Energy Minimization - Four Methods Using Mathcad

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Using $\Psi(\alpha, r) := \sqrt{\frac{\alpha^3}{\pi}} \cdot \exp(-\alpha \cdot r)$ as a trial wave function for the helium atom electrons leads to the following energy expression in terms of the variational parameter, α.

$$E(\alpha) := \alpha^2 - 4\cdot\alpha + \frac{5}{8}\cdot\alpha$$

The first term is electron kinetic energy, the second electron-nucleus potential energy and the final term electron-electron potential energy.

Mathcad provides four methods for energy minimization with respect to α. The second and third methods require a seed value for α.

First Method: $\alpha := \frac{d}{d\alpha}E(\alpha) = 0 \left| \begin{array}{l} \text{solve}, \alpha \\ \text{float}, 5 \end{array} \right. \rightarrow 1.6875$ $\quad E(\alpha) = -2.8477$

Second Method: $\alpha := 1$ $\quad$ Given $\quad \frac{d}{d\alpha}E(\alpha) = 0$ $\quad \alpha := \text{Find}(\alpha)$ $\quad \alpha = 1.6875$ $\quad E(\alpha) = -2.8477$

Third Method: $\alpha := 1$ $\quad \alpha := \text{Minimize}(E, \alpha)$ $\quad \alpha = 1.6875$ $\quad E(\alpha) = -2.8477$

Fourth Method: Clear memory of α and Z: $\quad \alpha := \alpha$ $\quad Z := Z$

$$En(\alpha, Z) := \alpha^2 - 2\cdot Z\cdot\alpha + \frac{5}{8}\cdot\alpha \qquad \frac{d}{d\alpha}En(\alpha, Z) = 0 \text{ solve}, \alpha \rightarrow Z - \frac{5}{16}$$

$$En(\alpha, Z) := \alpha^2 - 2\cdot Z\cdot\alpha + \frac{5}{8}\cdot\alpha \text{ substitute}, \alpha = Z - \frac{5}{16} \rightarrow -\frac{(16\cdot Z - 5)^2}{256}$$

$$En(\alpha, 2) = -2.8477 \qquad En(\alpha, 3) = -7.2227 \qquad En(\alpha, 4) = -13.5977$$

Two variables: a molecular orbital calculation yields the following result for the energy of the hydrogen molecule ion as a function of the internuclear separation and the orbital decay constant.

$$1s_a = \sqrt{\frac{\alpha^3}{\pi}}\cdot\exp(-\alpha\cdot r_a) \qquad 1s_b = \sqrt{\frac{\alpha^3}{\pi}}\cdot\exp(-\alpha\cdot r_b) \qquad S_{ab} = \int 1s_a \cdot 1s_b \, d\tau \qquad \Psi_{mo} = \frac{1s_a + 1s_b}{\sqrt{2 + 2\cdot S_{ab}}}$$

$$E(\alpha, R) := \frac{-\alpha^2}{2} + \frac{\left[\alpha^2 - \alpha - \frac{1}{R} + \frac{1 + \alpha\cdot R}{R}\cdot\exp(-2\cdot\alpha\cdot R) + \alpha\cdot(\alpha - 2)\cdot(1 + \alpha\cdot R)\cdot\exp(-\alpha\cdot R)\right]}{\left[1 + \exp(-\alpha\cdot R)\cdot\left(1 + \alpha\cdot R + \frac{\alpha^2\cdot R^2}{3}\right)\right]} + \frac{1}{R}$$

$\alpha := 1 \qquad R := 1 \qquad \begin{pmatrix} \alpha \\ R \end{pmatrix} := \text{Minimize}(E, \alpha, R) \qquad \begin{pmatrix} \alpha \\ R \end{pmatrix} = \begin{pmatrix} 1.2380 \\ 2.0033 \end{pmatrix} \qquad E(\alpha, R) = -0.5865$

$\alpha := 1 \qquad \text{Energy} := -2 \qquad \text{Given} \qquad \text{Energy} = E(\alpha, R) \qquad \frac{d}{d\alpha}E(\alpha, R) = 0 \qquad \text{Energy}(R) := \text{Find}(\alpha, \text{Energy})$

$R := .2, .25 .. 10 \qquad T(R) := -\text{Energy}(R)_1 - R\cdot\frac{d}{dR}\text{Energy}(R)_1 \qquad V(R) := 2\cdot\text{Energy}(R)_1 + R\cdot\frac{d}{dR}\text{Energy}(R)_1$