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In The Classroom

Integrating Molecular Modeling with Semiempirical Quantum Mechanical Calculations into the Upper-Level Inorganic Chemistry Course

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A stable calculation method and a good parameter set can produce results that are in agreement with experimental data.

The analysis of chemical bonding and reactivity from the perspective of molecular orbital theory is challenging for students at the undergraduate level. In an attempt to improve the instruction of this material in my upper-level inorganic chemistry course I developed a series of computational experiments using a molecular modeling program that can perform semiempirical quantum mechanical calculations. These exercises explore the chemistry of molecular systems through an analysis of the variation in the attractive and repulsive forces in the system as a function of structure or composition. The exercises challenge the analysis skills of the students by requiring them to consider how two or more factors contribute to the properties of the system. Examples of exercises that demonstrate different types of computational experiments are given. These sample exercises examine the structure of simple molecules, the reactivity of Lewis acids, and the bonding in transition metal complexes.

Introduction

Chemists, like most professionals, are limited by the quality of the tools that are available for a task at hand. When a chemist tries to understand the chemical reactivity of a molecule, bonding models are the tools that are used. Currently, valence bond theory and molecular orbital theory are the two bonding models for molecular systems that are taught at the undergraduate level. In introductory chemistry, valence bond theory is the model that is emphasized. This is appropriate due to the simplicity of the model and its ability to predict the structure of most organic and inorganic compounds. At the intermediate and upper levels of instruction, understanding the structure and the reactivity of compounds becomes important. Here, the limitations of valence bond theory become a problem and molecular orbital theory is often presented as a more robust model.

For a number of years I have taught molecular orbital theory in my upper-level inorganic chemistry course. I taught the subject from a qualitative point of view using the linear combination of atomic orbital method of defining molecular orbitals. The idea that the symmetry and energy of the atomic orbitals determined the contribution of each atomic orbital to the shape and energy of each molecular orbital was presented. Even though we could use the molecular orbitals produced in this way to qualitatively rationalize all of the chemistry presented in the course, some students were not convinced that molecular orbital theory was a better way to view bonding in compounds. I had a problem. Molecular orbital theory was more difficult to apply than valence bond theory, but students did not see the advantages as being worth the effort. The problem as I saw it was that I was still using a qualitative bonding model. The power of molecular orbital theory to quantitatively analyze the energy of a molecule was not being presented. A review of the current literature dealing with this problem uncovered a few papers describing the use of molecular modeling programs and programs that perform molecular orbital calculations in the quantitative presentation of molecular orbital theory [1–3]. Building upon these ideas, I developed a number computational experiments that were designed to explore the ways that quantitative results from molecular orbital calculations can address key topics in the advanced inorganic chemistry course. In this paper I present three examples of these computational experiments performed using the program HyperChem [4].

The Use of HyperChem at UWGB

Approximately six years ago we obtained our first copy of the computational chemistry program HyperChem. My colleagues and I quickly realized that computational chemistry would be a very important tool for the chemist of the future. Now, with this program, we had a reasonable way to introduce computational chemistry to our students. We currently have integrated molecular modeling using HyperChem into three parts of our program. Students are introduced to the HyperChem program in organic chemistry. Here, they gain experience in using the model building part of the program to define the molecular system that they want to investigate. This part of the program uses a modified structure-drawing program to define the way that atoms are connected. It then uses a “build molecule” command to generate an initial set of three-dimensional coordinates of the atoms in the molecular system. The program now allows the molecular system to be displayed using one of a number of different rendering types and for the system to be viewed from different angles and in different sizes. The students are also introduced to the concept of energy minimization and perform exercises to determine the coordinates of the atoms in their system at local energy minima using either a molecular mechanical or a semiempirical quantum mechanical method. When semiempirical methods are used for this calculation, HyperChem generates the energy and spatial characteristics of the molecular orbitals of their system. Students use this feature to visualize the pi orbitals of alkenes and conjugated pi systems and to determine the energy of these orbitals. After this two semester course the students have a very good grasp of the basic operation of the HyperChem program.

The skills that the students develop in the organic chemistry course are advanced in upper-level courses in inorganic chemistry and biochemistry. In Inorganic Chemistry a series of computational molecular modeling exercises is used to connect molecular orbital theory to the structure and reactivity of inorganic compounds, three of which are described in this paper. In Biochemistry students use both HyperChem and RasMol to visualize different types of biomolecules and to explore intramolecular and intermolecular bonding in these systems.

Background Material Presented to Students

Students are presented with the background material needed to perform the molecular modeling exercises described in this paper during the first few weeks of the upper level inorganic chemistry course. The material is presented on a qualitative level. The idea that in molecular orbital theory a molecule is considered a collection of nuclei that share a group of electrons is presented. The model is expanded with the idea that the energy of a molecular system is the sum of the repulsive energies between the positively charged nuclei, the repulsive energies between the negatively charged electrons, and the attractive energies between the nuclei and electrons. With this basis, students are presented with the concept of how HyperChem calculates the energy of a molecule using semiempirical quantum mechanical methods [5]. The basic ideas are as follows. First, only the valence electrons of the atoms in the molecule make significant contributions to the bonding in the molecule. The molecular system is therefore simplified by treating each atom as if it consisted of valence electrons and a single object composed of the nucleus plus the inner shell electrons. This object is called a core. Second, the determination of the repulsive energy between the cores is based upon the assumption that the cores do not move significantly within the molecule. Their kinetic energy term can be neglected and their position in the molecule can be used to determine the core–core repulsive forces using classical mechanics. Third, because of the rapid movement of the electrons, the energy term involving the electrons requires that wave mechanics and not classical mechanics be used to treat the electron–electron repulsive energies and the electron–core attractive energies. This requirement makes the exact calculation of the energies involving electrons impossible. Approximations for the molecular orbital wave equations for each of the valence electrons are produced by HyperChem using the linear combination of atomic orbital method. With these equations the electron–electron repulsion energy and the electron–core attraction energy can be estimated. The combination of these two energies is reported as the electronic energy term in HyperChem. The total energy of the molecule is reported by HyperChem as the sum of the electronic energy and the core–core energy.

Exercise I: Molecular Shapes, The Structure of H_2Y

The ability to predict the shape of molecular systems using valence bond theory is one of the major skills that is taught at the introductory level and developed in organic

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chemistry. After their second semester of organic chemistry, our students are very comfortable with this theory and can apply it very well. One of my greatest challenges in my upper-level inorganic chemistry course is to change the way that they think about bonding in molecules from the localized electron pair model of valence bond theory to the delocalized electron model of molecular orbital theory. One of my early computational exercises deals with the analysis of the factors that control the shape of a simple compound from a molecular orbital theory perspective. In this exercise the students are asked to analyze the structure of any hydride with the formula H_2Y. Energy calculations are performed on a molecule as a function of bond angle keeping the bond lengths fixed. The student is requested to analyze the contributions of the core–core energy, the electronic energy, the total energy and the energies of the occupied molecular orbitals to the shape of the molecule.

Students begin by defining the molecular system that they want to study in a new workspace in HyperChem. The drawing tool is used to create three bonded atoms in the workspace and then these atoms are defined as the elements of interest. The “Build Molecule” command puts the molecular system that the student has defined into a three-dimensional coordinate system. The student then follows the procedure that is presented in the handout for the exercise to perform the desired calculations. These instructions provide procedures that allow the student to define the bond length and the bond angle of the molecule and to determine the energy of each of the parameters of interest. The results of these calculations are stored in a series of text files. The information in the text files is then read in a word-processor program and analyzed in a spreadsheet program.

An example of the type of results generated in this exercise are given for water in Figures 1–4. These results were obtained using a fixed bond length of 0.9 Å and the semiempirical parameter set called AM1. In Figure 1 the total energy versus bond angle is presented. The minimum in the total energy curve gives the most stable bond angle for the compound at the defined bond length. The analysis of this curve can begin by comparing the predicted bond angle to literature values for the compound. One should be aware that the bond length used in the analysis can affect the position of the minimum in total energy curve.

Next, the factors that contribute to the shape of the total energy curve can be explored. The core–core energy, Figure 2, and the electronic energy, Figure 3, both contribute to

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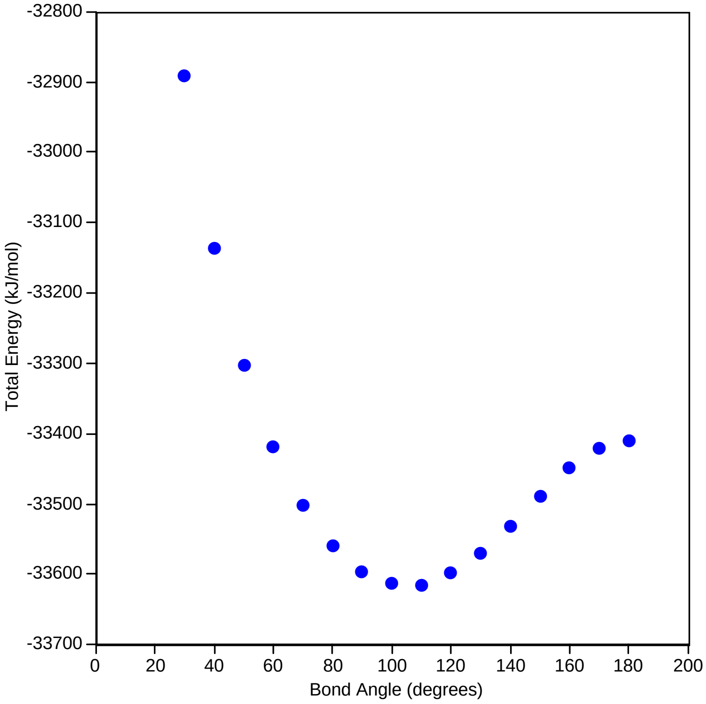

FIGURE 1. TOTAL ENERGY VERSUS BOND ANGLE FOR WATER WITH A FIXED BOND LENGTH OF 0.9 Å USING THE AM1 PARAMETER SET.

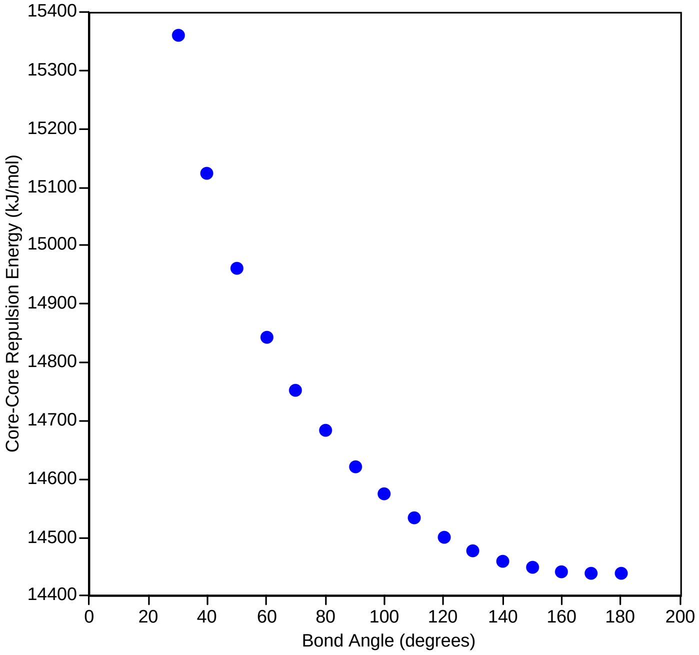

FIGURE 2. CORE-CORE REPULSION ENERGY VERSUS BOND ANGLE FOR WATER WITH A FIXED BOND DISTANCE OF 0.9 Å USING THE AM1 PARAMETER SET.

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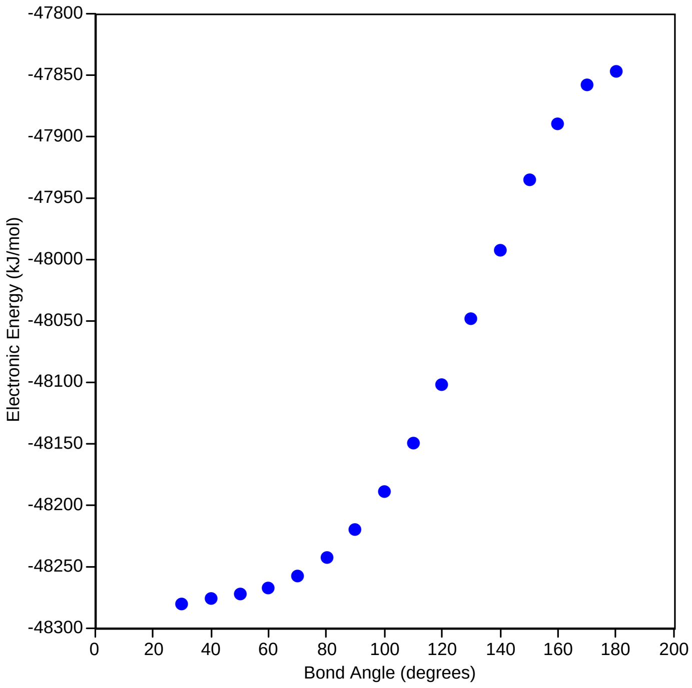

FIGURE 3. ELECTRONIC ENERGY VERSUS BOND ANGLE FOR WATER WITH A FIXED BOND LENGTH OF 0.9 Å USING AM1 PARAMETER SET.

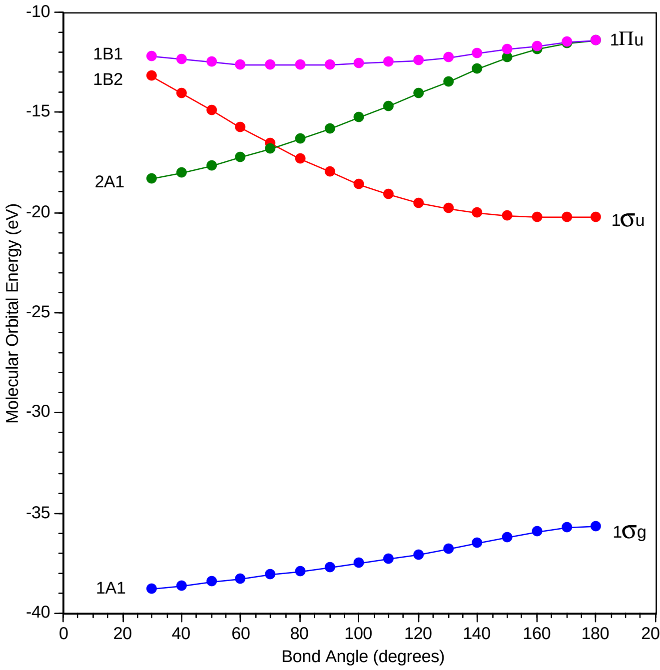

FIGURE 4. MOLECULAR ORBITAL ENERGY VERSUS BOND ANGLE FOR WATER WITH A FIXED BOND DISTANCE OF 0.9 Å CALCULATED USING THE AM1 PARAMETER SET.

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the total energy of the molecule. The trend in the core–core repulsion term is to increase as the bond angle decreases. In this computational experiment, the repulsion term between the hydrogen atoms and the Y atom remain constant due to the fixed bond length. The variation in the core–core term as a function of bond angle is, therefore, due to the increase in the hydrogen–hydrogen repulsion as the hydrogen nuclei approach each other. If this were the only factor affecting molecular shape, the molecule would be linear.

The trend for the electronic energy term is the opposite to that of the core–core energy. It becomes more negative as the bond angle decreases. If the effect of bond length on this parameter was also examined, one would find that the electronic energy also becomes more negative with decreasing bond length. The most stable conformation of the molecule with respect to the electronic energy would be when all of the cores combine into one nucleus. The opposite trends in the core–core energy and the electronic energy produce an energy minima at approximately 105º in this example.

The shape of the electronic energy curve can be further analyzed by looking at how the energies of the individual molecular orbitals change as a function of bond angle, Figure 4. For the majority of the H_2Y compounds, a maximum of four molecular orbitals is needed to explore the energies of the bonding electrons as a function of bond angle. The basic characteristics of this graph, often called a Walsh Diagram, is the same for each of the H_2Y compounds. Using the example given in Figure 4, one can see that the lowest energy MO decreases in energy as the bond angle decreases. The second MO for the molecule increases in energy as the bond angle decreases. The third MO decreases in energy as the bond angle decreases, and the fourth MO does not change significantly in energy with bond angle. The actual shape of each of these curves depends upon the compound being studied. The variation in the electronic energy of the compound as a function of bond angle will depend upon the distribution of electrons among these molecular orbitals. In general, H_2Y compounds with two, six, or eight valence shell electrons show large changes in electronic energy with bond angle, while compounds with four valence shell electrons show a flatter curve. Students can gain an understanding of the effect of the bond angle on the shape of these molecular orbitals by using the orbital rendering features of HyperChem. Included in the supporting materials are examples of the types of pictures that can be generated with this feature.

This exercise was designed to introduce students to the factors that control molecular shape from the perspective of a semiempirical molecular orbital analysis. The exercise can be expanded to look at the factors that affect the way that the electronic energy and the core–core energy change as a function of bond angle. For example, HyperChem predicts that water would have a bond angle of approximately 108° with a bond length of 0.96 Å. When the bond length is expanded to 1.34 Å, the approximate bond length in H_2S, the predicted bond angle decreases to 95°, approximately that of H_2S. When the shapes of the graphs of core–core energy versus bond angle and electronic energy versus bond angle are examined for these two bond lengths, one finds that the difference in the predicted bond angle for these two systems is influenced the greatest by the shift in the curve of the core–core energy graph. From these results, one could construe that the reason that H_2S has a smaller bond angle than H_2O is due to a decrease in the hydrogen–hydrogen repulsion energy as the bond length increases and not to a difference in the energy of molecular orbitals formed from oxygen atomic orbitals versus sulfur atomic orbitals.

Exercise II. The Strength of Lewis Acids

The Lewis acid base chemistry of inorganic compounds is a major theme of the upper-level inorganic chemistry course. Knowledge of the factors that contribute to the strength of a Lewis acid or a Lewis base is important to the understanding of a large number of chemical reactions. While the understanding of the Lewis acid chemistry of cations and the Lewis base chemistry of anions is fairly simple, the analysis of the Lewis acid base chemistry of molecular systems is often not trivial. This can be due to complex changes in the molecular orbital energy levels in both the Lewis acid and the Lewis base upon complex formation. In this exercise the reaction between two similar Lewis acids with a single Lewis base is examined in an attempt to develop an understanding of the factors that affect Lewis acid strength from a molecular orbital point of view.

In this exercise students are asked to analyze the factors that affect the Lewis acid strength of the boron trihalides. Molecular orbital energy calculations are performed on BF_3 and BCl_3, a Lewis base of the student's choice and the complexes between BF_3 and the Lewis base and BCl_3 and the Lewis base. The total energy, the core–core energy, the electronic energy, and the enthalpy of formation are used in the analysis.

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The exercise is performed by defining each of the molecular systems in HyperChem and performing a geometry optimization calculation on each structure using a semiempirical quantum mechanical method. Each of the desired energies is generated in this calculation and is saved in a text file. A sample data set is given in Table 1 for the exercise performed with fluoride as the Lewis base. The analysis of the data involves the calculation of the change in each of the energy terms for the formation of the Lewis acid base complex. The results from these calculations are presented in Table 2.

The interpretation of these results can begin by comparing the differences in the enthalpy of reaction for the formation of the two products. The enthalpy of reaction for the formation of BCl_3F^- from BCl_3 and F^- is more negative than that for the formation BF_4^- from BF_3 and F^- in agreement with the idea that BCl_3 is the stronger Lewis acid. This agreement with experimental data supports the further analysis of the results obtained in this exercise. As expected, the pattern seen for the enthalpy of reaction is mirrored by the change in the total energy for the reaction. The analysis of the change in the core–core energy and the change in the electronic energy for the reactions can be used to begin to explore the factors that may contribute to the relative Lewis acid strength of these two molecules.

The change in the electronic energy for the reaction can be viewed as the stabilization of the valence shell electrons of the reactants upon the formation of the complex. In the systems presented here, we find the formation of BF_4^- is associated with an electronic energy stabilization of 104,350 kJ mol^{-1}, while BCl_3F^- is stabilized by 86,523 kJ mol^{-1}. With respect to the change in the electronic energy for the reaction we find that the BF_3 is favored by 17,827 kJ mol^{-1}. From this result one could say that BF_3 is more capable of stabilizing the electron density offered by the Lewis base than is BCl_3. This is in agreement with the prediction made by most students that BF_3 is the stronger Lewis acid based upon the differences in the electronegativity of the halogen.

A similar analysis of the change in the core–core energy term for the formation of the two complexes favors BCl_3 by 17,916 kJ mol^{-1}. The core–core repulsion term contributes a factor that is often not stressed in the analysis of chemical reactivity. As the Lewis base approaches the boron atom, repulsive forces between the cores are created in addition to the attractive forces between the electrons and the cores. This analysis predicts that the repulsive forces created between BCl_3 and F^- are smaller than

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TABLE 1. Energy terms for individual species calculated from energy-minimized structures using the AM1 parameter set.

Species	Enthalpy of Formation (kJ/mol^{-1})	Total Energy (kJ/mol^{-1})	Electronic Energy (kJ/mol^{-1})	Core–Core Energy (kJ/mol^{-1})
BF_3	-1,139	-147,695	-286,429	138,733
BCl_3	-406	-115,223	-224,766	109,543
BF_4^-	-1,663	-194,832	-437,378	242,544
BCl_3F^-	-1,019	-162,448	-357,888	195,438
F^-	14	-46,599	-46,599	0

TABLE 2. Change in the various energy terms for the overall reaction based upon the energy terms for the individual species calculated from energy-minimized structures using the AM1 parameter set.

Reaction	Enthalpy of Reaction (kJ/mol^{-1})	Total Energy (kJ/mol^{-1})	Electronic Energy (kJ/mol^{-1})	Core–Core Energy (kJ/mol^{-1})
$BF_3 + F^- \text{->} BF_4^-$	-538	-538	-104,350	103,811
$BCl_3 + F^- \text{->} BCl_3F^-$	-624	-626	-86,523	85,895

those created between BF_3 and F^-. This result is due to the boron–chlorine bond distance being larger than the boron–fluorine bond distance. Considering these calculations, BCl_3 is the stronger Lewis acid because of the greater accessibility of the boron atom in BCl_3 than in BF_3.

This is a very different explanation for the relative Lewis acidities of BF_3 and BCl_3 than that presented in popular inorganic chemistry textbooks [6, 7, 8]. In these texts the most common explanation for the differences in the Lewis acid strength for these two

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compounds is that the pi-bonding system in BF_3 is stronger than that in BCl_3. The explanation continues by suggesting that in the formation of the Lewis acid base complex this pi-bonding system is disrupted due to the change in geometry around the boron atom from planar to tetrahedral or distorted tetrahedral. The stronger pi bond in BF_3 inhibits the distortion of the geometry around boron yielding a weaker Lewis Acid. In an advanced aspect of this exercise, this explanation can be investigated using the energies of the molecular orbitals to produce an orbital energy-level-mixing diagram for the two reactions. The analysis of the mixing of the molecular orbitals of the Lewis acid with the atomic orbitals of the Lewis base for the two reactions is not trivial and is often too complex for students at the undergraduate level.

Exercise III. Back Bonding in Pi-Bonding Ligands

The relative position of ligands in the spectrochemical series is often difficult for students to grasp. This is because of the need to apply molecular orbital theory to the analysis instead of a simpler theory. The need to use molecular orbital theory in this analysis makes this topic ideally suited to a quantum mechanical calculation exercise. In this exercise students are asked to explore the factors that contribute to the relative ligand strengths of a given series of ligands that have the ability to accept electron density from the metal using a molecular orbital with pi symmetry. The exercise requires that the student perform a semiempirical quantum mechanical calculation on each ligand and determine the energy of the highest occupied molecular orbital (HOMO), the energy of the lowest occupied molecular orbital (LUMO), the charge on the atom that binds to a metal, and the atomic orbital compositions of the HOMO and the LUMO. The student is then required to evaluate each of these energy terms to determine how each contributes to the trend, given with the exercise, in relative pi-bonding strength of the ligand.

The group of ligands that the students are asked to explore in this exercise are N_2, CO, CS, NO^+, and CN^-. These species are isoelectronic, allowing for a direct comparison to be made between them. Table 3 presents some of the results that are obtained from semiempirical quantum mechanical calculations using the AM1 parameter set. The ligands are listed in order of decreasing pi-acceptor strength, and the values for the energy of the LUMO and HOMO, the charge on the atom that bonds to the metal, and the percentage that this atom’s atomic orbitals contribute to the HOMO and the LUMO are given in the body of the table. From these results, one can see that only the energy

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TABLE 3. Analysis of pi-acceptor ligands.

Ligand	HOMO (eV)	LUMO (eV)	Bonding Atom Charge	Bonding atom contribution to HOMO	Bonding atom contribution to LUMO
CN^-	-3.13	10.13	-0.48	64%	60%
N_2	-14.32	1.00	0.00	50%	50%
CO	-13.31	0.94	0.20	72%	74%
CS	-10.42	-0.28	0.34	77%	70%
NO^+	-26.13	-9.62	0.65	65%	64%

of the LUMO follows the same trend as does the pi-acceptor strength of the ligand. This orbital is the one used in the pi-accepting process. If the energy of the metal-centered orbital that is donating electron density to the ligand is lower in energy than the LUMO of the ligand, then the interaction between these two orbitals should increase as the energy difference between them decreases.

Conclusions

I have presented a few of the exercises that I have used in my upper-level inorganic chemistry course to present molecular orbital theory in a quantitative fashion. This range of exercises demonstrates some of the techniques that can be used to explore chemical systems using a typical molecular modeling program that performs semiempirical quantum mechanical calculations. One can ask the question, “Do these calculations mean anything?”. The results of all molecular modeling calculations depend upon the type of calculation and the parameter set used in the calculation. Parameter sets contain the constants used in a calculation to make the results of the calculations match the experimental results for a set of compounds. A stable calculation method and a good parameter set can produce results that are in agreement with experimental data. When calculations are performed upon species that were not part of those used to generate the parameter set, great care should be used in the analysis of the results. Whenever possible the results of such a calculation should be supported by a comparison to experimental values. Even when one result, such as the heat of

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formation, compares favorably with the literature value, other results, such as electronic and core–core energies may not be partitioned correctly. In short, there are a number of factors that may contribute to inaccurate results being produced in the calculations being presented in this paper. At the undergraduate level, the greatest value of these calculations may not be in the individual results obtained in an analysis. Instead, the introduction that a student receives to the field of computational chemistry may be far more important. Combined with this is the practice that the students gain in performing critical-thinking exercises and their reintroduction to the idea that, even in the simplest of chemical systems, multiple factors are involved in the control of the properties of the system.

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