10.2: Energy Minimization - Four Methods Using Mathcad

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

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

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

$$\alpha=\frac{d}{d\alpha} E(\alpha)=0 |_{float,5}^{solve,\alpha} \rightarrow 1.6875$$

$E(\alpha)=-2.8477$

Second method

α = 1. Given $\frac{d}{d\alpha} E(\alpha)=0$ $\alpha=Find(\alpha)$ α = 1.685 $E(\alpha)=-2.8477$

Third method

α = 1. α : = Minimize(E, α) α = 1.685 $E(\alpha)=-2.8477$

Fourth method

Clear memory of α and X: α = α Z = Z

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

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

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

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.

$$1s_a=\frac{\alpha^3}{\pi} exp(-\alpha r_a)$$

$$1s_b=\frac{\alpha^3}{\pi} exp(-\alpha r_b)$$

$$S_{ab}=\int 1s_a 1s_b d\tau$$

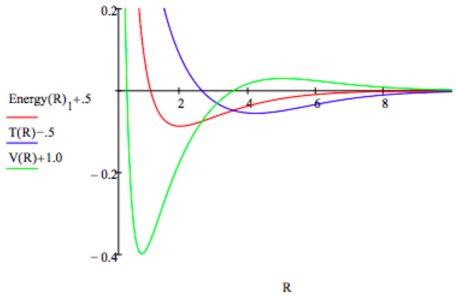
$$\psi_{mo}=\frac{1s_a+1s_b}{\sqrt{2+2S_{ab}}}$$

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

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

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

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


0.2
Energy(R)1+.5
T(R)−.5
V(R)+1.0
−0.2
−0.4
2
4
6
8
R