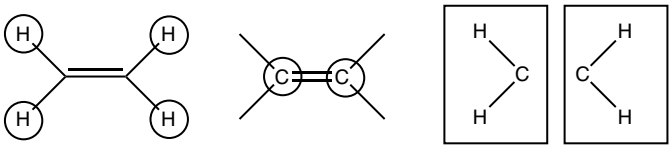
In-Class Problems / Self-study Problems / Test Preparation: Lecture 6

- **In-Class P1 (a)** determine the symmetry fragments for C_2H_4. **(b)** determine the molecular fragments for C_2H_4 and **(c)** which is the better one to use and why?



(a) Symmetry fragments (b) Molecular fragments

Figure 1 possible fragments for C_2H_4

  - the fragment pattern chosen to form the MO diagram could be either, but estimating the relative energy of the H_4 and C_2 fragment orbitals will be difficult. It is much easier to predict the orbital interactions when they are **degenerate** because the fragments are identical.

- **In-Class P2** draw and annotate an MO diagram of the diborane MO given, identify the bonding / antibonding interactions

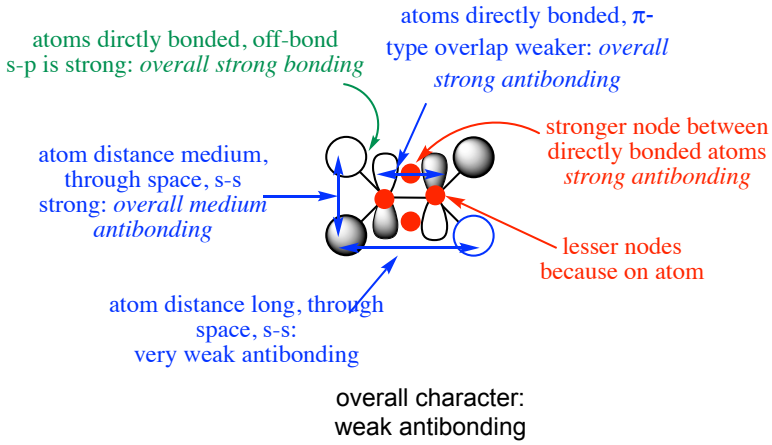


Figure 2 Assessing MO character

- **In-Class P3** draw the LCAO for MO24 and MO25

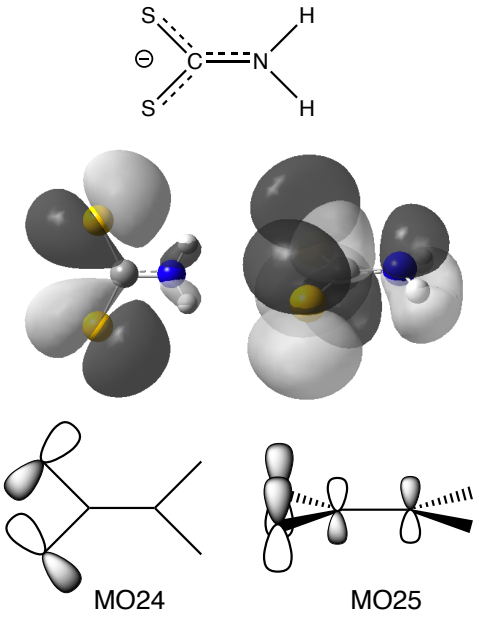


Figure 3 LCAOs

- **In-Class P4** draw the draw LCAOs for the computed MOs of BrF_3 below, on your diagram annotate features important for evaluating the MO bonding character

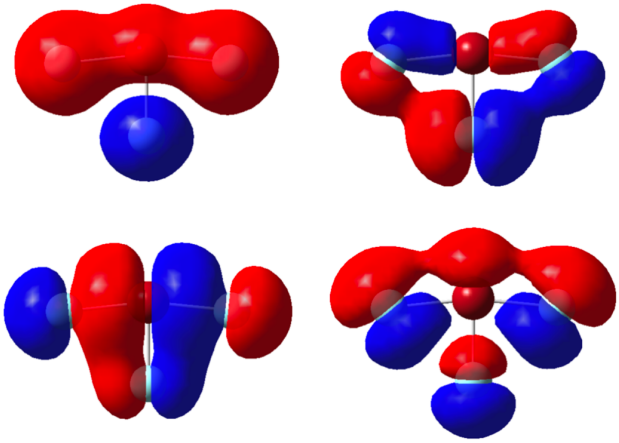
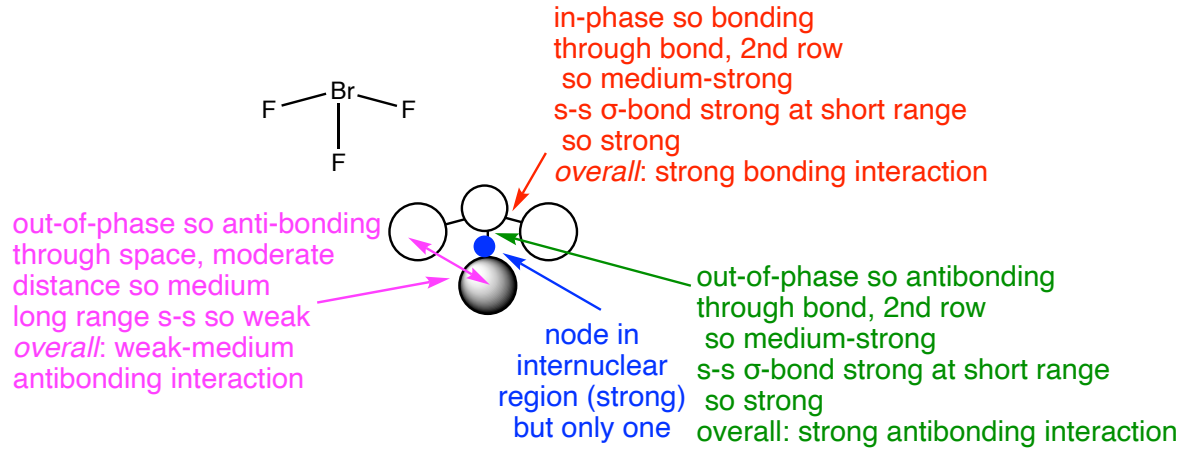
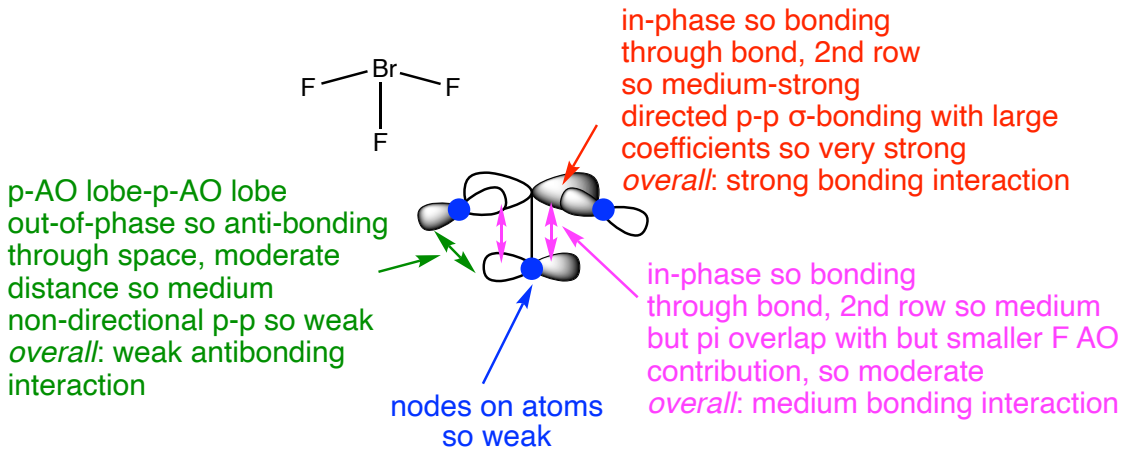


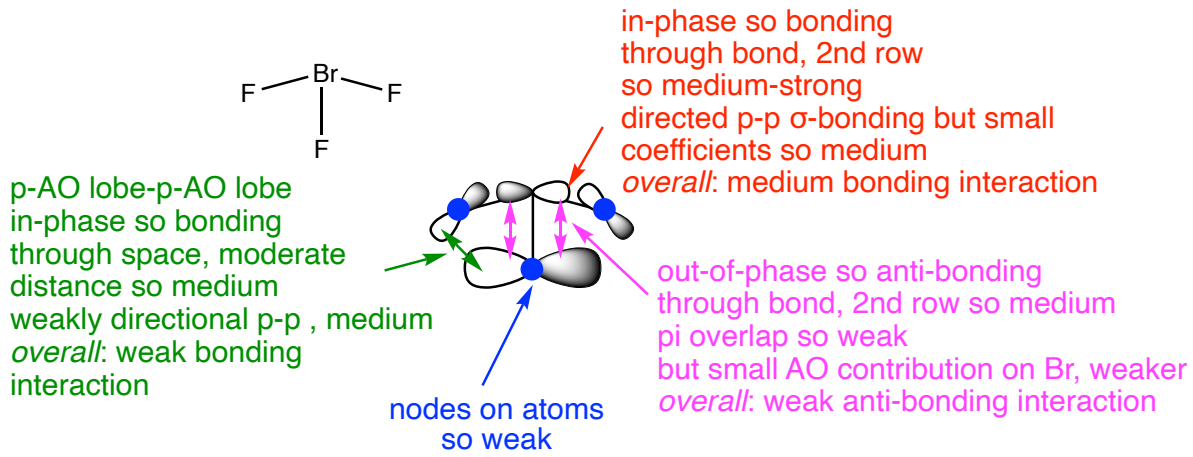
Figure 4 Selected computed MOs of BrF_3



- overall: 2 strong bonding interactions, 1 strong anti-bonding and 1 moderate antibonding, but sAOs, so moderate bonding



- overall: 2 strong σ- & 1 medium π- bonding interactions, 2 weak antibonding, so strongly bonding



- overall: 1 weak through-space and 2 moderate σ- bonding interactions, 1 weak π-antibonding, so weakly bonding

- **Q1** QM related questions
  - assuming $\varepsilon_a \neq \varepsilon_b$ and $S_{ab}=0$, what happens to the MO energy levels as $\Delta\varepsilon$ gets larger?

$$E_+ = \varepsilon_a - \frac{H_{ab}^2}{\Delta\varepsilon} \quad E_- = \varepsilon_b + \frac{H_{ab}^2}{\Delta\varepsilon}$$

  - the splitting energy is proportional to H_{ab} squared divided by $\Delta\varepsilon$ the energy difference between the two AOs, as $\Delta\varepsilon$ increases the stabilisation and destabilisation energy decrease until it is essentially zero (ionic bonding situation). As this occurs the FO contributions will start out essentially even and then become increasingly localised on one fragment until the energy gap is very large, at which point electron transfer occurs from one FO to the other

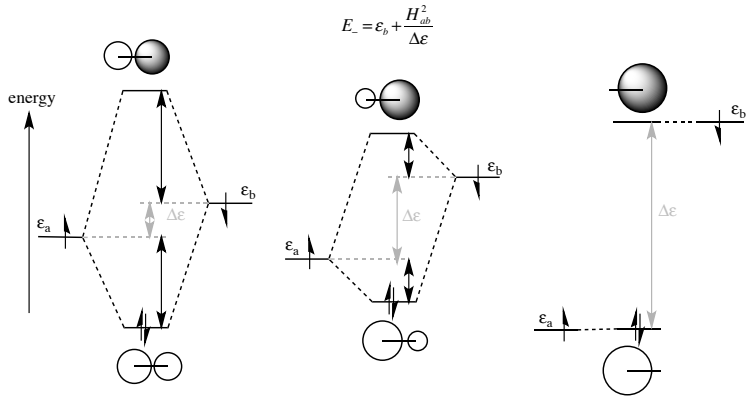


Figure 5 effect of increasing Δε

  - when is S_{ab} likely to be small?
  - S_{ab} is the orbital overlap it is highly distance dependents and will be zero if the orbitals ψ_a and ψ_b are "far apart" in reality this means, for first row atoms, if the atoms are more than one bond length apart. However, if the orbitals are diffuse they extend into space further and there can be through space overlap.
  - S_{ab} will also be zero if the orbitals are orthogonal
  - show that $c=1/\sqrt{2}$ when $S_{ab}=0$

$$c = \frac{1}{\sqrt{2(1 \pm S_{ab})}}$$

$$if \quad S_{ab} = 0$$

$$c = \frac{1}{\sqrt{2(1 \pm 0)}} = \frac{1}{\sqrt{2}}$$

- **Q2** (*advanced for experts, not examined*) First, solve the secular determinant for 3 overlapping p_z orbitals on a 3-atom chain (energies and wavefunctions). Draw the relevant MOs based on your mathematical equations. Then, draw a MO diagram (using the processes described in this course) using two p_z AOs as one fragment and a single p_z AO as the other fragment. Finally, check your answers by computing the MOs of the allene anion $(C_3H_5)^-$. Compare the maths, MO theory and computational results.

basis set 3pAOs

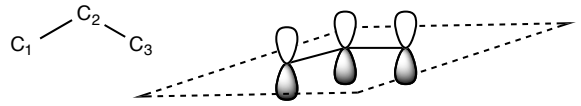


Figure 6 allene anion pAOs

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} \\ \beta_{21} & \alpha_2 - E & \beta_{23} \\ \beta_{31} & \beta_{32} & \alpha_3 - E \end{vmatrix} \rightarrow \begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix}$$

$$x = \frac{\alpha - E}{\beta}$$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \rightarrow x \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 0 \\ 1 & x \end{vmatrix} + 0 \begin{vmatrix} 1 & 0 \\ x & 1 \end{vmatrix} = 0$$

$$x(x \bullet x - 1 \bullet 1) - 1(1 \bullet x - 0 \bullet 1) + 0(1 \bullet 1 - 0 \bullet x) = 0$$

$$x^3 - x - x = 0 \rightarrow x(x^2 - 2) = 0$$

$$x = 0 \quad or \quad x^2 - 2 = 0 \rightarrow x = \pm\sqrt{2}$$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \quad and \quad x = 0, \pm\sqrt{2} \quad normalised \quad \sum C_n^2 = 1 = C_1^2 + C_2^2 + C_3^2$$

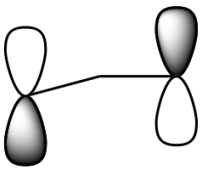
$$xC_1 + 1C_2 + 0C_3 = 0$$
$$1C_1 + xC_2 + 1C_3 = 0$$
$$0C_1 + 1C_2 + xC_3 = 0$$

$x = 0$

$0 + C_2 + 0 = 0 \rightarrow C_2 = 0$

$C_1 + 0 + C_3 = 0 \rightarrow C_1 = -C_3$

$0 + C_2 + 0 = 0$



$$\sum C_n^2 = C_1^2 + 0 + C_1^2 = 1 \rightarrow 2C_1^2 = 1 \rightarrow C_1 = \frac{1}{\sqrt{2}}$$

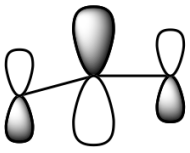
$$summary \quad C_1 = \frac{1}{\sqrt{2}} \quad C_2 = 0 \quad C_3 = -C_1$$

$x = \sqrt{2}$

$\sqrt{2}C_1 + C_2 + 0 = 0 \rightarrow C_2 = -\sqrt{2}C_1$

$C_1 + \sqrt{2}C_2 + C_3 = 0$

$0 + C_2 + \sqrt{2}C_3 = 0 \rightarrow C_2 = -\sqrt{2}C_3 \rightarrow C_1 = C_3$



$$\sum C_n^2 = C_1^2 + 2C_1^2 + C_1^2 = 1 \rightarrow 4C_1^2 = 1 \rightarrow C_1 = \frac{1}{2}$$

$$summary \quad C_1 = \frac{1}{2} \quad C_2 = -\sqrt{2}C_1 \quad C_3 = C_1$$

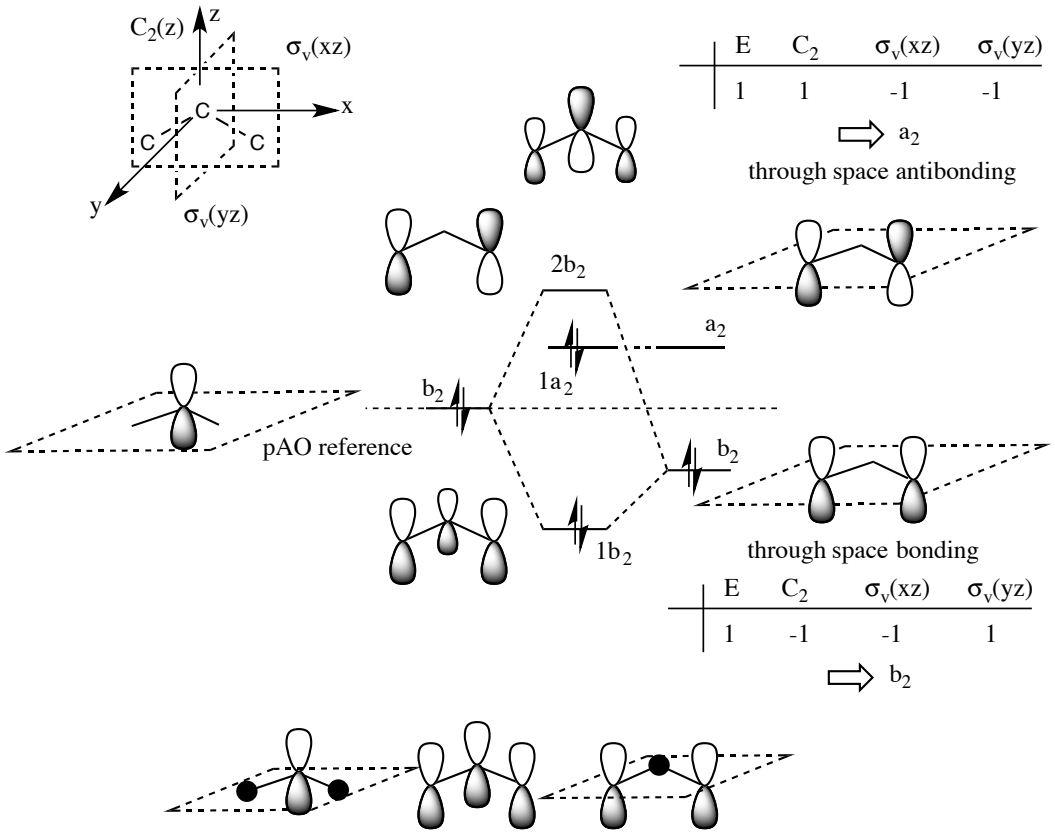


Figure 7 MO diagram

- note that the symmetry is C_{2v} and the principle axis must be the z-axis, therefore the out-of-plane pAO are actually p_y AOs
- in addition the orbital coefficients predicted by MO theory are not exactly the same as those predicted via Hückel theory
- below are the computed HOMO-1, HOMO and HOMO+4 for the allene anion.

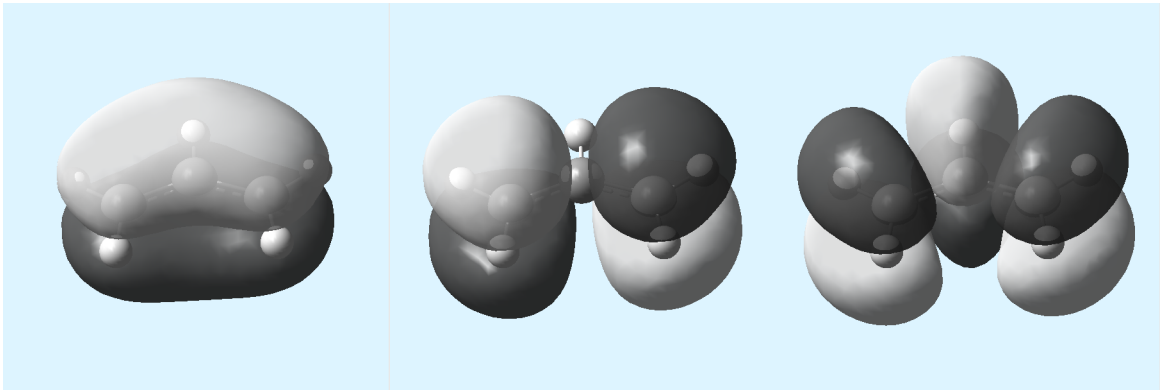
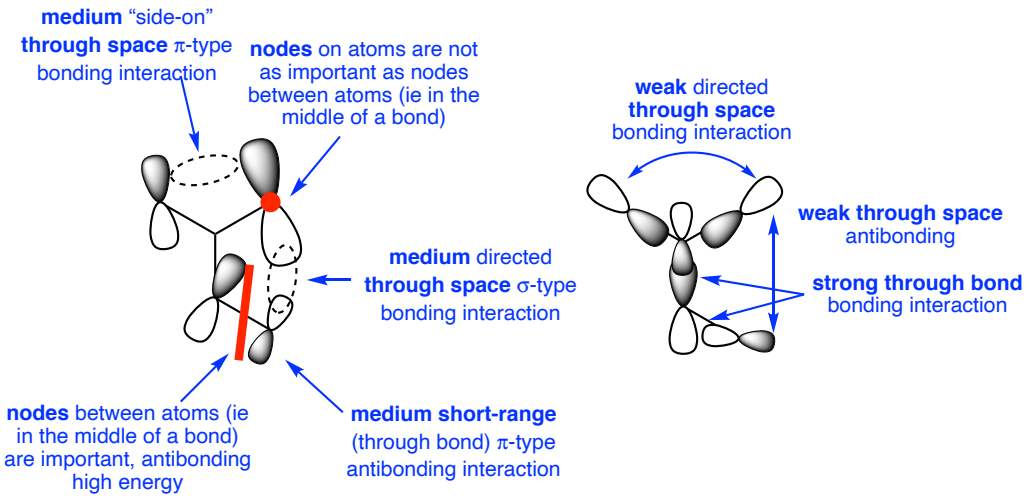


Figure 8 Computed MOs

- **Q3** Draw LCAOs for the computed MOs of planar NO_3F shown below. On your diagrams annotate features important for evaluating the orbital bonding character.
  - answers should always include reference to: through space vs through bond, types of node, bonding/antibonding, type of interaction (sigma, pi, s-s, directed, non-directed) and strength of interactions



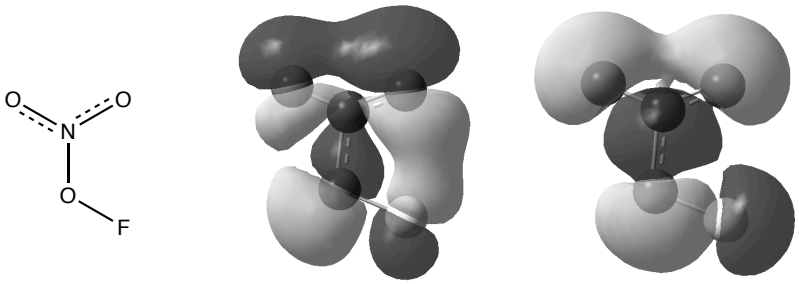


Figure 9 two computed MOs from planar NO_3F

- **Q4** Construct and annotate a valence MO diagram for $[H_2CN]^-$. Use your diagram to explain why the neutral radical is more stable than the anion
  - use the MO diagram check-list!!
  - shape is known, point group is C_{2v}
  - axial system and symmetry operations are shown in **Figure 10**
  - the best fragments to use are molecular fragments (CH_2) and N
  - use the MOs from the water model for CH_2
  - The neutral radical has lost one electron from an antibonding MO, this could be expected to stabilise the total energy of the molecule.
  - if you are interested, take a look at the real MOs below!

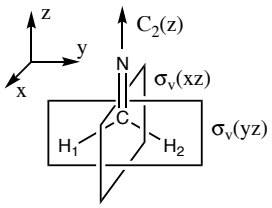


Figure 10 symmetry elements

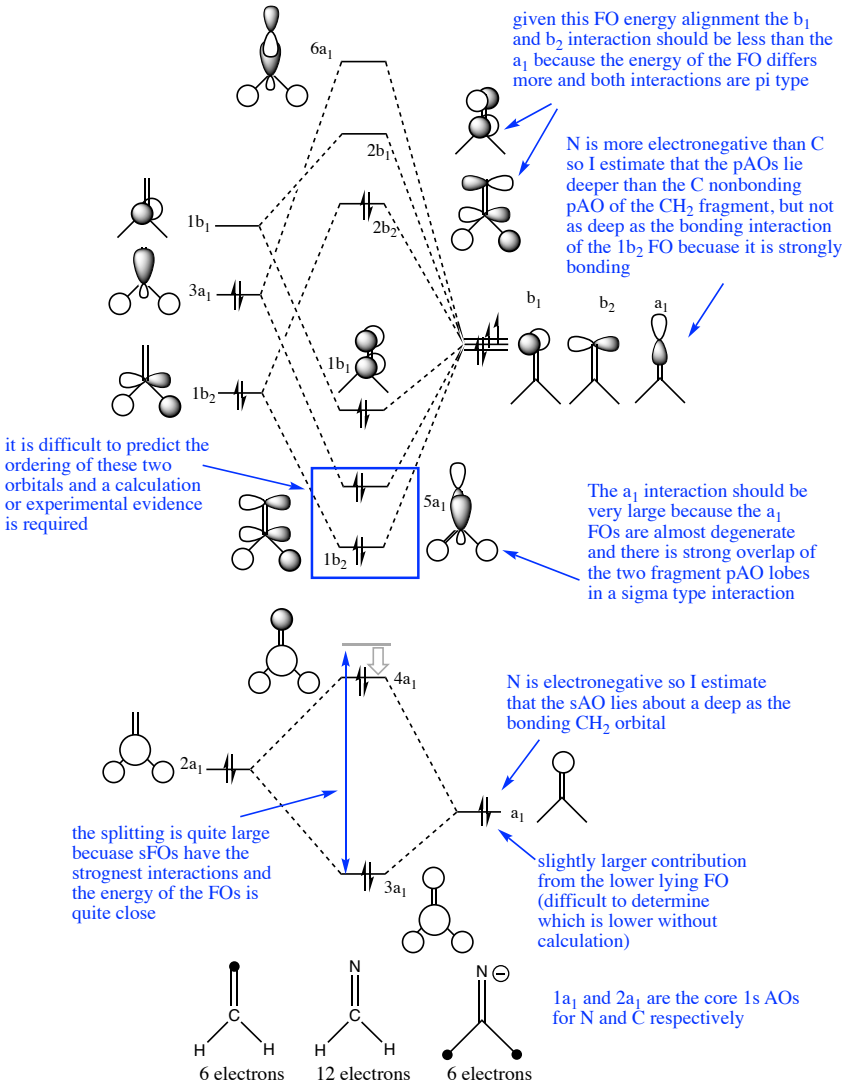


Figure 11 MO diagram for $[H_2CN]^-$

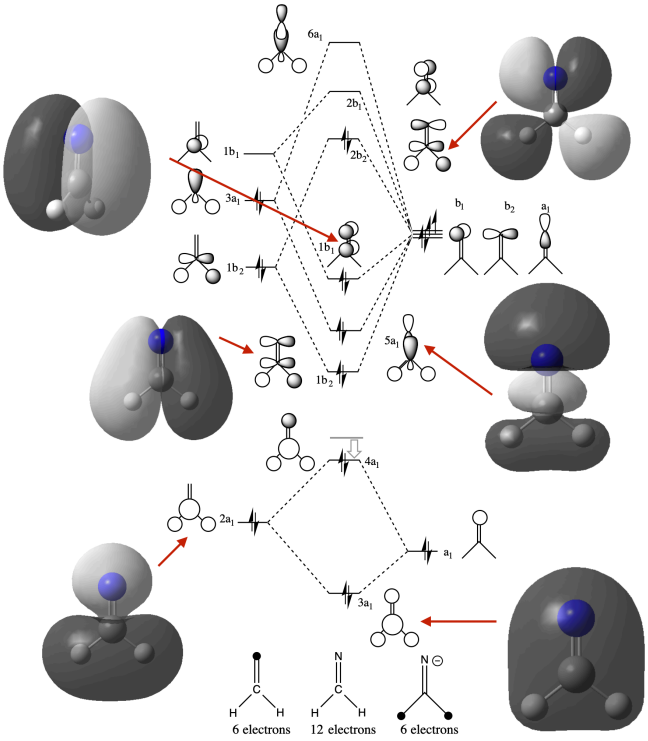


Figure 12 MO diagram for $[H_2CN]^-$ with computed MOs