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Using a Spreadsheet To Solve the Schrödinger Equations for the Energies of the Ground Electronic State and the Two Lowest Excited States of H₂

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Supporting Information

ABSTRACT: We have designed an exercise suitable for a lab or project in an undergraduate physical chemistry course that creates a Microsoft Excel spreadsheet to calculate the energy of the S₀ ground electronic state and the S₁ and T₁ excited states of H₂. The spreadsheet calculations circumvent the construction and diagonalization of the Fock matrix and thus can be accomplished by any undergraduate chemistry student with basic calculus skills. The wave functions of the S₀, S₁, and T₁ states of H₂ are constructed from the symmetry-adapted bonding and antibonding molecular orbitals (MO). All quantum mechanical integrals are estimated using the Monte Carlo integration method. Due to the stochastic nature of the spreadsheet calculations, 25 runs were carried out to obtain the mean energy of the S₀, S₁, and T₁ electronic states of H₂. The accuracy of the spreadsheet calculations is comparable to that of the HF/STO-3G calculations. The atomic and molecular orbitals and the energy components can be easily calculated and plotted for better visualization and understanding of essential quantum chemical concepts. This spreadsheet can also be adapted to tackle a wider range of quantum chemistry problems with different levels of complexity.

KEYWORDS: Upper-Division Undergraduate, Physical Chemistry, Computer-Based Learning, Quantum Chemistry, Computational Chemistry, MO theory

Q uantum chemistry is arguably the most daunting class for undergraduate chemistry students because it is highly mathematical and intangible. Efforts have been made to unveil details of self-consistent field (SCF) calculations for educational purposes: Szabo and Ostlund wrote a FORTRAN program to carry out the HF/STO-3G calculation for HeH⁺ to illustrate the SCF procedures.¹ In their FORTRAN program, the following Roothaan–Hall equation is solved iteratively:

\[ \text{FC} = \text{SCe} \]  (1)

where F is the Fock matrix, C the molecular orbital (MO) coefficient matrix, S the overlap matrix, and ε the diagonal matrix of the MO energies.¹ The preceding SCF algorithm was implemented on an Excel spreadsheet by Page et al., also for educational purposes.² Halpern and Glendening recently developed a spreadsheet to explore the nature of the H₂ bond by using the valence bond (VB), molecular orbital (MO), and molecular orbital–configuration interaction (MO-CI) methods.³,⁴ the authors suggest that students derive and then evaluate the analytical expressions of the kinetic energy and potential energy terms on a spreadsheet using the provided expressions of the seven fundamental integrals. However, a small chemistry program such as the one at the authors’ institution often lacks resources to cover both advanced calculus and linear algebra in depth. To circumvent the construction and diagonalization of the Fock matrix as described in the Page et al. paper² and the derivation of the analytical expressions of the energy components as described in Halpern and Glendening’s paper³, we designed a spreadsheet-aided exercise for students with very basic calculus skills to estimate the total energy and energy components of the ground and excited states of H₂. Matrix construction and operations in the SCF procedures are circumvented by constructing reasonably accurate total wave functions without optimization. Integral calculations are simplified by using the Monte Carlo integration method⁵,⁶ to estimate the quantum mechanical integrals. The optimization of the screening parameter is also skipped for simplicity. This hands-on exercise provides an alternative (and very simple) approach to tackle quantum chemistry problems and allows students to focus more on quantum mechanical postulates and several important concepts without being distracted by too much mathematical detail.

THEORY

One of the quantum mechanical postulates states that the expectation value of the energy of a quantum system can be calculated given its real wave function ψ using the following equation:

\[ \langle E \rangle = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^2 \, d\tau} \]  (2)

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where $\hat{H}$ is the Hamiltonian operator. When the exact wave function is unavailable, the variational theorem can be used to obtain the approximate wave function and energy through the minimization of $\langle E \rangle$. Herein, we introduce a hands-on exercise that allows students with basic calculus knowledge to solve eq 2 approximately for the ground and excited electronic states of H$_2$ on a spreadsheet. For simplicity, the variational theorem is not used to optimize the total wave function in the spreadsheet calculations. The molecular orbitals (MO) of H$_2$ are simply constructed through the linear combination of the exact exponential wave function of H atoms; the total wave function is then constructed from the MOs.

In the description of this exercise and in all spreadsheet calculations, four fundamental atomic units (au) are used for simplicity and clarity:

$$m_0 = 1\text{ au}$$

$$e = 1\text{ au}$$

$$h = \frac{\hbar}{2\pi} = 1\text{ au}$$

$$\frac{1}{4\pi\varepsilon_0} = 1\text{ au}$$

where $m_0$ is the mass of an electron, $e$ the charge of a proton, $h$ the Planck constant, $\hbar$ the reduced Planck constant, and $\varepsilon_0$ the dielectric constant in vacuum. The atomic units for length and energy can be derived from the above four fundamental atomic units:

$$1\text{ au of length} = \frac{(4\pi\varepsilon_0)^2\hbar}{m_0 e^2}$$

$$1\text{ au of energy} = \frac{m_0 e^4}{(4\pi\varepsilon_0)^2\hbar^2}$$

The total energy of H$_2$ consists of the nucleus–nucleus (N–N) repulsion energy and the electronic energy. The N–N repulsion in H$_2$ equals 1/$R_{AB}$, where $R_{AB}$ is the distance between the two H nuclei A and B. The electronic energy $E_{\text{elec}}$ of H$_2$ is calculated using the following equation:

$$\langle E_{\text{elec}} \rangle = \int \frac{\psi \hat{H} \psi}{\psi^2} \, dz$$

The terms enclosed within the first, second, and third parentheses are the quantum mechanical operators of kinetic energy, attraction, and repulsion of electrons, respectively. The analytical expressions of the integrals appearing in eq 9 are very complex when either exponential functions or Gaussian-type functions are used to construct the total wave function $\psi$. Therefore, we estimate all quantum mechanical integrals using the Monte Carlo integration method, a technique especially useful for high-dimensional integration. For example, the integral of a function $f$ of the $xyz$ coordinates of an electron can be estimated as follows:

$$\int_{-\infty}^{+\infty} f(x, y, z) \, dx \, dy \, dz \approx \frac{\sum_{k=1}^{N_{\text{sampling}}} f(x^k, y^k, z^k)}{N_{\text{sampling}}}$$
functions in eqs 12–14 can be neglected, and the following spatial functions are used to describe the first three electronic states of H₂ in the spreadsheet calculations:

$$\psi(S_0) = \sigma(1) \sigma(2)$$  

$$\psi(S_1) = \sigma(1) \sigma^*(2) + \sigma(2) \sigma^*(1)$$  

$$\psi(T_1) = \sigma(1) \sigma^*(2) - \sigma(2) \sigma^*(1)$$  

The spreadsheet calculations of the integrals of the electron density, attraction, and repulsion require no more than basic differential calculus. Taking the T₁ electronic state for example, the expectation value of the total kinetic energy of the two electrons can be calculated using the following equation:

$$\langle KE \rangle = \frac{\int \psi(T_1) \left( -\frac{1}{2} \nabla^2_1 + \frac{1}{2} \nabla^2_2 \right) \psi(T_1) \, d\tau}{\int \left| \psi(T_1) \right|^2 \, d\tau}$$

$$\approx \frac{\sum_{i=1}^{N_{\text{sample}}} \left[ \psi(T_1) \left( -\frac{1}{2} \nabla^2_1 + \frac{1}{2} \nabla^2_2 \right) \psi(T_1) \right]}{\sum_{i=1}^{N_{\text{sample}}} \left| \psi(T_1) \right|^2}$$

where $$\psi(T_1) = \sigma(1) \sigma^*(2) - \sigma(2) \sigma^*(1)$$. The numerator includes the kinetic energy terms of electrons 1 and 2 that can be evaluated numerically on the spreadsheet after the following derivations:

$$\left( -\frac{1}{2} \nabla^2_1 + \frac{1}{2} \nabla^2_2 \right) \psi(T_1)$$

$$= \frac{1}{2} \nabla^2_1 [\sigma(1) \sigma^*(2) - \sigma(2) \sigma^*(1)]$$

$$+ \frac{1}{2} \nabla^2_2 [\sigma(1) \sigma^*(2) - \sigma(2) \sigma^*(1)]$$

$$= \sigma^*(2) \left[ -\frac{1}{2} \nabla^2_1 \sigma(1) \right] - \sigma(2) \left[ -\frac{1}{2} \nabla^2_2 \sigma^*(1) \right]$$

$$+ \sigma(1) \left[ -\frac{1}{2} \nabla^2_2 \sigma^*(2) \right] - \sigma^*(1) \left[ -\frac{1}{2} \nabla^2_1 \sigma^*(2) \right]$$

Given $$\sigma(i) = \Phi_{A} + \Phi_{B}$$ and $$\sigma^*(i) = \Phi_{A} - \Phi_{B}$$ we have

$$\frac{-1}{2} \nabla^2_1 \sigma(i) = \frac{-1}{2} \nabla^2_1 \Phi_{A} + \frac{-1}{2} \nabla^2_1 \Phi_{B}$$  

$$\frac{-1}{2} \nabla^2_2 \sigma^*(i) = \frac{-1}{2} \nabla^2_2 \Phi_{A} - \frac{-1}{2} \nabla^2_2 \Phi_{B}$$

And it can be easily proven that

$$\frac{-1}{2} \nabla^2_1 \Phi_{A} = \frac{-1}{2} \nabla^2_1 \Phi_{B}$$

$$\frac{-1}{2} \nabla^2_2 \Phi_{A} = \frac{-1}{2} \nabla^2_2 \Phi_{B}$$

where $$i = 1, 2$$ and $$X = A, B$$. Therefore, eqs 21–24 can be used to calculate the numerical value of $$\psi(T_1) \left[ -\frac{1}{2} \nabla^2_1 \Phi_{A} + \frac{-1}{2} \nabla^2_2 \Phi_{B} \right]$$ at each randomly sampled point within the integral limits. The expectation value of the total kinetic energy of the two electrons can then be estimated using eq 20. The kinetic energy of the electrons in the S₀ and S₁ states can be obtained in a similar fashion.

Once the kinetic energy, N–e attraction, e–e repulsion, and N–N repulsion are calculated on the spreadsheet, the total energy can be easily obtained. We recommend repeating the above calculations multiple times to obtain the mean values of the energy components and the total energy because of the stochastic nature of the Monte Carlo integration method being used to estimate the integrals.

### RESULTS AND DISCUSSION OF SAMPLE CALCULATIONS

Due to the stochastic nature of the integral calculations through random sampling of the values of the integrand, we carried out a total of 25 runs on a spreadsheet for the H₂ molecule with a fixed bond distance of 1.5 au. Each run contains 40,000 randomly sampled data points within the x/y/z integral limits of 6/6/7.5 as the H₂ molecule is placed along the z axis illustrated in Figure 1.

![Figure 1. H₂ with a bond length of 1.5 au placed in a 6 × 6 × 7.5 box.](Image)

Note that the boundary of the box is at least 3 au away from the H nuclei. This distance of 3 au is chosen because the probability of finding the electron inside the sphere with a radius of 3 au is ~94% in a hydrogen atom. Therefore, we may assume that the electron probability density of the H₂ molecule is very small outside the 6 × 6 × 7.5 box. Meanwhile, the volume is still small enough that as many as 148 data points are sampled per atomic unit of volume (equivalent to ~1000 data/A³); this helps reduce the error introduced by the discrete approximation of integrals. The atomic orbitals and the bonding and antibonding molecular orbitals are presented in Figure 2 by plotting the numerical values of $e^{−σA}$, $e^{−σB}$, and $e^{−σA}$ ± $e^{−σB}$ versus the z coordinates of electron 1. Note that these atomic and molecular wave functions may adopt different...
The plots of the atomic orbitals are not exactly symmetrical because neither nucleus A or B is placed at the center of the z axis and also because the sampling of the positions of the electron is random. The constructive and destructive interferences between the two atomic orbitals are clearly illustrated in the plots of the bonding and antibonding molecular orbitals.

We have also carried out spreadsheet calculations to obtain the single-point energy of the S₀ state of H₂ at various internuclear distances ranging from 0.8 to 3.5 au of length. In each calculation, the x/y dimensions of the box are set to be 6 au of length; the z dimension is set to be 6 au plus the bond distance. The spreadsheet-calculated average energy and standard deviation are illustrated in Figure 3 in comparison with the HF/STO-1G, HF/STO-2G, and HF/STO-3G potential energy surfaces (PES). The HF/cc-pV6Z PES is also plotted serving as the benchmark within the realm of HF theory. All of the HF calculations were carried out using the GAMESS package. Note that the cc-pV6Z basis set (6s5p4d3f on H) is large enough to provide a close estimate of the HF limit. For example, at the 1.5 au bond distance, the HF limit (two-point extrapolation from the HF/cc-pVSZ and HF/cc-pV6Z energies) is −1.131387 au using the $E = A + B(L + 1)^{-4}$ equation or −1.131371 au using the $E = A + Be^{-\sqrt{L}}$ equation, where L is the number of the s-type functions. The HF/cc-pV6Z energy (−1.131368 au) agrees with these two extrapolated HF limits within 10⁻⁴ au of energy. Therefore, the HF/cc-pV6Z calculations are used as the benchmark hereafter.

Figure 3 shows the spreadsheet calculations are more accurate than the HF/STO-1G calculations and are comparable to the HF/STO-2G and HF/STO-3G calculations. The spreadsheet predictions are in better agreement with the HF/cc-pV6Z benchmark at stretched bond lengths because the exponential wave functions are the exact wave functions at the dissociation limit. It is worth noting that neither the HF PES curves nor the spreadsheet-calculated energies describe the dissociation limit properly. This is because in the HF calculations of the S₀ state of H₂ at the dissociation limit, the two electrons are forced to occupy the same spatial molecular orbitals (known as the restricted Hartree–Fock theory) while they are supposed to occupy two different orbitals each centered on a different nucleus. A proper description at stretched bond distances can be obtained by breaking the symmetry of the molecular orbitals using open-shell wave functions such as in an unrestricted HF (UHF) calculation. To further demonstrate the failure of the RHF theory and the success of the UHF theory at the dissociation limit of H₂, we used the spreadsheet to calculate the energies of the S₀, S₁, and T₁ electronic states at the bond distance of 10 au of length. The S₀, S₁, and T₁ energies are determined to be −(0.691 ± 0.131), −(0.394 ± 0.227), and −(1.000 ± 0.000) au, respectively. Our S₀ energy is close to the HF energy (−0.6875 au) at infinite bond distance calculated by Halpern and Glendening using the same exponential basis functions. For further comparison, the HF/cc-pV6Z energies of the S₀ and T₁ states are −0.768 and −1.000 au at the bond distance of 10 au, while the exact HF energies of the S₀ and T₁ states are supposed to be exactly −1 au at the dissociation limit.

Because the relative energy—rather than the absolute energy—is of more interest to chemists, binding energy (BE) is calculated using the $BE = |E(H₂) − 2E(H)|$ equation. The spreadsheet predicts the atomic energy of H to be exactly −0.5 au and the minimum energy of H₂ to be −(1.102 ± 0.023) au; thus the binding energy of H₂ in the ground state is determined to be 0.102 ± 0.023 au excluding the zero-point vibrational energy (ZPVE) correction. Our result is very close to Halpern and Glendening’s HF binding energy of 0.099 au using the same basis set but calculated in an analytical and deterministic manner. For comparison, the HF binding energies are 0.167, 0.185, 0.184, and 0.134 au using the STO-1G, STO-2G, STO-3G, and cc-pV6Z basis sets, respectively. Among the above HF energies, the HF/STO-1G energy is the closest to the experimental binding energy at 0 K (0.17446 au without the ZPVE correction) only because of the fortuitous cancellation of errors that originate from the very small basis set and from the lack of correlation in the molecular calculation. The spreadsheet-calculated binding energy contains the largest error of all partly because the error in the energy calculation for the H₂ molecule cannot be canceled by any error in the calculation for the H atom.

The spreadsheet-calculated PES reaches the minimum at the bond distance of ~ 1.5 au of length. This bond distance is reasonably close to the experimental bond distance of H₂ (1.401 au or 0.7414 Å) at equilibrium. It is also reasonably close to the equilibrium bond distance (1.603 au) calculated by

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Figure 2. Plots of 5000 randomly sampled numerical values of the atomic orbitals: (A) $e^{-r_{\alpha}}$ and (B) $e^{-r_{\beta}}$ and the molecular orbitals: (C) $e^{-r_{\alpha}} + e^{-r_{\beta}}$ and (D) $e^{-r_{\alpha}} - e^{-r_{\beta}}$.

Figure 3. Spreadsheet-calculated potential energy surface of H₂ in the S₀ electronic state versus those calculated at the HF level of theory with the STO-1G, STO-2G, STO-3G, and cc-pV6Z basis sets.
Halpern and Glendening using the same exponential basis functions in their MO calculations. Therefore, we made more detailed comparison of energy components at this bond distance between the spreadsheet calculations and the HF/STO-3G calculations in Figure 4. The HF/cc-pV6Z data are also plotted serving as the benchmark.

At the bond distance of 1.5 au, the average and standard deviation of the 25 spreadsheet calculations of the total energy of the $S_0$, $S_1$, and $T_1$ electronic states were $-(1.102 \pm 0.023)$, $-(0.410 \pm 0.035)$, and $-(0.682 \pm 0.018)$ in atomic units. The energies of the $S_0$, $S_1$, and $T_1$ electronic states are $-1.112$, $-0.222$, and $-0.591$ au at the HF/STO-3G level of theory and are $-1.131$, $-0.674$, and $-0.794$ au at the HF/cc-pV6Z level of theory. Although only one basis function is employed on each H atom in the spreadsheet calculations, the quality of the results is satisfactory: Figure 4A shows the spreadsheet calculations are slightly less accurate than the HF/STO-3G calculations for the ground state and are notably more accurate for the excited states; similar patterns of the ranking of accuracy are observed for each energy component illustrated in Figure 4B–E.

At the bond distance of 1.5 au, we also varied the value of $N_{\text{sampling}}$ to 20,000, 10,000, 5,000, and 2,500 to test the robustness of the spreadsheet calculations using fewer sampled data. Figure 5A shows that the mean values of the 25 runs are statistically the same regardless of the $N_{\text{sampling}}$ value used within the wide range from 2,500 to 40,000. Figure 5B shows that the standard deviation of the total energy is found to be asymptotically inversely proportional to the square root of the number of the sampled data per volume. Therefore, if the PES is of interest, we suggest using a sample size of 40,000 (or even more) data in each run to achieve a reasonable precision.
Even when a very large number of data are sampled, the computing time is not likely an issue because it takes only a split second to perform one run with 40,000 sampled data on a Windows PC with one CPU of 3.20 GHz frequency and the computing time scales linearly with \( N_{\text{sampling}} \).

### ADDITIONAL EXERCISES

Although this spreadsheet is designed to calculate the Hartree–Fock energies of the \( S_0 \), \( S_1 \), and \( T_1 \) electronic states of \( \text{H}_2 \) quantum chemistry instructors may also develop many other activities appropriate for students at different levels. For example, this spreadsheet can be easily modified to calculate the energies of one-electron systems such as the \( \text{H} \) atom and the \( \text{H}_2^+ \) molecule. Students may also estimate the energy of the first excited state using a Hartree product wave function, \( \sigma(1) \sigma^\alpha(2) \), which corresponds to the average of the \( S_1 \) state shown in eq 13 and the \( T_1 \) state with a zero magnetic quantum number shown in eq 14; they will be able to compare the Hartree-product wave function with the properly constructed wave functions for the \( S_1 \) and \( T_1 \) states. In this proposed spreadsheet calculations, the exponential coefficients in the atomic functions are fixed. The optimization of the exponential coefficients may further lower the energy of the \( S_0 \) state as shown in Halpern and Glendenning’s paper although a much larger sampling is required to achieve the desired accuracy in the stochastic spreadsheet calculations. Mathematically advanced students may calculate the energies of higher lying excited states of \( \text{H}_2 \) and \( \text{H}_2^+ \) using properly constructed wave functions. Because the proposed method and the density functional theory (DFT) method are similar in calculating discrete quantities weighted by electron probability density, students may modify the spreadsheet to conduct simple DFT calculations within the local density approximation (For example, by using the VWN exchange-correlation equation). Students with some programming experience and strong interest in computational chemistry may even implement the algorithm using FORTRAN or any other programming language they are comfortable with. The wide range of activities makes it possible for students at different levels to break down and assemble their own quantum chemistry computations.

### CONCLUSION

We have designed a spreadsheet to calculate the energy of the \( S_0 \), \( S_1 \), and \( T_1 \) electronic states of \( \text{H}_2 \). The spreadsheet calculations circumvent the need for knowledge of linear algebra and advanced calculus and hence constitute a suitable exercise for undergraduate physical chemistry students with very basic calculus skills. We suggest having students construct the spreadsheet themselves to learn how these complicated quantum calculations can be broken down into smaller, easily understood steps. The proposed spreadsheet calculations employed only one basis function on each \( \text{H} \) atom and did not involve the optimization of the exponential coefficients but are still nearly as accurate as the HF/STO-3G calculations for the ground state and are more accurate for the excited states. The atomic and molecular orbitals, the total energy, and the energy components of the \( \text{H}_2 \) molecule in the ground and excited states can be easily calculated and plotted by students to better visualize and understand some important quantum chemical concepts. The method presented in this work can also be extended to other problems of interest in quantum chemistry for upper-division students.

### ASSOCIATED CONTENT

#### Supporting Information

Text describing a sample exercise including the step-by-step instruction of the construction of the spreadsheet and the procedures of calculations and tables listing a Microsoft Excel spreadsheet that contains the sample calculations of the \( S_0 \), \( S_1 \), \( T_1 \) electronic states of \( \text{H}_2 \) and graphs and a much smaller EXCEL spreadsheet that contains only a template with 2500 sampled data. This material is available via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

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