

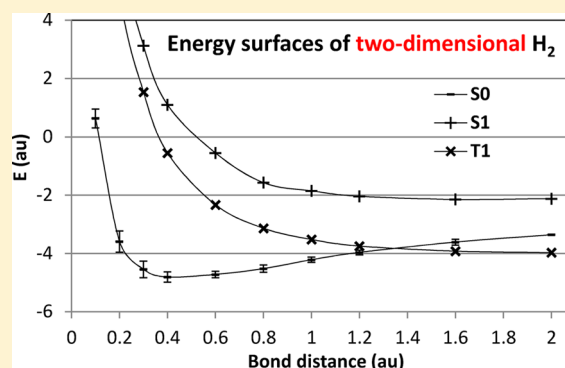
# Let Students Derive, by Themselves, Two-Dimensional Atomic and Molecular Quantum Chemistry from Scratch

Yingbin Ge\*

Department of Chemistry, Central Washington University, Ellensburg, Washington 98926, United States

## Supporting Information

**ABSTRACT:** Hands-on exercises are designed for undergraduate physical chemistry students to derive two-dimensional quantum chemistry from scratch for the H atom and H<sub>2</sub> molecule, both in the ground state and excited states. By reducing the mathematical complexity of the traditional quantum chemistry teaching, these exercises can be completed independently by students who have basic calculus skills. Students are expected to convert the Laplacian into the polar coordinates; solve the Schrödinger equations for the two-dimensional H atom; write out the electron configurations and atomic terms for many-electron atoms; solve the Schrödinger equations for the H<sub>2</sub> molecule; obtain its potential energy surfaces in the ground state and excited states; examine the individual kinetic, attractive, and repulsive energy components; and plot and visualize the bonding and antibonding molecular orbitals of the two-dimensional H<sub>2</sub>. In summary, various exercises are designed for students to derive quantum chemistry for atoms and molecules in two dimensions, from scratch, by themselves. These exercises help reinforce students' understanding of quantum chemistry of real atoms and molecules in three dimensions; they also challenge students to derive quantum chemistry for a fictitious two-dimensional world and to critically evaluate the validity of their derivations. These challenges may help students climb up Bloom's Taxonomy Pyramid of educational objectives toward its highest levels: synthesis of new knowledge and critical evaluation.



**KEYWORDS:** Upper-Division Undergraduate, Physical Chemistry, Computer-Based Learning, Quantum Chemistry, Computational Chemistry, Student-Centered Learning

## INTRODUCTION

Solving the Schrödinger equation of the H atom is an important topic in the teaching of undergraduate quantum chemistry because it allows students, for the first time, to see how the electronic structure of a real chemical system is computed. However, rarely do quantum chemistry instructors explain in detail how this Schrödinger equation is actually solved, possibly for one or more of the following reasons:

- The math is too hard; it involves converting the Laplacian from the Cartesian coordinates into the polar spherical coordinates (included in Appendix A in the Supporting Information) and solving Laguerre and Legendre differential equations.
- Even if an instructor takes the effort and time to illustrate the derivation in class, a significant portion, if not all, of the chemistry students may get overwhelmed and even intimidated by its mathematical complexity.
- A small portion of students who can follow the derivation, if there are any, will more likely be just following rather than actively learning.

To better teach this topic, it is necessary to reduce its mathematical complexity to involve the students in a more active learning process: students should not just sit back and

watch instructors derive on the board but also roll up sleeves and do the derivation themselves. One way to achieve these goals, assuming students make a reasonable amount of effort, is to reduce the dimensionality of the problem from three to two. Computation of the electronic structure of the two-dimensional H atom resembles its three-dimensional counterpart, but with much reduced mathematical complexity, while further reducing the problem to one dimension results in enhanced complexity because the ground state of the one-dimensional H atom disappears.<sup>1,2</sup> Students with basic calculus skills should be able to solve the easier two-dimensional Schrödinger equations and are expected to develop confidence in and even appreciation for learning this otherwise hard topic. In traditional quantum chemistry teaching, many-electron atoms and molecules are studied after the H atom. The same route is adopted in this paper to provide a more complete overview of atomic and molecular chemistry in two dimensions, which may help students through their learning of the real-world quantum chemistry. In addition, these exercises challenge students to derive quantum chemistry for a fictitious two-dimensional

Received: July 28, 2016

Revised: September 26, 2016

Published: October 12, 2016

world and to critically evaluate the results of their derivation; these challenges may help students climb up Bloom's Taxonomy Pyramid of educational objectives toward its highest levels, synthesis of new knowledge and critical evaluation.<sup>3</sup>

In the following sections, we will illustrate the construction and solution of the Schrödinger equation of the two-dimensional H atom, extend the quantum theory to many-electron atoms, study the ground and excited states of the H<sub>2</sub> molecule, and propose hands-on exercises suitable for undergraduate students. It is hoped that, by completing some or all of the proposed exercises, students may feel that learning quantum chemistry is not that hard, it is achievable, and sometimes, it can even be fun.

## THEORETICAL DERIVATION AND NUMERICAL COMPUTATION

### Hydrogen Atom

The two-dimensional Laplacian operator  $\nabla^2$  has a simple form in Cartesian coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \quad (1)$$

For convenience and clarity, subscripts of all partial derivatives are omitted with the assumption that when a partial derivative is taken with respect to an independent variable, all other respective independent variables are held constant.

The Cartesian coordinates  $x, y$  can be expressed in the polar coordinates as follows:

$$x = r \cos \phi \quad (2)$$

$$y = r \sin \phi \quad (3)$$

Using the chain rule,  $\frac{\partial}{\partial x}$  and  $\frac{\partial}{\partial y}$  can be expressed in terms of  $r$  and  $\phi$ :

$$\frac{\partial}{\partial x} = \cos \phi \frac{\partial}{\partial r} - \frac{\sin \phi}{r} \frac{\partial}{\partial \phi} \quad (4)$$

$$\frac{\partial}{\partial y} = \sin \phi \frac{\partial}{\partial r} + \frac{\cos \phi}{r} \frac{\partial}{\partial \phi} \quad (5)$$

The second derivatives  $\frac{\partial^2 f}{\partial x^2}$  and  $\frac{\partial^2 f}{\partial y^2}$  can thus also be expressed in terms of  $r$  and  $\phi$ :

$$\begin{aligned} \frac{\partial^2 f}{\partial x^2} = & \cos^2 \phi \frac{\partial^2 f}{\partial r^2} - \frac{2 \sin \phi \cos \phi}{r} \frac{\partial^2 f}{\partial r \partial \phi} + \frac{\sin^2 \phi}{r^2} \frac{\partial^2 f}{\partial \phi^2} \\ & + \frac{\sin^2 \phi}{r} \frac{\partial f}{\partial r} + \frac{2 \sin \phi \cos \phi}{r^2} \frac{\partial f}{\partial \phi} \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{\partial^2 f}{\partial y^2} = & \sin^2 \phi \frac{\partial^2 f}{\partial r^2} + \frac{2 \sin \phi \cos \phi}{r} \frac{\partial^2 f}{\partial r \partial \phi} + \frac{\cos^2 \phi}{r^2} \frac{\partial^2 f}{\partial \phi^2} \\ & + \frac{\cos^2 \phi}{r} \frac{\partial f}{\partial r} - \frac{2 \sin \phi \cos \phi}{r^2} \frac{\partial f}{\partial \phi} \end{aligned} \quad (7)$$

The two-dimensional  $\nabla^2$  can then be expressed as follows (more detailed derivation can be found in Appendix B in the Supporting Information):

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \quad (8)$$

The Schrödinger equation for the two-dimensional H atom in the atomic units is thus

$$\begin{aligned} -\frac{1}{2} \nabla^2 \psi - \frac{1}{r} \psi = & \frac{-1}{2} \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right) \psi - \frac{1}{r} \psi \\ = & E \psi \end{aligned} \quad (9)$$

It is assumed in the above equation that the kinetic energy of the nucleus is negligible and that the two-dimensional atomic units are the same as for its three-dimensional counterpart:

$$m_e = 1 \text{ au} \quad (10)$$

$$e = 1 \text{ au} \quad (11)$$

$$\hbar = \frac{h}{2\pi} = 1 \text{ au} \quad (12)$$

$$\frac{1}{4\pi\epsilon_0} = 1 \text{ au} \quad (13)$$

The derived atomic units for length and energy are also assumed to be the same as for their three-dimensional counterparts:

$$1 \text{ au of length} = \frac{(4\pi\epsilon_0)\hbar^2}{m_e e^2} \quad (14)$$

$$1 \text{ au of energy} = \frac{m_e e^4}{(4\pi\epsilon_0)^2 \hbar^2} \quad (15)$$

Setting  $\psi = R(r)\Phi(\phi)$  to separate the two variables in eq 9, we have

$$-\frac{1}{2} \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right) R\Phi - \frac{1}{r} R\Phi = ER\Phi \quad (16)$$

After rearranging the above equation to separate the variables, we have

$$-\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = \frac{1}{R} \left( r^2 \frac{\partial^2 R}{\partial r^2} + r \frac{\partial R}{\partial r} \right) + 2Er^2 + 2r \quad (17)$$

Because the left-hand side of the above equation is independent of  $r$  while the right-hand side is independent of  $\phi$ , both sides must be equal to a constant, which is set to be  $l^2$ :

$$-\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = l^2 \quad (18)$$

$$\Phi(\phi) = e^{im_l \phi} \quad (19)$$

Here,  $l$  is non-negative and  $m_l = \pm l$ . The physical meaning of  $l$  is the *magnitude* of the angular momentum, and  $l$  must be an integer to ensure the periodic boundary condition of the angular function  $\Phi$ . Unlike its three-dimensional counterpart (where  $m_l$  can adopt any integer value from  $-l$  to  $+l$ ), the values of  $m_l$  can only be  $\pm l$  for the two-dimensional H atom, which, we will show later, has a significant effect on writing the electron configurations and atomic terms for many-electron atoms. Although  $m_l$  alone is sufficient to describe the two-dimensional quantum rotation, the introduction of  $l = |m_l|$  as the *magnitude* of the angular momentum makes a parallel with its three-dimensional counterpart; it is also in accordance with the more general Laplacian in  $D$  dimensions developed by Louck.<sup>4</sup>

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{D-1}{r} \frac{\partial}{\partial r} + \frac{l(l+D-2)}{r^2} \quad (20)$$

From eqs 17 and 18, the differential equation for the radial function of H in two dimensions can be obtained:

$$r^2 \frac{\partial^2 R}{\partial r^2} + r \frac{\partial R}{\partial r} + (2Er^2 + 2r - l^2)R = 0 \quad (21)$$

Complete and partial solutions to the above equation can be found in various papers.<sup>5–10</sup> Nonetheless, students would benefit from solving this equation by themselves; however, they should be provided the form of the hydrogen atomic orbital functions, a product of an exponential function and an associated Laguerre polynomial function. With the 1s orbital of the two-dimensional H atom as example, its angular wave function is trivial:  $l = 0$ ,  $m_l = 0$ ,  $\Phi(\phi) = e^{im_l\phi} = 1$ , while its radial function can be obtained by solving the following equation:

$$r^2 \frac{\partial^2 R}{\partial r^2} + r \frac{\partial R}{\partial r} + (2Er^2 + 2r)R = 0 \quad (22)$$

We conjecture that  $R = e^{-br}$ , similar to its three-dimensional counterpart; the above differential equation is transformed to a polynomial equation:

$$(b^2 + 2E)r^2 + (-b + 2)r = 0 \quad (23)$$

For the above polynomial equation to hold true at all values of  $r$ , we have

$$b = 2 \quad (24)$$

$$E_{1s} = -\frac{b^2}{2} = -2 \quad (25)$$

$$\psi_{1s} = R(r)\Phi(\phi) = e^{-2r} \quad (26)$$

For clarity, the normalization factor is neglected in the above 1s wave function and all other wave functions in this paper. Note that the 1s orbital of the two-dimensional H atom is tighter with a more negative exponential coefficient than its 3D counterpart ( $e^{-2r}$  vs  $e^{-r}$ ) and has more negative energy ( $-2$  au vs  $-(1/2)$  au). The expectation value of the attraction energy is

$$\left\langle -\frac{1}{r} \right\rangle = \frac{\int_0^\infty e^{-2r} \left(-\frac{1}{r}\right) e^{-2r} r \, dr}{\int_0^\infty e^{-2r} e^{-2r} r \, dr} = \frac{-1/4}{1/16} = -4 \quad (27)$$

The expectation value of the kinetic energy of the 1s electron is thus  $E_{\text{kinetic}} = E - E_{\text{potential}} = (-2) - (-4) = 2$  au; the result is in accordance with the virial theorem.

For conciseness, the detailed derivations for the 2s, 2p, 3s, 3p, and 3d orbitals are included in Appendix C in the Supporting Information; the results, including the orbital wave functions and orbital energies, are summarized below in Table 1.

Table 1 shows that the atomic orbital wave functions in two dimensions are in general tighter (with more negative exponential coefficients) than their three-dimensional counterparts:  $e^{-r/(n-0.5)}$  (2D) versus  $e^{-r/n}$  (3D), and that the atomic orbital energies in two dimensions are more negative:  $-\frac{1}{2(n-0.5)^2}$  (2D) vs  $-\frac{1}{2n^2}$  (3D).

### Many-Electron Atoms

Like their three-dimensional counterparts, the two-dimensional many-electron atoms do not have analytical solutions.

**Table 1. Wave Functions and Corresponding Energies for the Two-Dimensional H Atom**

Orbital	Wave Function	Energy, au
1s	$e^{-2r}$	-2
2s	$\left(r - \frac{3}{4}\right)e^{-2/3r}$	$-\frac{2}{9}$
2p	$re^{-2/3r}e^{\pm i\phi}$	
3s	$\left(r^2 - 5r + \frac{25}{8}\right)e^{-2/5r}$	
3p	$\left(r - \frac{15}{4}\right)re^{-2/5r}e^{\pm i\phi}$	$-\frac{2}{25}$
3d	$r^2e^{-2/5r}e^{\pm 2i\phi}$	
In general <sup>a</sup>		
$n = 1, 2, 3, \dots$	$\psi = R_{n,l}(r)\Phi_{l,m_l}(\phi)$	
$l = 0, 1, 2, \dots, n-1$	$R_{n,l}(r) = f(r)e^{-r/n-\frac{1}{2}}$	$E = \frac{-1}{2\left(n - \frac{1}{2}\right)^2}$
$m_l = \pm l$	$\Phi_{l,m_l}(\phi) = e^{im_l\phi}$	

<sup>a</sup>Here,  $f(r)$  is an  $l$ -th order polynomial function of  $r$  with  $(n-1)$  distinctive positive roots, each of which corresponds to a circular node.

However, the electronic structures of the two-dimensional atoms can be constructed approximately using atomic orbitals similar to those of the H atom. The first three rows of a conjectured periodic table for the two-dimensional atoms are constructed using the Aufbau principle in Figure 1. Note that any orbital with  $l \geq 1$  can hold up to only four electrons because the values of  $m_l$  can only be  $\pm l$  in a fictitious two-dimensional world.

s-block									
1	2	p-block							
1s <sup>1</sup>	1s <sup>2</sup>								
3	4	5	6	7	8	d-block			
2s <sup>1</sup>	2s <sup>2</sup>	2s <sup>2</sup> 2p <sup>1</sup>	2s <sup>2</sup> 2p <sup>2</sup>	2s <sup>2</sup> 2p <sup>3</sup>	2s <sup>2</sup> 2p <sup>4</sup>				
9	10	11	12	13	14	15	16	17	18
3s <sup>1</sup>	3s <sup>2</sup>	3s <sup>2</sup> 3p <sup>1</sup>	3s <sup>2</sup> 3p <sup>2</sup>	3s <sup>2</sup> 3p <sup>3</sup>	3s <sup>2</sup> 3p <sup>4</sup>	3s <sup>2</sup> 3p <sup>4</sup> 3d <sup>1</sup>	3s <sup>2</sup> 3p <sup>4</sup> 3d <sup>2</sup>	3s <sup>2</sup> 3p <sup>4</sup> 3d <sup>3</sup>	3s <sup>2</sup> 3p <sup>4</sup> 3d <sup>4</sup>

**Figure 1.** Conjectured periodic table of two-dimensional atoms with valence electron configurations.

In the periodic table in Figure 1, electrons are conjectured to occupy the 3d orbitals before the 4s orbitals because of the larger energy spacing between  $n = 3$  and  $n = 4$  for the hydrogen-like atomic orbitals in two dimensions. However, the  $E_{3d} < E_{4s}$  energy ranking for atoms in two dimensions is merely a conjecture until various other factors are carefully analyzed as in the three-dimensional case.<sup>11</sup> The accurate energy ranking of the 3d and 4s orbitals may entail a serious effort of modifying existing computational chemistry software for the two-dimensional case.

Writing the atomic terms of atoms in two dimensions is easier than for its 3D counterpart. Taking the d<sup>2</sup> electron configuration as an example, its six microstates (compared with the 45 microstates of its 3D counterpart) and three atomic terms are illustrated in Table 2. A different rule of  $M_L = \pm L$  is applied to the two-dimensional case in comparison to the  $|M_L| \leq L$  rule for its three-dimensional counterpart.

**Table 2.** Six Microstates of the  $d^2$  Electron Configuration of Two-Dimensional Atoms

$m_l$		$M_L = \sum_i m_{l_i}$	$M_S = \sum_i m_{s_i}$	$L, S$	Atomic Term
-2	2				
$\downarrow\uparrow$		-4	0	4, 0	$^1G$
	$\downarrow\uparrow$	4	0		
$\uparrow$	$\uparrow$	0	1	0, 1	$^3S$
$\uparrow$	$\downarrow$	0	0		
$\downarrow$	$\downarrow$	0	-1		
$\downarrow$	$\uparrow$	0	0	0, 0	$^1S$

## H<sub>2</sub> Molecule

The transition from atomic chemistry to molecular chemistry is a crucial step in the learning of quantum chemistry. Exercises involving analytical derivation and spreadsheet calculation for solving the Schrödinger equation for the H<sub>2</sub> molecule were designed for students to better understand quantum chemistry,<sup>12,13</sup> so were the Monte Carlo integration enabled spreadsheet calculations of H<sub>2</sub> in its S<sub>0</sub>, S<sub>1</sub>, and T<sub>1</sub> electronic states.<sup>14</sup> Herein, the Monte Carlo integration method<sup>14</sup> is used to calculate the electronic energy of the two-dimensional H<sub>2</sub> molecule using the following equation

$$\langle E_{\text{ele}} \rangle = \frac{\int \psi \widehat{H}_{\text{ele}} \psi \, d\tau}{\int \psi^2 \, d\tau}$$

$$= \frac{\int \psi \left[ \left( \frac{-1}{2} \nabla_1^2 + \frac{-1}{2} \nabla_2^2 \right) + \left( \frac{-1}{r_{1A}} + \frac{-1}{r_{1B}} + \frac{-1}{r_{2A}} + \frac{-1}{r_{2B}} \right) + \left( \frac{1}{r_{12}} \right) \right] \psi \, d\tau}{\int \psi^2 \, d\tau} \quad (28)$$

where 1 and 2 are the two electrons, and A and B are the two H nuclei. The following antisymmetric wave functions are used for the singlet ground state (S<sub>0</sub>), the first excited singlet state (S<sub>1</sub>), and the first triplet excited state (T<sub>1</sub>)

$$\psi(S_0) = [\sigma(1)\sigma(2)] \cdot [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (29)$$

$$\psi(S_1) = [\sigma(1)\sigma^*(2) + \sigma(2)\sigma^*(1)] \cdot [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (30)$$

$$\psi(T_1) = [\sigma(1)\sigma^*(2) - \sigma(2)\sigma^*(1)] \cdot [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (31)$$

where  $\sigma$  and  $\sigma^*$  denotes the sigma bonding and antibonding molecular orbitals in H<sub>2</sub>.

The expectation value of each energy component is then estimated on a spreadsheet using the Monte Carlo integration method<sup>14</sup> taking the  $e-e$  repulsion as example:

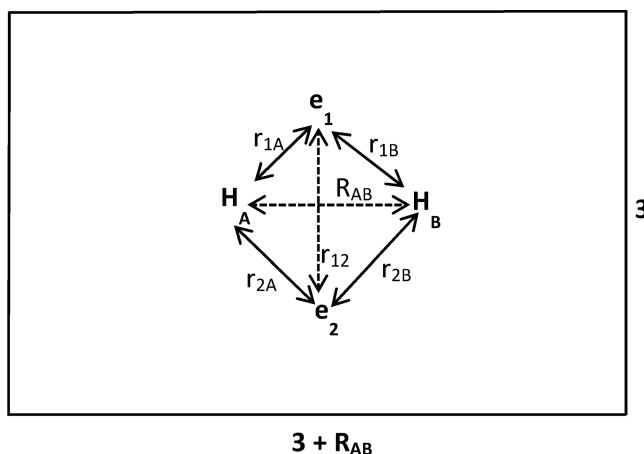
$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{\int \psi \frac{1}{r_{12}} \psi \, d\tau}{\int \psi^2 \, d\tau} \approx \frac{\sum_{k=1}^{N_{\text{sampling}}} (\psi^k)^2 \left( \frac{1}{r_{12}^k} \right) V^2}{\sum_{k=1}^{N_{\text{sampling}}} (\psi^k)^2 V^2}$$

$$\approx \frac{\sum_{k=1}^{N_{\text{sampling}}} (\psi^k)^2 \left( \frac{1}{r_{12}^k} \right)}{\sum_{k=1}^{N_{\text{sampling}}} (\psi^k)^2} \quad (32)$$

Here,  $V$  is the two-dimensional volume within which the positions of the two electrons are randomly sampled  $N_{\text{sampling}}$  times ( $N_{\text{sampling}} = 40,000$  for the calculations presented in this

paper).  $\psi^k$  is the wave function of the two electrons of the  $k$ -th sampling, and  $\frac{1}{r_{12}^k}$  is the respective  $e-e$  repulsion. The attractive terms between the electrons and the nuclei are estimated in a similar manner. The calculation of the kinetic energy of the electrons, however, requires some mathematical derivation beforehand with details presented in a previous paper.<sup>14</sup>

It is impractical to sample the positions of the electrons in an infinitely large two-dimensional space. Instead, we decide to perform the Monte Carlo integration within a rather small area of  $V = 3 \times (3 + R_{\text{AB}})$  as illustrated in Figure 2, where  $R_{\text{AB}}$  is the



**Figure 2.** Two-dimensional H<sub>2</sub> with a bond length of  $R_{\text{AB}}$  placed in a box. The dimensions of the box, also in au, illustrate the limits of the integrals calculated on the spreadsheet.

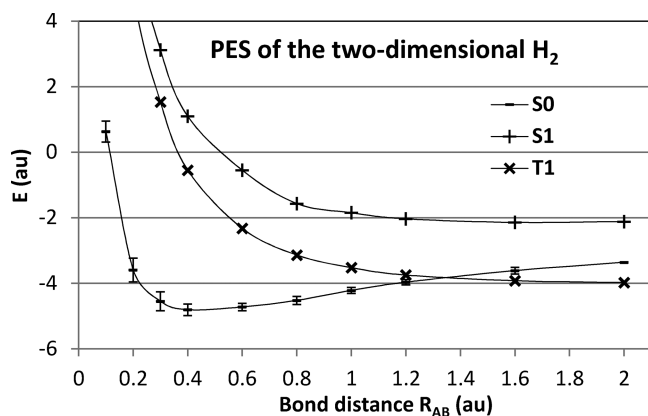
internuclear distance. This is because 98.3% of the 1s electron density of the H atom is contained within the shell of a 1.5 au radius:

$$\frac{\int_0^{1.5} e^{-4r} r \, dr}{\int_0^{\infty} e^{-4r} r \, dr} = \frac{0.06142}{0.0625} = 98.3\% \quad (33)$$

Also, in the H<sub>2</sub> molecule, electrons are attracted even more toward the center of the H<sub>2</sub> bond owing to the attraction from two H nuclei compared with only one in the atomic case.

Spreadsheet calculations were carried out for the two-dimensional H<sub>2</sub> using the Monte Carlo integration method.<sup>14</sup> The calculated potential energy surfaces (PES) of the S<sub>0</sub> ground state and the S<sub>1</sub> and T<sub>1</sub> excited states are presented in Figure 3. Note that the PES in the ground state does not level off properly at the dissociation limit because a single-determinant wave function that forces the pairing of the bonding electrons is insufficient to describe a severely stretched bond. However, the PES in the T<sub>1</sub> excited state, in which the two electrons are not forced to be paired, levels off properly at the dissociation limit to  $E = -4$  au, which equals the total energy of two separate H atoms in two dimensions.

For students to dissect the energy profile of the H<sub>2</sub> molecule in the ground and excited states, the kinetic energy, attraction, and  $e-e$  repulsion energy components are presented in Figure 4. The electrons in the S<sub>1</sub> and T<sub>1</sub> excited states of H<sub>2</sub> have much higher kinetic energy than those in the S<sub>0</sub> state at the equilibrium bond distance of 0.4 au, and the difference increases/decreases rapidly as the H<sub>2</sub> bond is compressed/stretched. The attraction energy difference between the excited states and the ground state is relatively small, and this difference



**Figure 3.** Potential energy surfaces (PES) of the two-dimensional  $H_2$  in the  $S_0$ ,  $S_1$ , and  $T_1$  electronic states. Error bars are plotted only for the  $S_0$  ground state for better clarity of the graph.

diminishes as the bond distance approaches zero or infinity: when  $R_{AB} \rightarrow 0$ , each of the four attractive terms approaches  $-4$  au in the  $S_0$ ,  $S_1$ , and  $T_1$  states; when  $R_{AB} \rightarrow \infty$ , only two attractive terms approach  $-4$  au while the other two terms approach zero. In the  $e-e$  repulsion plot, the nearly 2 au difference between the  $S_1$  and  $T_1$  states originates from the exchange energy.

After the bond distance of the two-dimensional  $H_2$  is optimized using the PES in Figure 3, the bonding ( $\sigma$ ) and antibonding ( $\sigma^*$ ) molecular orbitals of the two-dimensional  $H_2$  molecule at the equilibrium bond distance ( $R_{eq} = 0.4$  au) are calculated at intervals of 0.2 au in both  $x$  and  $y$  dimensions on a separate spreadsheet using the following equations:

$$\sigma = 1s_A + 1s_B = e^{-2r_A} + e^{-2r_B} \quad (34)$$

$$\sigma^* = 1s_A - 1s_B = e^{-2r_A} - e^{-2r_B} \quad (35)$$

where

$$r_A = \sqrt{(x + 0.2)^2 + y^2} \quad (36)$$

$$r_B = \sqrt{(x - 0.2)^2 + y^2} \quad (37)$$

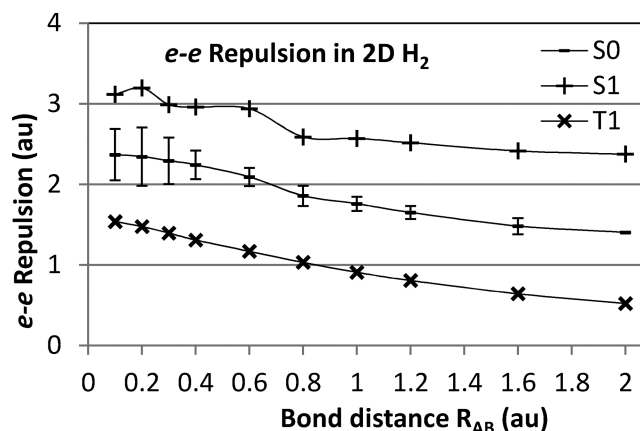
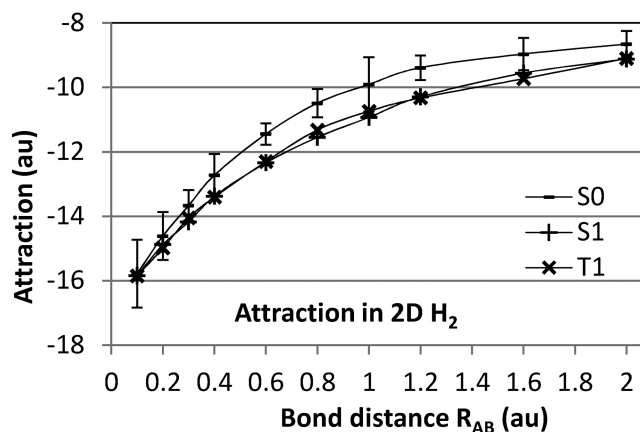
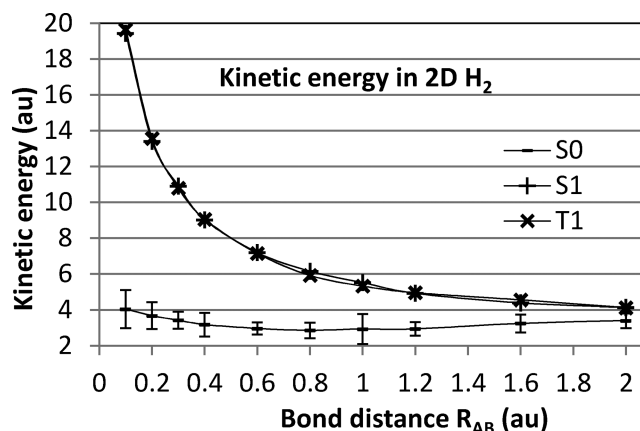
Due to the lower dimensionality of the 2D  $H_2$  molecule, its molecular orbitals in their entirety, rather than the cut views, can now be illustrated in Figure 5.

## EXERCISES FOR STUDENTS

The exercises for students are categorized into two parts: Part I, Atomic Chemistry, and Part II, Molecular Chemistry. Both parts are proposed for students to accomplish independently or with as little external help as possible.

### Part I. Atomic Chemistry

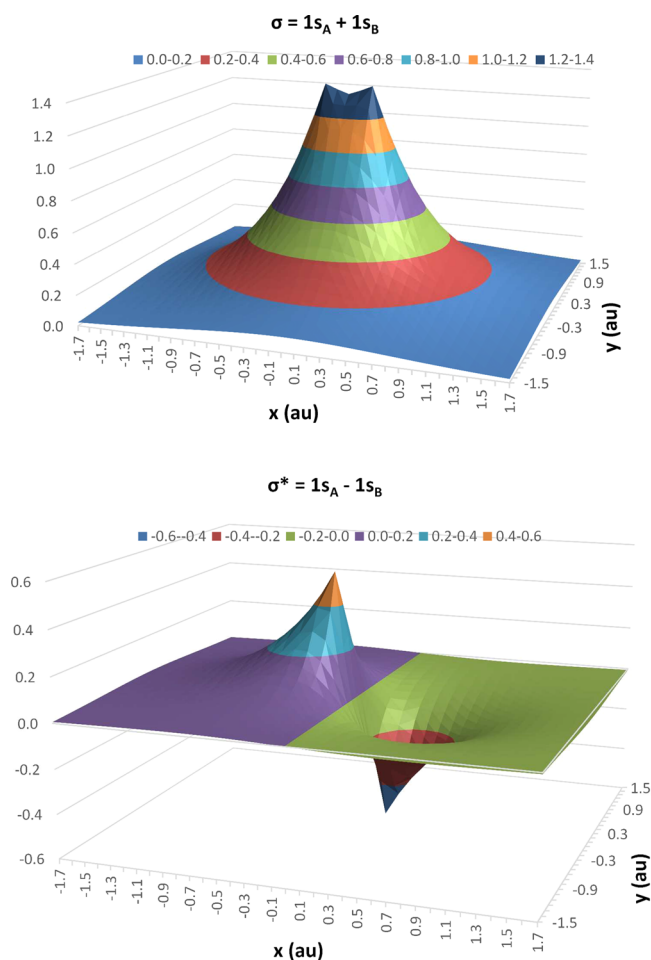
Students should be able to convert the Laplacian from the two-dimensional Cartesian coordinates to the polar coordinates, solve the Schrödinger equation for two-dimensional H atom to obtain the 1s and higher-energy atomic orbitals, obtain the corresponding atomic orbital energies, analyze the individual energy components, and write out electron configurations and atomic terms for the two-dimensional many-electron atoms. Detailed derivations are included in Appendices B and C in the Supporting Information in case students need additional help to complete these exercises.



**Figure 4.** Energy components of the two-dimensional  $H_2$  in the  $S_0$ ,  $S_1$ , and  $T_1$  electronic states. Error bars are plotted only for the  $S_0$  ground state for better clarity of the graphs.

### Part II. Molecular Chemistry

Students should be able to solve the Schrödinger equation for the two-dimensional  $H_2$  on a spreadsheet, plot and visualize the potential energy surfaces and energy components of the ground and excited states of the two-dimensional  $H_2$ , and plot the molecular orbitals of the two-dimensional  $H_2$ . More specific instructions for students to complete this part are included in the Supporting Information of a previous paper.<sup>14</sup> Minor modifications should be made: only the  $xy$  coordinates of electrons should be used, and the 1s wave function in two dimensions is tighter ( $\psi_{1s} = e^{-2r}$ ).



**Figure 5.** Bonding ( $\sigma = 1s_A + 1s_B$ ) and antibonding ( $\sigma^* = 1s_A - 1s_B$ ) molecular orbitals of the two-dimensional  $H_2$  at equilibrium bond distance ( $R_{eq} = 0.4$  au).

Instructors are recommended to *selectively* assign these 2D quantum chemistry exercises, *before or after* their 3D counterparts are taught. Whether or when to assign an exercise should depend on multiple factors: students' background, desired learning outcomes, topics to be covered, and the amount of time students are expected to spend on learning these topics. For example, students may be asked to convert the 2D Laplacian into the polar coordinates *before* they are introduced to the 3D Laplacian conversion; this way, students will better appreciate the results of the 3D conversion, even if the actual

derivation is not presented in class or worked out by themselves. On the other hand, the exercise of solving the Schrödinger equation for the H atom in two dimensions is better assigned *after* students see the 3D solutions because it requires prior knowledge of the form of the radial functions. Although this 2D exercise does not constitute a complete rigorous solution to the Schrödinger equation, it offers students an opportunity for tackling new quantum chemistry problems by connecting them to old ones. The exercises regarding the electron configurations and atomic terms of atoms, as well as the ones regarding the  $H_2$  molecule, closely resemble their three-dimensional counterparts, but students may be encouraged to work on these exercises as well, if time permits, because completing these exercises would force students to think critically and creatively: For example, they need to explain why in a fictitious two-dimensional world the 3d orbitals can accommodate up to only four electrons.

In addition to the exercises proposed above, motivated students may be encouraged to solve the Schrödinger equation for the H atom in various dimensions ( $D = 1, 2, 3, 4$ ) and compare the results to “observe” the quantum confinement effect from an interesting perspective by varying the dimensionalities. Table 3 summarizes the 1s and 2s orbitals in  $D$  dimensions ( $D = 1, 2, 3, 4$ ); detailed derivation is included in Appendix D in the Supporting Information. The quantum confinement effect is illustrated by the dimensionality-dependent energy spacing between the 1s and 2s orbitals. Beyond atoms, students may also be challenged to think outside the (3D) box with the task of studying the PES of the  $H_2$  molecule in *four* dimensions.

## CONCLUSIONS

It has been demonstrated that two-dimensional quantum chemistry of the H atom and the  $H_2$  molecule can be derived from scratch using only basic calculus skills. The derivation from the Cartesian coordinates to the polar coordinates becomes much more tractable than its three-dimensional counterpart; the quantum descriptions of the H atom and the  $H_2$  molecule in two dimensions may pave an alternative path for students to better understand the real-world three-dimensional quantum chemistry. The additional exercise about the electronic structures of the *four*-dimensional H atom and  $H_2$  molecule may further challenge the students to truly think outside the (3D) box. Finally, the proposed exercises constitute a complement to the existing “dry” laboratories of quantum chemistry (which are few); these exercises can also be used for homework problems,

**Table 3.** 1s and 2s Orbitals and Energies in au in  $D$  Dimensions ( $D = 1, 2, 3, 4$ )

Orbital or Energy	1D <sup>a</sup>	2D	3D	4D
$\psi_{1s}$	$\delta(r)^\alpha$	$e^{-2r}$	$e^{-r}$	$e^{-2/3r}$
$\psi_{2s}$	$re^{-r}$	$\left(r - \frac{3}{4}\right)e^{-2/3r}$	$(r - 2)e^{-1/2r}$	$\left(r - \frac{15}{4}\right)e^{-2/5r}$
$E_{1s} = -\frac{2}{(D-1)^2}$	$-\infty$	-2	$-\frac{1}{2}$	$-\frac{2}{9}$
$E_{2s} = -\frac{2}{(D+1)^2}$	$-\frac{1}{2}$	$-\frac{2}{9}$	$-\frac{1}{8}$	$-\frac{2}{25}$
$\Delta E_{1s \rightarrow 2s} = \frac{8D}{(D^2 - 1)^2}$	$\infty$	1.778	0.375	0.142

<sup>a</sup>Where  $\delta$  denotes the Dirac delta function.

collaborative projects, or exam questions in the undergraduate level quantum chemistry lecture courses.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: [10.1021/acs.jchemed.6b00572](https://doi.org/10.1021/acs.jchemed.6b00572).

Appendices A–D (PDF, DOCX)

Sample spreadsheet to illustrate the calculation of the electronic energy of the two-dimensional H<sub>2</sub> (XLSX)

Spreadsheet to construct the molecular orbitals of the H<sub>2</sub> (XLSX)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [yingbin@cwu.edu](mailto:yingbin@cwu.edu).

### Notes

The author declares no competing financial interest.

## ■ ACKNOWLEDGMENTS

Y.G. thanks his undergraduate physical chemistry students from the past eight years for their suggestions to make quantum chemistry learning more tractable and more fun. Hao Jiang is thanked for providing feedback on the paper from a student's perspective. Reviewers' comments were very helpful for the revision and improvement of the paper and are greatly appreciated.

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