2.50: The SCF Method for Two Electrons

Self-consistent field calculations have great historical significance and play a major role in contemporary quantum chemistry. Therefore, the purpose of this exercise is to illustrate with an interactive example the simplest possible self-consistent field calculation for atomic systems. The SCF method is particularly transparent in the Mathcad programming environment as will be shown below.

Under the orbital approximation [$\Phi(1,2) = \Psi(1)\Psi(2)$] the two-electron Schrödinger Equation can be decoupled into two one-electron equations with effective Hamiltonian operators of the form,

$$H_i = -\frac{1}{2r_1}\frac{d^2}{dr_i^2}r_i - \frac{Z}{r_i} + \int_0^\infty \Psi_j \frac{1}{r_j}d\tau_j$$

Here the subscripts i and j are used to distinguish the two electrons.

The first term on the right side represents the kinetic energy of the ith electron, the second term is its interaction with the nucleus, and the third term is its average interaction with the jth electron. If it is assumed that the jth electron is in a Slater-type orbital with scale factor β,

$$\Psi_j = \sqrt{\frac{\beta^3}{\pi}}\exp\left(-\beta r_j j\right)$$

the effective Hamiltonian for the ith electron becomes,

$$H_i = -\frac{1}{2r_1}\frac{d^2}{dr_i^2} - \frac{Z}{r_1} + \frac{1}{r_1}\left[1 - (1 + \beta r_1)\exp\left(-2\beta r_i\right)\right]$$

This Hamiltonian is then used with the variational method to calculate the orbital energy of the ith electron,

$$\varepsilon_i = \int_0^\infty \Psi_i H_i \Psi_i d\tau_i$$

If the ith electron is also assumed to be in a Slater-type orbital but with a different scale factor α,

$$\Psi_i = \sqrt{\frac{\alpha^3}{\pi}}\exp\left(-\alpha r_i\right)$$

the variational integral for the orbital energy upon evaluation is,

$$\varepsilon_i = \frac{\alpha^2}{2} - Z\alpha + \frac{\alpha\beta\left(\alpha^2 + 3\alpha\beta + \beta^2\right)}{(\alpha + \beta)^3}$$

The SCF calculation proceeds by minimizing εi with respect to α given an initial value for β. This amounts to finding the orbital energy and wavefunction of the ith electron in the average electrostatic field created by the jth electron. Now we turn our attention to the jth electron. By identical arguments to those given above for the ith electron, it can be shown that the orbital energy of the jth electron is

$$\varepsilon_j = \frac{\beta^2}{2} - Z\beta + \frac{\alpha\beta\left(\alpha^2 + 3\alpha\beta + \beta^2\right)}{(\alpha + \beta)^3}$$

The value of α just obtained for the ith electron serves as the seed value as εj is minimized with respect to β in order to obtain the orbital energy and wavefunction of the jth electron. One cycle has now been completed and this procedure is continued until self-consistency is achieved. This occurs when the orbital energies and the wavefunctions of the two electrons converge to the same values. After each iteration the energy of the atom or ion is calculated as the sum of orbital energy of one of the electrons plus the kinetic and nuclear potential energy of the other electron.

$$E_{atom} = \varepsilon_i + \frac{\beta^2}{2} - Z\beta$$

To summarize: After making a guess for the wavefunction of the jth electron the variation method is used to determine the orbital energy and wavefunction of the ith electron. Using this output wavefucntion as the input wavefunction in the second iteration, the orbital energy and wavefunction of the jth electron is calculated. The procedure is repeated until self-consistency is achieved; that is until $\Psi_i = \Psi_j$ and $\varepsilon_i = \varepsilon_j$. This is also the point at which the energy of the atom has achieved a minimum value in compliance with the variational theorem. This is clearly shown in the output of the third method.

Note that the final SCF result is the same as that achieved in a variational calculation which places both electrons in the same Slater orbital from the beginning. This calculation results in the familiar expression

$$E = \alpha^2 - \left(2Z - \frac{5}{8} \right) \alpha$$

which when minimized with respect to α yields, α = Z - 5/16 and $E_{atom} = -\alpha^2$.

The reason for using the indirect procedure outlined here is that it provides an unusually simple and direct example of the SCF method. This example should be helpful in understanding what is going on behind the scenes in much more complicated quantum mechanical calculations performed with comprehensive commercial programs like Spartan.

SCF Calculation for Two Electron Atoms and Ions

1. Supply nuclear charge and an input value for β:

$$Z = 2 \quad \beta = 2 \quad \alpha = Z$$

2. Define orbital energies of the electrons in terms of the variational parameters:

$$\varepsilon_{1s\alpha}(\alpha,\ \beta) = \frac{\alpha^2}{2} - Z\alpha + \frac{\alpha\beta(\alpha^2+3\alpha\beta+\beta^2)}{(\alpha+\beta)^3} \qquad \varepsilon_{1s\beta}(\alpha,\ \beta) = \frac{\beta^2}{2} - Z\beta + \frac{\alpha\beta(\alpha^2+3\alpha\beta+\beta^2)}{(\alpha+\beta)^3}$$

3. Minimize orbital energies with respect to α and β:

$$\text{Given} \quad \frac{d}{d\alpha}\varepsilon_{1s\alpha}(\alpha,\ \beta) = 0 \quad \alpha = \text{Find}(\alpha) \quad \alpha = 1.5999 \quad \varepsilon_{1s\alpha}(\alpha,\ \beta) = -0.8116$$

$$\text{Given} \quad \frac{d}{d\beta}\varepsilon_{1s\alpha}(\alpha,\ \beta) = 0 \quad \beta = \text{Find}(\beta) \quad \beta = 1.5999 \quad \varepsilon_{1s\beta}(\alpha,\ \beta) = -0.9250$$

4. Calculate the energy of the atom:

$$E_{atom} = \frac{\alpha^2}{2} + \frac{\beta^2}{2} - Z\alpha - Z\beta + \frac{\alpha\beta(\alpha^2+3\alpha\beta+\beta^2)}{(\alpha+\beta)^3} \qquad E_{atom} = -2.8449$$

5. Record results of the SCF cycle and return to step 1 with the new and improved input value for β.
6. Continue until self-consistency is achieved.
7. Verify the results shown below for He. Repeat for Li$^+$, Be^{2+} and B^{3+}.

Recommend tabular form for results of each SCF cycle:

$$\begin{pmatrix} \beta(\text{input}) & \alpha & \varepsilon_{1s\alpha} & \beta & \varepsilon_{1s\beta} & E_{atom} \\ 2.000 & 1.5999 & -0.8116 & 1.7126 & -0.9250 & -2.8449 \\ 1.7126 & 1.6803 & -0.8887 & 1.6895 & -0.8987 & -2.8476 \\ 1.6895 & 1.6869 & -0.8959 & 1.6877 & -0.8967 & -2.8477 \\ 1.6877 & 1.6874 & -0.8964 & 1.6875 & -0.8965 & -2.8477 \\ 1.6875 & 1.6875 & -0.8965 & 1.6875 & -0.8965 & -2.8477 \end{pmatrix}$$