Problem Set #2
Solutions

1) Molecular orbitals for each of the species are generated by overlap of 1s orbitals:

\[ \sigma^* \]

\[ 1s \quad - \quad - \quad 1s \]

2 atomic orbitals give two M.O.'s \((\sigma \text{ and } \sigma^*)\)

\[ \text{H}_2^+ \text{ contains one electron:} \]

\[ \sigma^* \]

\[ \sigma \]

Bond order = \( \frac{1-0}{2} = \frac{1}{2} \)

There is "half a bond" (i.e. a one-electron bond)
$\text{He}_2^+$ contains three electrons
+ $\sigma^*$
\[ \text{B.O.} = \frac{2-1}{2} = \frac{1}{2} \]
+ $\sigma$

$\text{He}_2$ contains four electrons
+ $\sigma^*$
\[ \text{B.O.} = \frac{2-2}{2} = 0 \]
+ $\sigma$

We don't expect $\text{He}_2$ to hold together! No net bonding.

2. Bond formed by $\text{sp}^3$-$\text{sp}^3$ overlap

Each carbon $\text{sp}^3$-hybridized

$\sigma^*$

--- Extra node ---

$\sigma$

$\text{C}_{\text{sp}^3}$

*Yes, cyl. sym.*

$\Rightarrow \sigma$-type
3. Selected views of ethane, propane, and \( n \)-butane. Use models to inspect.

- Ethane (Staggered)

- Propane (eclipsed)

- \( n \)-butane (anti)

- \( n \)-butane (gauche)
4. \[ H \, 1s^1 \]

\[ F \, 1s^2 \, 2s^2 \, 2p_x^2 \, 2p_y^2 \, 2p_z^1 \]

Let's form H-F bond by overlapping \( H_{1s} \) and \( F_{2p_z} \).

\[ \text{EXTRA NODE} \]

\[ \text{ANTI-BONDING} \]

\[ \text{NODE} \]

\[ F_{2p_z} \]

\[ H_{1s} \]

\[ \text{BONDING} \]

\[ \text{NODE} \]

\( \sigma \)-type means:

look down inter-nuclear axis, see cylindrically symmetric

\[ \rightarrow \text{We might be more sophisticated and use } sp^3 \text{-hybrid orbitals for } F, \text{ but the above treatment is a good first guess.} \]
5. **Step 1**

\[ \begin{align*}
\text{Add 104 Kcal/mole} \\
\text{Add 104 Kcal/mole} \\
\text{ENDOTHERMIC}
\end{align*} \]

\[ \begin{align*}
\text{H} & \quad \text{H} \\
\quad & \quad \rightarrow \\
\text{H} & + \quad \text{H}
\end{align*} \]

**Step 2**

\[ \begin{align*}
\text{Add energy,} \\
\text{but how much?} \\
\text{Need BDE for one of bonds} \\
\text{in C=O}
\end{align*} \]

\[ \begin{align*}
\text{BDE} & = (175 - 87) \text{ Kcal/mole} \\
\text{BDE} & \quad \text{for C=O} \\
\text{BDE} & \quad \text{for C-O}
\end{align*} \]

\[ \begin{align*}
& = 88 \text{ Kcal/mole} \\
\text{ENDOTHERMIC}
\end{align*} \]
Step 3:

\[
\begin{align*}
&\text{(97 + 110) Kcal/mole} \\
&\text{Forming two bonds. Energy is released}
\end{align*}
\]

\[\Delta H = -207 \text{ Kcal/mole}\]

Exothermic

Overall

\[\Delta H = (+104 + 88 - 207) \text{ Kcal/mole} \]

\[= -15 \text{ Kcal/mole}\]

Exothermic overall.

Acetaldehyde

\[\text{ethanol}\]

\[\text{This is a "hydrogenation" reaction.}\]