Why inhomogeneous magnetic field...??

Otherwise the force acting is zero!!

No splitting

\[ E = -\mu B \]

\[ F_z = -\frac{\partial}{\partial z}(-\mu B) = \mu \frac{\partial B_z}{\partial z} \]

\[ \frac{\partial B_z}{\partial z} = 0 \]

For Homogeneous magnetic field
Molecular Electronic Structure: Bonding

Chemical Bond Formation
Stabilization due to Bond-formation

\[
E(4 \text{ charges @ } \infty) - E(2 \text{ H-Atoms}) = \sim 2642 \text{ kJ/mole}
\]

\[
E(2 \text{ H-Atoms @ } \infty) - E(\text{H}_2 \text{ molecule}) = \sim 436 \text{ kJ/mole}
\]

\[\rightarrow \text{ Chemical bond lowers the total energy by only } \sim 17\%\]

Charge distribution in \(\text{H}_2\) molecule not very different from Superposition of the charge distribution of individual atoms
Simplest Molecule: $H_2^+$ - 1 electron

2 Nuclei + 1 Electron

$H_2^+$ Molecule Ion Exists, Stable (Experimentally)
Bond length $\sim 1\text{Å} (2a_0)$; Bond Energy $\sim 270 \text{kJ/mole} (0.1E_H)$

One more electron complicate matters to great extent!
Just like many electron atoms - So, we need to build a Model with $H_2^+$ and get insight into chemical bonding

Then extend model for other multi-electronic molecules
Simplest Molecules: $H_2^+$ and $H_2$

$H_2^+$ Molecule Ion (2 Nuclei + 1 Electron):

$$\hat{H}(H_2^+) \sim (-\nabla^2_A - \nabla^2_B) + (-\nabla^2_{1e}) + \left( \frac{1}{r_{1A}} - \frac{1}{r_{1B}} \right) + \left( \frac{1}{R_{AB}} \right)$$

For $H_2$ Molecule (2 Nuclei + 2 Electrons):

$$\hat{H}(H_2) \sim (-\nabla^2_A - \nabla^2_B) + (-\nabla^2_{1e} - \nabla^2_{2e}) + \left( \frac{1}{r_{1A}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}} \right) + \left( \frac{1}{R_{AB}} + \frac{1}{r_{12}} \right)$$
Born-Oppenheimer Approximation

Nuclei are stationary wrt electronic motion

\[ \hat{H}(H_2^+) \sim \left( -\nabla_A^2 - \nabla_B^2 \right) + \left( -\nabla_{1e}^2 \right) + \left( -\frac{1}{r_{1A}} - \frac{1}{r_{1B}} \right) + \left( \frac{1}{R_{AB}} \right) \]

\[ \hat{H}_{H_2^+} \sim \left( -\nabla^2 \right) - \frac{1}{r_{e1A}} + \frac{1}{R_{AB}} - \frac{1}{r_{e1B}} = \hat{H}_{H(1e)} + \frac{1}{R_{AB}} - \frac{1}{r_{eB}} \]

TISE for \( H_2^+ \)

\[ \hat{H}_{H_2^+} \left( \vec{r}; R \right) \Psi_{H_2^+} \left( \vec{r}; R \right) = E_{H_2^+} \left( R \right) \Psi_{H_2^+} \left( \vec{r}; R \right) \]

Very difficult, but possible to solve the TISE under elliptical polar coordinates. Numerically easier!
Bonding: Valence Bond and Molecular Orbital Approaches
Valence Bond Theory

• Extension of Lewis electron dot model
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Valence Bond Theory

- Extension of Lewis electron dot model
- Overlap of atomic orbitals and sharing of electron pairs
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*Delocalization*: Resonance
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- Set up the Hamiltonian: Exactly solvable for $H_2^+$ but not for more complex molecules
- Molecular orbitals: Linear combination of Atomic Orbitals (*LCAO*)
- Can handle delocalization, excited states. *A general theory*
- A bit too general at times (*ionic structure for H$_2$, for example*)
Model 1: Valence Bond Theory (VBT)

1 electron in H1

2 electron in H2

Inclusion of ionic terms

“Resonance”

$\Psi = \Psi_{A(1)} \Psi_{B(2)}$

$\Psi = \Psi_{A(1)} \Psi_{B(2)} + \Psi_{A(2)} \Psi_{B(1)}$

$\Psi = \Psi_{A(1)} \Psi_{B(2)}$

$\Psi = \Psi_{A(1)} \Psi_{B(2)} + \Psi_{A(2)} \Psi_{B(1)} + \lambda \Psi_{A(1)} \Psi_{A(2)} + \lambda \Psi_{B(1)} \Psi_{B(2)}$

$\Psi = \Psi_{cov} + \lambda \Psi_{H^+H^-} + \lambda \Psi_{H^-H^+}$

Table 3.7 Energies and equilibrium distances for VB wave functions

<table>
<thead>
<tr>
<th>Type of wave function</th>
<th>Energy (kJ mol$^{-1}$)</th>
<th>Distance (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncorrected, $\Psi = \Psi_A \Psi_B$</td>
<td>24</td>
<td>90</td>
</tr>
<tr>
<td>Heitler-London”</td>
<td>303</td>
<td>86.9</td>
</tr>
<tr>
<td>Addition of shielding</td>
<td>365</td>
<td>74.3</td>
</tr>
<tr>
<td>Addition of ionic contributions</td>
<td>388</td>
<td>74.9</td>
</tr>
<tr>
<td>Observed values</td>
<td>458.0</td>
<td>74.1</td>
</tr>
</tbody>
</table>
Both VBT and MOT are used frequently – each of them work good for certain systems, respectively, and often are not so good for other systems!
Molecular Orbital Theory: LCAO

Linear Combination of Atomic Orbitals (LCAO)

\[ \psi_{MO} = \psi_{\text{Approx}} = c_1 \psi_{1S_A} + c_2 \psi_{1S_B} = c_1 \psi_1 + c_2 \psi_2 \]

\[ \psi_{MO}^2 = c_1^2 \psi_1^2 + c_2^2 \psi_2^2 + 2c_1c_2 \psi_1 \psi_2 \]

Symmetry: \( c_1^2 = c_2^2 \), \( \Rightarrow \) \( c_1 = \pm c_2 \)

For \( c_1 = c_2 = c_b \), \( \psi_b^2 = c_b^2 (\psi_1 + \psi_2)^2 \) \( \Rightarrow \) \( \psi_b = \pm c_b (\psi_1 + \psi_2) \sim 1S_A + 1S_B \)

For \( c_2 = -c_1 = -c_a \), \( \psi_a^2 = c_a^2 (\psi_1 - \psi_2)^2 \) \( \Rightarrow \) \( \psi_a = \pm c_a (\psi_1 - \psi_2) \sim 1S_A - 1S_B \)