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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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Article

Using a Spreadsheet To Solve the Schrödinger Equations for the Energies of the Ground Electronic State and the Two Lowest Excited States of H_2

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S *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 S_0 ground electronic state and the S_1 and T_1 excited states of H_2. 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 S_0, S_1, and T_1 states of H_2 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 S_0, S_1, and T_1 electronic states of H_2. 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.
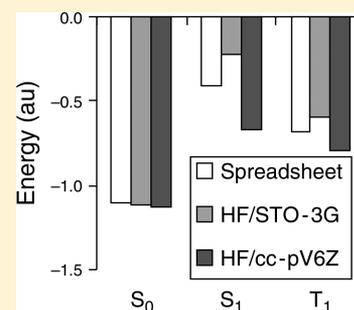
KEYWORDS: *Upper-Division Undergraduate, Physical Chemistry, Computer-Based Learning, Quantum Chemistry, Computational Chemistry, MO theory*

Quantum 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:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \tag{1}$$

where $\mathbf{F}$ is the Fock matrix, $\mathbf{C}$ the molecular orbital (MO) coefficient matrix, $\mathbf{S}$ the overlap matrix, and $\boldsymbol{\varepsilon}$ 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 H_2 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. paper[2] and the derivation of the analytical expressions of the energy components as described in

Halpern and Glendening's paper,[3] 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 H_2. 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 method[5,6] 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:

$$\langle E \rangle = \frac{\int \psi \hat{H} \psi \, d\tau}{\int \psi^2 \, d\tau} \tag{2}$$

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:

$$m_e = 1 \text{ au} \tag{3}$$

$$e = 1 \text{ au} \tag{4}$$

$$\hbar = \frac{h}{2\pi} = 1 \text{ au} \tag{5}$$

$$\frac{1}{4\pi\varepsilon_0} = 1 \text{ au} \tag{6}$$

where m_e is the mass of an electron, e the charge of a proton, h the Planck constant, $\hbar$ the reduced Planck constant, and ε_0 the dielectric constant in vacuum. The atomic units for length and energy can be derived from the above four fundamental atomic units:

$$1 \text{ au of length} = \frac{(4\pi\varepsilon_0)\hbar^2}{m_e e^2} \tag{7}$$

$$1 \text{ au of energy} = \frac{m_e e^4}{(4\pi\varepsilon_0)^2 \hbar^2} \tag{8}$$

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_{elec} of H_2 is calculated using the following equation:

$$\langle E_{elec} \rangle = \frac{\int \psi \widehat{H_{elec}} \psi \, d\tau}{\int \psi^2 \, d\tau}$$

$$= \frac{\int \psi \left[\left(\frac{-1}{2}\nabla_1^2 + \frac{-1}{2}\nabla_2^2 \right) + \left(\frac{-1}{r_{1A}} + \frac{-1}{r_{1B}} + \frac{-1}{r_{2A}} + \frac{-1}{r_{2B}} \right) + \left(\frac{1}{r_{12}} \right) \right] \psi \, d\tau}{\int \psi^2 \, d\tau} \tag{9}$$

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[3] or Gaussian-type functions[2] are used to construct the total wave function ψ. Therefore, we estimate all quantum mechanical integrals using the Monte Carlo integration method,[5,6] 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:

$$\iiint\limits_{-\infty}^{+\infty} f(x, y, z) \, dx \, dy \, dz \approx \frac{\sum_{k=1}^{N_{sampling}} f(x^k, y^k, z^k)}{N_{sampling}} V \tag{10}$$

where x^k, y^k, and z^k are Cartesian coordinates of the kth randomly sampled position of the electron within a box of a given volume V. The approximation is reasonable if (a) the integrand is a fast decaying function, (b) the volume V is large enough that the value of the integrand outside the volume is negligible, and (c) the number of sampled points $N_{sampling}$ per volume ($N_{sampling}/V$) is reasonably large (this poses a practical limit to the volume). Two-electron integrals can be calculated in a similar fashion. For example, the expectation value of the repulsion between two electrons can be calculated using the following equation:

$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{\int \psi \frac{1}{r_{12}} \psi \, d\tau}{\int \psi^2 \, d\tau}$$

$$\approx \left(\frac{\sum_{k=1}^{N_{sampling}} (\psi^k)^2 \left(\frac{1}{r_{12}^k} \right)}{N_{sampling}} V^2 \right) \Big/ \left(\frac{\sum_{k=1}^{N_{sampling}} (\psi^k)^2}{N_{sampling}} V^2 \right)$$

$$= \frac{\sum_{k=1}^{N_{sampling}} (\psi^k)^2 \left(\frac{1}{r_{12}^k} \right)}{\sum_{i=1}^{N_{sampling}} (\psi^k)^2} \tag{11}$$

where $\psi = \psi(x_1, y_1, z_1, x_2, y_2, z_2)$ and $d\tau = dx_1 \, dy_1 \, dz_1 \, dx_2 \, dy_2 \, dz_2$. The volume appearing in the preceding equation is squared both in the numerator and denominator because the integrands are functions of the $x/y/z$ coordinates of two electrons. The ψ^k and r_{12}^k are the numerical values of ψ and r_{12} at the kth randomly sampled positions of the two electrons. Note that the numerator in the last term of the above equation is simply the weighted sum of the repulsion between the two electrons, where the weight, $(\psi^k)^2$, is the probability density of finding the two electrons at their corresponding positions.

In the spreadsheet calculations, the total wave function ψ is constructed from MOs that are linear combinations of real exponential functions (e^{-r}). Note that e^{-r} is the exact solution to the H atom, where r is in the atomic unit of length (1 au = 0.529177 Å). The following antisymmetric wave functions are used for the H_2 singlet ground state (S_0), the first excited singlet state (S_1), and the first triplet excited state (T_1) with a magnetic quantum number of zero:[7]

$$\psi(S_0) = [\sigma(1)\,\sigma(2)][\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)] \tag{12}$$

$$\psi(S_1) = [\sigma(1)\,\sigma*(2) + \sigma(2)\,\sigma*(1)][\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)] \tag{13}$$

$$\psi(T_1) = [\sigma(1)\,\sigma*(2) - \sigma(2)\,\sigma*(1)][\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)] \tag{14}$$

where σ and $\sigma*$ denote the unnormalized symmetry-adapted bonding and antibonding orbitals:

$$\sigma(i) = \Phi_{iA} + \Phi_{iB} = e^{-r_{iA}} + e^{-r_{iB}} \tag{15}$$

$$\sigma*(i) = \Phi_{iA} - \Phi_{iB} = e^{-r_{iA}} - e^{-r_{iB}} \tag{16}$$

where $i = 1, 2$ denotes the coordinates of the ith electron in H_2, $\Phi_{iA} = e^{-r_{iA}}$ is the atomic function of nucleus A, and $\Phi_{iB} = e^{-r_{iB}}$ is the atomic function of nucleus B. The α and β spin functions are orthonormalized.

In eqs 12−14, the spin part of the total wave function is separated from the spatial part and thus the spin integrals can be separated and canceled in eq 2 because the Hamiltonian operator does not contain spin coordinates. Therefore, the spin

functions in eqs 12−14 can be neglected, and the following spatial functions are used to describe the first three electronic states of H_2 in the spreadsheet calculations:

$$\psi(S_0) = \sigma(1)\,\sigma(2) \tag{17}$$

$$\psi(S_1) = \sigma(1)\,\sigma^*(2) + \sigma(2)\,\sigma^*(1) \tag{18}$$

$$\psi(T_1) = \sigma(1)\,\sigma^*(2) - \sigma(2)\,\sigma^*(1) \tag{19}$$

The spreadsheet calculations of the integrals of the electron density, attraction, and repulsion require no more than algebraic skills. Students may derive and simplify the analytical expression of the expectation value of the repulsion in the T_1 electronic state and should understand that the negative exchange energy originates from the negative cross-terms $(-2\int \sigma(1)\,\sigma^*(1)\,\sigma(2)\,\sigma^*(2)/r_{12}\,d\tau)$ that appear in the numerator. Numerical values of these cross-terms and the corresponding exchange energy can be estimated by slightly modifying the spreadsheet. Motivated students may resort to more advanced quantum chemistry textbooks such as Szabo and Ostlund's *Modern Quantum Chemistry* to better understand exchange (and even correlation).[8]

The kinetic energy integral calculations require a simple derivation that employs basic differential calculus. Taking the T_1 electronic state for example, the expectation value of the kinetic energy of the two electrons can be calculated using the following equation:

$$
\langle KE \rangle = \frac{\int \psi(T_1)\left(\frac{-1}{2}\nabla_1^2 + \frac{-1}{2}\nabla_2^2 \right)\psi(T_1)\,d\tau}{\int [\psi(T_1)]^2\,d\tau}
$$
$$
\approx \frac{\sum_{i=1}^{N_{sampling}} \left[\psi(T_1)\left(\frac{-1}{2}\nabla_1^2 + \frac{-1}{2}\nabla_2^2 \right)\psi(T_1) \right]}{\sum_{i=1}^{N_{sampling}} [\psi(T_1)]^2} \tag{20}
$$

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:

$$
\left(\frac{-1}{2}\nabla_1^2 + \frac{-1}{2}\nabla_2^2 \right)\psi(T_1)
$$
$$
= \frac{-1}{2}\nabla_1^2[\sigma(1)\,\sigma^*(2) - \sigma(2)\,\sigma^*(1)]
$$
$$
+ \frac{-1}{2}\nabla_2^2[\sigma(1)\,\sigma^*(2) - \sigma(2)\,\sigma^*(1)]
$$
$$
= \sigma^*(2)\left[\frac{-1}{2}\nabla_1^2\sigma(1) \right] - \sigma(2)\left[\frac{-1}{2}\nabla_1^2\sigma^*(1) \right]
$$
$$
+ \sigma(1)\left[\frac{-1}{2}\nabla_2^2\sigma^*(2) \right] - \sigma^*(1)\left[\frac{-1}{2}\nabla_2^2\sigma(2) \right] \tag{21}
$$

Given $\sigma(i) = \Phi_{iA} + \Phi_{iB}$ and $\sigma^*(i) = \Phi_{iA} - \Phi_{iB}$, we have

$$
\frac{-1}{2}\nabla_i^2\sigma(i) = \frac{-1}{2}\nabla_i^2\Phi_{iA} + \frac{-1}{2}\nabla_i^2\Phi_{iB} \tag{22}
$$

$$
\frac{-1}{2}\nabla_i^2\sigma^*(i) = \frac{-1}{2}\nabla_i^2\Phi_{iA} - \frac{-1}{2}\nabla_i^2\Phi_{iB} \tag{23}
$$

And it can be easily proven that

$$
\frac{-1}{2}\nabla_i^2\Phi_{iX} = \frac{-1}{2r_{iX}^2}\left[\frac{\partial}{\partial r_{iX}}\left(r_{iX}^2 \frac{\partial}{\partial r_{iX}} \right) \right]e^{-r_{iX}} = \left(\frac{1}{r_{iX}} - \frac{1}{2} \right)e^{-r_{iX}} \tag{24}
$$

where $i = 1, 2$ and $X = A, B$. Therefore, eqs 21−24 can be used to calculate the numerical value of $\psi(T_1)[(-1/2)\nabla_1^2 + (-1/2)\nabla_2^2]\psi(T_1)$ 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 S_0 and S_1 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 H_2 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 H_2 molecule is placed along the z axis illustrated in Figure 1.
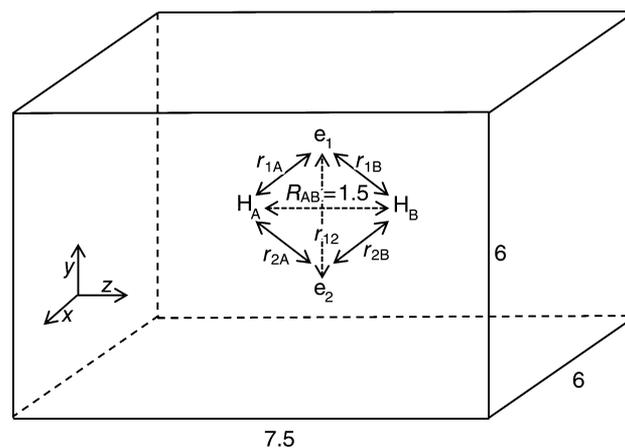

Figure 1. H_2 with a bond length of 1.5 au placed in a $6 \times 6 \times 7.5$ box. The dimensions of the box, also in au, illustrate the limits of the integrals calculated on the spreadsheet.

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 H_2 molecule is very small outside the $6 \times 6 \times 7.5$ 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/Å³); 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 $e^{-r_{1A}}$, $e^{-r_{1B}}$, and $e^{-r_{1A}} \pm e^{-r_{1B}}$ versus the z coordinates of electron 1. Note that these atomic and molecular wave functions may adopt different
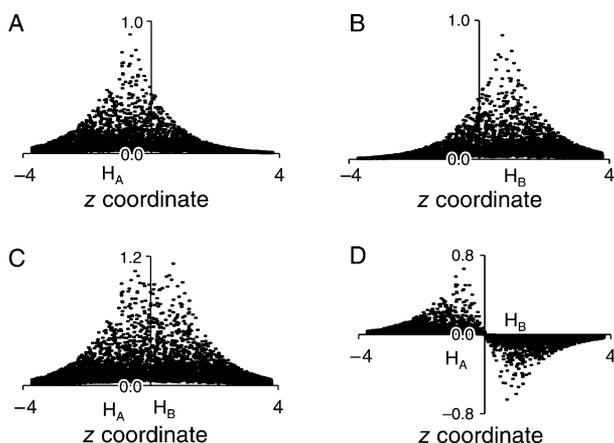
Figure 2. Plots of 5000 randomly sampled numerical values of the atomic orbitals: (A) $e^{-r_{1A}}$ and (B) $e^{-r_{1B}}$ and the molecular orbitals: (C) $e^{-r_{1A}} + e^{-r_{1B}}$, and (D) $e^{-r_{1A}} - e^{-r_{1B}}$.

numerical values at a fixed value of z because x and y coordinates are randomly sampled.

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 S_0 state of H_2 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
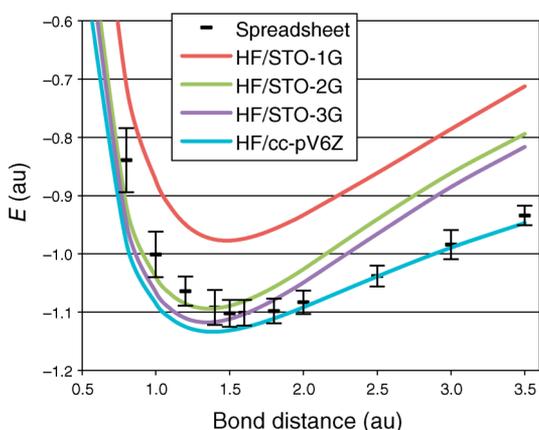

Figure 3. Spreadsheet-calculated potential energy surface of H_2 in the S_0 electronic state versus those calculated at the HF level of theory with the STO-1G, STO-2G, STO-3G, and cc-pV6Z basis sets.

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.[9,10] 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-pV5Z and

HF/cc-pV6Z energies) is -1.131387 au using the $E = A + B(L + 1)^{-4}$ equation[11] or -1.131371 au using the $E = A + Be^{-9\sqrt{L}}$ equation,[12] 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 S_0 state of H_2 at the dissociation limit, the two electrons are forced to occupy the same spatial molecular orbitals (known as the restricted Hartree–Fock or RHF 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.[13] To further demonstrate the failure of the RHF theory and the success of the UHF theory at the dissociation limit of H_2, we used the spreadsheet to calculate the energies of the S_0, S_1, and T_1 electronic states at the bond distance of 10 au of length. The S_0, S_1, and T_1 energies are determined to be $-(0.691 \pm 0.131)$, $-(0.394 \pm 0.227)$, and $-(1.000 \pm 0.000)$ au, respectively. Our S_0 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.[3] For further comparison, the HF/cc-pV6Z energies of the S_0 and T_1 states are -0.768 and -1.000 au at the bond distance of 10 au, while the exact HF energies of the S_0 and T_1 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 $= |E(H_2) - 2E(H)|$ equation. The spreadsheet predicts the atomic energy of H to be exactly -0.5 au and the minimum energy of H_2 to be $-(1.102 \pm 0.023)$ au; thus the binding energy of H_2 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.[3] 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[14]) 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 H_2 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 H_2 (1.401 au or 0.7414 Å)[14] at equilibrium. It is also reasonably close to the equilibrium bond distance (1.603 au) calculated by
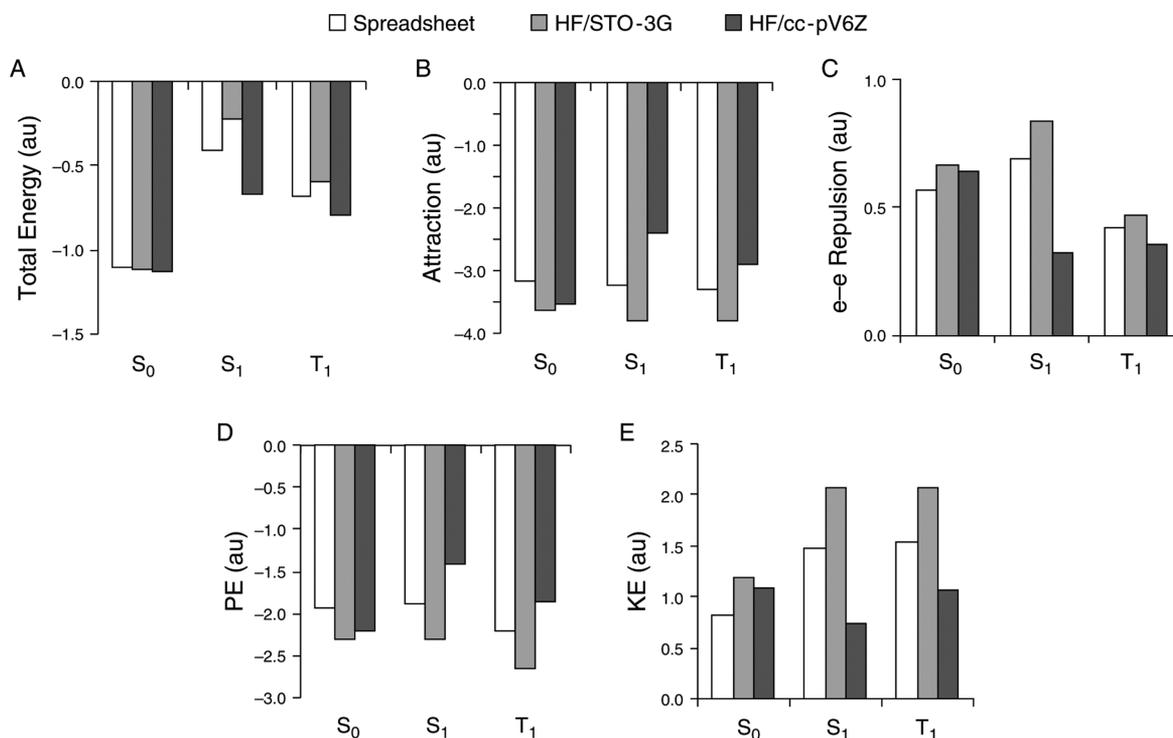
Figure 4. Spreadsheet versus HF/STO-3G calculated results for H_2 at the bond distance of 1.5 au: (A) total energy, (B) attraction, (C) $e-e$ repulsion, (D) potential energy, and (E) kinetic energy. The HF/cc-pV6Z data are plotted serving as the benchmark.
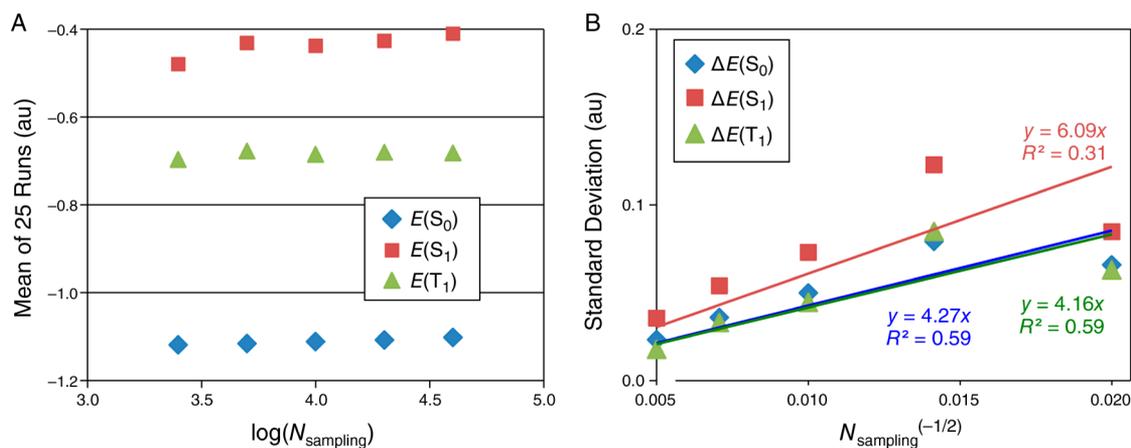

Figure 5. The mean (A) and the standard deviation (B) of the total energy of the S_0, S_1, and T_1 electronic states of H_2 with various numbers of sampled data ($N_{sampling}$ = 2,500, 5,000, 10,000, 20,000, 40,000).

Halpern and Glendening using the same exponential basis functions in their MO calculations.[3] 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 $N_{sampling}$ 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 $N_{sampling}$ 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_{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 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 H atom and the H_2^+ molecule. Students may also estimate the energy of the first excited state using a Hartree product wave function, $\sigma(1)$ $\sigma^*(2)$, 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 Glendening's paper[3] 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 H_2 and 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[15]). 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 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 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 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

S 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 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.

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Notes

The authors declare no competing financial interest.

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