Documentation for

Restricted Hartree-Fock SCF Calculations Using Microsoft Excel

Taylor R. Page, Cortney A. Boots, and Mark A. Freitag

Background

All of the mathematical background is summarized in the accompanying print submission (Boots, Page, and Freitag, "Restricted Hartree-Fock SCF Calculations Using Microsoft Excel") to the *Journal of Chemical Education.* This paper is based on the theoretical background found in Szabo & Ostlund's *Modern Quantum Chemistry.*[1]

The spreadsheet has been tested on the Microsoft Office XP, Office 2003, and Microsoft Excel 2004 for Mac. The specific instructions here will refer to Excel 2004 for Mac. Macros are used to copy data and highlight relevant parts of the SCF calculation, and so they should be enabled when the spreadsheet is opened by clicking *Enable Macros* on the warning window that typically opens with the spreadsheet.

In addition, the spreadsheet makes use of the error function. To enable this function in Excel, go to the *Tools* menu, click on *Add Ins…*, and then ensure that the *Analysis ToolPak* is checked in the resulting window. If the *Analysis ToolPak* is not available, the user will have to install it from the original Excel installation disks.

Instructions for Use

All of the following instructions refer to the control and results panel on the *Front* worksheet:

I. To Perform a Basic SCF Calculation

- Use the pull down menu to the right of *Choose basis set* (D5): to select the STO-1G, STO-2G, or STO-3G basis set. The selected contraction coefficients and Gaussian exponents will be automatically updated in the *Custom Basis Set Entry* box (J3:M16). (The *Show All* option in the pull-down menu refers to the individual STO-1G, STO-2G, and STO-3G worksheets. This option would be used to demonstrate the exponential increase in computational work that occurs as the basis set is increased, and should not normally be selected.)

- Choose the first atom to be hydrogen or helium using the pull-down menu under *Atom* (B8). Set the *x*-, *y*-, and *z*-coordinates for the first atom by entering the coordinates in cells C8 to E8. The distance units are Bohr (a.u.).

- Choose the second atom to be hydrogen or helium using the pull-down menu under *Atom* (B9). Set the *x*-, *y*-, and *z*-coordinates for the first atom by entering the coordinates in cells C9 to E9. The distance units are Bohr (a.u.).

- Set the convergence energy threshold in cell D11. When the change in the electronic energy is less than this value, the SCF calculation is considered converged. A threshold of 1×10^{-6} a.u. (Hartree) is adequate for the purposes of this spreadsheet.

- Choose which wave functions you wish to plot during the SCF procedure in the *Molecular Orbitals* box (N4:P16). Ψ_1 is the highest occupied molecular orbital (HOMO), and Ψ_2 is the lowest unoccupied molecular orbital (LUMO). Checking the box to the left of each wave function will cause it to be plotted. One can also choose to plot the wave function squared. The color key for each wave function is given to the right, along with the energy of each orbital in atomic units (Hartrees). The magnitude of the normalized wave function (or the wave function squared) along the *z*-axis is plotted. To plot the wave function along another axis, change the orientation of the diatomic in cells C8:E9. The wave function being plotted can be changed at any time by clicking or unclicking the appropriate box.

- To enter an initial guess for the molecular wave function, enter the MO coefficients C_{11} (cell G11), C_{12} (cell H11), C_{21} (cell G12), and C_{22} (cell H12). The MO coefficients are related to the MOs according to the following equations:

$$\psi_1 = C_{11}\phi_1 + C_{21}\phi_2$$
$$\psi_2 = C_{12}\phi_1 + C_{22}\phi_2$$

where ϕ_1 and ϕ_2 are the atomic orbitals defined by the chosen STO-*n*G minimal basis set. (See Eqs. (2-3) in the accompanying *JCE* paper.) If these cells are left blank, the spreadsheet will calculate an initial guess by diagonalizing the core Hamiltonian. (See Eq. (12) in the accompanying *JCE* paper.)

- Click the green *Iterate* button. The total electronic energy, the density matrix (**P**), and MO coefficients (**C**) are updated along with any selected wave function plots.

- Click the green *Iterate* button again. The new electronic energy, density matrix and MO coefficient matrix is given, along with the change in electronic energy from the previous iteration.

- Continue clicking the green *Iterate* button until the wave function converges. When this happens, the *Iterate* button will turn red and will read *Converged*. The final electronic, nuclear, and total energies will be displayed. [There is no guarantee of convergence in the

SCF method, but this can be used as a 'teaching moment' to discuss the various convergence accelerators and enhancers that are available; e.g. damping, direct inversion of the iterative subspace (DIIS), second-order SCF (SOSCF), etc. See 'Teaching Tips' below.]

- When all relevant data has been observed and/or recorded, click the *Reset* button to return the spreadsheet to its original starting point.

II. To Perform a Detailed SCF Calculation

- Follow the instructions given above for a **basic** SCF calculation, but instead of clicking the green *Iterate* button, click the orange *Show Iteration Details* button. The spreadsheet will walk the user through the steps of one SCF iteration cycle. Explanations are given on the spreadsheet, and further information can be found in *The SCF Procedure* section of the accompanying *JCE* paper. Note that all cells on the *Calculations* and *STO-nG* worksheets that have a red triangle in the upper right-hand corner are additional comments about the calculation. Put the cursor over the red triangle to view the comments. Numbered equations in these comments refer to equations in the accompanying *JCE* paper.

III. To Modify the Basis Set

There are two ways to modify the standard built-in STO-nG basis sets: scale the Gaussian exponents, and explicitly change the contraction coefficients and Gaussian exponents to any desired value.

- By default, the spreadsheet uses the standard scaling factors of $\zeta = 1.24$ for hydrogen and $\zeta = 1.69$ for helium. These values return the standard STO-nG basis sets that are used by GAMESS. To change the scaling factor ζ, click the box to the right of *Change the Default ζ*. Then, enter the values you wish to use in cells H8 and H9 for atoms 1 and 2, respectively.

- Checking the box to the right of *Apply Custom Basis Set* will allow the user to do just that. Once this box is checked, the custom values entered in the *Custom Basis Set Entry* box will be used in the calculation. We suggest entering values *without* this box checked to allow comparison with the standard basis set. Once the user decides on new values, checking the *Apply Custom Basis Set* box will make the change. Note that if this option is selected, a value must be entered for *all* relevant coefficients and exponents.

Example Exercises

I. Create a Potential Energy Surface (PES)

By changing the bond distance in HeH$^+$ and performing RHF calculations at each distance, one can easily generate a potential energy surface for this diatomic molecule:
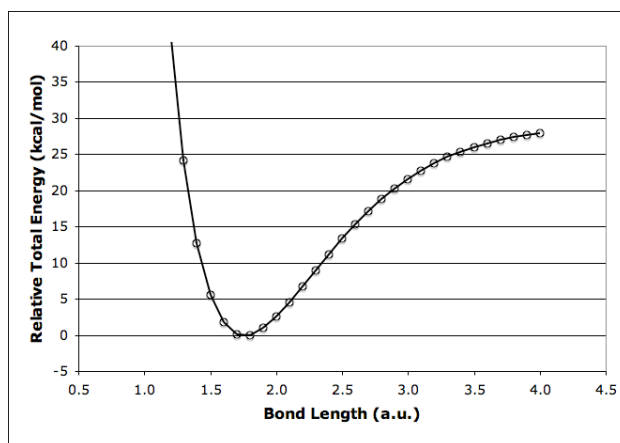
Note that HeH$^+$ is one of the few molecules that the RHF method models correctly in the limit of dissociation.[2]

In this way, a student can—in a sense—perform their own Born-Oppenheimer calculation.

II. Demonstrate the Variational Principle

The variational theorem states that, given a time-independent Hamiltonian $\hat{H}$, and a normalized, well-behaved wave function that obeys the boundary conditions of the system (ψ), then

$$E_1 \leq \int \psi^* \hat{H} \psi \, d\tau$$

where E_1 is the exact ground-state energy of the system.[3] One important consequence of this theorem is the following: if ψ can be modified such that the total energy of the system goes down (the right-hand side of the above equation), then the new ψ must be a better wave function that the old ψ.

Given the ability to scale the exponents in the basis functions that make up ψ, it is easy to demonstrate this property. (Compare what follows with the discussion on p. 168 in Szabo and Ostlund, reference 1.) Calculate the energy of H_2 with the STO-3G basis set and a bond distance of 1.4 a.u. By changing the value of ζ (and thus ψ), one obtains the following results:

ζ	Energy (a.u.)
1.0	-1.081642454
1.1	-1.110891885
1.2	-1.119119673
1.3	-1.107137342

Szabo and Ostlund point out that $\zeta = 1.19$ would be the optimal value for the H_2 molecule with a bond length of 1.4 a.u.

III. Demonstrate Dependence on the Initial MO Orbital Guess

The professional computational chemist knows all too well about convergence difficulties. Indeed, there is no guarantee that an RHF calculation will converge. There are many algorithms available that increase the likelihood and speed of convergence: the damping method, the direct inversion of the iterative subspace (DIIS), etc. The current spreadsheet has no such convergers built in; it simply uses unfiltered iterations. However, all *ab initio* calculations can be made more reliable by giving the program a good starting guess wave function. For example: if you attempt to calculate the energy of the H_2 molecule at $R = 3.5$ a.u. using the STO-3G basis set, it will take 13 iterative cylces to converge, and there are some oscillations in the cycles. (This can be seen best by watching the wave function change by selecting the desired MOs in the *Molecular Orbitals* box.) However, if you take the final MOs from a calculation at $R = 3.0$ a.u. and use them as the starting MO guess in cells G11:H12, then the calculation at $R = 3.5$ a.u. converges in only three steps. (Of course, convergence problems can also be due to the inappropriateness of the wave function, so the instructor should take care in applying this feature.)

Teaching Tips

- Select orbitals to plot *during* the SCF cycle. Many times convergence problems and oscillations in the MOs can be seen visually. This can be done by checking the desired orbitals to plot in the *Molecular Orbitals* section of the Front sheet.

- The default convergence threshold is that suggested by Szabo and Ostlund. For more precise work, a smaller threshold should be chosen. However, for pedagogical purposes, a larger one could be chosen to cut down on the number of iterations a student needs to perform for a given energy calculation.

- Don't use the *Show All* option in the basis set pull-down menu unless you want to show how much more work there is for STO-3G vs. STO-1G.

- Make a back-up copy of the spreadsheet right away in case some of the cell formulas are accidentally deleted. None of the cells are write protected!

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[1] Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Dover Publications: Mineola, New York, 1989.

[2] See, for example: Jensen, F. *Introduction to Computational Chemistry*; John Wiley & Sons: Chichester, 1999, p. 111.

[3] Levine, I. N. *Quantum Chemistry*; Prentice Hall: New Jersey, 1991, 4th Ed. p. 189.