Restricted Hartree-Fock SCF Calculations Using Microsoft Excel

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An Excel spreadsheet that calculates Restricted Hartree-Fock Self-Consistent Field energies for H_2, HeH^+, or He_2^{2+} using the STO-nG (n = 1,2,3) basis sets is presented. All calculations are carried out using standard Excel cell formulas to facilitate understanding of the SCF method. The student can input a custom contracted minimal basis set with up to three primitive Gaussian functions. Gaussian exponents can also be scaled by the user, and the molecular orbitals can be plotted during the SCF cycle. The initial molecular orbital guess can be input by the student to demonstrate accelerated convergence with a better initial guess of the wave function.

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Introduction

The power and availability of high-performance computers is increasing at such a high rate that computational chemistry calculations are becoming increasingly common. Accordingly, the study of the theoretical foundations of computational chemistry is no longer reserved exclusively for graduate school. Today, many undergraduate institutions routinely offer instruction in computational chemistry using programs like Spartan,(*1*) HyperChem,(*2*) Gaussian(*3*) and GAMESS.(*4*) While these programs and others offer graphical user interfaces to facilitate the *execution* of quantum chemical calculations, there is a real danger that the calculations themselves will be reduced to a 'black box' exercise. Advanced courses in computational chemistry will cover the derivation of the restricted Hartree-Fock (RHF) integro-differential equations, and discuss the idea of solving these equations by constructing molecular orbitals (MOs) as a linear combination of atomic orbitals (LCAO), where the atomic orbitals are commonly defined by contracted Gaussian basis sets. Within this framework, the resulting equations must be solved iteratively using the self-consisted field (SCF) method. However, the

details of such a computation are far too extensive to be realistically covered for even the simplest two-electron diatomic molecule. To date, very useful programs have been created to illustrate the basic nature of the SCF method: Hoffman(*5*) has created a spreadsheet that illustrates the Hartree-Fock SCF procedure for an atomic, two-electron system, but outside of the commonly used LCAO framework. Rioux(*6*) has shown how to model two-electron SCF calculation on helium atom within the LCAO-MO formalism using Mathcad. This article presents a full RHF-SCF calculation for a two-electron, two-center molecular system (H_2, HeH^+, or $HeHe^{2+}$) using an Excel spreadsheet. Further, it makes use of contracted Gaussian minimal basis sets (STO-1G, STO-2G, or STO-3G). Contracted Gaussian basis sets are standard in nearly all *ab initio* computational chemistry calculations, but their actual, practical usage can be difficult to demonstrate in an understandable way. In addition, performing SCF calculations on a diatomic molecule opens up the very important notion of the potential energy surface (PES) and the practical application of the Born-Oppenheimer approximation.

The purpose of this project is to create a learning tool that can be understood and used by advanced undergraduate and graduate students. While programs like Mathcad and Mathematica are very powerful and can present SCF calculations elegantly, we have chosen to perform all the calculations in Microsoft Excel. Almost all undergraduate students are intimately familiar with spreadsheets, and the visual nature of the sheet makes it much easier to see how a particular value is calculated. The spreadsheet allows all calculations to be explicitly shown rather than hidden in code, and the progression of the calculation can be viewed step by step using the built-in macro functionality in Excel. Macros are used to present and clarify data, but *all* calculations are carried out using standard Excel cell formulas.

Theory

The detailed derivation of the restricted Hartree-Fock self-consistent field method is a standard topic in most advanced undergraduate or graduate level quantum chemistry courses. A particularly good source, and common graduate textbook, is by Szabo and Ostlund.(7) For the benefit of the student and the instructor, the actual working equations will be presented here, with explicit references (in brackets) to the analogous numbered equations in Szabo and Ostlund. (To our knowledge, many of these full, working equations are presented no where else in the literature.)

The Hartree-Fock equations are a set of integro-differential equations [3.132]:

$$\hat{f}(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = \varepsilon_i\psi_i(\mathbf{r}_1) \qquad i = 1,2,3,\cdots,K \qquad (1)$$

where $\hat{f}(\mathbf{r}_1)$ is the Fock operator, which is a function of the coordinates of electron 1 ($\mathbf{r}_1$), ψ_i is one of the set of K molecular orbitals for the system, and ε_i is the energy of the ith molecular orbital. Since no efficient numerical methods are known for solving these equations, the most common computational technique in *ab initio* quantum chemistry is to introduce a linear combination of atomic orbitals (LCAO) to construct molecular orbitals (ψ_i) [3.133]:

$$\psi_i = \sum_{\mu=1}^{K} C_{\mu i}\phi_\mu \qquad i = 1,2,3,\cdots,K \qquad (2)$$

Here, the $C_{\mu i}$ are a set of coefficients that must be determined by the SCF procedure. In practice, the sets of atomic orbitals (AOs – ϕ_μ) used to construct MOs are given by defined Gaussian basis sets, of which there are many varieties.(8) To increase computational efficiency,

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the great majority of basis sets are contracted, meaning that each AO is itself a linear combination of P primitive Gaussian functions [3.212]:

$$\phi_\mu(\mathbf{r}_1) = \sum_{p=1}^{P} d_{p\mu} \left(\frac{2\alpha_{p\mu}}{\pi} \right)^{3/4} e^{-\alpha_{p\mu}|\mathbf{r}_1 - \mathbf{R}_\mu|^2} \tag{3}$$

In Eq. (3), the "$(\mathbf{r}_1)$" refers to the coordinates of electron 1, given explicitly by the vector $\mathbf{r}_1$. These coordinates will become the integration variables for the one-electron integrals that follow. The $d_{p\mu}$ are contraction coefficients that are defined for a given basis set, and $\mathbf{R}_\mu$ is the point where ϕ_μ is centered. One of the major computational advantages of contracted basis sets is the fact that the product of two Gaussian functions is another Gaussian. For example [3.208]:

$$\phi_\mu(1)\phi_\nu(1) = \left[\sum_{p=1}^{P} d_{p\mu} \left(\frac{2\alpha_{p\mu}}{\pi} \right)^{3/4} e^{-\alpha_{p\mu}|\mathbf{r}_1 - \mathbf{R}_\mu|^2} \right] \left[\sum_{q=1}^{Q} d_{q\nu} \left(\frac{2\alpha_{q\nu}}{\pi} \right)^{3/4} e^{-\alpha_{q\nu}|\mathbf{r}_1 - \mathbf{R}_\nu|^2} \right]$$

$$= \sum_{p=1}^{P} \sum_{q=1}^{Q} \left[\frac{2\alpha_{p\mu}\alpha_{q\nu}}{\pi(\alpha_{p\mu} + \alpha_{q\nu})} \right]^{3/4} e^{-\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu} + \alpha_{q\nu}} R_{\mu\nu}^2} \left[\frac{2(\alpha_{p\mu} + \alpha_{q\nu})}{\pi} \right]^{3/4} e^{-(\alpha_{p\mu} + \alpha_{q\nu})|\mathbf{r}_1 - \mathbf{R}_\rho|^2} \tag{4}$$

where [3.210]

$$\mathbf{R}_\rho = \frac{\alpha_{p\mu}\mathbf{R}_\mu + \alpha_{q\nu}\mathbf{R}_\nu}{\alpha_{p\mu} + \alpha_{q\nu}} \tag{5}$$

$R_{\mu\nu}$ is the distance between the two nuclei, and can be found using the formula [1.5]:

$$R_{\mu\nu} = |\mathbf{R}_\mu - \mathbf{R}_\nu|$$

$$= \sqrt{(R_{\mu,x} - R_{\nu,x})^2 + (R_{\mu,y} - R_{\nu,y})^2 + (R_{\mu,z} - R_{\nu,z})^2} \tag{6}$$

where, for example, $R_{\mu,x}$ is the x Cartesian coordinate for point where ϕ_μ is centered.

By introducing the basis set, Eq. (2), into Eq. (1), one arrives at the Roothaan equations [3.193]:

$$\mathbf{FC} = \mathbf{SC}\varepsilon \tag{7}$$

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Here, **C** is the $K \times K$ matrix of LCAO coefficients [3.140], and $\boldsymbol{\varepsilon}$ is a diagonal matrix of the MO energies [3.141].

S is the overlap matrix, which results from the fact that most basis sets are not constructed to be orthogonal. (If the basis set was orthogonal, then **S** would be equal to the unit matrix, **1**.) The elements of **S** are given by [3.136 and A.9]

$$S_{\mu\nu} = \int d\mathbf{r}_1 \, \phi_\mu^*(1) \, \phi_\nu(1)$$
$$= \sum_{p=1}^{L} \sum_{q=1}^{M} d_{p\mu} d_{q\nu} \left(\frac{\pi}{\alpha_{p\mu} + \alpha_{q\nu}} \right)^{3/2} e^{-\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}} R_{\mu\nu}^2} \tag{8}$$

F is the Fock matrix, whose elements are given by [3.154]:

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + G_{\mu\nu} \tag{9}$$

The Fock matrix is the sum of two terms: the core-Hamiltonian matrix and the two-electron integral matrix. The core-Hamiltonian matrix is constructed from one-electron kinetic energy and potential energy integrals [3.153]:

$$H_{\mu\nu}^{\text{core}} = T_{\mu\nu} + V_{\mu\nu}^{\text{nucl}} \tag{10}$$

where [3.151 and A.11]:

$$T_{\mu\nu} = -\tfrac{1}{2} \int d\mathbf{r}_1 \, \phi_\mu^*(1) \, \nabla_1^2 \, \phi_\nu(1)$$
$$= \sum_{p=1}^{L} \sum_{q=1}^{M} d_{p\mu} d_{q\nu} \left(\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}} \right) \left(3 - \frac{2\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}} R_{\mu\nu}^2 \right) \left(\frac{\pi}{\alpha_{p\mu}+\alpha_{q\nu}} \right)^{3/2} e^{-\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}} R_{\mu\nu}^2} \tag{11}$$

and [3.152 and A.33]:

$$V_{\mu\nu}^{\text{nucl}} = -\sum_{A=1}^{N} \int d\mathbf{r}_1 \, \phi_\mu^*(1) \left[\frac{Z_A}{|\mathbf{r}_1 - \mathbf{R}_\mu|} \right] \phi_\nu(1)$$
$$= -\sum_{A=1}^{N} \sum_{p=1}^{L} \sum_{q=1}^{M} \left(\frac{d_{p\mu} d_{q\nu} \pi Z_A}{\alpha_{p\mu}+\alpha_{q\nu}} \right) e^{-\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}} R_{\mu\nu}^2} \left[\frac{\pi}{(\alpha_{p\mu}+\alpha_{q\nu}) R_{\mu\rho}^2} \right]^{1/2} erf\left[\sqrt{\alpha_{p\mu}+\alpha_{q\nu}} R_{\mu\rho} \right] \tag{12}$$

The second term in the Fock matrix is the two-electron integral matrix, defined as [3.154]:

$$G_{\mu\nu} = \sum_{\lambda=1}^{K}\sum_{\sigma=1}^{K} P_{\lambda\sigma}\left[(\mu\nu|\sigma\lambda) - \tfrac{1}{2}(\mu\lambda|\sigma\nu)\right] \tag{13}$$

where the density matrix, $P_{\lambda\sigma}$, is defined for a closed-shell wave function as [3.145]:

$$P_{\lambda\sigma} = 2\sum_{a=1}^{N_e/2} C_{\lambda a} C_{\sigma a}^{*} \tag{14}$$

and the two-electron integrals are given by [3.155 and A.41]:

$$(\mu\nu|\sigma\lambda) = \iint d\mathbf{r}_1 d\mathbf{r}_2\, \phi_\mu^{*}(1)\, \phi_\nu(1)\left(\frac{1}{r_{12}}\right)\phi_\sigma^{*}(2)\,\phi_\lambda(2)$$

$$= \sum_{p=1}^{P}\sum_{q=1}^{Q}\sum_{r=1}^{R}\sum_{s=1}^{S}\left\{ \begin{array}{l} d_{p\mu} d_{q\nu} d_{r\sigma} d_{s\lambda}\, \dfrac{\pi^{5/2}}{\left(\alpha_{p\mu}+\alpha_{q\nu}\right)\left(\alpha_{r\sigma}+\alpha_{s\lambda}\right)\sqrt{\alpha_{p\mu}+\alpha_{q\nu}+\alpha_{r\sigma}+\alpha_{s\lambda}}} \\[2ex] \times\; e^{-\frac{\alpha_{p\mu}\alpha_{q\nu}}{\alpha_{p\mu}+\alpha_{q\nu}}R_{\mu\nu}^2 - \frac{\alpha_{r\sigma}\alpha_{s\lambda}}{\alpha_{r\sigma}+\alpha_{s\lambda}}R_{\sigma\lambda}^2}\;R_{\rho\theta}\sqrt{\dfrac{\pi\left(\alpha_{p\mu}+\alpha_{q\nu}+\alpha_{r\sigma}+\alpha_{s\lambda}\right)}{\left(\alpha_{p\mu}+\alpha_{q\nu}\right)\left(\alpha_{r\sigma}+\alpha_{s\lambda}\right)}} \\[2ex] \times\; erf\left[\sqrt{\dfrac{\left(\alpha_{p\mu}+\alpha_{q\nu}\right)\left(\alpha_{r\sigma}+\alpha_{s\lambda}\right)}{\left(\alpha_{p\mu}+\alpha_{q\nu}+\alpha_{r\sigma}+\alpha_{s\lambda}\right)}}\,R_{\rho\theta}\right] \end{array}\right\} \tag{15}$$

In Eq. (15), "erf" is the error function, which is a standard formula in Excel once the Analysis ToolPak has been turned on. (Tools → Add Ins…) $R_{\rho\theta}$ is the distance between point $\mathbf{R}_\rho$, given in Eq. (5), and point $\mathbf{R}_\theta$, defined by

$$\mathbf{R}_\theta = \frac{\alpha_{r\sigma}\mathbf{R}_\sigma + \alpha_{s\lambda}\mathbf{R}_\lambda}{\alpha_{r\sigma}+\alpha_{s\lambda}} \tag{16}$$

By considering Eqs. (9), (13), and (14), it is clear that the Fock matrix, $\mathbf{F}$, depends on the LCAO coefficients, $\mathbf{C}$. However, as shown in the SCF procedure below, the coefficients are calculated from a given Fock matrix. This is the essence of the SCF procedure: make a guess at $\mathbf{C}$, calculate a Fock matrix, use that $\mathbf{F}$ to recalculate $\mathbf{C}$, and repeat until self-consistency is

reached. The total energy can be used as a criterion for self-consistency, since it can be calculated at any point during the iterative process using [3.184]:

$$E = \frac{1}{2} \sum_{\mu=1}^{K} \sum_{\nu=1}^{K} P_{\mu\nu} \left(H_{\mu\nu}^{\text{core}} + F_{\mu\nu} \right) \tag{17}$$

At any point during the iterative process, a particular molecular orbital can be plotted by combining Eqs. (2) and (3):

$$\psi_i(0,0,z) = \sum_{p=1}^{P} \sum_{\mu=1}^{K} C_{\mu i} d_{p\mu} \left(\frac{2\alpha_{p\mu}}{\pi} \right)^{3/4} e^{-\alpha_{p\mu} \left(r_{1,z} - R_{\mu,z} \right)^2} \tag{18}$$

Eq. (18) will give the value of the wave function along the z-axis, which is particularly useful if the z-axis corresponds to the internuclear axis.

The SCF Procedure

The SCF procedure, following Szabo and Ostlund(9), and as implemented here, has the following steps:

1. Specify the molecule (H_2, HeH$^+$, or HeHe^{2+}) by giving the Cartesian coordinates of each atom. Specify the basis set (STO-1G, STO-2G, or STO-3G). In practice, this means specifying values for the contraction coefficients and exponents α in Eq. (3).

2. Calculate the one- and two-electron integrals: Eqs. (8), (10), and (15).

3. Diagonalize $\mathbf{S}$ [Eq. (8)] to form [3.167] $\mathbf{X} = \mathbf{S}^{-1/2}$. $\mathbf{X}$ is used to orthogonalize the basis set such that the Roothaan equations can be written as [3.178] $\mathbf{F'C'} = \mathbf{C'\varepsilon}$, where [3.177] $\mathbf{F'} = \mathbf{X}^\dagger \mathbf{F X}$ and [3.174] $\mathbf{C} = \mathbf{XC'}$. For the two-electron systems we are considering here, $\mathbf{S}$ will always be a 2×2 Hermitian matrix, and can be diagonalized using the following unitary matrix [1.104]:

$$\mathbf{U} = \begin{pmatrix} \cos\theta & \sin\theta \\ \sin\theta & -\cos\theta \end{pmatrix} \tag{19}$$

where [1.105]

$$\theta = \frac{1}{2}\tan^{-1}\left(\frac{2S_{12}}{S_{11}-S_{22}}\right) \tag{20}$$

The eigenvalues of $\mathbf{S}$ are given by [1.106]

$$s_1 = S_{11}\cos^2\theta + S_{22}\sin^2\theta + S_{12}\sin(2\theta)$$
$$s_2 = S_{11}\cos^2\theta + S_{22}\sin^2\theta - S_{12}\sin(2\theta) \tag{21}$$

Note that Eqs. (20) and (21) are applicable to any 2×2 Hermitian matrix, not just $\mathbf{S}$. (E.g. $\mathbf{H}^{\text{core}}$, $\mathbf{F}$.)

In practice, a canonical orthogonalization is used, wherein the $\mathbf{X}$ matrix is defined as [3.169]

$$\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2} \tag{22}$$

In the case where $\mathbf{S}$ has unity along the diagonal, this reduces to

$$\mathbf{X} = \begin{pmatrix} \dfrac{1}{\sqrt{2(1+S_{12})}} & \dfrac{1}{\sqrt{2(1-S_{12})}} \\ \dfrac{1}{\sqrt{2(1+S_{12})}} & -\dfrac{1}{\sqrt{2(1-S_{12})}} \end{pmatrix} \tag{23}$$

4. Diagonalize the $\mathbf{H}^{\text{core}}$ matrix, Eq. (10), using Eqs. (20)-(21) to obtain an initial guess for $\mathbf{P}$. The initial guess for $\mathbf{P}$ is the unitary matrix that diagonalizes $\mathbf{H}^{\text{core}}$. Since $\mathbf{P}$ is constructed from $\mathbf{C}$, this is equivalent to guessing the MO coefficients $\mathbf{C}$. (Alternatively, the student can provide their own guess for $\mathbf{P}$. This option allows for the demonstration that SCF convergence isn't guaranteed, and that convergence can be improved by a better initial guess.)

5. Calculate $\mathbf{G}$, Eq. (13), from the density matrix and the previously calculated two-electron integrals, Eq. (15).

6. Calculate the Fock matrix using Eq. (9).

7. Calculate the transformed Fock matrix: $\mathbf{F}' = \mathbf{X}^{\dagger}\mathbf{F}\mathbf{X}$ [3.177].

8. Diagonalize $\mathbf{F'}$ to find $\mathbf{C'}$ and $\boldsymbol{\varepsilon}$: $\mathbf{C'^\dagger F' C'} = \boldsymbol{\varepsilon}$, where $\boldsymbol{\varepsilon}$ is a diagonal matrix of the MO energies, Eq. (1).

9. Back-transform $\mathbf{C'}$ to find $\mathbf{C}$: $\mathbf{C} = \mathbf{XC'}$ [3.174].

10. Using the new $\mathbf{C}$, recalculate the density matrix using Eq. (14).

11. Has the total energy, Eq. (17), converged? If not, go back to step 5.

12. Repeat until the change in the total energy from iteration to iteration is below a chosen threshold.

Spreadsheet Features

The spreadsheet is designed to provide easy user interface while maintaining the user-friendly and transparent characteristics of Excel. There are two main features that lead the user through the SCF calculations. The first is the actual SCF calculation itself. On the front page, the user inputs the system for which the energy is to be calculated (step 1 in the SCF procedure, above). The one-electron integrals are immediately calculated using the basic Excel functions on one of two sub-worksheets. One sub-worksheet corresponds to a particular choice of basis set (STO-1G, STO-2G, or STO-3G). The user then clicks the *Iterate* button and the first iteration of the calculation is completed, returning the electronic energy and the new density matrix. The user continues the iterative process by clicking *Iterate* until the energy converges to within a selected convergence threshold. At this point, the total energy of the system is displayed as well as the electronic and nuclear energies, the final density matrix, and the final MO coefficients.

The second feature of the spreadsheet is a walkthrough of one iteration of the SCF cycle. Using macros, the matrices and corresponding explanations for each step of the SCF cycle are laid out on the front page. With each click of the button, the next step of the procedure is

displayed. This feature not only allows the user to read about the procedure, but also provides for an interactive exploration by the student.

The calculations involved in the SCF procedure are entirely computed with basic built-in Excel functions. No calculations take place within macros. At all times, the student can trace the calculations of each cell and view the formula associated. The macros are employed exclusively for a more user-friendly and attractive way of presenting information.

Applications and Extensions

The spreadsheet can be further utilized by constructing a potential energy surface (PES). This is a concrete application of the Born-Oppenheimer approximation, where the electronic energy of the molecule is calculated as a function of bond distance, as shown in Fig. 1
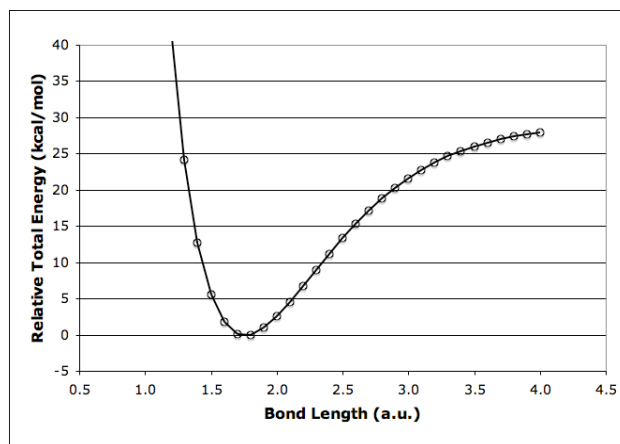

Figure 1. The potential energy surface (PES) for HeH$^+$. Energies are relative to the minimum, and are calculated at intervals of 0.1 Bohr (a.u.).

The diatomic PES is the starting point for models of molecular vibrations, most notably the harmonic oscillator. It should be noted here that the spreadsheet contains no tools to assist

convergence of the RHF wave function, and there is no guarantee that it will converge;[10] indeed, convergence depends greatly on the suitability of the initial guess, especially as the bond length becomes large. However, this apparent drawback provides a pedagogical opportunity: if the student uses the converged wave function at a smaller bond distance as the initial guess for a wave function at a larger bond distance, convergence can be achieved, whereas it was not possible with the default guess (the diagonalization of $\mathbf{H}^{\text{core}}$).

Given a PES for a diatomic, it is straightforward to calculate a dissociation energy for the molecule. However, it is well known that the RHF method usually predicts the wrong dissociation limit[11] because it forces the electrons to remain paired, whereas most molecules dissociate homolytically in the gas phase. The simplest diatomic for which RHF predicts the correct dissociation limit is HeH$^+$, since this molecule dissociates into helium atom and a proton. This molecule can be analyzed using the spreadsheet, and there is an extensive discussion of this calculation in Szabo and Ostlund.[12]

While many molecular properties are built into the spreadsheet, many more can be calculated from the spreadsheet data by the student. For example, using Eqs. (2) and (3), it can be shown that the condition for orthonormality of the MOs is given by

$$\int \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1)\,d\mathbf{r}_1 = \delta_{ij} = \sum_{\mu=1}^{K}\sum_{\nu=1}^{K} C_{\mu i}^* C_{\nu j} S_{\mu\nu} \tag{24}$$

where δ_{ij} is the Kronecker delta. The $\mathbf{C}$ and $\mathbf{S}$ matrices are standard output from the spreadsheet, and can be used with the above equation to demonstrate orthonormality explicitly. Given the density matrix $\mathbf{P}$ and the overlap matrix $\mathbf{S}$, a Mullikan population analysis can be performed using [3.196]

$$q_A = Z_A - \sum_{\mu \in A} (\mathbf{PS})_{\mu\mu} \tag{25}$$

Here, q_A is the Mullikan charge on nucleus A, Z_A is the atomic number of nucleus A, and the sum is over all atomic orbitals centered on $\mathbf{R}_A$. The standard matrix multiply function (MMULT) in Excel makes this calculation particularly straightforward. Similarly, the Löwdin population analysis can be calculated [3.201]

$$q_A = Z_A - \sum_{\mu \in A} \left(\mathbf{S}^{1/2} \mathbf{P} \mathbf{S}^{1/2}\right)_{\mu\mu} \tag{26}$$

The charge density is the probability of finding an electron in a given region of space, and can be plotted in a manner similar to the wave function itself using [3.193]:

$$\rho(\mathbf{r}_1) = \sum_{\nu=1}^{K} \sum_{\mu=1}^{K} \sum_{p=1}^{P} \sum_{q=1}^{Q} P_{\mu\nu} d_{p\mu} d_{q\nu} \left(\frac{2\alpha_{p\mu}}{\pi}\right)^{3/4} \left(\frac{2\alpha_{q\nu}}{\pi}\right)^{3/4} e^{-\alpha_{p\mu}|\mathbf{r}_1 - \mathbf{R}_\mu|^2} e^{-\alpha_{q\nu}|\mathbf{r}_1 - \mathbf{R}_\nu|^2} \tag{27}$$

Finally, the spreadsheet could simply be used as a model for the student to write their own RHF-SCF spreadsheet using the equations presented here.

Conclusions

Working equations and a full outline of the RHF-SCF procedure with minimal contracted Gaussian basis sets has been presented, along with an Excel spreadsheet that carries out the calculation for H_2, HeH^+, or He_2^{2+}. This spreadsheet can be used to take the mystery out of a typical *ab initio* SCF calculation by explicitly showing all the relevant operations using standard Excel cell formulas. Macros are used to present and clarify data, but not to calculate any quantities.

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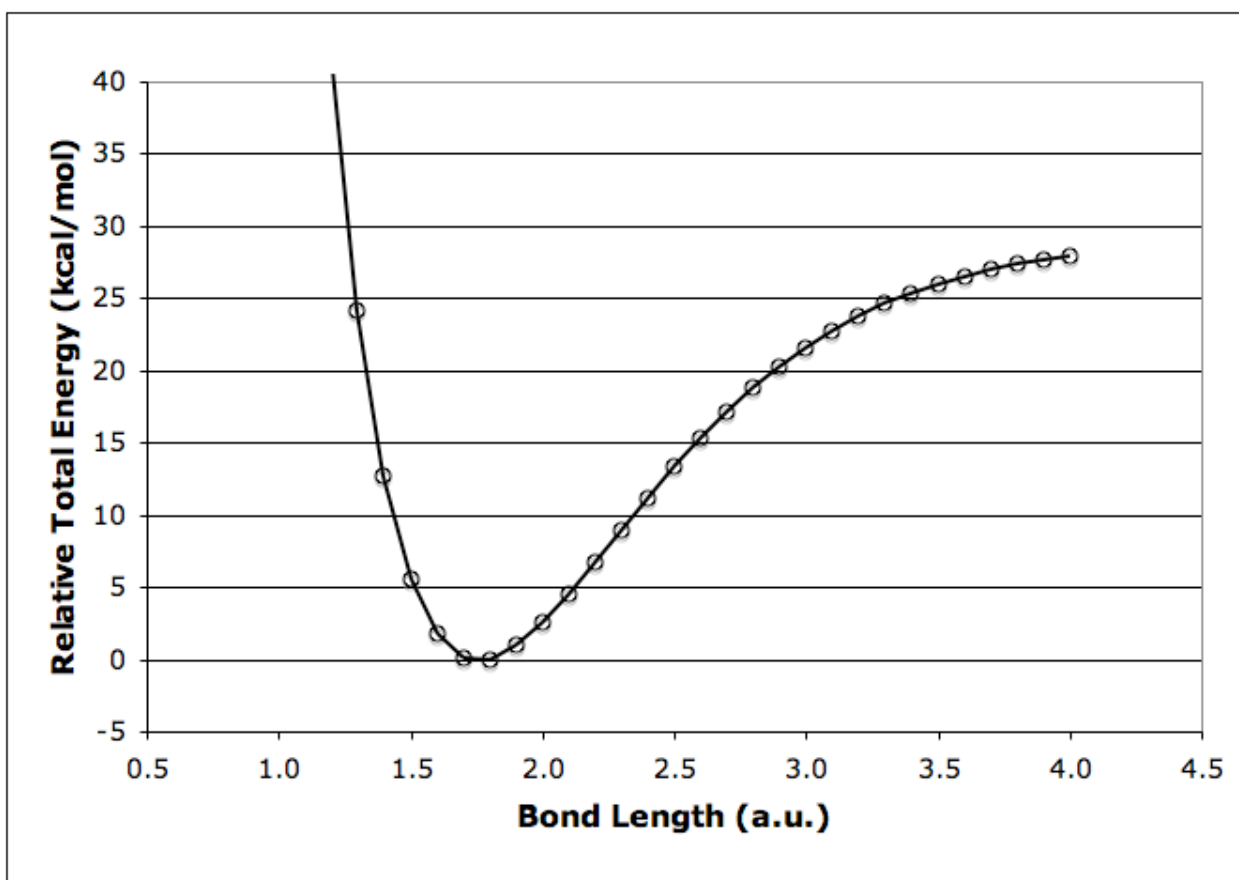
Figure 1

Figure Caption

Figure 1. The potential energy surface (PES) for HeH$^+$. Energies are relative to the minimum,

and are calculated at intervals of 0.1 Bohr (a.u.).