An Interactive SCF Calculation

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This is an outline of the Mathcad implementation of a two-electron SCF calculation published in JCE by Snow and Bills. [Snow, R. L.; Bills, J. L. *J. Chem. Educ.* **1975**, *52*, 506.]

Under the orbital approximation, $\Psi(1,2) = \Phi(1)\Phi(2)$, the two-electron Schrodinger equation for helium can be decoupled into two, one-electron Hartree differential equations. The individual helium atom electrons are assumed to occupy an orbital which is a linear combination of two Slater 1s orbitals,

$$\Phi = C_1 \cdot f_1 + C_2 \cdot f_2 \qquad (1)$$

$$f_1 = \sqrt{\frac{\alpha^3}{\pi}} \cdot \exp(-\alpha \cdot r) \qquad \text{and} \qquad f_2 = \sqrt{\frac{\beta^3}{\pi}} \cdot \exp(-\beta \cdot r) \qquad (2)$$

The effective Hamiltonian for the i^{th} electron is,

$$H_i = -\frac{1}{2 \cdot r^2} \cdot \frac{d}{dr}\left(r^2 \cdot \frac{d}{dr} \blacksquare \right) - \frac{2}{r_i} + \int_0^{\infty} (Cj_1 \cdot f_1 + Cj_2 \cdot f_2) \cdot \frac{1}{r_{ij}} \cdot (Cj_1 \cdot f_1 + Cj_2 \cdot f_2) \, d\tau \qquad (3)$$

where the Cjs are the coefficients of the j^{th} electron.

Assuming that the i^{th} electron is also in an orbital of the form given in equation (1), the variational method yields the following expression for the energy of the i^{th} electron.

$$\varepsilon_i = \frac{\int_0^{\infty} (Cj_1 \cdot f_1 + Cj_2 \cdot f_2) \cdot H_i \cdot (Cj_1 \cdot f_1 + Cj_2 \cdot f_2) \, d\tau}{\int_0^{\infty} (Cj_1 \cdot f_1 + Cj_2 \cdot f_2)^2 \, d\tau} = \frac{Ci_1^{\,2} \cdot H_{11} + 2 \cdot Ci_1 \cdot Ci_2 \cdot H_{12} + Ci_2^{\,2} \cdot H_{22}}{Ci_1^{\,2} + 2 \cdot Ci_1 \cdot Ci_2 \cdot S_{12} + Ci_2^{\,2}} \qquad (4)$$

The optimum values for the orbital scale factors are given below. The user can change these values to demonstrate that they do indeed yield a minimum energy for the trial wavefunction chosen.

$$\alpha := 1.45 \qquad \beta := 2.90$$

Evaluation of integrals given values for the scale factors, α and β, of the Slater type orbitals follows (See Snow and Bills for details):

$$\tau := \frac{\alpha - \beta}{\alpha + \beta} \qquad \tau 1 := \frac{\alpha - \beta}{3 \cdot \alpha + \beta} \qquad \tau 2 := \frac{\alpha - \beta}{\alpha + 3 \cdot \beta}$$

Kinetic energy integrals:

$$T_{11} := \frac{\alpha^2}{2} \qquad T_{22} := \frac{\beta^2}{2} \qquad T_{12} := \frac{1}{8} \cdot (\alpha + \beta)^2 \cdot \left(1 - \tau^2\right)^{2.5}$$

Electron-nucleus potential energy integrals:

$$V_{11} := -2\cdot\alpha \qquad V_{22} := -2\cdot\beta \qquad V_{12} := -(\alpha+\beta)\cdot\left(1-\tau^2\right)^{1.5}$$

Electron-electron repulsion integrals:

$$V_{1111} := \frac{5}{8}\cdot\alpha \qquad V_{2222} := \frac{5}{8}\cdot\beta \qquad V_{1212} := \frac{5}{16}\cdot\left(1-\tau^2\right)^3\cdot(\alpha+\beta)$$

$$V_{1122} := \frac{1}{16}\cdot\left(1-\tau^2\right)\cdot\left(5-\tau^2\right)\cdot(\alpha+\beta) \qquad V_{1222} := \frac{1}{32}\cdot\left(1-\tau^2\right)^{1.5}\cdot\left(1-\tau2^2\right)\cdot\left(5-\tau2^2\right)\cdot(\alpha+3\cdot\beta)$$

$$V_{1112} := \frac{1}{32}\cdot\left(1-\tau^2\right)^{1.5}\cdot\left(1-\tau1^2\right)\cdot\left(5-\tau1^2\right)\cdot(3\cdot\alpha+\beta)$$

Overlap integral: $S_{12} := \left(1-\tau^2\right)^{1.5}$

Having evaluated the integrals, the next step is the calculation of the matrix elements that appear in equation (4).

$$\begin{aligned} H_{11} &:= T_{11} + V_{11} + Cj_1{}^2\cdot V_{1111} + 2\cdot Cj_1\cdot Cj_2\cdot V_{1112} + Cj_2{}^2\cdot V_{1122} \\ H_{12} &:= T_{12} + V_{12} + Cj_1{}^2\cdot V_{1112} + 2\cdot Cj_1\cdot Cj_2\cdot V_{1212} + Cj_2{}^2\cdot V_{1222} \\ H_{22} &:= T_{22} + V_{22} + Cj_1{}^2\cdot V_{1122} + 2\cdot Cj_1\cdot Cj_2\cdot V_{1222} + Cj_2{}^2\cdot V_{2222} \end{aligned} \qquad (5)$$

Given initial values for the coefficients of the j^{th} electron (these are declared below in a more convient location using Mathcad's global equal sign), minimization of the orbital energy simultaneously with respect to the coefficients of the i^{th} electron yields the orbital energy of the i^{th} electron and its coefficients. These output coefficients become the input coefficients of the next iteration when the orbital energy of the j^{th} electron is calculated. The procedure is repeated until self-consistency is achieved. This occurs when the output coefficients are equal to the input coefficients, or to put it another way, when the coefficients of the two electrons are identical.

In the numeric mode Mathcad requires seed values for all variable which appear in the expression to be evaluated in a **Given/Find** solve block. The seed values for the coefficients shown below are arbitrarily set at 0.5.

$$Ci_1 := .5 \qquad Ci_2 := .5$$

The variational integral for the electron orbital energy:

$$\varepsilon\left(Ci_1, Ci_2\right) := \frac{Ci_1{}^2\cdot H_{11} + 2\cdot Ci_1\cdot Ci_2\cdot H_{12} + Ci_2{}^2\cdot H_{22}}{Ci_1{}^2 + 2\cdot Ci_1\cdot Ci_2\cdot S_{12} + Ci_2{}^2}$$

Minimization of the variational integral simultaneously with respect to the coefficients plus the normalization condition

Given $\quad \frac{d}{dCi_1}\varepsilon\left(Ci_1, Ci_2\right) = 0 \qquad \frac{d}{dCi_2}\varepsilon\left(Ci_1, Ci_2\right) = 0 \qquad Ci_1{}^2 + 2\cdot Ci_1\cdot Ci_2\cdot S_{12} + Ci_2{}^2 = 1$

yields the output coefficients and the orbital energy:

$$\begin{pmatrix} Ci_1 \\ Ci_2 \end{pmatrix} := \mathrm{Find}(Ci_1, Ci_2) \qquad \begin{pmatrix} Ci_1 \\ Ci_2 \end{pmatrix} = \begin{pmatrix} 0.809249 \\ 0.219060 \end{pmatrix}$$

In the SCF method the output coefficients become the input coefficients in the next iteration.

Display the orbital energy: $\varepsilon(Ci_1, Ci_2) = -0.984326$

The energy of the atom at this point in the calculation is the orbital energy of the ith electron plus the kinetic and nuclear potential energy of the jth electron.

$$E_{atom} := \varepsilon(Ci_1, Ci_2) + Cj_1^{\,2}\cdot(T_{11} + V_{11}) + 2\cdot Cj_1\cdot Cj_2\cdot(T_{12} + V_{12}) + Cj_2^{\,2}\cdot(T_{22} + V_{22}) \qquad E_{atom} = -2.833076$$

Input coefficients: $\begin{pmatrix} Cj_1 \\ Cj_2 \end{pmatrix} \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

Paste new input coefficients after each iteration.

Summary of the SCF results for the following initial input coefficients: $\begin{pmatrix} Cj_1 \\ Cj_2 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

Iteration	Ci_1	Ci_2	$\varepsilon(Ci_1, Ci_2)$	E_{atom}
1	0.809249	0.21906	−0.984326	−2.833076
2	0.847034	0.176951	−0.90556	−2.860616
3	0.839638	0.185241	−0.920653	−2.86163
4	0.841091	0.183615	−0.917676	−2.86167
5	0.840806	0.183934	−0.918258	−2.861672
6	0.840862	0.183871	−0.918144	−2.861672
7	0.840851	0.183884	−0.918167	−2.861672
8	0.840853	0.183881	−0.918161	−2.861673
9	0.840852	0.183882	−0.918164	−2.861672
10	0.840852	0.183882	−0.918164	−2.861672