Wave Equations of Polyatomic Molecules

- Approximate wave functions are sought by combining atomic wave functions for the bonded atoms.

- Several different approaches have been taken to constructing trial wave functions.

- Valence Bond (VB) - Heitler & London (1927)
$$\Psi_{bond} = \psi_a \psi_b$$

  - Hybrid orbitals - Pauling (1920s)

- Molecular Orbital (MO) - Hund, Mulliken (1920s)
$$\Psi_{MO} = a\psi_A \pm b\psi_B$$

  - LCAOs - Lennard-Jones (1929)

Slater Overlap Criterion

- When two orbitals on different atoms A and B overlap, the nature and effectiveness of their interaction is given by the *Slater overlap integral*

$$S = \int \Psi_A \Psi_B d\tau$$

 which can be evaluated precisely only for H_2.

☞ For our purposes we only need to recognize when certain interactions of orbitals have $S > 0$, $S = 0$, or $S < 0$
  - $S > 0$ – bonding interaction
  - $S = 0$ – nonbonding interaction
  - $S < 0$ – antibonding interaction
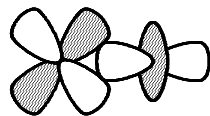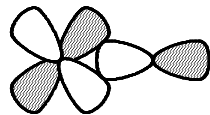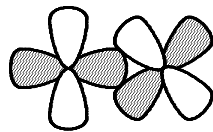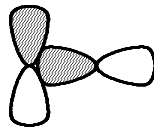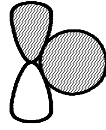
- The sense of S is evident from simple pictures of interacting orbitals.
  - $S > 0$ – reenforcing overlap between nuclei
  - $S = 0$ – equally reenforcing and cancelling overlaps
  - $S < 0$ – cancelling overlap between nuclei

Examples of $S > 0$, $S = 0$, and $S < 0$
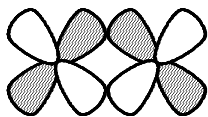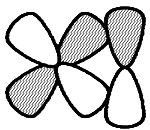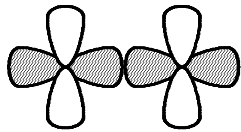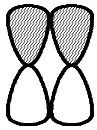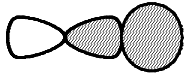
| $S > 0$ | $S = 0$ | $S < 0$ |
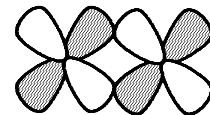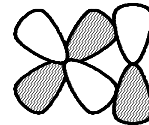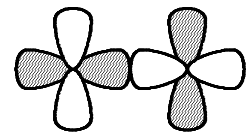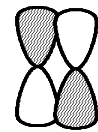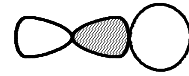
AO Shape and Symmetry

- All AOs with the same value of l have the same symmetry, regardless of n.

- As isolated orbitals, each type can be identified with a particular point group.
    $$s = R_3$$
    $$p = C_{\infty v}$$
    $$d = D_{2h} \text{ ("cloverleaf") or } D_{\infty h} \ (d_{z^2})$$

- Orbitals that have bonding combinations usually have the same kind of symmetry with respect to the internuclear axis.

- If a bonding combination can be identified for any pair of orbitals, there must also be an antibonding combination.

- Nonbonding orbitals are oriented relative to each other such that they do not have the same kind of symmetry relative to the internuclear axis.

Symmetry Definition of Sigma, Pi, and Delta Interactions

- Sigma interactions are symmetrical relative to a C_2 axis collinear with the internuclear axis.
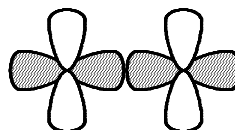
- Pi interactions are antisymmetric (Ψ changes sign) with respect to C_2 collinear with the internuclear axis and with respect to σ_v coplanar with the shared nodal plane.
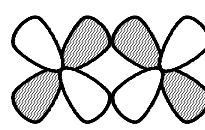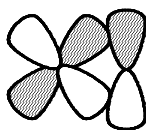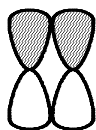
- Delta interactions are symmetric to C_2 and antisymmetric to C_4.
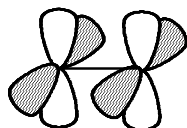
- Bonding and antibonding interactions of the same type have the same symmetry with respect to the internuclear axis.
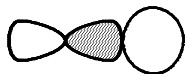
σ bonding σ^* antibonding π bonding π^* antibonding

Molecular Orbitals for Polyatomic Molecules

- 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) with the general form

$$\Psi_i = N_i\{\psi_a \pm \psi_b \pm ... \psi_n\}$$

- If $S > 0$, a bonding MO results; if $S < 0$, an antibonding MO results; if $S = 0$, a nonbonding MO results.

Normalization Requirement

- From the Copenhagen interpretation we associate the probability of finding the electron in a vanishingly small volume element ("a point") as
$$P \propto \Psi\Psi^*$$

- The electron has unit probability over all space:
$$\int \Psi\Psi^* d\tau = 1$$

- To ensure that any trial wave function, ψ, meets this criterion we generally must multiply by a *normalization constant*, N, such that

$$\int (N\psi)(N\psi^*)d\tau = N^2 \int \psi\psi^* d\tau = 1$$

- If ψ is a solution to the Schrödinger equation, then so too is $N\psi$, and E in $\mathcal{H}\psi = E\psi$ is unaffected.

Localized MOs for BeH₂

- 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.
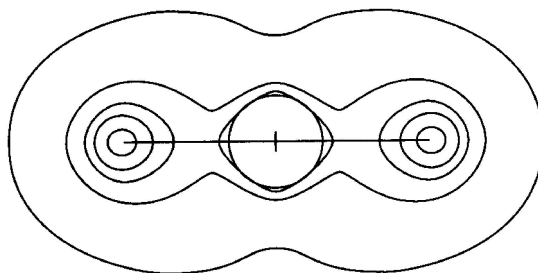
Contours at 0.01, 0.07, 0.13, 0.19, and 0.25

$$\text{H''——Be——H'}$$

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

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

$$\sigma_2 = a[sp(2)_{\text{Be}}] + b[1s_{\text{H''}}]$$

$$\sigma_3^* = a[sp(1)_{\text{Be}}] - b[1s_{\text{H'}}]$$

$$\sigma_4^* = a[sp(2)_{\text{Be}}] - b[1s_{\text{H''}}]$$

Qualitative Localized MO Scheme for BeH$_2$

Be   BeH$_2$ 2 H
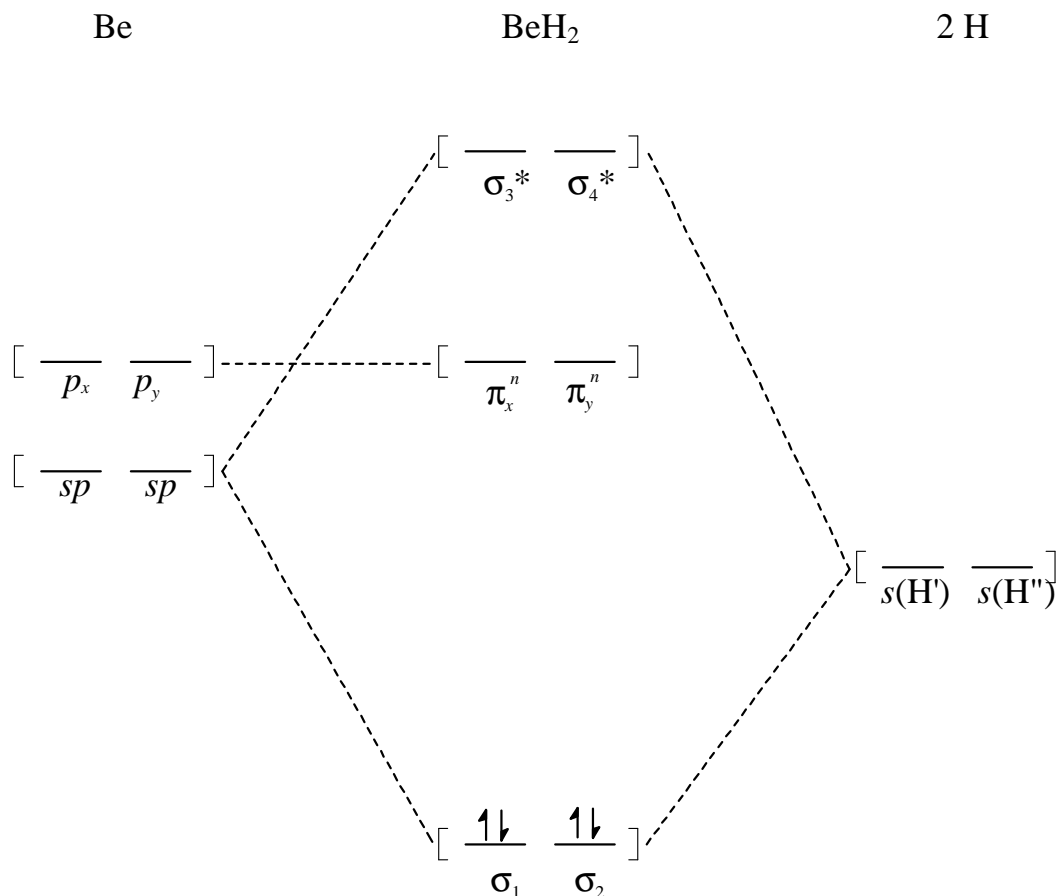
✔ The two π^n MO are just the unused $2p$ orbitals on Be, perturbed by the presence of the two H nuclei.

☞ The equal-energy 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 AX$_n$ Molecules

- To construct delocalized MOs we write LCAOs that combine central-atom AOs with combinations of pendant-atom AOs, called SALCs:

$$\Psi_{MO} = a\psi_{AO}(A) \pm b\psi_{SALC}(nX)$$

☞ SALC = Symmetry Adapted Linear Combination
$$\psi_{SALC} = c_1\psi_1 \pm c_2\psi_2 \pm c_3\psi_3 \pm \ldots \pm c_n\psi_n$$

- 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.

General Method Using Group Theory
Setting Up the Problem and Forming SALCs

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 nonshifted by each class of operations of the group. Each vector shifted through space contributes 0 to the character for the class. Each nonshifted vector contributes 1 to the character for the class. A vector shifted into the negative of itself (base nonshifted 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. The number of SALCs, including members of degenerate sets, must equal the number of AOs taken as the basis for the representation.

4. 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.

General Method Using Group Theory
Forming LCAO MOs

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

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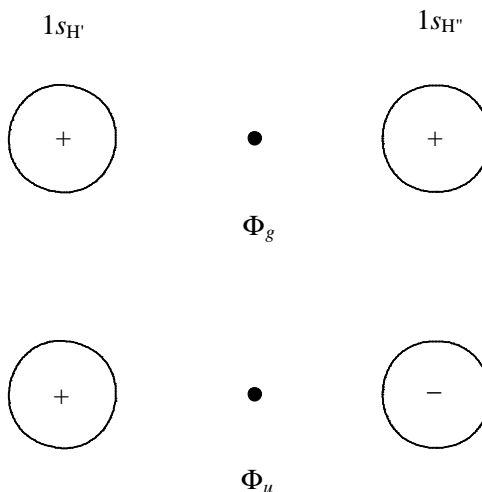
General MOs for BeH$_2$

Forming the Hydrogen SALCs

$\longrightarrow$ $\longleftarrow$

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

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

SALC Equations:

Σ_g^+: $\qquad\qquad \Phi_g = \dfrac{1}{\sqrt{2}}(1s_{H'} + 1s_{H''})$

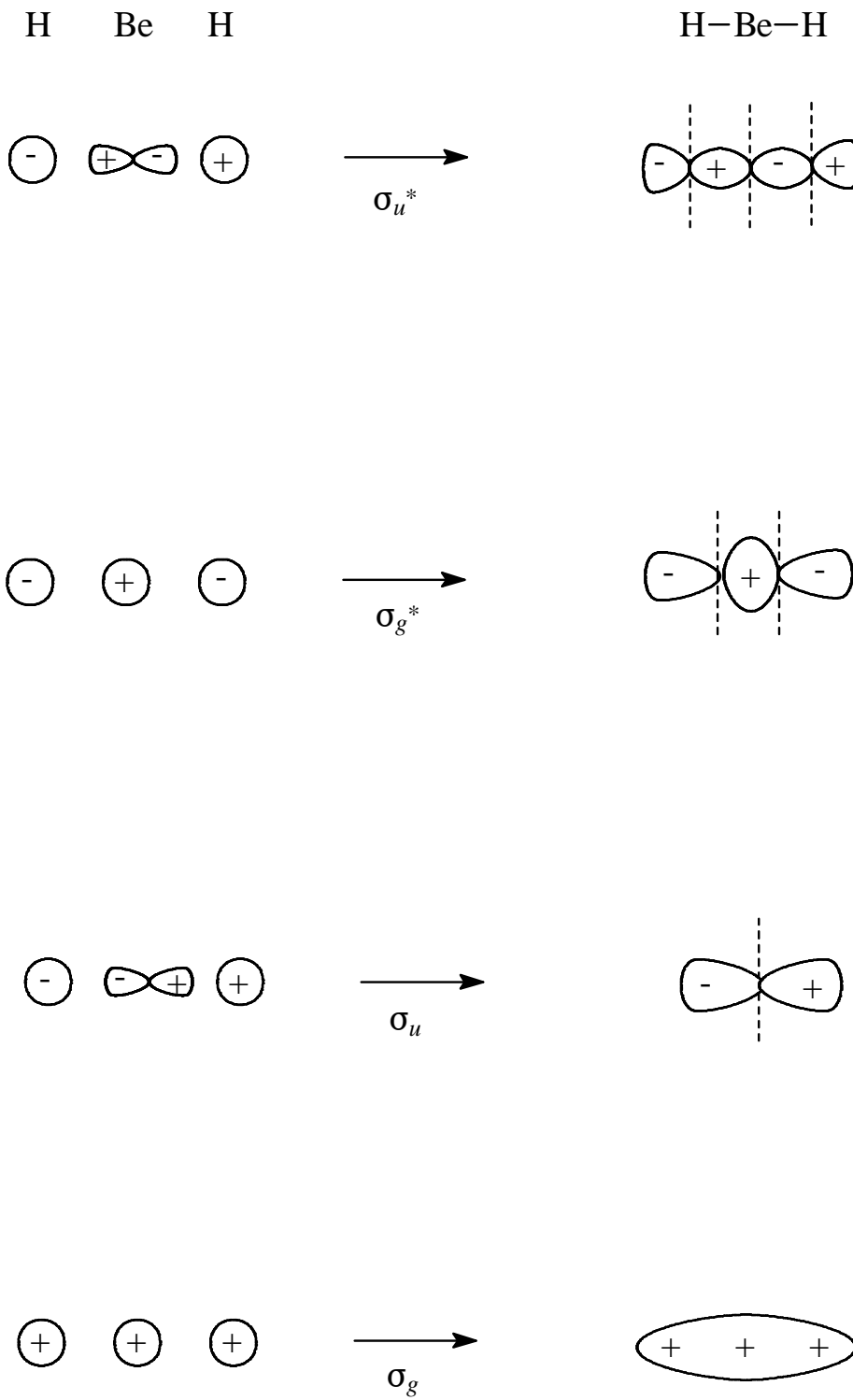Σ_u^+: $\qquad\qquad \Phi_u = \dfrac{1}{\sqrt{2}}(1s_{H'} - 1s_{H''})$

Identifying the Central Atom (Be) AO Symmetries

✔ From the listed unit vector transformations in the $D_{\infty h}$ character table

$$s = \Sigma_g^+ \qquad p_z = \Sigma_u^+ \qquad (p_x, p_y) = \Pi_u$$
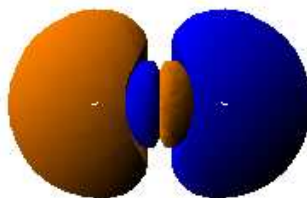
☞ Σ_g^+: Be $2s$ forms σ and σ^* combinations with Φ_g SALC.

☞ Σ_u^+: Be $2p_z$ forms σ and σ^* combinations with Φ_u SALC.

☞ Π_u: Be $2p_x$ and $2p_y$ (Π_u) are a degenerate pair of nonbonding π^n MOs.

Delocalized LCAO MOs for BeH$_2$

H   Be   H

H$-$Be$-$H

$\sigma_u{}^*$

$\sigma_g{}^*$

σ_u

σ_g

Cut-Away Models of BeH$_2$ Bonding and Antibonding MOs

σ_u^*

σ_g^*

σ_u
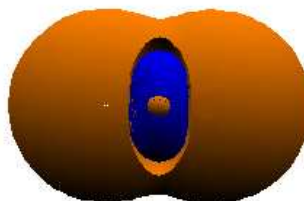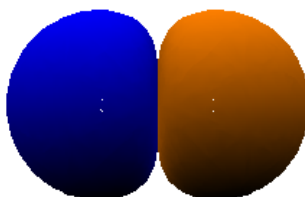
σ_g
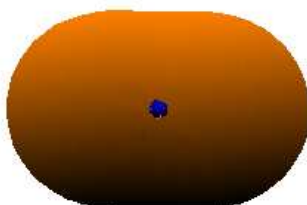
Qualitative Delocalized MO Scheme for BeH$_2$

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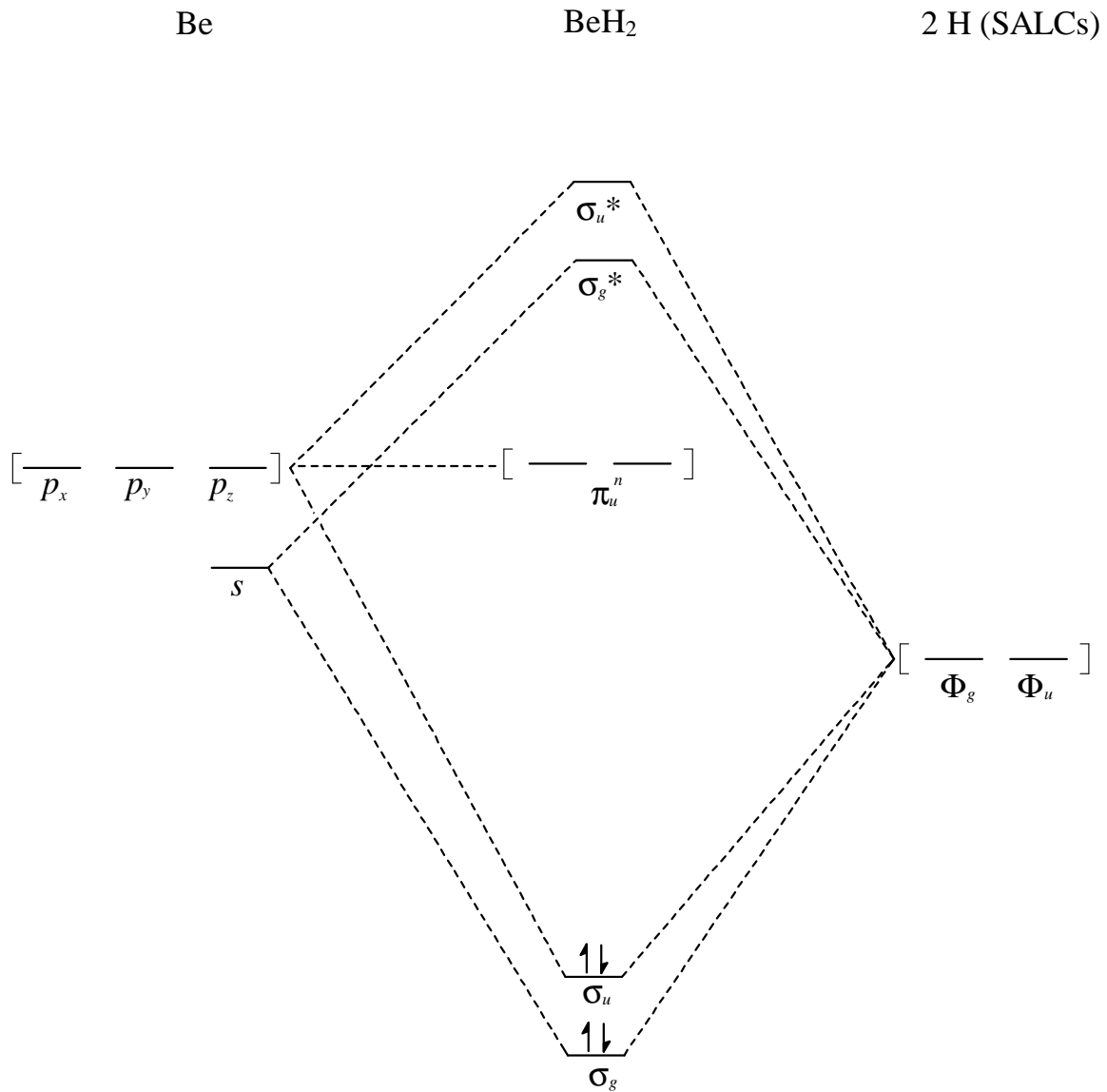
☞ Separate energy levels for the two bonding electron pairs is a more realistic representation, consistent with observations in many other MX$_n$ cases.

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

4. MO energies tend to rise as the number of nodes increases. Therefore, MOs with no nodes tend to lie lowest, and those with the greatest number of nodes tend to lie highest in energy.

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