

Interactively Applying the Variational Method to the Dihydrogen Molecule: Exploring Bonding and Antibonding

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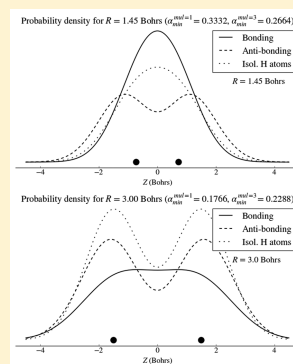
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Supporting Information

ABSTRACT: In this work we are going to present how an interactive platform can be used as a powerful tool to allow students to better explore a foundational problem in quantum chemistry: the application of the variational method to the dihydrogen molecule using simple Gaussian trial functions. The theoretical approach for the hydrogen atom is quite straightforward, however, the level of complexity increases considerably for the dihydrogen molecule. Although, as shown in this work, it is possible to obtain an analytical expression for the dihydrogen molecule variational integral by “pen-and-paper”, this expression cannot be completely appreciated without the proper tools. In this work the “dry” analytical equations were implemented into an interactive platform that allows the students to visualize results (like probability densities and meaningful graphs), play with parameters, and thus gain a deeper understanding of the problem itself. Having an interactive environment is also important as a way of minimizing complex equations, testing analytical results with numerical calculations, among other things, that otherwise would be unachievable by “pen and paper” only. Additionally, in this work the bonding and antibonding behaviors of the dihydrogen molecule were investigated and evaluated in detail. As a final outcome, this article shows that important properties regarding the dihydrogen molecule (like equilibrium bond length and favorability of formation) can be explained and approximated with the variational method.

KEYWORDS: Quantum Chemistry, Atomic Properties/Structure, Computational Chemistry, Computer-Based Learning, Graduate Education/Research, Physical Chemistry



INTERACTIVE PLATFORM FOR TEACHING QUANTUM CHEMISTRY

There is a considerable discrepancy between the apparent “ease of use” of some quantum chemistry software packages on one hand, and the often challenging math underlying quantum mechanics on the other hand. It is thus not surprising that to many students and researchers, quantum chemistry is like an impenetrable “black box”, where deeper understanding appears unattainable. It is undeniable that a fundamental knowledge of quantum chemistry cannot be achieved without “pen and paper” derivations. At the same time, it is also important for students to gain an appreciation for the immense power of computational approaches not only in solving quantum chemistry problems but also as a visualization tool. In fact, computer algorithms can greatly assist student learning not only by visualizing data output but by aiding understanding of mathematical relations, and carrying out a large number of calculations for systematic exploration of parameters. A number of educational software packages (e.g., Mathematica, Maple, Matlab) can perform some of these tasks. In this work, we are going to use the *IPython* interactive computing environment¹ as a platform for teaching quantum chemistry. The *IPython notebook* format was chosen because of some attractive features as: it is open-source and freely available; it runs within a web browser interface; it allows inclusion of explanatory text, tables, images, and mathematical equations in LaTeX format; and it

includes powerful libraries for symbolic mathematical operations (SymPy), numerical operations (NumPy, SciPy), data visualization (Matplotlib, Mayavi), and even quantum chemistry operations (QuTiP).^{2,3}

SCOPE OF THIS WORK

The aim of this work is to present an interactive environment that allows students to better explore the application of the variational method^{4–6} to the dihydrogen molecule using simple Gaussian trial functions. The analytical calculations performed were implemented into an *IPython notebook* program (which is available as [Supporting Information](#), as well as installation and running instructions). The application of the variational method to the hydrogen atom is a classic textbook example in quantum chemistry classes. The solution to this problem can be reached entirely by “pen and paper”, following primarily calculus rules.

The application of the variational method to the dihydrogen molecule involves a number of nontrivial derivations and assumptions. Several papers on the literature discuss different applications of the variational method,^{7–15} including to the dihydrogen molecule.^{16,17} However, to our knowledge, the

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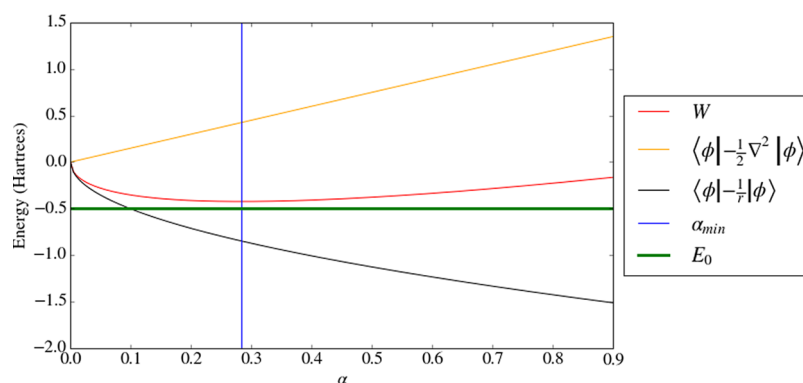


Figure 1. Variational integral, the kinetic term, and the electron-nuclear attraction term as a function of α .

derivation of the dihydrogen molecule variational integral using Gaussian trial functions has not been published to date. This article will focus on some key equations and results of this derivation. More details on the mathematical derivations can be found in the [Supporting Information](#). The *IPython notebook* program allows an interactive visualization of the wave functions and the energy of the dihydrogen molecule to compare bonding and antibonding behaviors, among other things.

It is expected that the *IPython notebook* program, along with this article, can be used in quantum chemistry and/or physical chemistry classes to give the students a more interactive learning experience on this key problem in quantum mechanics, which involves not only the variational theorem itself but also other fundamental concepts in quantum chemistry, such as Pauli's principle, the Born–Oppenheimer approximation, and the combination of atomic orbitals. It is hoped that this notebook can serve as a hands-on introduction to implementing quantum chemistry computations and that it will encourage students to develop other educative interactive programs on other quantum chemistry topics (e.g., Perturbation Theory, Hartree–Fock method).

This *IPython notebook* program together with this manuscript was tested in class as a homework given to the students of the undergraduate course CHM 4412—Physical Chemistry, Quantum Mechanics and Spectroscopy, at the University of Florida. The students were junior/seniors, with no previous experience in *IPython*. The students were asked to comment on their learning experience and they wrote that through this educational experience they were able to “easily visualize bonding and anti-bonding wavefunctions”, “better understand orbitals overlap”, and “found it interesting to see how the formation of the H₂ molecule chemical bond can be justified by using simple Gaussian functions and the variational method”. This is an example of pedagogical value and practical student learning enhancement gained from the material presented in this manuscript.

VARIATIONAL THEOREM

The variational method is an approximation method in quantum chemistry. It involves a trial function, which is optimized by minimizing its energy in order to approach as close as possible the true ground state solution. This happens because according to the variational theorem:

$$W = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \geq E_0 \quad (1)$$

where W is called the variational integral, $|\phi\rangle$ is a trial function, H is the system's Hamiltonian, and E_0 is the exact ground state energy. This inequality becomes an equality when the trial function equals the exact ground state wave function, i.e., $|\phi\rangle = |\psi_0\rangle$. The proof for this inequality is straightforward and can be found in the [Supporting Information](#).

APPLYING THE VARIATIONAL METHOD TO THE H ATOM

We know from the solution of the Schrödinger equation that the exact wave function has the form $e^{-\alpha r}$, therefore if we apply the variational method for a trial wave function in this form we will get the exact solution. Let us use instead a Gaussian function as a normalized trial wave function given that the analytical solutions to Gaussian-based electronic structure integrals are well-known (see [Supporting Information](#)):

$$\phi(r) = N_\alpha e^{-\alpha r^2} \quad (2)$$

where N_α is the normalization factor, α is a decay factor, and r is electron–nucleus distance.

The Hamiltonian in atomic units (i.e., units chosen in such a way that $\hbar = 1$, $m_e = 1$, $q_e = 1$, and $1/4\pi\epsilon_0 = 1$) for the hydrogen atom is:

$$H = -\frac{1}{2}\nabla^2 - \frac{1}{r} \quad (3)$$

where $-1/2\nabla^2$ accounts for the kinetic energy, and $-1/r$ for the electron–nuclear attraction.

It can be shown that the variational integral (eq 1) for the hydrogen atom is (see [Supporting Information](#)):

$$W = \frac{3}{2}\alpha - \sqrt{\frac{8}{\pi}}\sqrt{\alpha} \quad (4)$$

where $3/2\alpha$ accounts for the kinetic energy, and $-\sqrt{\frac{8}{\pi}}\sqrt{\alpha}$ accounts for the electron–nuclear attraction energy.

We see that W depends on α , which means that W can be minimized with respect to α . It can be shown that the α value that gives the minimum value for W and the minimum value of W are respectively (see [Supporting Information](#)):

$$\alpha_{\min} = \alpha_H = \frac{8}{9\pi} \approx 0.2829 \quad (5)$$

$$W_{\min} = W_H = \frac{3}{2}\alpha_{\min} - \sqrt{\frac{8}{\pi}}\sqrt{\alpha_{\min}} = -\frac{4}{3\pi} \approx -0.4244 \quad (6)$$

As the exact energy is $E_0 = -0.5$, we see that $W_H > E_0$ as expected, and that W_H and E_0 differ by 15%.

Let us now see all this graphically by plotting the variational integral (W), the kinetic contribution ($\langle\phi| -1/2 \nabla^2|\phi\rangle$), and the electron–nuclear attraction contribution ($\langle\phi| -1/r|\phi\rangle$) to W as a function of α .

As Figure 1 shows, the minimum for W arises due the competing effects of the electron kinetic energy on one hand, and the electron–nuclear attraction on the other. As α increases, the wave function decays faster, meaning that the electron density closer to the nucleus increases. We see that as the electron gets closer to the nucleus on average (i.e., when α increases) its kinetic energy increases (i.e., the electron speeds up) and the electron–nuclear attraction becomes stronger as one would expect.

■ APPLYING THE VARIATIONAL METHOD TO THE H₂ MOLECULE

Setting the Problem

The electronic Hamiltonian in atomic units for the H₂ molecule is:

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{|\vec{r}_1 - \vec{R}_A|} - \frac{1}{|\vec{r}_1 - \vec{R}_B|} - \frac{1}{|\vec{r}_2 - \vec{R}_A|} - \frac{1}{|\vec{r}_2 - \vec{R}_B|} + \frac{1}{|\vec{r}_1 - \vec{r}_2|} \quad (7)$$

where the first two terms account for the kinetic energy of each electron, the other terms with negative signs account for electrons–nuclei attractions, the last term accounts for electron–electron repulsion. ∇_1^2 acts on the coordinates of electron 1 (\vec{r}_1) and ∇_2^2 acts on the coordinates of electron 2 (\vec{r}_2). \vec{R}_A and \vec{R}_B denote, respectively, the coordinates of the nuclei A and B. A schematic representation is shown in Figure 2.

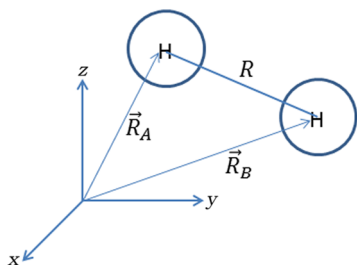


Figure 2. Schematic representation of the coordinate space and of the atomic orbitals for the dihydrogen molecule.

Let us use as the trial wave function a Gaussian orbital around each nucleus:

$$\phi_A(\vec{r}_1) = N_A e^{-\alpha_A |\vec{r}_1 - \vec{R}_A|^2} \quad (8)$$

$$\phi_B(\vec{r}_2) = N_B e^{-\alpha_B |\vec{r}_2 - \vec{R}_B|^2} \quad (9)$$

As both orbitals describe one electron around an H atom of the H₂ molecule it is natural to assume that these two orbitals are equivalent and so:

$$\alpha_A = \alpha_B = \alpha \quad (10)$$

It can be shown that in order for ϕ_A and ϕ_B to be normalized we have:

$$N_A = N_B = N = \left(\frac{2\alpha}{\pi}\right)^{3/4} \quad (11)$$

regardless of the values of \vec{R}_A and \vec{R}_B .

In order for the total wave function to obey Pauli's principle, it has to be antisymmetric with respect to the exchange of electrons. The total wave function is a product of a spatial wave function and a spin wave function. In case the spin multiplicity is 1, that is, when we have one electron with spin up and the other with spin down, the spin wave function is antisymmetric and therefore the spatial wave function has to be symmetric. In case the spin multiplicity is 3, that is, when we have both electrons with spin up or both with spin down, the spin wave function is symmetric and therefore the spatial wave function must be antisymmetric. Our trial function $\Phi(\vec{r}_1, \vec{r}_2)$ is a spatial wave function, so let us write it as a product in the following way:

$$\Phi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\phi_A(\vec{r}_1)\phi_B(\vec{r}_2) \pm \phi_B(\vec{r}_1)\phi_A(\vec{r}_2)) \quad (12)$$

where the plus sign applies for multiplicity 1 (bonding) and the minus sign for multiplicity 3 (antibonding).

It is important to emphasize that although $\phi_A(\vec{r})$ and $\phi_B(\vec{r})$ are normalized functions, $\Phi(\vec{r}_1, \vec{r}_2)$ is not normalized because $\phi_A(\vec{r})$ and $\phi_B(\vec{r})$ are not orthogonal to each other.

It can be shown that the expression for W becomes (the most enthusiastic and curious readers are encouraged to go through the long but beautiful derivation steps of this expression, which can be found in more details at the Supporting Information):

$$W = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \left\{ 3\alpha \pm (3 - \alpha R^2)\alpha e^{-\alpha R^2} - 4\sqrt{\frac{2\alpha}{\pi}} \times \left[1 + \frac{1}{2R}\sqrt{\frac{\pi}{2\alpha}} \operatorname{erf}(R\sqrt{2\alpha}) \right] \mp \frac{8}{R} e^{-\alpha R^2} \operatorname{erf}\left(R\sqrt{\frac{\alpha}{2}}\right) + 2\sqrt{\frac{\alpha}{\pi}} \left[\frac{1}{R}\sqrt{\frac{\pi}{\alpha}} \operatorname{erf}\left(R\sqrt{\frac{\alpha}{4}}\right) \pm e^{-\alpha R^2} \right] \right\} \frac{1}{1 \pm e^{-\alpha R^2}} \quad (13)$$

where the error function is $\operatorname{erf}(x) = 2/\sqrt{\pi} \int_0^x e^{-v^2} dv$, the upper sign accounts for spin multiplicity 1 (bonding) and the lower sign accounts for spin multiplicity 3 (antibonding). It is interesting to note that in the limit where $R \rightarrow \infty$ the expression of W goes to two times the expression we had for the hydrogen atom (see eq 4), as one would expect. This is true regardless of the spin multiplicity.

The choice for the positions of the nuclei is arbitrary. Here, we are going to place the nuclei symmetrically along the z axis by making $\vec{R}_B = -\vec{R}_A = (R/2)\hat{z}$.

We can also derive an expression for the probability density $P(x, y, z)$ of finding an electron in an infinitesimal volume element $d\tau$ around a point $\vec{r} = x\hat{x} + y\hat{y} + z\hat{z}$:

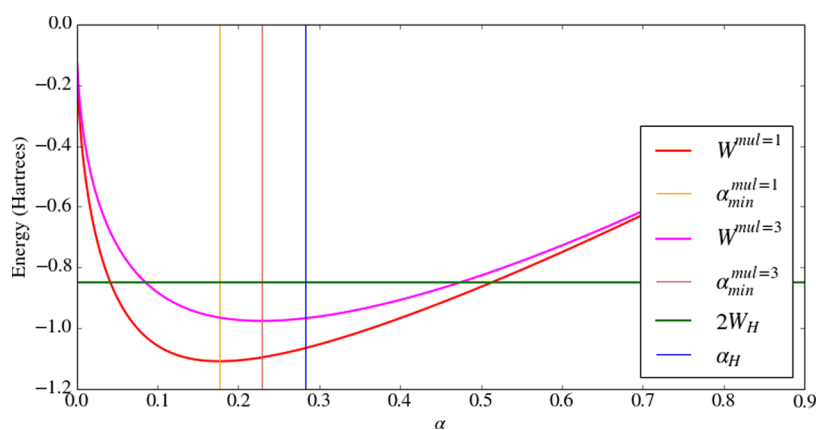


Figure 3. Variational integral of the dihydrogen molecule as a function of α for $R = 3$ Bohr ($1 \text{ Bohr} = 0.5292 \times 10^{-10} \text{ m}$). This figure was generated by the *IPython notebook* program. The reader may go to the program to generate this figure for other values of R .

$$P(x, y, z) = \frac{\int |\Phi(\vec{r}, \vec{r}_2)|^2 d\tau_2}{\int \int |\Phi(\vec{r}_1, \vec{r}_2)|^2 d\tau_1 d\tau_2} = \frac{1}{2} \left(\frac{2\alpha}{\pi} \right)^{3/2} \frac{e^{-2\alpha(x^2+y^2)}}{1 \pm e^{-\alpha R^2}} [e^{-2\alpha(z-R/2)^2} \pm 2e^{-2\alpha z^2} e^{-\alpha R^2} + e^{-2\alpha(z+R/2)^2}] \quad (14)$$

Using an Interactive Platform To Test and Visualize Results

The integrals necessary to solve in order to get the final expression for the variational integral (eq 13) were implemented numerically using *IPython notebook* and the results were compared with the ones we got analytically. This was a really important step in order to detect possible errors in the calculations, which in such large and complex analytical calculations are not unlikely to happen.

As eq 13 shows, the variational integral W is a function of α , R , and the spin-multiplicity. Finding the optimum value of α that gives the minimum value of W (for a given spin-multiplicity and value of R) would be a really tough task by “pen and paper” because the expression for W involves error functions, which makes it unfeasible to obtain an analytical expression for α_{\min} as a function of R and the spin-multiplicity. This problem, however, can be easily solved numerically within the interactive platform. An example is shown in Figure 3.

In Figure 3 α_H and W_H are the optimum values for the hydrogen atom obtained using the variation method (see eqs 5 and 6). For $R = 3$ Bohr we see that α_{\min} is lower than α_H for both spin-multiplicities. In a similar way, the α_{\min} value for different values of R can be determined for the bonding and antibonding wave functions. By plugging α_{\min} into eq 14 one can visualize how the optimum trial wave functions look like. In Figure 4, the probability densities of the optimized trial wave functions are shown plotted as heat maps as a function of x and z (with $y = 0$) for different values of R and for both the bonding and antibonding wave functions. For comparison, the probability density of the hydrogen atoms as if they were isolated is also shown. The probability density $P_{2H}(x, y, z)$ for two isolated hydrogen atoms is straightforward to obtain:

$$P_{2H}(x, y, z) = \frac{|\phi_A(\vec{r})|^2 + |\phi_B(\vec{r})|^2}{2} = \frac{1}{2} \left(\frac{2\alpha_H}{\pi} \right)^{3/2} e^{-2\alpha_H(x^2+y^2)} [e^{-2\alpha_H(z+R/2)^2} + e^{-2\alpha_H(z-R/2)^2}] \quad (15)$$

Naturally, the expression for $P(x, y, z)$ presented on eq 14 converges to $P_{2H}(x, y, z)$ for sufficiently large values of R and for $\alpha = \alpha_H$.

For not too large values of R we can clearly see a bonding behavior for spin-multiplicity 1 exemplified by the presence of probability density between the nuclei, as opposed to an antibonding behavior for spin-multiplicity 3 that can be seen by the presence of a node in the probability density between the nuclei. It is intriguing to note that the bonding probability density “looks like” two isolated hydrogen atoms for small values of R ($R \sim 1.45$ Bohr), however for intermediate values of R ($R \sim 4$ Bohr) it is the antibonding probability density that “looks like” two isolated hydrogen atoms. It is also interesting to note that the probability density for the optimum trial wave function for small or intermediate values of R is never equal to the sum of the probability densities of the two isolated hydrogen atoms (as can be clearly seen for $R = 1.45$ Bohr and $R = 2.5$ Bohr). On the other hand, we also see that as R gets larger both the bonding and the antibonding wave functions tend to behave as two isolated hydrogen atoms and $\alpha_{\min} \rightarrow \alpha_H$.

Another simple way to visualize the probability density of the optimum trial wave functions is by plotting it as a function of z only (by setting $x = y = 0$ in eq 14, for instance). This is shown in Figure 5, and as in this plot the probability density was not integrated over x and y , one cannot expect the graphs to be normalized. In addition to the bonding and antibonding probability densities, we also plot the probability density for the hydrogen atoms as if they were isolated (eq 15).

For $R = 3.0$ Bohr $\alpha_{\min}^{\text{mul}=1} = 0.1766 < \alpha_H$ which means that, in comparison to the isolated hydrogen atoms, in the bonding situation the electrons get farther away from the nuclei. As a result, the probability density in between the nuclei becomes more equally distributed for the bonding trial wave function. For $R = 1.45$ Bohr $\alpha_{\min}^{\text{mul}=1} = 0.3332 > \alpha_H$ which means that in the bonding situation the electrons get closer to the nuclei in comparison to the isolated hydrogen atom. We see that at this distance the maximum of the probability density lies at the middle position between the nuclei. For $R = 6$ Bohr both the

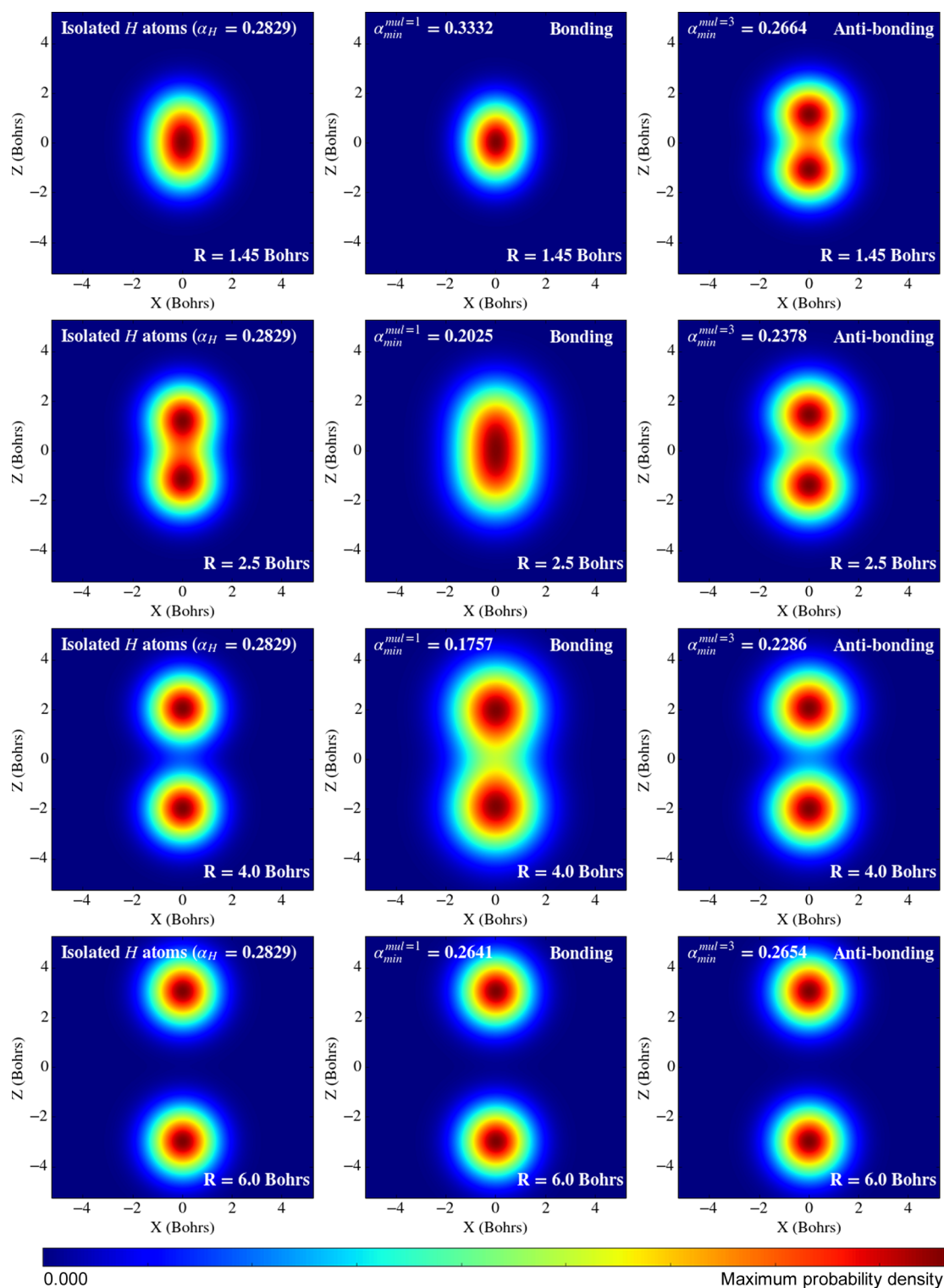


Figure 4. Probability density of the bonding (spin-multiplicity 1, at the center) and antibonding (spin-multiplicity 3, at the right) optimum trial wave functions (plotted as heat maps in the $y = 0$ plane) for the dihydrogen molecule for some values of R . The probability density of the two isolated hydrogen atoms is also presented (at the left). These density plots were generated by the *IPython notebook* program. The reader may go to the program to generate these plots for other values of R .

bonding and antibonding wave functions behave almost like isolated hydrogen atoms (as the reader can verify on the *IPython notebook* program, for $R \approx 8$ Bohr and larger, the probability density plots for the bonding, antibonding, and isolated atoms are identical).

Besides the plots of the wave functions we can also use the computational environment to produce some insightful graphs as the ones shown in Figure 6, which depicts some of the trends in the optimum α_{min} and different types of contribution to the W (see eq 25 of the Supporting Information) as a function of R .

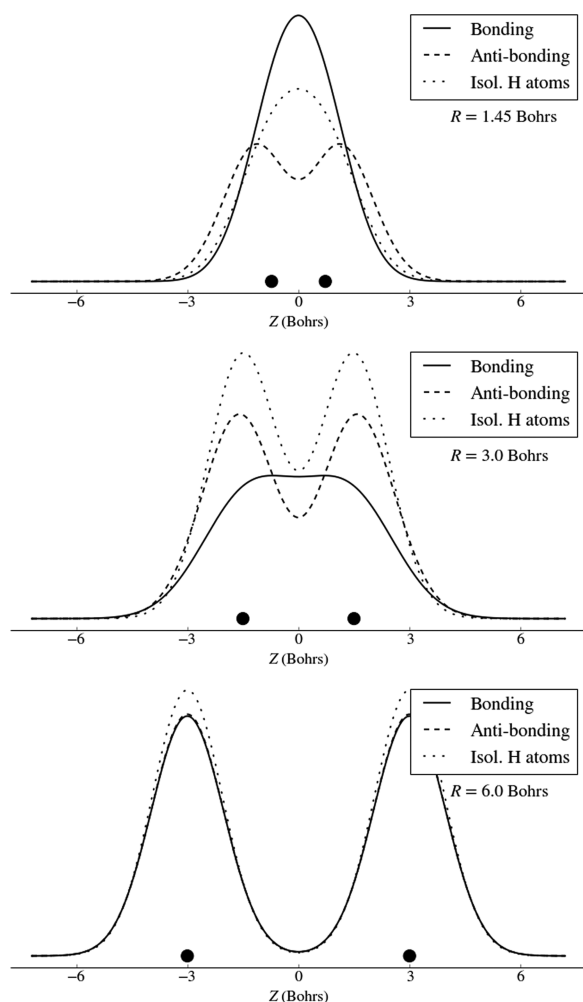


Figure 5. Trial wave function as a function of z for $x = y = 0$ and for some values of R . These density plots were generated by the *IPython notebook* program. The reader may go to the program to generate these plots for other values of R .

Figure 6a shows that $\alpha_{\min}^{\text{mul}=1}$ is higher than α_H for $R < \sim 1.73$ Bohr and lower than α_H for $R > \sim 1.73$ Bohr; $\alpha_{\min}^{\text{mul}=3}$ is lower than α_H except for $R < \sim 0.64$ Bohr, where it is slightly higher. For both the bonding and antibonding wave functions α_{\min} converge to α_H at large values of R .

Figure 6b and c shows for both the bonding and antibonding trial wave functions the minimum value of W_{\min} as well as the kinetic, electron–nuclear attraction, and electron–electron repulsion contributions to W_{\min} , all as a function of R . These figures show that the kinetic contribution is higher in energy than the electron–electron repulsion contribution and that both are positive. The figure also shows that the electron–nuclear attraction contribution is negative and higher in magnitude than the sum of the other two because W_{\min} is negative.

At a first sight, it may be counterintuitive that W_{\min} is lower in energy than $2W_H$ for the antibonding case or that the graph of W_{\min} as a function of R does not have a minimum for the bonding situation. It is very important to note then that the Hamiltonian we are dealing with in eq 7 does not include the nuclear repulsion interaction. As the wave function we are considering depends only parametrically on the nuclei coordinates (see eq 12), this means that if we added nuclear repulsion ($1/R$) to the Hamiltonian it would only add a constant (because it would not depend on α) equal to $1/R$ to our expression for the variational integral at eq 13. Within the Born–Oppenheimer approximation, the nuclei and electronic motions can be separated, and that is exactly the approximation we are making when we do not include an explicit nuclear dependence on the wave function expression. Therefore, both the Hamiltonian in eq 7 and the wave function in eq 12 can be considered as electronic quantities within the Born–Oppenheimer approximation.

Figure 6d presents the minimized values of the variational integral plus the nuclear repulsion term. A comparison of the plots for both the bonding and antibonding cases with two times the energy of an isolated hydrogen atom (W_H , minimum value of the energy for the hydrogen atom also obtained using the variational method, see eq 6) is extremely insightful in

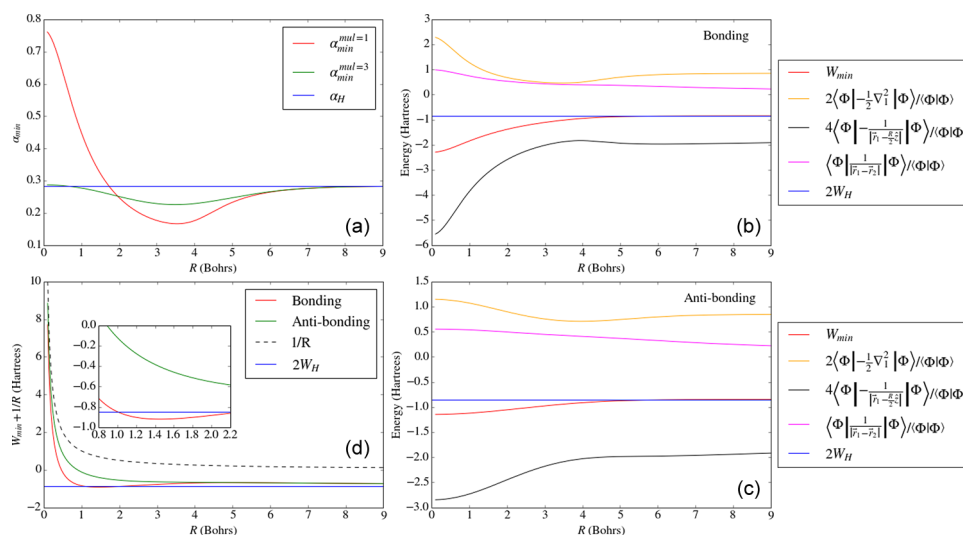


Figure 6. (a) Optimum Gaussian decay factor (α_{\min}) as a function of R for both spin-multiplicities; (b) and (c) Optimum values of the variational integral (W_{\min}) as a function of R for both spin-multiplicities as well as the kinetic, electron–nuclear attraction, and electron–electron repulsion contributions to W_{\min} . (d) Optimum values of the variational integral plus nuclear repulsion ($W_{\min} + 1/R$) as a function of R for both spin-multiplicities. These figures were generated by the *IPython notebook* program.

terms of understanding the bond formation. If we consider the process $H + H \rightarrow H_2$, the energy difference between $W_{\min} + 1/R$ and $2W_H$ is going to tell us whether this process is favorable or unfavorable. As Figure 6d shows, for the antibonding wave function $W_{\min} + 1/R$ is always higher in energy than $2W_H$, which means that the process is unfavorable and a bond will not be formed (that is, that hydrogen prefers to be as two isolated hydrogen atoms rather than as a dihydrogen molecule for any value R). For the bonding wave function, however, Figure 6d shows that this process is favorable (and thus a bond will be formed) for approximately $1.00 \geq R \geq 2.32$ Bohrs (the process is unfavorable for all other values of R).

It is interesting to note that, regardless of the spin state, at larger values of R the curves for $W_{\min} + 1/R$ converges to $2W_H$. Although the Hamiltonian (see eq 7) does not have any spin dependence, the spin (inserted in the spatial wave function through Pauli's principle, see eq 12) is an important property. The hydrogen atoms can come together in two different ways: when both have the same spin state (antibonding, spin-multiplicity 3), or when both have different spin states (bonding, spin-multiplicity 1). We see that in both cases when the atoms are far apart the behavior is equivalent, but when they get close together the behavior is different for the two situations. This observation is in agreement with what is taught on Molecular Orbital Theory in General Chemistry, as illustrated in Figure 7.

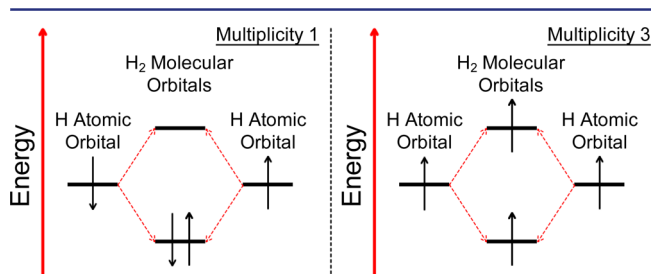


Figure 7. Atomic and molecular energy diagrams for the dihydrogen molecule.

As our results show and Figure 7 illustrates, when the atoms come together with each atom having a different spin state (spin-multiplicity 1), depending on the internuclear distance R , a bond is formed because the molecule is more stable in energy than the isolated atoms. However, when the atoms come together with each atom having the same spin state (spin-multiplicity 3) the interaction has a repulsive (antibonding) behavior and a bond cannot be formed.

As Figure 6d shows, the curve for $W_{\min} + 1/R$ has a minimum for the bonding optimum trial wave function. This minimum represents the equilibrium position of the nuclei, and as can be seen from the figure (see the inset of Figure 6d) it is equal to $R_{\text{eq}} = 1.45$ Bohrs; probability density plots of the optimum trial wave function at this equilibrium position is shown in Figures 4 and 5. In comparison, the experimental value for the bond length of the dihydrogen molecule is 1.40 Bohrs,^{4,18} which is in fairly good agreement with the value we obtained by using the variational method with Gaussian trial functions. Similarly, the bond energy is determined from the difference of $W_{\min} + 1/R$ at R_{eq} and $2W_H$, which is equal to -44.946 kcal/mol. This value underestimates in magnitude the experimentally determined bond energy for the dihydrogen molecule which is -109.5 kcal/mol.^{4,18}

CONCLUSIONS

This work shows that important features of the dihydrogen molecule can be explained with the variational method and simple Gaussians as trial wave functions. Among other things, we are able: to show that the favorability of formation of the dihydrogen molecule from two hydrogen atoms can be seen in the results; talk about the bonding and antibonding behaviors of the dihydrogen molecule (that is, when the multiplicity is 1 and when it is 3); obtain an equilibrium bond length for the dihydrogen molecule which is in close agreement with the experimental one.

Although the variational integral for the dihydrogen molecule presented in this article was obtained analytically, the *IPython notebook* platform had a fundamental role in testing the derivations, on visualizing results (for example, the wave functions), and on deriving some important results that would be unreachable by only “pen and paper” (like the equilibrium bond length). Therefore, this work is an example that the combination of a computational environment and “pen and paper” can be powerful in complex analytical derivations as well as it can be a nice way to teach quantum chemistry/physical chemistry to students in class.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00017.

The mathematical derivation details not presented in the article regarding the analytical calculations, information on how to install *IPython notebook* and all the libraries necessary to run the program, some general instructions on how to execute the program, and links to good reading material on *IPython notebook* (PDF). The *IPython notebook* program written for this article which focuses on generating all the plots for the dihydrogen molecule interactively (ZIP).

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Notes

The authors declare no competing financial interest. This work started as a student project for a quantum chemistry graduate course (CHM 6470-Chemical Bonding and Spectra I) at the University of Florida.

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