Types of Covalent Bonds

- What are the symmetries?
- Where are the nodes?
- What are the relative energies?
- How $S$ changes with $R_{AB}$?
- What are the $Y$(MO)?
Dihydrogen Molecule ($\text{H}_2$)

\[ \hat{H}_{\text{H}_2} \sim \left( -\nabla_1^2 - \frac{1}{r_{1A}} \right) + \left( -\nabla_2^2 - \frac{1}{r_{2B}} \right) - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{R_{AB}} \]

\[ \hat{H}_{\text{H}_2} = \hat{H}_{\text{H}(1e)} + \hat{H}_{\text{H}(1e)} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{R_{AB}} + \frac{1}{r_{12}} \]

Can not be solved exactly $\rightarrow$ Approximate

Place 2e with opp. spin in bonding orbital of $\text{H}_2^+$

\[ \varphi_{b}^{1e} = \frac{1}{\sqrt{2(1+S)}} \left[ 1s_A + 1s_B \right] \]

**Spatial part!**

\[ \varphi_{\text{H}_2}^{\text{MO}} = \frac{1}{2(1+S)} \left[ 1s_A (1) + 1s_B (1) \right] \left[ 1s_A (2) + 1s_B (2) \right] \]

\[ \varphi_{\text{H}_2}^{\text{MO}} = \frac{1}{2(1+S)} \left[ 1s_A (1)1s_A (2) + 1s_B (1)1s_B (2) + 1s_A (1)1s_B (2) + 1s_B (1)1s_A (2) \right] \]

MOT overemphasizes ionic terms in a covalent bond! VBT better?
Dihydrogen Molecule: One more electron goes to bonding orbital

Bond strength increases: Bond order=1

Effective nuclear charge changes the absolute Energy levels and the orbitals!

Matching of energies of AO important for LCAO-MO
If energies are not close to each other, they would Not interact to form MOs.
Energies of $\text{H}_2^+$, $\text{H}_2$, $\text{He}_2^+$, $\text{He}_2$

Molecular properties of $\text{H}_2^+$, $\text{H}_2$, $\text{He}_2^+$, and $\text{He}_2$.

<table>
<thead>
<tr>
<th>Species</th>
<th>Number of electrons</th>
<th>Ground-state electron configuration</th>
<th>Bond order</th>
<th>Bond length/pm</th>
<th>Binding energy/ kJ·mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2^+$</td>
<td>1</td>
<td>$(\sigma_g 1s)^1$</td>
<td>1/2</td>
<td>106</td>
<td>268</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>2</td>
<td>$(\sigma_g 1s)^2$</td>
<td>1</td>
<td>74</td>
<td>457</td>
</tr>
<tr>
<td>$\text{He}_2^+$</td>
<td>3</td>
<td>$(\sigma_g 1s)^2(\sigma_g 1s)^1$</td>
<td>1/2</td>
<td>108</td>
<td>241</td>
</tr>
<tr>
<td>$\text{He}_2$</td>
<td>4</td>
<td>$(\sigma_g 1s)^2(\sigma_g 1s)^2$</td>
<td>0</td>
<td>$\approx 6000$</td>
<td>$\ll 14$</td>
</tr>
</tbody>
</table>
Matching of AO energies for MO

Due to large difference in energy of 1s(H) and 1s(F), LCAO-MO for both 1S is not feasible in HF. Rather, 2Pz(F) and 1S(H) form a sigma bond.

Both symmetry and energy matching is required for MO.

Valence electrons are most important for bonding.

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Electron Density Maps/Contours
MO Contours show electron density maps

H₂

Li₂: core 1s

Li₂: core 1s*

Li₂: Valence 2s

2s and 2s*

3s and 1p

1p*

Total

HOMO (e): Highest Occupied Molecular Orbital

Li₂: Total

LUMO: Lowest Unoccupied Molecular Orbital
Expected MO and Energies for Dinitrogen

Are these MO and correct energy level diagram for $N_2$?

There is a problem! Spectroscopy says NO!
Mixing of 2S and 2P orbital occur because of small energy gap between them. 2s and 2p electrons feel not so different effective nuclear charge.
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s-p Mixing: $B_2$ magnetism confirms it!

Incorrect!

Boron is paramagnetic. This can only happen if the two electrons with parallel spin are in the $p$-orbitals → $p$-bonding energies lower than $s^*$?