Application of LCAO for H_2^+

Using the LCAO-MO approximation, the wave function for H_2^+ is written as.

$\psi = N(c_1\phi_A + c_2\phi_B)$ where N is normalisation constant. —— (1)

According to the normalisation condition for real ψ (using Dirac's bra and ket notation) —— (2)

$$\int \psi^2 d\tau = \langle \psi | \psi \rangle = 1$$

Incorporating the value of ψ from eqn (1) in eqn (2) we have

$$N^2 \langle c_1\phi_A + c_2\phi_B | (c_1\phi_A + c_2\phi_B) \rangle = 1$$

or, $c_1^2[\langle\phi_A|\phi_A\rangle] + c_2^2[\langle\phi_B|\phi_B\rangle] + 2c_1c_2[\langle\phi_A|\phi_B\rangle] = \frac{1}{N^2}$ —— (3)

Assuming ψ_A and ψ_B are normalised, i.e.

$\langle\phi_A|\phi_A\rangle = \int \phi_A^2 d\tau = 1$ and $\langle\phi_B|\phi_B\rangle = \int \phi_B^2 d\tau = 1$ —— (4)

We have, $c_1^2 + c_2^2 + 2c_1c_2S = \frac{1}{N^2}$, Where S is the Overlap Integral —— (5)

defined as, $S = \langle\phi_A|\phi_B\rangle = \int \phi_A\phi_B d\tau$ —— (6)

So that $N = (c_1^2 + c_2^2 + 2c_1c_2S)^{-1/2}$

Hence from equ-(1)

$\psi = (c_1^2 + c_2^2 + 2c_1c_2S)^{-1/2}(c_1\phi_A + c_2\phi_B)$ —— (7)

But we know that for BMO (Bonding Molecular Orbital)

$c_1 = c_2$ and ABMO, $c_1 = -c_2$

Hence from equation (7)

$$\psi_{BMO} = \frac{1}{\sqrt{2(1+S)}}(\phi_A + \phi_B)$$

and for ABMO (Anti Bonding Molecular Orbital)

$$\psi_{ABMO} = \frac{1}{\sqrt{2(1-S)}}(\phi_A - \phi_B)$$