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A Simple Hartree SCF Calculation on a One-Dimensional Model of the He Atom

It has been noted frequently that it is very difficult for undergraduates to come to grips with the fundamentals of quantum theory. Undoubtedly, this difficulty is related to the fact that there are not very many examples of meaningful, yet simple, quantum calculations that can be performed by undergraduates. Like many other activities, it is easier to learn quantum chemistry if you actually do it. This situation has been improved recently by the publication of several papers in *this Journal* outlining calculations of varying complexity which can be performed by undergraduates and which illustrate important computational methods in quantum chemistry (1–3). In this paper we present a numerical self-consistent field calculation on a one-dimensional model for the helium atom appropriate for a typical undergraduate level course in physical chemistry. We have chosen a one-dimensional model so that mathematical complexities will not obscure the fundamental principles of the numerical SCF method. Similar calculations for two particles in a one-dimensional box have been described by Boleman (4).

Numerical calculations in quantum chemistry generally are not discussed in physical chemistry texts or elementary expositions on quantum chemistry. This omission is unfortunate because numerical calculations have both historical and contemporary significance. In addition numerical solutions are general and can be used in those cases for which analytical solutions are either very difficult to obtain or are unobtainable. Numerical methods also have the added advantage that they keep physical principles directly before the student because they emphasize the critical role of boundary conditions in quantum mechanical problems.

The Model

The one-dimensional potential well shown in Figure 1 will be used as a model for the electron-nucleus electrostatic interaction of the helium ion and atom. For positive values of x (the position of the electron relative to the nucleus) the electron-nucleus interaction is $-2/x$. For x less than zero the potential energy is set at infinity.

In the proposed exercise the students warmup by numerically integrating the Schrödinger equation for the one-dimensional helium ion. This calculation is very simple and serves as an introduction to the technique of numerical integration. It also serves as an aid to understanding the somewhat more complex SCF calculation.

The Helium Ion

On the basis of the model of Figure 1, the Schrödinger equation for He$^+$ is

$$[-\tfrac{1}{2} \, d^2/dx^2 - 2/x] \, Y(x) = E \, Y(x) \qquad (1)$$

The analytical solution (5) of this equation is straightforward and yields the following normalized wavefunction and ground-state energy.

$$Y(x) = \sqrt{32} \, x \, \exp(-2x)$$

$$E_{He^+} = -2.0 \text{ hartrees}$$

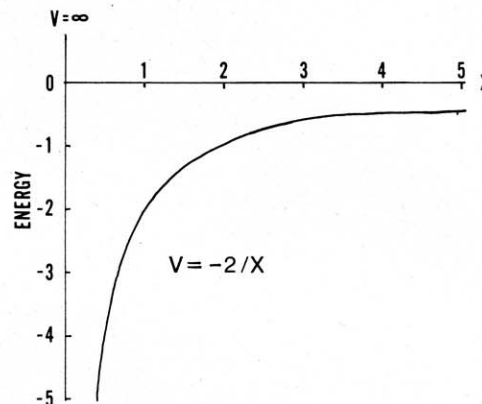To facilitate numerical integration of Schrödinger's equation it is re-written as

Figure 1. One-dimensional model of the electron-nucleus interaction in He$^+$ and He. Energy in hartrees and distance in bohrs.

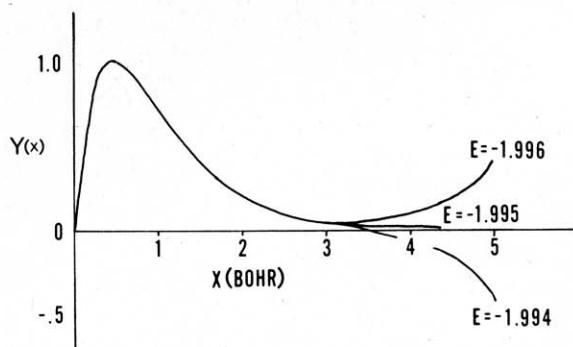Figure 2. Summary of numerical integration of Schrödinger's equation for He$^+$. Energy in hartrees.

$$Y''(x) = -2(2/x + E) \, Y(x) \qquad (2)$$

At this point an algorithm for integration must be chosen and Euler's method is recommended because of its simplicity. It is described briefly in Appendix A. Since the primary goal of this exercise is to introduce the numerical SCF method Euler's method is adequate, although the students should be made aware of its limitations (6).

The results of the numerical integration of eqn. (2) using Euler's method are summarized in Figure 2 for the ground state of the He atom. After completing the numerical integration the students are asked to compare their results with the analytical solution for He$^+$.

The Helium Atom

For the atom there are two electrons in the potential well, and it is assumed that they interact through a truncated coulombic potential of the form

$$V_{12} = 1.0/(|x_1 - x_2| + A) \qquad (3)$$

The truncation parameter, A, is introduced to prevent the mathematical problem of V_{12} becoming infinite when $x_1 = x_2$. The Schrödinger equation for this model of the helium atom is

$$[-\tfrac{1}{2}d^2/dx_1{}^2 - 2/x_1 - \tfrac{1}{2}d^2/dx_2{}^2 - 2/x_2$$
$$+ 1/(|x_1 - x_2| + A)]\, Y(1,2) = E\, Y(1,2) \quad (4)$$

Due to the presence of the electron-electron interaction term which involves the coordinates of electrons 1 and 2, eqn. (4) cannot be solved exactly. Hartree (7) suggested that the two-electron Schrödinger equation could be approximated by two one-electron equations of the form (see appendix B)

$$[-\tfrac{1}{2}\, d^2/dx_i{}^2 - 2/x_i + V_{12}(x_i)]\, Y_i(x_i) = \epsilon_i\, Y_i(x_i) \quad (5)$$

where

$$V_{12}(x_i) = \int_0^\infty \frac{Y_j{}^2(x_j)\, dx_j}{|x_i - x_j| + A}$$

and ϵ_i is the energy of the ith electron. Thus, we see that for the He atom the Hartree SCF method assumes that the individual electrons are moving in the field of the nucleus and an additional field which represents the average effect of the other electron. Approximation of the instantaneous electron-electron interaction by an average does not adequately take into account the fact that electrons, having the same charge tend to correlate their motions. This interaction introduces an error in the determination of the ground-state energy which is called the correlation energy.

To facilitate integration eqn. (5) is re-written

$$Y_i{}''(x_i) = 2\left[\int_0^\infty \frac{Y_j{}^2(x_j)\, dx_j}{|x_i - x_j| + A} - 2/x_i - \epsilon_i\right] Y_i(x_i) \quad i = 1,2 \quad (7)$$

Notice that to solve the Hartree equation for ϵ_1 and Y_1, it is necessary to know the wavefunction for electron 2, Y_2. Similarly, to obtain ϵ_2 and Y_2, it is necessary to know Y_1. The crux of the Hartree SCF calculation lies, therefore, in making an initial guess (see appendix C) for Y_2 and using it to obtain ϵ_1 and Y_1 by numerically integrating eqn. (7). Y_1 is then used to get an improved Y_2 and so on until the calculation is self-consistent. Because the electrons in the helium atom are assumed to occupy the same spatial orbital, the calculation is considered to be self-consistent when $Y_1 = Y_2$ and $\epsilon_1 = \epsilon_2$. The diagram in Figure 3 summarizes the algorithm for the numerical SCF calculation on the one-dimensional helium atom. Further details on the use of boundary conditions are presented in Appendix A.

For this exercise the students are presented with the following subroutines:

1) A subroutine which calculates the initial guess for the wavefunction (see Appendix C).
2) A subroutine which evaluates the potential energy integral in eqn. (7), $V_{12}(x_1)$, using Simpson's method.
3) A subroutine which normalizes a wavefunction using Simpson's method.
4) A subroutine which uses Simpson's method to evaluate the final electron-electron potential energy integral in eqn. (8).

The students are then asked to use these subroutines plus the program they wrote to integrate Schrödinger's equation to put together a main program that carries out the SCF calculation as outlined in the flow chart of Figure 3.

The SCF calculation was performed on a HP-2000 series computer which carries six or seven significant digits. The programming language was BASIC and a typical calculation required an hour of terminal (time-share) time. The programming and the calculation can be completed easily in one 4-hr laboratory period. The results of the calculation are summarized in Figure 4 and Tables 1 and 2.

Table 1 shows that it required eight iterations to achieve self-consistency. The criteria for self-consistency were that the boundary conditions be satisfied and that the one-electron energies be equal to four significant figures. Figure 4 compares the electron density, Y^2, for the He^+ ion with the one-electron SCF density for the He atom. This figure shows graphically the effect of placing a second electron into the potential well. For distances from the nucleus less than 1 bohr, the one-electron density in the atom is less than in the ion. For dis-
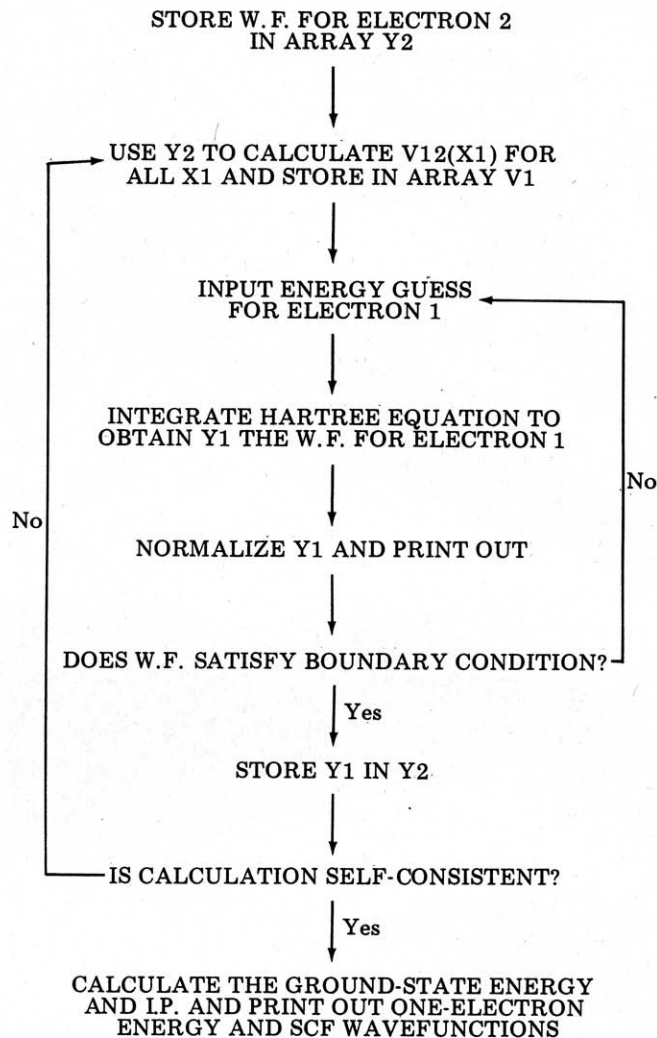
FLOW CHART

Figure 3. Algorithm for SCF calculation on the 1-D He atom.

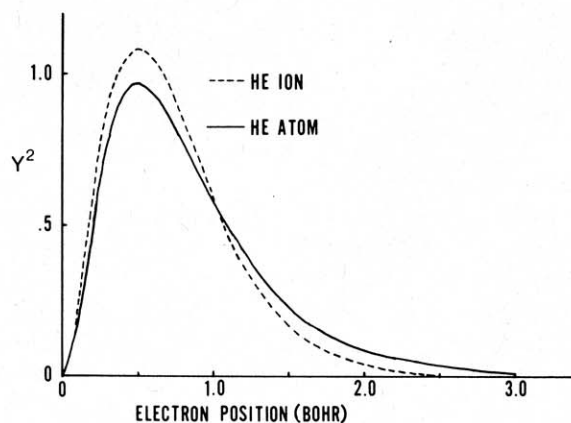Figure 4. Comparison of one-electron probability densities for He^+ and He.

tances greater than 1 bohr the one-electron density is greater in the atom than in the ion. The presence of the additional electron reduces electron density near the nucleus and increases it for positions more distant from the nucleus.

The ground-state energy of the helium atom is twice the one-electron energy minus the average electron-electron potential energy.

Table 1. Convergence of One-Electron Energies [a]

Iteration	One-Electron Energy
1	$E_1 = -0.8847$
2	$E_2 = -0.8329$
3	$E_1 = -0.8501$
4	$E_2 = -0.8445$
5	$E_1 = -0.8461$
6	$E_2 = -0.8454$
7	$E_1 = -0.8458$
8	$E_2 = -0.8458$
9	$E_1 = -0.8458$

[a] Energy in hartrees. 1 hartree = 27.19 e.v.

Table 2. Summary of the SCF Calculation [a]

The He$^+$ Ion Ground-State Energy	-1.9950
SCF One-Electron Energy	-0.8458
The Electron-Electron PE	1.1178
The He Atom Ground-State Energy	-2.8094
The He Atom Ionization Energy	0.8144

[a] Energy in hartrees.

$$E_{\text{He}} = 2e - \int_0^\infty V_{12}(x_1)\, Y_1{}^2(x_1)\, dx_1$$

$$E_{\text{He}} = 2e - \int_0^\infty \int_0^\infty \frac{Y_1{}^2(x_1)\, Y_2{}^2(x_2)\, dx_1\, dx_2}{|x_1 - x_2| + A} \qquad (8)$$

The electron-electron potential energy is subtracted because it is contained in the one-electron energies, ϵ, and, therefore, not to subtract it would be to count it twice. The He atom ionization energy is obtained by subtracting the ground-state energy for the atom from that of the ion.

The energy calculations depend on the value chosen for the truncation parameter, A. A value of 0.5 yielded the results summarized in Table 2. This value was chosen because it yielded a ground-state energy which was reasonably close to the correct value for the three-dimensional helium atom. In addition to the calculations outlined above, one may want to discuss with the students the relationships between the SCF one-electron energies, the ionization energy, and Koopmans' approximation (1).

Conclusion

We believe that the exercise outlined here is of the type that will help to "bridge the gap between the formalism of quantum theory and its computational aspects" (3). The calculations are conceptually and mathematically simple and insure that the student will get a clear picture of the SCF method. Also the exercise introduces students to important numerical techniques which they are unlikely to otherwise encounter in their first exposure to quantum chemistry. We also believe that this calculation serves as an important complement to the analytical SCF calculation of Snow and Bills (1).

A listing of the subroutines which are given to the students plus a listing of the complete program will be provided by the authors upon request.

Appendix A—Euler's Algorithm

If $Y(x_0)$ and $Y'(x_0)$ are known the value of $Y(x_0 + \Delta)$ can be determined approximately using the definition of the first derivative.

$$Y(x) = Y(x_0) + Y'(x_0)(x - x_0) \qquad \text{A1}$$

where $x = x_0 + \Delta$. Using the definition of the second derivative Schrödinger's eqn. (2) can be re-cast as

$$Y'(x) = Y'(x_0) - 2(2/x + E)Y(x)(x - x_0) \qquad \text{A2}$$

Equations A1 and A2 are employed in an iterative algorithm to find solutions (E and Y) for eqn. (2).

This solution is accomplished by using one boundary condition to make intelligent guesses for $Y(x_0)$ and $Y'(x_0)$. For He$^+$, for example, $Y(0) = 0$ because the potential energy goes to infinity at this point. $Y'(0)$ is positive and can be given some reasonable value, say 5. At this point a guess for the energy is made and the iterative process employed. Equation A1 is used to calculate $Y(x_0 + \Delta)$ and A2 is used to determine a new slope $Y'(x_0 + \Delta)$. Then A1 is used to calculate $Y(x_0 + 2\Delta)$ and A2 is used to get a new slope $Y'(x_0 + 2\Delta)$ and so on. If the wavefunction satisfies the second boundary condition, $Y(\infty) = 0$, the energy guess, E, represents the energy eigenvalue. If not, a new guess is made and the process described above is repeated. Figure 2 illustrates how the second boundary condition is used to bracket the correct energy eigenvalue.

In the calculations described here "infinity" was taken to be 5 bohr for He$^+$ and 7 bohr for He. The increment was set at 0.05 for He$^+$ and 0.1 for He. A BASIC program consisting of 18 steps was used to integrate eqn. (2).

The choice of increment is determined by three considerations: (1) algorithm accuracy (Euler's method is most accurate for small increments); (2) computer round-off error; and (3) computing time (6). Extremely small increments can lead to significant round-off error and consumption of large amounts of computer time. The increment of 0.1 for the He atom calculation was dictated by considerations of computing time. The numerical evaluation of the electron-electron potential energy integral, eqn. (6), is time consuming. Thus, a rather large increment was used to keep time demands within reason. In the He$^+$ ion calculation time is not a constraint and an increment of 0.05 was chosen because it gave reasonable accuracy.

Several algorithms, more accurate than Euler's method, have been discussed in the literature (8–11). The finite difference algorithm described by Bolemon (11) is particularly well-suited to SCF calculations.

Appendix B—Hartree's Approximation

Assuming that the two-electron wavefunction Y(1,2) can be written as a product of two normalized, one-electron wavefunctions, Y(1)Y(2), Schrödinger's eqn. (4) can be written as,

$$[\hat{T}_1 + \hat{T}_2 + \hat{V}_{N1} + \hat{V}_{N2} + \hat{V}_{12}]\, Y(1)Y(2) = E\, Y(1)Y(2) \qquad \text{C1}$$

Multiplication on the left by Y(2) followed by integration over the coordinates of electron 2 yields after rearrangement,

$$[\hat{T}_1 + \hat{V}_{N1} + \langle Y(2)\,|\,\hat{V}_{12}\,|\,Y(2)\rangle]Y(1) = [E - \langle T_2\rangle - \langle V_{N2}\rangle]\,Y(1) \qquad \text{C2}$$

where

$$\langle T_2\rangle = \int_0^\infty Y(2)\,|\,\hat{T}_2\,|\,Y(2)\,dx_2$$

$$\langle V_{N2}\rangle = \int_0^\infty Y(2)\,|\,\hat{V}_{N2}\,|\,Y(2)\,dx_2$$

Identifying $[E - \langle T_2\rangle - \langle V_{N2}\rangle]$ as the orbital energy of electron one, ϵ_1, yields Hartree's eqn. (5).

Appendix C—Initial Wavefunction Guess

The analytical solution for the one-dimensional hydrogen atom with $V = -1/x$ is $Y(x) = \sqrt{2}\, x\, \exp(-x)$. Since the electrons in the He atom will experience an effective nuclear charge less than +2 but greater than +1, a reasonable first guess for the wavefunction would be some normalized function intermediate between the H atom function and the He$^+$ ion function. We chose $Y(x) = \sqrt{13.5}\, x\, \exp(-1.5\,x)$.

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