JOURNAL OF CHEMICAL EDUCATION
Activity
pubs.acs.org/jchemeduc

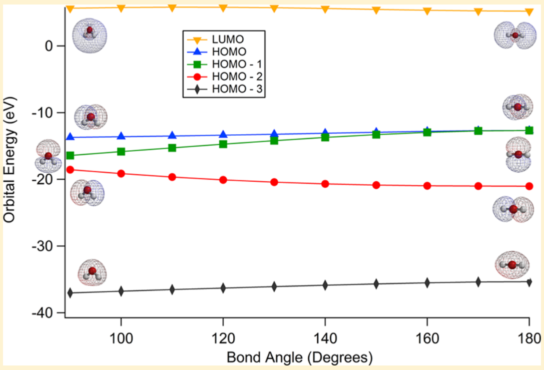
Walsh Diagrams: Molecular Orbital and Structure Computational Chemistry Exercise for Physical Chemistry

Carrie S. Miller*,† and Mark Ellison‡

†Department of Biology and Chemistry, Azusa Pacific University, Azusa, California 91702, United States
‡Department of Chemistry, Ursinus College, Collegeville, Pennsylvania 19426, United States

Supporting Information

ABSTRACT: The increasing importance of computational chemistry in modern chemistry provides an impetus to increase the incorporation of computational exercises in the undergraduate chemistry curriculum. Herein, a computational chemistry exercise that can be used in a physical chemistry course is described. In this exercise, students build a series of AH_2 molecules in the computational chemistry software Spartan and construct Walsh diagrams for the molecules from calculations of the molecular orbital energies as a function of bond angle. The Walsh diagrams are then used to predict the bond angle of the ground state of each molecule. The exercise focuses on creating a connection between molecular orbital theory and molecular structure and investigating the effects of using different methods and basis sets on the molecular orbital energies. This exercise provides a means for students to visualize and explore the molecular orbitals of small molecules.



KEYWORDS: *Computational Chemistry, Physical Chemistry, MO Theory, Molecular Properties/Structures, Computer-Based Learning, Upper-Division Undergraduate*

The growing importance of computational chemistry in modern research has led to a corresponding need to include computational experiences in the undergraduate curriculum, focusing on activities or laboratories primarily for upper-division courses.[1−10] This article describes an exercise using three computational methods, namely, Hartree−Fock (HF), density functional theory (DFT), Møller−Plesset (MP2), and multiple basis sets to generate Walsh diagrams for a set of triatomic AH_2 molecules for a computational exercise for an upper-division physical chemistry course. Students learn how to construct and optimize simple molecules in Spartan (Wavefunction, Inc.), a commonly available software package. After calculating orbital energies at different bond angles, students construct Walsh diagrams to determine the ideal bond angle of the molecule. Visualizations of the calculated molecular orbitals help students to bridge the conceptual gap between calculations in the lab and the molecular orbital (MO) theory that they learn in class.

In 1953, Arthur Walsh proposed a means of using electronic orbitals to predict the shapes of polyatomic molecules of the type AH_2. Walsh focused on binding energy (the energy required to remove an electron from the highest occupied orbital) as the primary determiner of molecular structure.[11] His argument assumes that the sum of the total one-electron orbital energies equals the total energy. Although this is not strictly true, the sum of the orbital energies is correlated with the total energy.[12] Modern approaches focus on the total energy of the occupied electronic orbitals to investigate the structure of a variety of small polyatomic molecules.[13−16]

MO theory provides a description of delocalized orbitals that span the molecule. In their basic formulation, the MOs of a molecule are formed by linear combinations of atomic orbitals, and the labels of the MOs are based on their symmetry. The MOs of a bent AH_2 molecule are constructed as outlined in Table 1.[17] Although this paper presents results for second row hydrides ($n = 2$), it would be possible to do the exercise with third row hydrides ($n = 3$). As shown in Figure 1b, as the bond angle is increased from 90° to 180°, the $2a_1$ orbital changes into the $2\sigma_g$, the $1b_2$ changes into the $1\sigma_u$, and finally the $3a_1$ and $1b_1$ change into the $1\pi_u$ orbitals. A plot showing the orbital energies as a function of the bond angle is called a Walsh diagram, as

Table 1. Construction of Molecular Orbitals of AH_2-Type Molecules from Linear Combinations of Atomic Orbitals

Bent Geometry		Linear Geometry	
Molecular Orbital	Linear Combination	Molecular Orbital	Linear Combination
$2a_1$	$ns_A + 1s_H + 1s_H$	$2\sigma_g$	$ns_A + 1s_H + 1s_H$
$1b_1$	$np_{x,A} + 1s_H - 1s_H$	$1\sigma_u$	$np_{x,A} + 1s_H - 1s_H$
$3a_1$	$np_{z,A} + 1s_H + 1s_H$	$1\pi_u$	$np_{z,A} + 1s_H + 1s_H$
$1b_2$	$np_{y,A}$	$1\pi_u$	$np_{y,A}$

DOI: 10.1021/ed500813d
J. Chem. Educ. XXXX, XXX, XXX−XXX

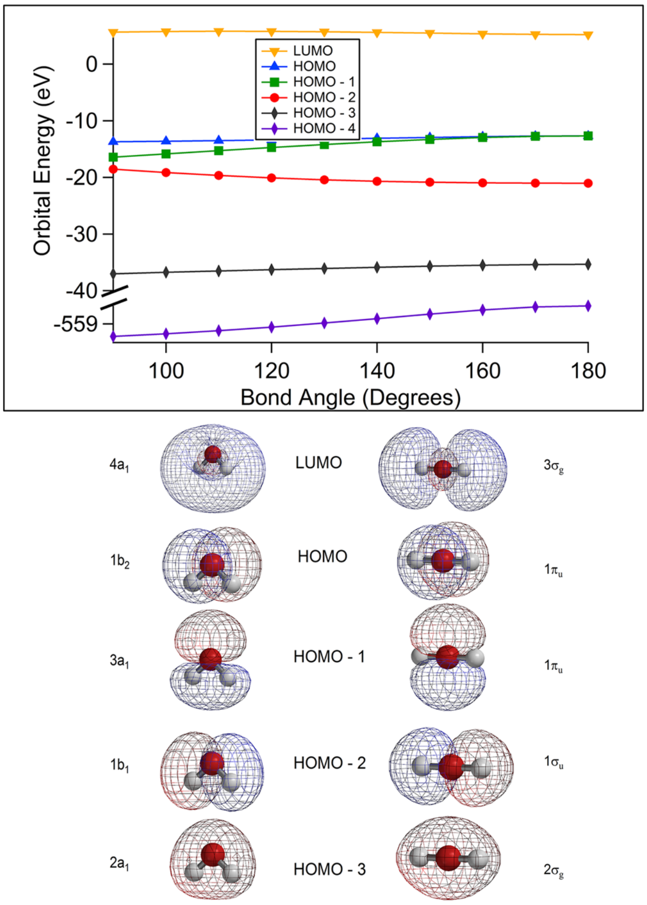


Figure 1. (a) Walsh diagram calculated using the Hartree–Fock method with 6-31G* basis set in Spartan, showing the orbital energies of OH_2. (b) Orbital representations of bent (left) and linear (right) orbitals, including symmetry designations. Isovalues represent 90% probability.

seen in Figure 1a for water. These diagrams are powerful visual tools for determining the qualitative bond angles of AH_2 molecules in the ground and excited states.

■ LEARNING GOALS

The calculation of Walsh diagrams as an exercise in physical chemistry can accomplish several important learning goals. As described in the example exercise in the Supporting Information, we expect that, after finishing this exercise, students will be able to do the following:

- Calculate the equilibrium geometry of a molecule.
- Calculate the orbital energies of a molecule.
- Identify the symmetry designation of an orbital of a triatomic molecule.
- Construct a Walsh diagram for a triatomic molecule.
- Use a Walsh diagram to predict the bond angle of a triatomic molecule in its ground state.
- Compare the speed, qualitative, and quantitative results from three different computational methods.

Before entering a physical chemistry course, many students learn in general chemistry the importance of MO theory for determining characteristics such as bond order or paramagnetism or diamagnetism in diatomic molecules.[18−21] Through the exercise presented here, these students will see for themselves that MO theory can also be used to make testable predictions about other molecular properties. The exercise can be presented to students as a laboratory experiment in computational chemistry or as an out-of-class assignment.

■ CALCULATING WALSH DIAGRAMS

Models of AH_2 (A = Be, B, C, N, and O) are built in Spartan'10 molecular modeling software (Wavefunction, Inc. version 1.1.0). The optimized geometry for each molecule is found for each computational method using the 6-31G* basis set. Then, the bond angle is varied from 90° to 180° in 10° steps. For the DFT calculations, the bond lengths are allowed to vary at each angle,[12] whereas for the HF and MP2 calculations, the bond lengths are fixed at the value found for the optimized geometry of the molecule. At each step, the energies of the lowest energy valence orbital through the LUMO are computed and recorded. Additional details of the computational process for Spartan and full student instructions are available in the Supporting Information. For BeH_2 and H_2O, the spin multiplicity is singlet, whereas for BH_2 and NH_2 it is doublet. For CH_2, both singlet and triplet spin multiplicities are used in the calculations.

Spartan and Gaussian Results

A comparison of Gaussian[22] and Spartan calculation results shows that the orbital energies calculated by the two programs are quite similar, with average and maximum absolute percent differences of 0.02% and 1.44%, respectively. This close agreement indicates that either program can be used to carry out the exercises described here. (Other software, such as GAMESS[23] could also be used, although we did not compare its results against Gaussian or Spartan.) As a representative example, Figure 1a shows the orbital energies calculated by Spartan for OH_2. Figure 1b shows the calculated orbitals (90% probability) for the 90°and 180° bond angles, with the corresponding symmetry designations. In general, the orbital energies calculated by Spartan qualitatively agree with the results of Walsh. Specifically, the energies of the LUMO ($4a_1$), HOMO ($1b_2$), and HOMO-3 ($2a_1$) are essentially independent of bond angle. The energy of the HOMO-1 ($3a_1$) increases as the bond angle goes from 90° to 180°, whereas the energy of the HOMO-2 ($1b_1$) decreases. Contrary to the results of Walsh, the HOMO-1 is not lower in energy than the HOMO-2 at 90°. As seen in Figure 1a, the energy of the HOMO-4 core (localized) orbital is significantly lower than the valence orbitals. Thus, the core orbitals are left out of the Walsh diagrams and bond angle calculations. Similar results are obtained for all of the other molecules tested in this work, as shown in Figures S2–S7 and S10–S15 (Supporting Information).

Physical Interpretation of the Walsh Diagram

The orbital correlation diagram in Figure 1b can help students understand how the MOs of a molecule influence molecular properties, starting with the variation of the orbital energy as a function of bond angle. For the HOMO ($1b_2$), which corresponds to a π orbital in the linear geometry, bending the molecule does not change the overlap between the 1s orbitals on the H atoms and the p orbital on the central atom. Thus, this orbital does not significantly change its energy as the molecule moves from a linear to a bent geometry. In contrast, for the HOMO-1 ($3a_1$), which also corresponds to a π orbital in the linear geometry, bending the molecule causes the 1s orbitals on the H atoms to overlap preferentially with one lobe of the p_z

Table 2. Bond Angles of AH_2-Type Molecules Predicted from the Computational Optimum Geometry and from the Walsh Diagrams Using Spartan with the 6-31G* Basis Set

Method		Predicted Bond Angles of Molecules, °					
		BeH_2	BH_2	Singlet CH_2	Triplet CH_2	NH_2	OH_2
Hartree–Fock (HF)	Calculated	180	126.6	103.1	130.7	104.5	105.5
	Walsh Diagram	180	130	90	120	90	90
Density Functional Theory (DFT)	Calculated	180	127.9	100.3	133.1	104.5	103.7
	Walsh Diagram	180	150	90	140	90	90
Møller–Plesset (MP2)	Calculated	180	127.6	102.1	131.5	103.3	103.9
	Walsh Diagram	180	130	90	120	90	90

orbital on the central atom. For the $3a_1$ orbital, this causes an increase in favorable overlap because the 1s orbitals and the lobe of the p_z orbital have the same phase. This, in turn, lowers the energy of the orbital, so the energy of the $3a_1$ orbital decreases as the bond angle gets smaller. The $1b_1$ orbital, with its contribution from the $p_{x,A}$ orbital, will have maximum overlap (and thus lowest energy) with the $1s_H$ orbitals at 180°, so the energy of the $1b_1$ orbital will increase as the bond angle gets smaller. For the $2a_1$ changing the bond angle does not significantly change the orbital overlap because of the minimal contribution from the oxygen p_z; consequently, its energy does not significantly change with bond angle. Thus, using basic orbital overlap arguments, the qualitative trends of orbital energies in Walsh diagrams can be explained.

Comparison of HF, MP2, and DFT Results

The Walsh diagrams of the AH_2 series of molecules were calculated using three methods: HF, MP2, and DFT. Table 2 lists the optimum bond angle predicted by each computational method (Calcd) and the angle predicted by the Walsh diagrams (Walsh) calculated using Spartan.

For BeH_2, all of the methods correctly predict a bond angle of 180°. For BH_2, the Walsh diagrams for HF and MP2 predict a bond angle of 130°, in excellent agreement with the computational prediction near 127°, whereas DFT predicts an angle of 150°, which is only qualitatively in agreement. For triplet CH_2, DFT again overestimates the bond angle whereas HF and MP2 underestimate it, although both are within 10° of the calculated value of 131°. For the rest of the molecules, the Walsh diagrams predict a bond angle of 90°, which is 10–15° smaller than the computational prediction in each case. Still, the Walsh diagrams make at least a qualitatively correct prediction that, for these molecules, the most favorable geometry is a bond angle significantly less than 180°.

■ EXERCISE

Walsh diagrams are presented in many physical chemistry textbooks.[24−26] The use of computational software allows students to produce their own Walsh diagrams and explore the relationships between orbital energies and bond angles and between methods and basis sets. Because each Walsh diagram is constructed using a particular method/basis set combination, students can explore the effects of choosing either different methods or different basis sets.

Ab initio calculations can be presented to physical chemistry students as approximations to the Schrödinger equation. The method provides a description of the Hamiltonian, and the basis set approximates the wave function. Conceptually, HF is a fairly straightforward method of self-consistently creating one-electron wave functions in a mean field created by the many-electron Coulomb potential. MP2 is a postself-consistent-field method that builds on the HF methodology while including a better description of electron correlation. DFT takes a distinctly different approach by equating a minimum-energy electron density to the solution of the Schrödinger equation. By doing the same Walsh diagram calculations with these three different methods, students can directly compare their results for these systems. Similarly, the exercise can involve the use of multiple basis sets for a given method. In that instance, students can compare the effects on the calculations' speed and accuracy when using a minimal basis set, a routine basis set (with polarizability), and a large basis set (with both diffuse functions and polarizability).

As previously described, students build the full set of AH_2 molecules (A = B, Be, C, N, O). Students perform a geometry optimization on each molecule in order to determine the optimized bond length and the optimized bond angle predicted by a particular method and basis set. Holding the bond length fixed at the optimized distance, students calculate the molecular orbitals of each molecule at H−A−H bond angles of 90°−180° in 10° increments. The energies of the occupied and unoccupied (virtual) orbitals can be found in the output file and then plotted against the bond angle (optionally, the energies, generally reported in hartrees, could be converted to a unit more familiar to the students, such as joules). To show their results, students create plots of molecular orbital energy versus bond angle for each molecule. For molecules in a doublet or triplet state, the α and β orbital energies should be plotted together. Next, the sum of the energies of the occupied orbitals are plotted against the bond angle. The minimum of the summed orbital energies determines the predicted bond angle of the structure in its ground state.

■ CONCLUSIONS

In this article, we present an exercise that helps students explore molecular orbital theory and computational chemistry at the upper level of the chemistry curriculum. This laboratory can be completed using commercially available software on personal computers, and it meets several learning goals. Constructing Walsh diagrams from molecular orbital calculations helps bridge the conceptual gap between MO theory and molecular structure. The ability to visualize orbitals of small molecules also improves students' intuitive understanding of molecular orbitals. Moreover, physical chemistry students explore different computational methods by comparing HF, MP2, and DFT results.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Physical chemistry student exercise; Spartan and Gaussian computational details and results. This material is available via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cmiller@apu.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Amanda Smith and Yara Arnouk for their work running select Gaussian calculations. We thank Erica Ellison for a critical proofreading of the manuscript. We acknowledge the anonymous reviewers for valuable suggestions to improve the manuscript.

■ REFERENCES

(1) Anderson, B. D. Cyclic Polyynes as Examples of the Quantum Mechanical Particle on a Ring. *J. Chem. Educ.* **2012**, *89*, 724−727.

(2) Karpen, M. E.; Henderleiter, J.; Schaertel, S. A. Integrating Computational Chemistry into the Physical Chemistry Laboratory Curriculum: A Wet Lab/Dry Lab Approach. *J. Chem. Educ.* **2004**, *81*, 475−477.

(3) Martin, N. H. Integration of Computational Chemistry into the Chemistry Curriculum. *J. Chem. Educ.* **1998**, *75*, 241−243.

(4) Montgomery, C. D. Factors Affecting Energy Barriers for Pyramidal Inversion in Amines and Phosphines: A Computational Chemistry Lab Exercise. *J. Chem. Educ.* **2013**, *90*, 661−664.

(5) Simpson, S.; Autschbach, J.; Zurek, E. Computational Modeling of the Optical Rotation of Amino Acids: An "in Silico" Experiment for Physical Chemistry. *J. Chem. Educ.* **2013**, *90*, 656−660.

(6) Simpson, S.; Lonie, D. C.; Chen, J.; Zurek, E. A Computational Experiment on Single-Walled Carbon Nanotubes. *J. Chem. Educ.* **2013**, *90*, 651−655.

(7) Ziegler, B. E. Theoretical Hammett Plot for the Gas-Phase Ionization of Benzoic Acid versus Phenol: A Computational Chemistry Lab Exercise. *J. Chem. Educ.* **2013**, *90*, 665−668.

(8) Ruddick, K. R.; Parril, A. L.; Petersen, R. L. Introductory Molecular Orbital Theory: An Honors General Chemistry Computational Lab As Implemented Using Three-Dimensional Modeling Software. *J. Chem. Educ.* **2012**, *9*, 1358−1363.

(9) Linenberger, K. J.; Cole, R. S.; Sarkar, S. Looking Beyond Lewis Structures: A General Chemistry Molecular Modeling Experiment Focusing on Physical Properties and Geometry. *J. Chem. Educ.* **2011**, *88*, 962−965.

(10) Feller, S. E.; Dallinger, R. F.; McKinney, P. C. A Program of Computational Chemistry Exercises for the First-Semester General Chemistry Course. *J. Chem. Educ.* **2004**, *81*, 283−287.

(11) Walsh, A. D. The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part I. AH_2 Molecules. *J. Chem. Soc.* **1953**, 2260−2266.

(12) March, N. H. Foundations of Walsh's rules for molecular shape. *J. Chem. Phys.* **1981**, *74*, 2973−2974.

(13) Tarroni, R.; Clouthier, D. J. Heavy atom nitroxyl radicals. I: An ab initio study of the ground and lower electronic excited states of the $H_2As{=}O$ free radical. *J. Chem. Phys.* **2009**, *131*, 114310.

(14) Chen, E-h.; Chang, T.-C. Walsh diagram and the linear combination of bond orbital method. *J. Mol. Struct.* **1998**, *431*, 127−136.

(15) Yarkony, D. R.; Schaefer, H. F., III Walsh Diagram for Zinc Difluoride. *Chem. Phys. Lett.* **1972**, *15*, 514−520.

(16) Hayes, E. F. Bond Angles and Bonding in Group IIa Metal Dihalides. *J. Phys. Chem.* **1966**, *70*, 3740−3742.

(17) For the symmetry labels of the molecular orbitals, Spartan places the molecule in the *xz* plane, whereas Walsh put the molecule in the *yz* plane. Thus, in Walsh's paper, the orbitals are labeled in increasing energy as $1a_1$, $2a_1$, $1b_2$, $3a_1$, and $1b_1$. By placing the molecule in the *xz* plane, Spartan interchanges the $1b_2$ and $1b_1$ labels. The Spartan output, therefore, in increasing energy is $1a_1$, $2a_1$, $1b_1$, $3a_1$, and $1b_2$. To help students and instructors avoid confusion, we adopt the Spartan convention in this article.

(18) McMurry, J. E.; Fay, R. C. *Chemistry*, 5th ed.; Prentice Hall: Upper Saddle River, NJ, 2008.

(19) Burdge, J. *Chemistry*, 3rd ed.; McGraw Hill Publishing Company: New York, 2014.

(20) Brown, T. L.; Le May, H. E., Jr; Bursten, B. E.; Murphy, C. J. *Chemistry: The Central Science*; Prentice Hall: Upper Saddle River, NJ. 2009.

(21) Tro, N. J. *Chemistry: A Molecular Approach*, 3rd ed.; Pearson Education: New York, NY, 2014.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision D.01; Gaussian, Inc., Wallingford CT, 2009.

(23) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347−1363.

(24) McQuarrie, D. A.; Simon, J. D. *Physical Chemistry: A Molecular Approach*, 1st ed.; University Science Books: Sausalito, CA, 1997.

(25) Engel, T.; Reid, P. *Physical Chemistry*, 3rd ed.; Prentice Hall: San Francisco, 2012.

(26) Berry, R. S.; Rice, S. A.; Ross, J. *Physical Chemistry*, 1st ed.; Wiley & Songs: New York, 1980.