

# Roothaan's Method in One-Dimension

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Quantum mechanical calculations in one dimension are useful because they are conceptually and mathematically simple. Because of these characteristics they facilitate the classroom development of fundamental principles. In this paper we describe a calculation on a one-dimensional model of the helium atom using Roothaan's (1) analytical procedure, which has been outlined recently by Snow and Bills (2).

The calculation presented here and a Hartree numerical SCF calculation on the same one-dimensional model (3) have been used as computer laboratory exercises to augment classroom work on quantum chemistry in a junior-senior level physical chemistry course. Undergraduates can perform every step of this calculation, from the evaluation of the matrix elements to the necessary computer programming. This provides them with the satisfaction of doing a SCF calculation in its entirety and prepares them for much of the literature in quantum chemistry.

The one-dimensional model employed is as follows: (1) an infinite potential barrier is present at the nucleus; (2) for positive values of  $x$ , the electron-nuclear potential energy is  $-2/x$ ; (3) the electron-electron potential energy,  $V_{12}$ , is described by a truncated coulombic interaction,  $1/(|x_1 - x_2| + A)$ . Truncated potentials similar to this one have been employed by others (4, 5) in the study of one-dimensional system. The truncation parameter prevents  $V_{12}$  from becoming infinite when  $x_1 = x_2$ . A value of 0.5 for  $A$  yields a reasonable value for the ground-state energy of the helium atom.

Schrödinger's equation for this model is, in atomic units,

$$[-\frac{1}{2}d^2/dx_1^2 - 2/x_1 - \frac{1}{2}d^2/dx_2^2 - 2/x_2 + 1/(|x_1 - x_2| + A) - E]\phi(1,2) = 0 \quad (1)$$

Assuming that  $\phi(1,2)$  can be written as a product of one-electron orbitals,  $\psi(1)\psi(2)$ , which in turn are linear combinations of atomic orbitals

$$\psi(1) = \sum c_j f_j(1) \quad (2)$$

and following the method outlined by Snow and Bills, yields the usual set of linear simultaneous equations

$$\sum_{j=1}^N c_j (h_{ij} + g_{ij} - \epsilon s_{ij}) = 0 \quad i = 1, 2, \dots \quad (3)$$

Non-trivial solutions are obtained for eqn. (3) only if the determinant of the coefficients is zero.

$$|h_{ij} + g_{ij} - \epsilon s_{ij}| = 0 \quad (4)$$

where

$$h_{ij} = \langle f_i | -\frac{1}{2}d^2/dx_1^2 - 2/x_1 | f_j \rangle \quad (5)$$

$$g_{ij} = \sum_k \sum_l c_k c_l \langle f_i f_j | \hat{V}_{12} | f_k f_l \rangle = \sum_k \sum_l c_k c_l \langle ij | kl \rangle \quad (6)$$

$$s_{ij} = \langle f_i | f_j \rangle \quad (7)$$

The basis set chosen for this calculation

$$\psi = \sum_{j=1}^N c_j (2j^{3/2}) x \exp(-jx) \quad (8)$$

is truncated after two terms giving

$$\psi = c_1 2x \exp(-x) + c_2 \sqrt{32} x \exp(-2x) \quad (9)$$

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This truncation can be rationalized on physical grounds. The first term on the right is the eigenfunction for the one-dimensional hydrogen atom ( $H = -\frac{1}{2}d^2/dx^2 - 1/x$ ). The exponential parameter is 1, reflecting the fact that the electron experiences a nuclear charge of +1. The second term is the eigenfunction for the one-dimensional helium ion ( $H = -\frac{1}{2}d^2/dx^2 - 2/x$ ). The exponential parameter is 2, reflecting the fact that the electron experiences a nuclear charge of +2. Due to shielding effects, it is reasonable to assume that the electrons in the atom will experience an effective charge between +1 and +2. This suggests that a linear combination of the H atom eigenfunction and the He<sup>+</sup> ion eigenfunction should serve as a good approximation for the wavefunction for the electrons in the He atom.

The  $h_{ij}$  and  $s_{ij}$  matrix elements are not difficult to evaluate. Using

$$\int_0^\infty x^n \exp(-ax) dx = n!/a^{n+1}$$

it will be easy for undergraduates to verify the following values:

$$h_{11} = 4 \int_0^\infty x e^{-x} |h| x e^{-x} dx = -1.5$$

$$h_{12} = h_{21} = -1.6761$$

$$h_{22} = -2.00$$

$$s_{11} = s_{22} = 1.00$$

$$s_{12} = s_{21} = 0.8381$$

Due to the presence of the truncation parameter in  $V_{12}$  the  $g_{ij}$  matrix elements must be evaluated numerically. Setting  $A$  equal to 0.5 and using Simpson's method, the following values are obtained for the integrals of eqn. (6):

$$\langle 11 | 11 \rangle = 0.902392 \quad \langle 11 | 22 \rangle = 0.913088$$

$$\langle 11 | 12 \rangle = 0.785299 \quad \langle 12 | 22 \rangle = 0.924484$$

$$\langle 12 | 12 \rangle = 0.750574 \quad \langle 22 | 22 \rangle = 1.18784$$

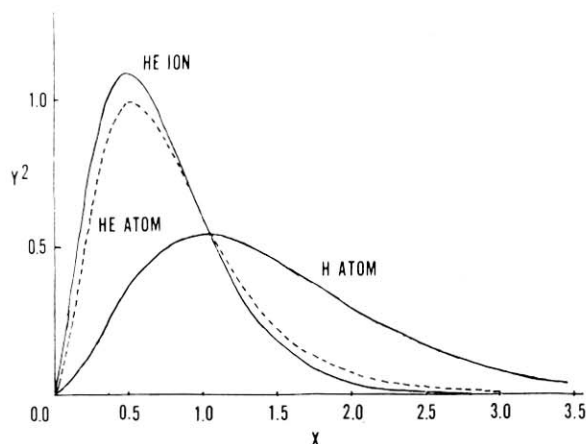
The students are asked to write a computer program to verify the values of these integrals.

From here the calculation proceeds as outlined by Snow and Bills. The table indicates that the calculation becomes self-consistent with respect to the coefficients and the orbital energy within 10 iterations when the initial values of the coefficients are  $c_1 = 0$  and  $c_2 = 1$ . The accompanying figure

Successive Values of the Coefficients and Energies <sup>a</sup> for Ten Iterations of Roothaan's Equation.

Iteration	$c_1$	$c_2$	$\epsilon$	$V_{ee}$	$E_{He}$
1	0.0000	1.0000	-0.8266	1.1529	-2.8266
2	0.2024	0.8242	-0.8556	1.1327	-2.8350
3	0.1527	0.8685	-0.8473	1.1390	-2.8357
4	0.1654	0.8573	-0.8493	1.1385	-2.8357
5	0.1622	0.8602	-0.8488	1.1380	-2.8357
6	0.1630	0.8594	-0.8489	1.1378	-2.8357
7	0.1628	0.8596	-0.8489	1.1378	-2.8357
8	0.1629	0.8596	-0.8489	1.1378	-2.8357
9	0.1628	0.8596	-0.8489	1.1378	-2.8357
10	0.1628	0.8596	-0.8489	1.1378	-2.8357

<sup>a</sup> Energy in hartrees.



Comparison of the He atom SCF wavefunction with  $f_1$  and  $f_2$  of the basis set.

compares the resulting SCF wavefunction with the basis set functions.

The ground-state energy of the 1-D He atom, which is given in the last column of the table, is equal to twice the one-electron orbital energy minus the electron-electron potential energy.

$$E_{\text{He(SCF)}} = 2\epsilon - V_{ee} = -2.8357 \text{ hartrees}$$

Because the  $h_{22}$  matrix element corresponds to the ground-state energy of the  $\text{He}^+$  ion, it is possible to calculate the ionization potential of the atom as follows,

$$\begin{aligned} I. P. &= E_{\text{He}^+} - E_{\text{He(SCF)}} \\ I. P. &= -2.00 - (-2.8357) = 0.8357 \text{ hartrees} \end{aligned}$$

The initial values chosen for the coefficients were  $c_1 = 0.0$  and  $c_2 = 1.0$ . This amounts to trying to place both electrons in an  $\text{He}^+$  ion orbital. The optimum values of the coefficients are  $c_1 = 0.1628$  and  $c_2 = 0.8596$ , essentially making the orbital larger and reducing the electron-electron potential energy.

This calculation also can be used to demonstrate the difficulty with which even modest improvements in the calculated ground-state energy are obtained. For example, using a trial wavefunction consisting of the first three terms of the basis set (8) yields a ground-state energy of  $-2.8413$ . Compared with the two-term calculation this represents an improvement of only 0.2% in the total energy. This improvement is obtained at substantially greater computational effort. For the two-term wavefunction it is necessary to evaluate six electron-electron repulsion integrals, while for the three-term wave-

function 15 additional electron-electron integrals are required. The additional computational effort is commonly justified on the basis that small improvements in ground-state energies often yield large improvements in the determination of experimentally verifiable quantities such as the ionization potential. For instance, here a 0.2% change in total energy led to a 0.7% improvement in the ionization energy.

Listings of sample programs used in this exercise are available upon request from the authors.

## Appendix

The following derivation of eqn. (3) has been used to introduce Roothaan's method to the students. Using a shorthand operator notation and assuming that  $\phi(1,2)$  can be factored into a product of one-electron orbitals,  $\psi(1)\psi(2)$ , allows equation (1) to be written as

$$(\hat{T}_1 + \hat{V}_{N1} + \hat{T}_2 + \hat{V}_{N2} + \hat{V}_{12})\psi(1)\psi(2) = E\psi(1)\psi(2) \quad (10)$$

Multiplication of (10) on the left by  $\psi(2)$  followed by integration over the coordinate of electron 2 yields after rearrangement

$$(\hat{T}_1 + \hat{V}_{N1} + \langle \psi(2) | \hat{V}_{12} | \psi(2) \rangle)\psi(1) = (E - \langle T_2 \rangle - \langle V_{N2} \rangle)\psi(1) \quad (11)$$

where

$$\begin{aligned} \langle T_2 \rangle &= \langle \psi(2) | \hat{T}_2 | \psi(2) \rangle \\ \langle V_{N2} \rangle &= \langle \psi(2) | \hat{V}_{N2} | \psi(2) \rangle \end{aligned}$$

Recognizing  $(E - \langle T_2 \rangle - \langle V_{N2} \rangle)$  as the orbital energy of electron 1 yields,

$$(\hat{T}_1 + \hat{V}_{N1} + \langle \psi(2) | \hat{V}_{12} | \psi(2) \rangle)\psi(1) = \epsilon_1\psi(1) \quad (12)$$

This is generally referred to as Hartree's equation and the energy operator on the left is the one-electron effective Hamiltonian,  $H_1^{\text{eff}}$ . A similar Hartree equation can be written for electron 2.

Roothaan solved eqn. (12) by expressing  $\psi(1)$  as a linear combination in a complete basis set of functions represented by eqn. (2). Substitution of eqn. (2) into eqn. (12) followed by multiplication on the left by each member of the basis set in turn and integration over the coordinate of electron 1 yields eqn. (3).

## Literature Cited

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