A Computational Approach to Walsh Correlation Diagrams for the Inorganic Chemistry Curriculum

William W. Kennerly,*,†,‡ Kyle B. Billings,‡ Andrew D. Geragotelis,‡ and Jodi L. O'Donnell‡

†Department of Chemistry, Skidmore College, Saratoga Springs, NY 12866, wkennerl@skidmore.edu;
‡Department of Chemistry and Biochemistry, Siena College, Loudonville, NY 12211

Abstract: This article demonstrates how students can use quantum chemistry software to calculate correlation diagrams (also called Walsh diagrams) used to understand chemical bonding in the inorganic chemistry curriculum. Specifically, students can calculate how molecular orbital energetics change as dintrogen is stretched and as the bond angles of water and ammonia are distorted. The theoretical method B3LYP/6-31G* is suitable for this purpose. Comparison to HF/6-31G* results and correlation diagrams from the literature are made, to point out that computational methods and different authors disagree on some details.

Introduction

Constructing molecular orbital diagrams has become an important part of the inorganic chemistry curriculum. Using symmetry operators, students typically learn how to construct molecular orbitals (MOs) of polyatomic molecules from atomic and small fragment orbitals and then estimate and rank MO energies. The value of this rather complicated analysis is that MO energy diagrams allow us to predict molecular spectra, structure, and reactivity, particularly items that elude simple VSEPR ideas. For example, in general chemistry, students are taught that H_2O has a 104.5° bond angle, rationalized as a reduction from the VSEPR-predicted tetrahedral 109.5° due to strong lone pair repulsion forcing together the bonding pairs. The same prediction would be made for the remaining group 16 hydrides. But that is not correct: H_2S, H_2Se, and H_2Te have decreasing bond angles all near 90° [1]. Indeed, the bond angle in H_2O is the exception, not the rule. In an inorganic chemistry course, the intellectual emphasis shifts to using chemical periodicity and molecular orbital theory to understand bonding trends. (A MO explanation of the group 16 hydride bond angle trend does exist [2].)

Students learn to construct MO energy diagrams based on several qualitative principles [3], chiefly that only orbitals of (1) appropriate symmetry and (2) approximately the same energy can interact to form bonding-antibonding MO pairs. However, once molecules start to get more complicated (even second-row diatomics), ad-hoc rationalizations are introduced under the guise of rules to justify the energetic ordering of MOs. This allows the instructor and student to stumble through a few simple classroom cases, but those rules apply only to those particular molecules and often are not useful in general. The most familiar example is invocation of s-p mixing to explain why the MO diagrams of N_2 and O_2 are different. But almost all MO diagrams contain subtleties that deny construction from rules derived based on experience with smaller molecules. Perceptive students will feel that the grand machinery of point group symmetry and MO analysis is useless since they have no way to unambiguously predict the MO diagram of an arbitrary molecule.

Moreover, different popular inorganic chemistry textbooks make different recommendations on how to employ the qualitative MO machinery. For example, Miessler and Tarr (p. 145) suggest that "atomic orbitals with energy differences greater than about 10 eV to 14 eV usually do not interact significantly" [1]. Housecroft and Sharpe (p. 47) approach it qualitatively, suggesting that as two atomic orbitals diverge in energy, the interaction becomes less and less efficient until there is essentially no overlap, or the original atomic orbitals can be considered non-bonding without a quantitative statement about what divergence in energy might cause this effect [4]. Shriver and Atkins (Ch. 6) also suggest qualitatively assessing atomic orbital energy differences when constructing MO diagrams, but recommend doing a calculation afterwards to check [5].

In a wider context, an MO diagram is just one part of a full correlation diagram, which shows how MO energies change as molecular geometry changes, be it a bond length, bond angle, or dihedral angle. (In the cases of angles, these are often called Walsh diagrams [6].) Correlation diagrams are most often used to understand and predict how molecular geometry changes as electrons are added or removed. They can also be applied to chemical reactivity, such as acid-base chemistry by looking at how orbitals interact as a proton and base approach [1], and how dienes and dienophiles approach in a Diels-Alder reaction [7]. However, like MO diagrams, correlation diagrams can be difficult to qualitatively predict correctly.

Using widely available quantum chemistry software, students can calculate their own MO correlation diagrams. Indeed, such diagrams are theoretical predictions only rigorously possible using quantum mechanics and solving Schrödinger's equation. In this article, we show how to calculate and interpret three correlation diagrams relevant to the inorganic chemistry curriculum: (1) dinitrogen bond length, (2) water bond angle, and (3) ammonia bond angle.

Just as there are ambiguities in constructing MO diagrams that lead to different results, correlation diagrams differ from

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* Address correspondence to this author.
† Dept. of Chemistry, Skidmore College, Saratoga Springs, NY.
‡ Dept. of Chemistry and Biochemistry, Loudonville, NY.

book to book. Below, our calculated results are compared to a variety of literature sources. This emphasizes that there is not one accepted correlation diagram—or even MO energy diagram—in each of these simple molecules. A qualitative diagram is always subject to the author's sources of experimental data, judgment on how to interpret that data, and intuition. While calculated diagrams may appear deterministic and rigorous they suffer discrepancies when different methods are used. Using computational tools blindly can lead to laughably incorrect or contradictory results. In this article and the accompanying exercises, we probe and try to answer why different methods produce different results.

Our immediate goal is to introduce practical tools for students to calculate their own MO and correlation diagrams seen in their inorganic chemistry courses. Where qualitative methods fall short, computational tools provide results. Our overarching goal is to help students intelligently use quantum computational methods to solve their problems, no matter the chemistry subfield. Even in physical chemistry courses, where one might expect to see this material, students seldom learn computational chemistry [8, 9].

Methods

Quantum chemistry calculations are specified by a theory and a basis set, denoted by the shorthand "THEORY/BASIS" indicating which theoretical method and basis set are used. Schrödinger's equation cannot be solved exactly for any multielectron molecule or atom due to the electron-electron interaction term in the Hamiltonian operator. So, many different theories have been developed to account for that interaction. These theories result in equations and algorithms that approximately solve Schrödinger's equation. Two commonly used theories are Hartree-Fock (HF) and density functional theory with Becke's 3-parameter exchange functional combined with the Lee-Yang-Parr correlation functional (B3LYP). The basis set is a list of orbitals that one thinks should be included in the calculation for good results. Infinitely many orbitals would be required for an exact calculation at a given level of theory, so we approximate by selecting a subset of orbitals that should describe the chemical problem. The larger this set, the longer the calculation will take. The orbitals in a basis set should be thought of as modeling a molecule in the way building blocks model a tall tower: a larger supply with more varied types of blocks allows you to build a more realistic tower. A common basis set, and adequate for our purposes, is 6-31G*. A thorough description of computational quantum chemistry and its terminology are provided by Bell et al. [10] and several textbooks [11–14].

We use B3LYP/6-31G* for our exercises. This choice is made because it is fast enough that students will not need to wait more than a few minutes for calculations to finish (all three activities can be completed within a three hour lab), and so that results agree with the course textbook, Miessler and Tarr [1] when applicable. On this latter point, the reader should be aware that the energetic ordering of molecular orbitals, particularly unoccupied MOs above the LUMO, can be different depending on the method and basis set chosen. For this reason, the portion of the exercise on diatomic molecules asks students to compare results from B3LYP/6-31G* and HF/6-31G*, so they see the discrepancy and learn that a single computation cannot be blindly trusted. Furthermore, there are several minor discrepancies between the correlation diagrams

presented here and those found in the literature, which will be discussed below. Usually, much work through understanding the methods, comparing related calculations, and verification with experimental data is required to develop confidence in computational results.

There are more sophisticated methods and larger basis sets that typically produce more accurate results (at the expense of longer computing times). However both HF and B3LYP are widely used, cited, and often the first-listed options in the software packages mentioned below. First-time computationalists will try them initially. It would be reasonable to explore those more accurate options. But for our purposes here, HF/6-31G* and B3LYP/6-31G* provide a useful starting point for students learning computational chemistry.

Available Software Packages

Almost any quantum chemistry software package can perform the calculations for our exercises. The main differences between them are cost, workflow simplicity, and how the software is made available to students. Below we discuss two common choices for computational chemistry software in undergraduate education, but we do not purposefully exclude other packages that work.

To complete our exercises, the required software functionality is to (1) compute energies and display pictures of molecular orbitals and (2) automatically recompute energies and molecular orbitals as the molecular geometry is systematically changed, for example by increasing a bond length from 1 Å to 2 Å in steps of 0.1 Å. By exporting the energy data to a spreadsheet program correlation diagrams are easily constructed.

We use Spartan 2008 (Wavefunction Inc.), a full-featured computational chemistry package that integrates a graphical interface with the computational engine. One unique, but not essential, feature of Spartan is that it can show "movies" of molecular orbitals evolving as molecular geometry changes. Spartan also publishes a student edition that can be purchased for less than $100. Additionally, Spartan Student is bundled and integrated with a popular physical chemistry text [12].

Software typically used for research such as Gaussian (Gaussian, Inc.), GAMESS (Gordon research group, Iowa State University), and NWChem (Pacific Northwest National Laboratory) may also be used. Gaussian is expensive, while the latter two are free and open-source. However for easy student use these all require a separate graphical interface to draw molecules, start calculations, and view results. WebMO (WebMO, LLC), which is used through any web browser, serves in this role. WebMO must be installed on a web server, so installation is more complicated, but it need only be installed on one computer no matter how many students use it. Likewise, only a single copy of Gaussian, GAMESS, or NWChem need be installed on one server. WebMO facilitates student access to that one server for their calculations, though jobs may only be able to run consecutively (i.e. students must wait) while each job finishes, depending on the hardware configuration. WebMO has a free version available, however for correlation diagrams and MO visualization, the "Pro" version must be purchased.

We have successfully completed these exercises with Spartan 2008, Spartan 2010, Spartan Student, and Gaussian 2009.
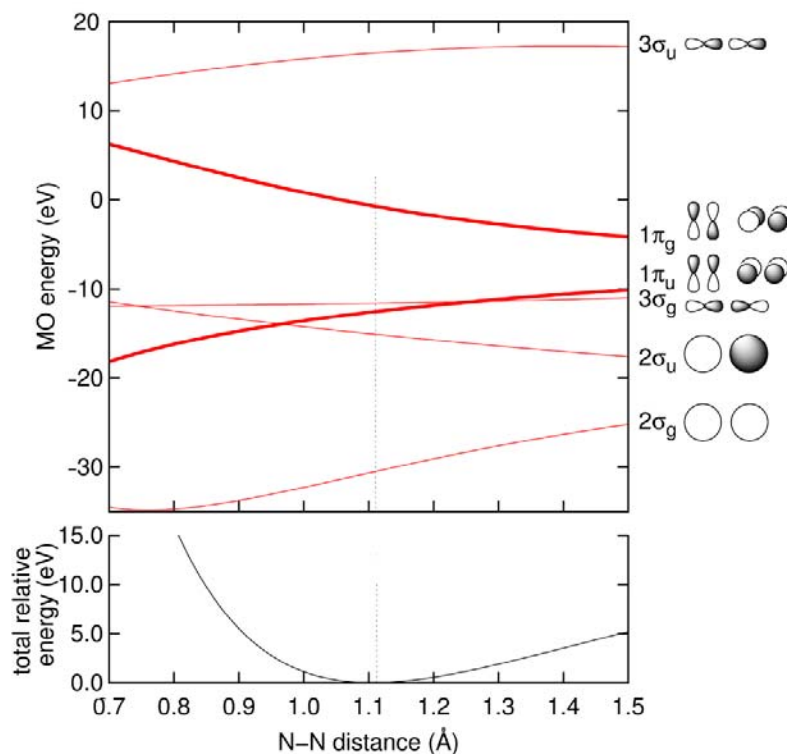
Figure 1. Correlation diagrams as N_2 is stretched, as calculated by B3LYP/6-31G*: (top) valence molecular orbital energies and (bottom) total energy, relative to the ground state minimum. The thick curves indicate doubly-degenerate states (π_g or π_u MOs). The vertical dashed lines indicate the calculated optimum bond length of 1.11 Å.

Diatomics—Stretching N_2

Molecular orbital diagrams for homonuclear diatomic molecules are the same in every textbook, drawn from interpreting experimental photoelectron spectra. The diagrams' character must be split between the heavier species (O_2, F_2, Ne_2) and the lighter ones (Li_2 through N_2). The only change is swapping the π (2p) and σ ($2p_z$) bonding molecular orbitals. Textbooks invoke the magic wand of strong "s-p mixing" in the lighter diatomics since they have the "wrong" orbital order. The extent of s-p mixing is affected both by bond length and nuclear charge. Miessler and Tarr (p. 142) summarize the orbital energetics of all second-row homonuclear diatomics with one correlation diagram, which correlates the extremes of united-atom (fused nuclei) orbitals and fully separated atomic orbitals [1]. (This plot originates long ago with Herzberg on p. 329 [15].) However this is a rather complicated plot, as the orbital energy swaps (called "crossings") needed to match with experimental results are drawn manually. A correlation diagram for a single diatomic molecule is simpler and can easily be computed to understand how bond length affects MO ordering for that particular diatomic.

Figure 1 shows the correlation diagram for the MO energies of N_2 as the bond is stretched from 0.7 Å to 1.5 Å. It is important not to extend to longer bond lengths, since the computational methods used here do not accurately treat broken bonds and radical species. ("Unrestricted" methods should be used for those cases.) The bottom plot in Figure 1 shows the total molecular energy as the bond stretches, which

clearly shows the most stable structure calculated for N_2 is when the bond length is 1.11 Å.

The skeptical chemist might be wondering why B3LYP/6-31G* is the appropriate method among hundreds that could be chosen. Other methods may work, too. To illustrate one that does not, consider Figure 2, which compares B3LYP to Hartree-Fock (HF) using the same basis set. While both are common methods, generally B3LYP would be considered more likely to be accurate since it explicitly includes electron correlation, which HF lacks. There are three salient differences between the results. First, the energies are uniformly higher in the B3LYP calculation. This discrepancy (which could be higher, or lower, depending on the molecule) is common when comparing DFT and HF MO energies, and there can be discrepancies among DFT results from different functionals as high as 10 eV [16, 17]. Second, the predicted HF bond length is shorter than B3LYP (1.08 Å vs. 1.11 Å where the experimental result is 1.098 Å) [18]. This is the usual situation; HF almost always predicts bond lengths shorter than they actually are [19]. (There is not a significant systematic bias in B3LYP bond lengths.) Since the HF method does not include electron correlation, the internuclear electrons are not calculated to repel as much as they should, so the nuclei can move closer together. Third, observe how the central triangle in Figure 2, formed by three MO degeneracies (the crossings) at different bond lengths, changes. For the HF calculation the crossing lengths shorten just enough so that the HF MO energies are ordered differently (at the HF predicted bond length) compared to B3LYP. HF predicts the incorrect MO diagram, as textbooks might say, with orbitals not strongly affected by s-p mixing. B3LYP gets this right.
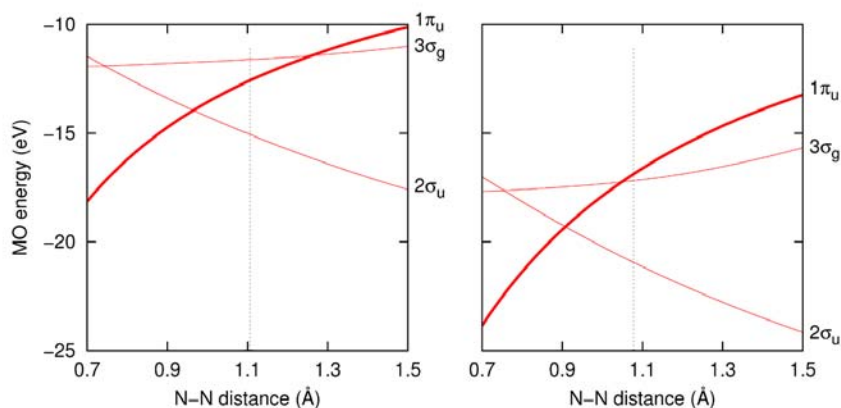
Figure 2. Close-up of the N_2 molecular orbital correlation diagram showing the four highest energy occupied molecular orbitals: (left) B3LYP/6-31G* and (right) HF/6-31G* results. The thick curves indicate doubly-degenerate states (π_u MOs). The dashed vertical lines indicate the optimized bond length from each method, 1.11 Å and 1.08 Å, respectively.
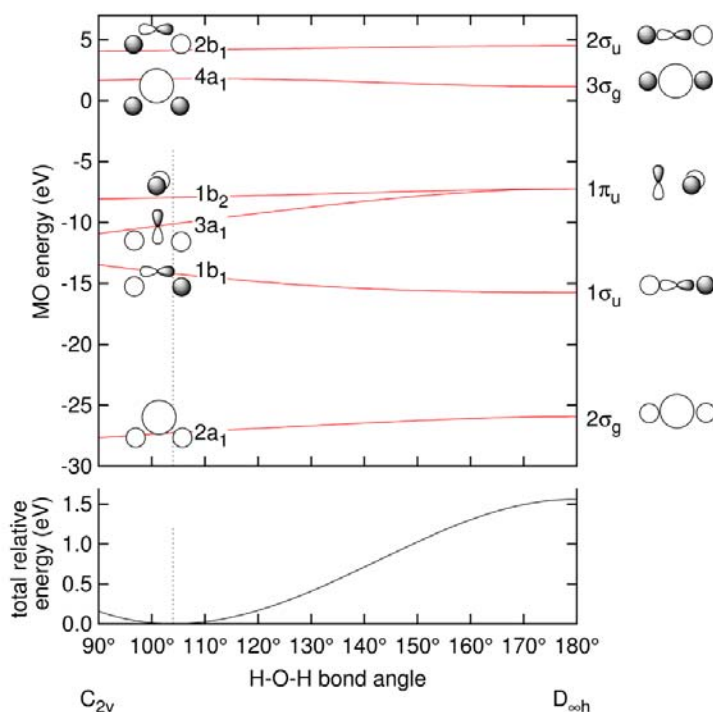

Figure 3. Correlation diagrams as bent H_2O becomes linear, calculated at B3LYP/6-31G*: (top) valence molecular orbital energies and (bottom) total energy, relative to the ground state minimum. The vertical dashed lines indicate the calculated optimum bond angle of 104.0°.

Triatomics—Bending H₂O

With a third atom comes the need to study how bond angle affects MO energies. Water is universally featured in textbooks, but typically only to show its MOs and energy levels at the experimental bond angle 104.5°. Here we calculate how MO energies change as the molecule transverses bent (bond angle 90°) to linear (180°) geometries. The point group symmetry correspondingly changes from C_{2v} to $D_{\infty h}$.

Textbook authors have a bit of trouble agreeing on the MO diagram details. The most commonly stated valence MO configuration—and the one calculated at B3LYP/6-31G*—is $(2a_1)^2(1b_1)^2(3a_1)^2(1b_2)^2(4a_1)^0(2b_1)^0$. (These symmetry

designations assume the principal rotation axis is in the z direction, and the molecule lies in the x-z plane. Not all books, or computed results, use this convention.)

For the standard MO diagram at the equilibrium geometry, both Ballhausen and Gray [20] and DeKock and Gray [21] switch the unoccupied MOs $4a_1$ and $2b_1$, compared to our results and most books. Since LUMO identities and energies are often used to determine reactivity or properties (hardness, etc.) this discrepancy leads to divergent conclusions about chemical behavior—this is not just a computational oddity to be shrugged off.

Figure 3 shows our calculated correlation diagram. Three books (Shriver & Atkins, Winter, and DeKock & Gray) have a
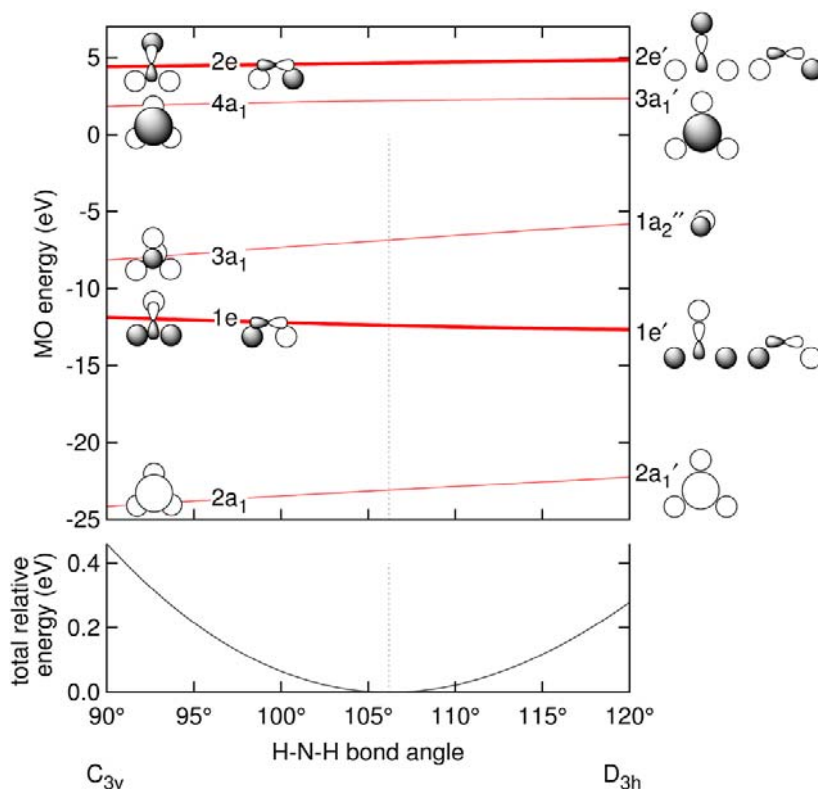
Figure 4. Correlation diagrams as pyramidal NH_3 becomes planar, calculated at B3LYP/6-31G*: (top) valence molecular orbital energies and (bottom) total energy, relative to the ground state minimum. The thick curves indicate doubly-degenerate states (e or e' MOs). The vertical dashed lines indicate the calculated optimum bond angle of 106.2°.

similar one, but with a crossing between occupied orbitals $1b_1$ and $3a_1$ levels near bond angle 110° [5, 21, 22]. This diagram may have been inherited from Walsh's original paper [6], where he interprets spectral data to justify the crossing as the molecule bends. However Walsh also states that the interpretation could be wrong, and indeed he states other authors had suggested so, meaning the crossing may not be real. Jean, Volatron, and Burdett instead show a crossing between the unoccupied orbitals $4a_1$ and $2b_1$ [23]. Our calculated results, and the correlation diagram of Albright, Burdett and Whangbo [2] do not show any crossings.

Tetratomics—Planarizing Ammonia

Depending on geometry, adding a fourth atom could require examining several different molecular distortions. Here we use a popular case, examining how ammonia is affected when changing from pyramidal geometry (H−N−H angle 90°) to planar (120°), C_{3v} to D_{3h} symmetry, placing the optimum bond angle near the middle of the diagram in Figure 4. Only the bond angle is varied; the N−H bond length is held fixed at 1.01 Å during the calculation. This is a way of calculating the inversion barrier of ammonia [24].

The textbooks all agree on the valence MO configuration of equilibrium ammonia as $(2a_1)^2(1e)^4(3a_1)^2(4a_1)^0(2e)^0$ without serious disagreement or puzzles about how the MOs are constructed, unlike the previous exercises. However, three textbooks show Walsh diagrams with crossings, unlike our B3LYP/6-31G* results in Figure 4. DeKock and Gray [21] show the two highest occupied and bonding 1e and $3a_1$ MOs crossing at 95°. Albright and Burdett [2] show the lowest

unoccupied 2e and $4a_1$ MOs crossing at 95°, as do Jean, Volatron and Burdett [23] though at an unspecified angle. Both Walsh and Herzberg do not show any crossings [25, 26].

Discussion and Conclusions

We have shown that MO and correlation diagrams used in inorganic chemistry courses can be reproduced with simple quantum mechanical calculations. Determining the single "correct" diagram through exhaustive calculations and reference to experiment would be quite a task, but B3LYP/6-31G* performs well in comparison to existing literature and is convenient for student use.

However, textbooks disagree on the fine details of these diagrams. There are two likely sources for these discrepancies. One is that textbook correlation diagrams are constructed in terms of a generic molecule, for example any trihydride AH_3, whereas we calculate in particular the properties of NH_3. A generic diagram is valuable if it can be applied to any trihydride such as BH_3 or the methyl radical. However since changing nuclei also changes the atomic orbital energetics from whence the diagrams originate, it is likely that details of correlation diagrams (ordering of unoccupied orbitals, crossing points) would change. Combining results from several different molecules into one diagram is not a rigorous process and some variability between author's discretion would be introduced.

Secondly, the very notion of a Walsh diagram rests on the energies being plotted, which are ill defined. It may surprise the reader that Walsh himself plotted what he called "orbital binding energies" but never rigorously defined them. A steady

trickle of authors have tried to make Walsh's idea concrete, but with no firm resolution [27]. Nevertheless, many use Walsh diagrams and assume they are made from energy eigenvalues obtained from solving the Schrödinger equation by an accurate ab initio technique. Not much harm is done, apparently. This opens up another avenue of debate, however, since we used density functional methods that optimize the electron density in the calculation, not the molecular orbital wavefunctions. So-called Kohn-Sham orbitals result from the DFT calculation, but these are not rigorously equivalent to MOs from a proper ab initio calculation, such as Hartree-Fock. Kohn-Sham and ab initio orbitals have been compared in the literature, and they usually correspond well, but there can be differences [16, 17].

With all of this said, it is not surprising there are discrepancies between diagram details in the literature, but we feel B3LYP/6-31G* is a reliable method for calculating the MO and correlation diagrams presented here, as encountered in the inorganic chemistry curriculum.

Prior work on incorporating computational methods into the inorganic chemistry curriculum complement, and can be extended by, our methods. Lyon used the AM1 semiempirical (partially quantum mechanical, partially experimental-fitted) method to plot the H_2O correlation diagram [27]. Both Lyon and Nataro et al. used AM1 to compute Lewis acid-base properties based on HOMO and LUMO energies [28, 29]. Martin used Spartan and density functional theory to explore crystal-field splitting in inorganic complexes [30]. Any of these student activities could be extended by computationally producing correlation diagrams as presented here. Furthermore, students with a particular interest in computational work could study how larger basis sets and more accurate theoretical methods affect the results shown here.

Learning Outcomes, Implementation, Evaluation

Learning how to construct and interpret molecular orbital diagrams for polyatomic molecules is a standard part of the modern inorganic chemistry curriculum. Students completing this activity reinforce their classroom experiences with symmetry groups and MO energy ordering. Studying correlation diagrams helps students understand that molecular geometry affects molecular orbital diagrams, which are usually constructed by estimating the degree of overlap between adjacent atomic orbitals. Moreover, they gain practical skills in using molecular modeling software. They learn that different computational methods exist, produce different results, and it is the user's responsibility to understand which method is most appropriate.

Before this activity, our students had approximately 10 hours of Spartan experience. In general chemistry they had a one-hour exercise and a three-hour lab. In second-year inorganic chemistry they completed several exercises with Spartan. The exercises discussed here are completed at the same time students are learning about polyatomic molecular orbital construction for third-year inorganic chemistry.

Students completed these exercises in a 3-hour session for a third-year physical and inorganic chemistry lab course. (The activities could alternatively be completed in two or three 1-hour sessions.) The students worked in groups of two or three in a computer lab with Spartan 2008 and Excel, with free access to the instructor and each other for advice. The students followed a very detailed procedure to calculate MOs and

produce correlation diagrams. The students had a list of questions to answer during the activity. The questions prompted students to observe the calculated results and compare to their classroom experience and textbook, particularly when recognizing MO symmetry and energetic trends. A couple questions probed the difference between HF and DFT results for N_2.

Supporting Materials. Detailed instructions for students to construct correlation diagrams of N_2, H_2O, and NH_3 in Spartan 2008 are provided. Also provided are questions for students to answer during the exercise (http://dx.doi.org/10.1333/s00897122411a).

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