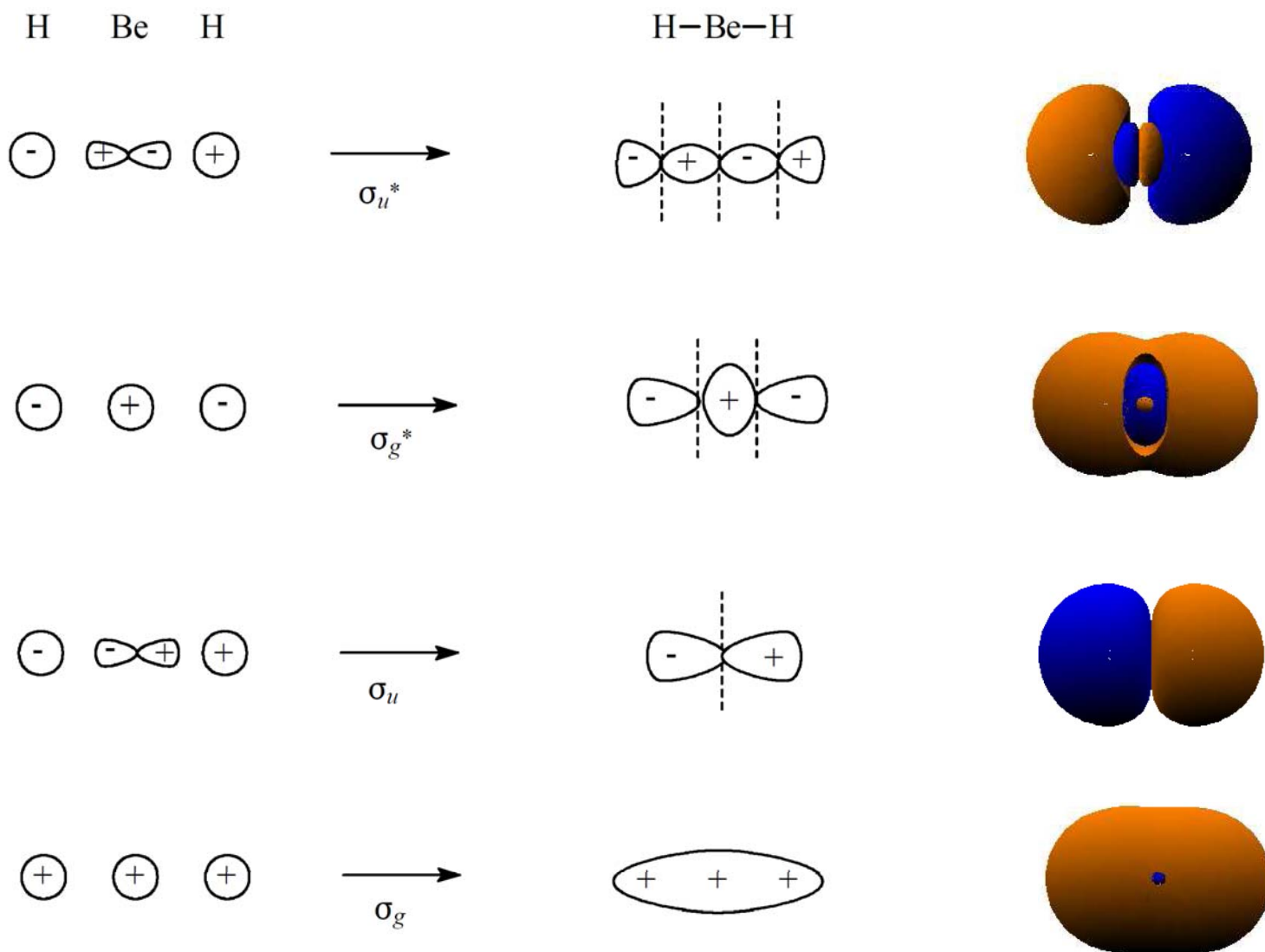
Φ_u

Identifying the Central Atom (Be) AO Symmetries

- From the listed unit vector transformations in the D_{4h} character table

$$s = \Sigma_g^+ \qquad p_z = \Sigma_u^+ \qquad p_{x,y} = \Pi_u$$

➤ $s = \Sigma_g^+$ Be 2s forms σ and σ* combinations with Φ_g SALC.

➤ $p_z = \Sigma_u^+$ Be 2p_z forms σ and σ* combinations with Φ_u SALC.

➤ $p_{x,y} = \Pi_u$ Be 2p_x and 2p_y (Π_u) are a degenerate pair of nonbonding π^n MOs.

Delocalized LCAO MOs for BeH$_2$

Qualitative <u>Delocalized</u> MO Scheme for BeH_2

Be BeH$_2$ 2 H (SALCs)
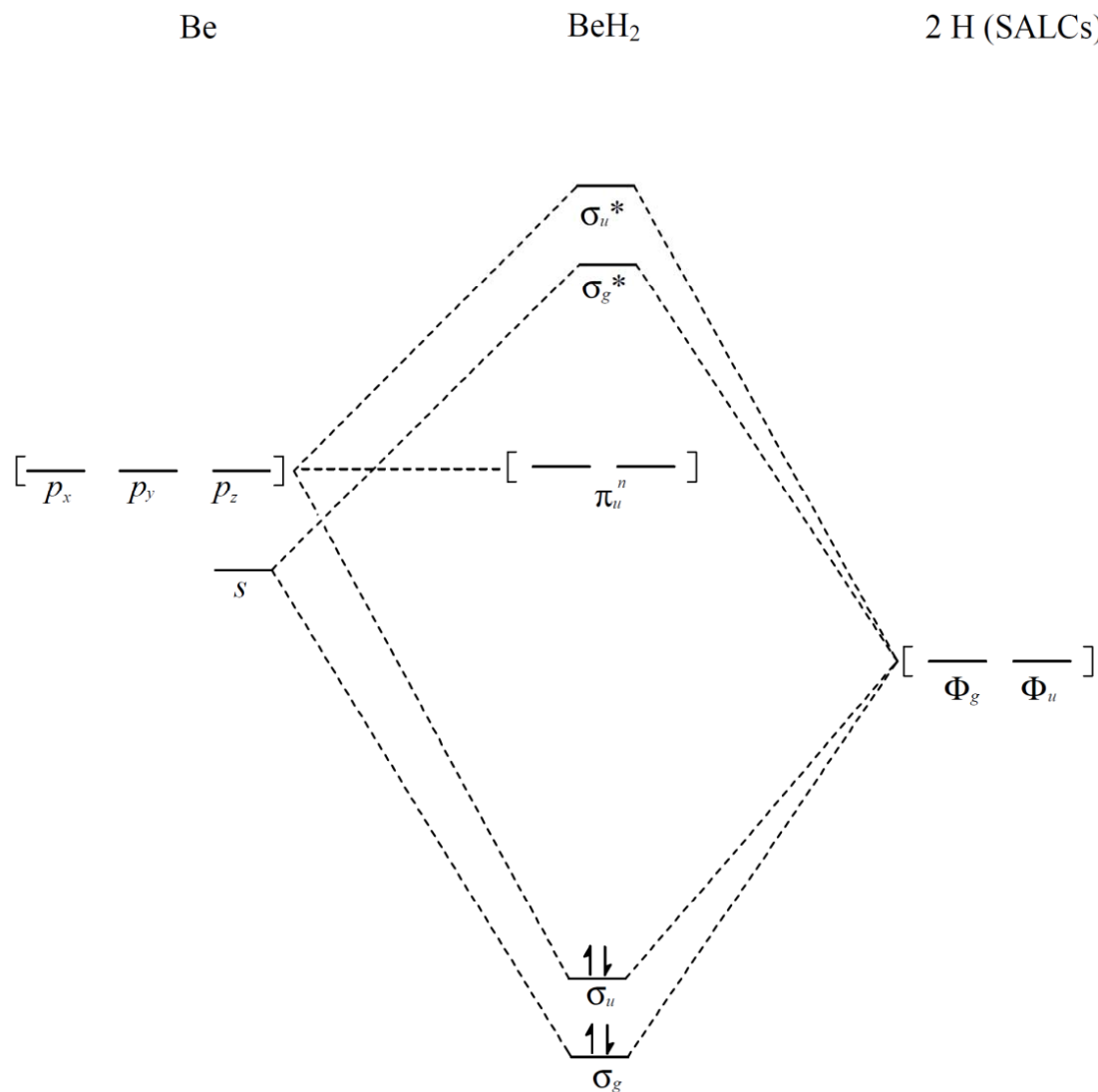
- Separate energy levels for the two bonding electron pairs is a more realistic representation, consistent with observations in many other MX$_n$ *cases.*

Guidelines for Constructing MO Schemes

1. Bonding MOs always lie lower in energy than the antibonding MOs formed from the same AOs.

2. Nonbonding MOs tend to have energies between those of bonding and antibonding MOs formed from similar AOs.

3. $\pi-$interactions tend to have less effective overlap than sigma interactions. Therefore, π-bonding MOs tend to have higher energies than σ-bonding MOs formed from similar AOs.

4. Likewise, π^* MOs tend to be less antibonding and have lower energies than σ^* MOs formed from similar AOs.

5. MO energies tend to rise as the number of nodes increases.

6. Therefore, MOs with no nodes tend to lie lowest, and those with the greatest number of nodes tend to lie highest in energy.

7. Among σ-bonding MOs, those belonging to the totally symmetric representation tend to lie lowest.

Problem

Determine the sets of specific atomic orbitals that can be combined to form hybrid orbitals with the following geometries:

(a) Trigonal planar

(b) Square planar

(c) Trigonal bipyrimidal

(d) Octahedral

Problem

Determine the sets of specific atomic orbitals that can be combined to form hybrid orbitals with the

following geometries:

(a) Trigonal planar

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ	3	0	1	3	0	1

$$\Gamma = A_1' + E'$$

$$A_1': s, d_{z^2} \qquad E': (p_x, p_y), (d_{xy}, d_{x^2-y^2})$$

A_1'	E'	Notation
s	(p_x, p_y)	sp^2
s	$(d_{xy}, d_{x^2-y^2})$	sd^2
d_{z^2}	(p_x, p_y)	$p^2d \equiv dp^2$
d_{z^2}	$(d_{xy}, d_{x^2-y^2})$	d^3

Problem

Determine the sets of specific atomic orbitals that can be combined to form hybrid orbitals with the
following geometries:

(b) Square planar

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	4	0	0	2	0	0	0	4	2	0

$$\Gamma = A_{1g} + B_{1g} + E_u$$

A_{1g}: s, d_{z^2} B_{1g}: $d_{x^2-y^2}$ E_u: (p_x, p_y)

A_{1g}	B_{1g}	E_u	Notation
s	$d_{x^2-y^2}$	(p_x, p_y)	dsp^2
d_{z^2}	$d_{x^2-y^2}$	(p_x, p_y)	d^2p^2

Problem

Determine the sets of specific atomic orbitals that can be combined to form hybrid orbitals with the following geometries:

(c) Trigonal bipyrimidal

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ	5	2	1	3	0	3

$$\Gamma = 2A_1' + A_2'' + E'$$

A_1': s, d_{z^2} A_2'': p_z E': $(p_x, p_y), (d_{xy}, d_{x^2-y^2})$

$2A_1'$	A_2''	E'	Notation
s, d_{z^2}	p_z	$(p_x, p_y),$	dsp^3
s, d_{z^2}	p_z	$(d_{xy}, d_{x^2-y^2})$	d^3sp

Problem

Determine the sets of specific atomic orbitals that can be combined to form hybrid orbitals with the following geometries:

(d) Octahedral

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ	6	0	0	2	2	0	0	0	4	2

$$\Gamma = A_{1g} + E_g + T_{1u}$$

$$A_{1g}: s \quad E_g: (d_{z^2}, d_{x^2-y^2}) \quad T_{1u}: (p_x, p_y, p_z)$$

Only possibility is d^2sp^3.