Appendix 1 : Minimization of the Expression for the Orbital Energy

Rearrangement of the equation for determining the expectation value of the orbital energy yields:

$$E\int \psi^2 .d\tau = \int \psi \hat{H} \psi .d\tau$$

which, as shown on page 4.5, may (for two orbital overlap) be written in the form.

$$E(c_1^{\;2} + c_2^{\;2} + 2c_1c_2S) = c_1^{\;2}\alpha_1 + 2c_1c_2\beta_{12} + c_2^{\;2}\alpha_2 \qquad [1]$$

To minimize *E* with respect to *c*₁ : we need to differentiate eqtn.[1] with respect to c_1 and set $\frac{\partial E}{\partial c_1} = 0$.

Derivative of LHS $= E(2c_1 + 2c_2S) + \frac{\partial E}{\partial c_1}(c_1^{\;2} + c_2^{\;2} + 2c_1c_2S)$ (using the chain rule)

Derivative of RHS $= 2c_1\alpha_1 + 2c_2\beta_{12}$

Hence, when we set $\frac{\partial E}{\partial c_1} = 0$, the differentiated form of eqtn.[1] becomes

$$E(2c_1 + 2c_2S) = 2c_1\alpha_1 + 2c_2\beta_{12}$$

$$\Rightarrow \qquad \underline{c_1(\alpha_1 - E) + c_2(\beta_{12} - ES) = 0}$$

To minimize *E* with respect to *c*₂ : we need to differentiate eqtn.[1] with respect to c_2 and set $\frac{\partial E}{\partial c_2} = 0$.

Derivative of LHS $= E(2c_2 + 2c_1S) + \frac{\partial E}{\partial c_2}(c_1^{\;2} + c_2^{\;2} + 2c_1c_2S)$ (using the chain rule)

Derivative of RHS $= 2c_2\alpha_2 + 2c_1\beta_{12}$

Hence, when we set $\frac{\partial E}{\partial c_2} = 0$, the differentiated form of eqtn. [1] becomes

$$E(2c_2 + 2c_1S) = 2c_2\alpha_2 + 2c_1\beta_{12}$$

$$\Rightarrow \qquad \underline{c_1(\beta_{12} - ES) + c_2(\alpha_2 - E) = 0}$$