M.O. approach continued... Lecture 11-12

Graphical representation of LCAO method:

The wave function is expressed as a sum of 1s wave functions of hydrogen atom.

\[ \Psi_{M0+} = C_1 \Psi_{1sA} + C_2 \Psi_{1sB} \]

The resulting \( \Psi_{M0+} \) has a net electron density at the \( A-B \) nuclear axis. This is also viewed as constructive interference of the atomic wave functions!

The \( \Psi_{M0+} \) has a cylindrical symmetry and the change in sign of coordinates (\( r \rightarrow -r \)) does not change the sign of \( \Psi_{M0+} \), i.e., it is an even function.

\( \Psi \Rightarrow \) Cylindrical Symmetry

The subtractive combination:

\[ \Psi_{M0} = C_1 \Psi_{1sA} - C_2 \Psi_{1sB} \]

has a net electron density of zero along the nuclear axis. Cylindrical Symmetry \( \Rightarrow \)
Normalization of \( \Psi_{m0+} \) = \( C \left( \Psi_{15A} + \Psi_{15B} \right) \) where \( C = C^* \)

\[ c^2 \int \Psi_{m0+}^* \Psi_{m0+} \, dx = \left( \int 1 + 1 + 2 \int \Psi_{15A}^* \Psi_{15B} + 2 + 2 \beta \right) = 1 \]

Where \( \beta = \text{Overlap integral} = \int \Psi_{15A}^* \Psi_{15B} \, dx \)

\[ 1 = \int \Psi_{15A}^* \Psi_{15A} \, dx = \int \Psi_{15B}^* \Psi_{15B} \, dx \]

All functions are real!

\[ \therefore \quad C^* = \frac{1}{\sqrt{2(1+\beta)}} \]

\[ \quad \Psi_{m0+} = \frac{1}{\sqrt{2(1+\beta)}} \left( \Psi_{15A} + \Psi_{15B} \right) \]

The energies of \( \Psi_{m0+} \) are quite comparable to experimental values. These can be improved further by adding additional terms \( \Psi_{2S,2p}, \ldots \) to the linear combination.

\[ \Psi_{m0+} = N_1 e^{-\frac{Z \alpha}{a_0}} + N_2 e^{-\frac{Z \alpha}{a_0}} \]

In a good trial function, and using variational theorem can be applied to determine \( Z \).
Additional MOs are obtained by combining \( n=2, 3 \) states wavefunctions. (Fig. 11.8)

H₂ - Molecule

\[
H_{\text{H}_2} = -\frac{1}{2me} \left[ V_1 + V_2 \right] - \frac{e^2}{4\pi\varepsilon_0} \left[ \frac{1}{r_{A1}} + \frac{1}{r_{B2}} + \frac{1}{r_{A2}} + \frac{1}{r_{B1}} - \frac{1}{R_{AB}} \right]
\]

As a first approximation, we can use the MOs of \( \text{H}_2^+ \) to describe \( \text{H}_2 \). This is similar to the application of orbital approximation to obtain wave functions for elements.
\[ \Psi_{m_0} = \left[ 1s_A(1) + 1s_B(1) \right] \left[ 1s_A(2) + 1s_B(2) \right] \]

\[ \text{For electron } 1 \quad \text{For electron } 2 \]

\[ = 1s_A(1)1s_A(2) + 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) + 1s_B(1)1s_B(2) \]

The binding energy calculated here corresponds to only \( \sim 60\% \). More refined \( \Psi_{m_0} \) is

\[ \Psi_{m_0} = \left[ C_1(1s_A(1) + 1s_A(2)) + C_2(1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)) \right] \]

\[ + C_1(1s_B(1)1s_B(2)) \]

Ionic Structures

Covalent Structures

\( C_1 \) and \( C_2 \) can be evaluated using variation theorem and the new \( \Psi_{m_0} \) predicts much better binding energy! (\( \sim 85\% \)).

This can be improved even further by adding additional terms in the \( \Psi_{m_0} \) but that will result in a loss of that will lack a clear intuitive understanding of the \( \Psi_{m_0} \).