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Integrated Applications of Electronic Structure Computations in the Undergraduate Chemistry Curriculum

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Abstract: This paper describes the integrated use of electronic structure computations in the undergraduate chemistry curriculum including organic, physical, and analytical chemistry courses. This computational tool is used to enhance student learning and understanding of chemical principles along with exposing students to a modern research tool in chemistry. The electronic structure computations are used for homework, classroom activities (including examinations), and laboratory experiments (both computational and wet-lab). Some examples of these uses of electronic structure computations in organic, analytical, and physical chemistry courses are discussed.

Key Words: Academic Computing, Chemistry, Electronic Structure Computations, Undergraduate Chemistry Curriculum
Category: J

1 Introduction

The use of electronic structure computations in chemistry is not novel. The study of chemistry is based upon the fact that chemical behavior is dependent upon structure, especially electronic structure. Therefore, the behavior of a particular chemical species can be predicted on the basis of its structure. Molecular electronic computations have become an important aspect of both experimental and theoretical chemical research. Computational chemistry is fast becoming a tool as important as nuclear magnetic resonance (NMR) spectrometry. just as no one would argue the importance of including the theory, use, and interpretation of NMR in the undergraduate chemistry curriculum, computational chemistry, especially molecular electronic computations, has become just as important.

As computers became powerful enough to handle large structures, chemists began refining calculations in order to make accurate predictions about the chemical properties of reactants and products. This is becoming increasingly important in the ability to inhibit or promote biological reactions based upon molecular recognition. It is also extremely important to be able to predict potential drug activity and bioavailability in the area of pharmaceuticals. Therefore, being able to make accurate predictions about the products of specific reactions and the medicinal potential of a target product is sociologically and economically desirable.

The use of computers has made a drastic change in teaching and learning from the primary grades all the way into college. Most freshmen enter our institutions of higher learning with a high degree of computer literacy. It is becoming common for educational institutions to require that incoming students purchase a laptop computer that will be used for their academic careers. Those institutions that do not require such a purchase are under pressure to provide computer facilities adequate for constant student use. Given the increasing importance of computational chemistry, the availability of computers in the academic setting, and reasonably priced electronic structure computational software, it seems both appropriate and necessary that we in academia employ such programs in the undergraduate chemistry curriculum. The most obvious reason for using such computational programs in the classroom is the thesis that students learn and retain by seeing and doing. Perhaps the best scenario is for students to be able to build molecules and perform computations at their own seats in the classroom along with an instructor. Analyzing the data allows students to discover for themselves the concept being presented, and the instructor can confirm the conclusion and offer more detailed explanations as to why and how. The second reason for incorporating electronic structure computations in the undergraduate chemistry curriculum is to provide students with “hands-on” experience using such programs. Clearly, computational chemistry is becoming increasingly important in the corporate and academic worlds, and the professionals of tomorrow can benefit from exposure to these tools today.

The purpose of this paper is to provide examples of how we have integrated use of an electronic structure computational program into the undergraduate chemistry curriculum in an institution that requires all incoming students to purchase a laptop computer with a standard software suite. The use of such a program in an undergraduate organic chemistry course sequence is obvious because such courses are based on the fact that chemical behavior and reactivity arise from molecular structure and conformation.

However, organic chemistry is not the only course sequence that finds electronic structure computations a valuable instructional tool. Computational programs are capable of calculating thermodynamic properties and geometries of molecules, complexes, and radicals. Molecular parameters such as dipole moments, vibrational frequencies, and vibrational modes can be used to interpret and predict spectra. And, computed electron densities of molecules can be used to explain the mechanistic details of chemical reactions from a modern quantum mechanical perspective rather than relying on traditional classical mechanical spring models or “memorized” group functionalities. We suggest that these capabilities can be utilized in courses throughout the undergraduate curriculum, and we present examples of how we have used electronic structure computations in organic, physical, and analytical chemistry courses. The examples we present arise from using *PC-Spartan+* [Wavefunction, Inc.] in an undergraduate chemistry curriculum composed of chemistry and chemical engineering majors with individual copies of the program installed on their laptop computers. We remind the reader that there is other comparable computational software on the market, and we do not intend to recommend this specific package over any other.

2 Organic Chemistry

Organic chemistry is generally the second course sequence for students majoring in chemistry or chemical engineering. In some programs it is taken in the second term of the first year. In others it is taken in the second year simultaneously with the first course in analytical chemistry. Regardless of the timing, however, many students experience organic chemistry as radically different from any of their prior learning experiences. One reason is that it is seldom related more than superficially to the chemistry students studied in high school. Another reason why so many students find this a particularly challenging course is that it demands a higher degree of chemical intuition than the general chemistry sequence. Conceptually organic chemistry is not as mathematical or quantitative as the introductory course. And, while competency in critical thinking is one of the overall goals most educators seek to inculcate in their students by the time the students' college careers *end*, at the Sophomore level, students are, on average, not mature enough to wrestle effectively with the abstract critical thinking demanded by organic chemistry. Over the years a variety of tools have been developed to help students meet this challenge. Hand-held models rank near the top of the list for ease of manipulation and for providing reasonably accurate 3-dimensional spatial information about molecules. It seems apparent from the rapid incursion of molecular modeling programs into instructional settings that what has been lacking in such common tools, at least for organic chemistry, is far more than the colorful 3-dimensional animation the electronic medium provides. Even for molecular structure and modeling software that is least sophisticated in its underlying mathematical complexity, the appeal and the intrinsic pedagogical value lies in the presentation of fundamental physical-chemical principles designed in such a way as to visually display readily recognizable atomic/electronic features about the structure from which students can make concrete connections to the abstract principles associated with the properties and reactivity of that structure. By frequently encountering the same or similar connections, students can more rapidly learn to make credible, critically developed *predictions* about properties and reactivity of molecules or in situations or systems for which *they have never had an example* 'explained' to them.

2.1 Fundamentals of Structure-Reactivity Relationships

From their first courses in chemistry, all students have at least a rudimentary knowledge of acids as proton donors. Thus, a simple computational exercise they can carry out the first time they use modeling software is one in which they construct a set of related organic protic acids and model electronic charge density associated with the acid proton. The visual displays are valuable for revealing the impact of changing electron density as structure changes. These data are plotted as a function of literature pK_a values (provided *or* student-searched), and with a high degree of certainty students can predict either the pK_a or the electronic charge for additional structures in the set. Equally as important as exhibiting the predictive ability of these computations, students can be assisted to focus on the fundamental concept of the relationship of structure at the molecular level to the property displayed at the macroscopic level. Other introductory exercises are available in many publications [see Hehre et al. 1996]. They involve both physical-structural and electro-magnetic considerations. These activities have utility either as in-class activities culminating in discussion of the unifying principles, or as out-of-class assignments that make students responsible for bringing their own data into class where they must share their understanding as part of the class discussion.

2.2 Experimental Design and Formulation of Testable Hypotheses

We have used two other somewhat less usual pedagogical applications of the computational features of modeling software to support the laboratory portion of the organic chemistry course. One is to have students use the computational information to plan the experimental design of the laboratory experiment. The second is to use modeling data as the entrée for instructing students in the skill of articulating a hypothesis, then *critiquing* the hypothesis once the experimental data are in hand. Tied together, these features provide the instructor with a two-dimensional approach to instruction. First, it moves beyond many published exercises that serve to illustrate reactions that are not practical for students in an academic laboratory. Second, this approach is an attempt to replace entirely the use of predefined-outcomes, the so-called verification laboratory exercise, with guided, but open-ended laboratory experiences.

For one of these applications we have added a computational exercise as a precursor to a more traditional experiment involving thin layer chromatography (TLC). In the stand-alone experiment a set of related compounds is ordered according to dipole moment by carrying out a specified sequence of paired TLC elutions. We do *not* provide the dipole moment data *or* the specified sequence. Rather, we discuss some of the theory of solvent-solute interactions, describe the overall intent, and provide some guidelines for the experiment. Students must extract the relevant dipole moment information from modeling computations. Using their own data and their understanding of the theory, students formulate a hypothesis about how the paired elutions can be done efficiently to illustrate the theory. Prior to going into the lab some time is devoted to a class discussion of the various plans. This gives the class an opportunity to hear how others have approached the problem, particularly in terms of an efficient use of time, and to hear the kinds of affirmations or questions the instructor raises about the various ideas. The amount of pre-lab or class time spent on this discussion can be varied according to individual situations, but we have discovered that such discussion does assist some students in seeing that there are some "easier" and some "harder", more cumbersome, ways of getting this work done.

Whether they collaborate on a plan or not, students are responsible for articulating their own written hypothesis, describing the logic of the sequence they use, carrying out the experiment, and critiquing the hypothesis and limitations of the experiment against their own results. Because the hypothesis must be reported before they carry out the experiment, students cannot "work backward", making their hypothesis "look good" when they know what the outcome is. Their critique is not expected to be self-deprecating, but students are asked to deal with revealed gaps in their thinking. An additional feature of this exercise is that the concepts and the conclusions related to TLC are reiterated in a slightly different context when students study gas chromatography and liquid chromatography in analytical chemistry (*vide infra*).

2.3 Transition States and Reaction Mechanisms

More complex applications of electronic structure computations have been devised for the latter part of a year's course. From about mid-way through a first course in organic chemistry references to reaction mechanism, transition state structures, and the interplay of thermodynamic control and kinetic control are frequent. By this time in the course students are thoroughly familiar with such things as the relative structure-stability relationships of primary, secondary and tertiary species, strong and weak nucleophiles, nucleophile-electrophile interactions, the relationship between energy and stability, and the *disjunction* between thermodynamic stability and rate. They are also capable of utilizing the software fully. Computations for such structural features as electron-rich and electron-poor reaction sites, the way in which bond formation and bond breaking can affect transition state structure, and the thermodynamic parameters associated with these structures can be incorporated into guided discussions of almost any common synthetic organic laboratory exercise. What this permits is, again, moving away from verification; i.e., *not* providing students with the identity of all species nor all the steps in a given reaction, but letting them explore, discover and propose some of these pieces for themselves. This can be done by referring students to only the general nature of the reaction then asking them to model the structures of reactants and potential products and to use molecular geometry and electron density to predict the reactive sites. From this they can move to the construction of one or two possible transition states, computing the energy demanded to attain such a structure, and then reflecting on what the relative energy values convey about the relative ease with which such a structure would form. While focusing on thermodynamics, students need to be urged to keep in mind the *absence* in modeling of *kinetics* information, and they can be asked to think about ways in which they might be able to test reaction rates. Finally, the discussion can move to using all their information, both thermodynamic and kinetic and including the limitations they have recognized, to form a hypothesis about the product they think they will isolate when they carry out the reaction under consideration. What this approach "costs" in time and in terms of perhaps doing fewer experiments of the verification type is, we believe, more than compensated for in what it "pays" in dividends gained in breadth and depth of experience and understanding.

3 Physical Chemistry

The physical chemistry curriculum can be divided into the following major segments: thermodynamics and thermochemistry, chemical kinetics, and quantum chemistry. Within this section, applications of molecular electronic computations in each of these major areas will be described. However, the applications presented here are not implied to be all-inclusive. The possibilities are limitless.

3.1 Quantum Chemistry

When using most electronic structure computational packages, the user is faced with a number of different computational approaches: molecular mechanics, ab-initio, semi-empirical, and density functional. An important focus in an undergraduate physical chemistry course is to introduce the differences in the approaches amongst these various computational methods along with the inherent advantages and disadvantages of each. As an example, if structure is the desired outcome, all of the approaches provide reasonably accurate results. Hence using the fastest computational approach (*i.e*. molecular mechanics) is superior. If thermochemical comparisons are needed between different molecules or reaction pathways, the semi-empirical approach is the most computationally economical. These various examples lead to different computational strategies that make using the computational tools more effective. Using electronic structure computations in instructing quantum chemistry makes the subject come alive for students and helps them see the practical importance of quantum chemistry in every field of chemistry.

3.2 Thermochemistry

An important topic in physical chemistry is the ability to obtain thermochemical information on unstable species or reaction intermediates and transition state structures. Here is where electronic structure computational methods are most certainly indispensable. Students learn how to construct intermediate structures and perform computations. In addition, students can use fundamental information such as rotational, vibrational, and electronic energies to obtain various thermochemical properties such as heats of formation, total energy, entropy, and free energy via statistical thermodynamic computations. For these computations, a student obtains the molecular information from the electronic structure computation and then uses suitable spreadsheet software to perform the various statistical thermodynamic computations. This assignment not only provides students with a useful research skill, but it helps students understand thermodynamic principles from a molecular level.

3.3 Chemical Kinetics

An excellent example of using electronic structure computations is to have students construct a potential energy diagram along a reaction pathway. A specific example is the elementary gas-phase reaction of $H + F_2 \rightarrow HF + F$. Students initially build a structure of F-F—H whereby the distance between the fluorine atoms is the normal bond length of a fluorine molecule and the distance between the fluorine and the hydrogen atom is essentially infinite (i.e. in the order of 3 – 4 Angstroms). These distances between the atoms along with angles (180°) are constrained, and the energy of this structure is calculated. The Hamiltonian employed in the calculation depends on the computational platform available to the students. Depending on the Hamiltonian employed, the computation can become quite lengthy. Additional points are obtained along the reaction pathway by increasing the distance between the fluorine atoms and decreasing the distance between the hydrogen and fluorine atoms. At each point, the distances and angles between the atoms are constrained and the energy obtained. Students obtain numerous energy points along the reaction pathway from which a three dimensional plot can be constructed: the F-F distance verses the H-F distance verses energy. (Suitable programs for constructing 3-D plots include algebraic software such as *Maple* [Waterloo Maple Inc.].) From this plot, students can identify the transition state structure along with the activation energy of this reaction. Since the computational activity is quite involved, it is helpful to make this into a group assignment (groups composed of three to four students) so the computational effort can be shared. These computations can be further manipulated through animation features that help students visualize vibrational modes that lead successfully to products.

The applications of electronic structure computations to undergraduate physical chemistry courses are endless. Not only is incorporation of these types of computations integral to an undergraduate chemistry curriculum, but they also bring many chemical principles to life for students. Not only do students leave these courses with a valuable research skill, but they appreciate the importance of the fundamental principles taught in physical chemistry.

4 Analytical Chemistry

The use of computers in analytical chemistry is obvious with respect to data acquisition. Most analytical instruments are interfaced to computers, and data acquisition and analysis are carried out through this interface. Spreadsheet programs are also used often in analytical chemistry for the purpose of constructing calibration curves and performing statistical analyses on data. However, we suggest that computers can be used for more than developing calibration equations. Specifically, we provide examples of how electronic structure computations can be used to provide students with a basic understanding of principles in chromatography and spectroscopy, important concepts and topics in analytical chemistry. We also remind the reader that analytical chemistry is very much laboratory-driven, and the examples we present are employed in conjunction with actual experiments that students perform in the analytical laboratory.

4.1 Chromatography

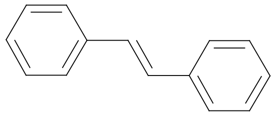
As our first example, we describe how electronic structure computations can be used effectively in developing a student's understanding of chromatographic separations. Students learn in organic chemistry through a computational/laboratory exercise involving TLC (described earlier) that elution order in chromatographic separations can be predicted based on relative polarities of solutes. This also holds true for gas and liquid chromatographic separations based on partitioning (preferential solubility). One of the first "rules" that students learn in general chemistry is "like dissolves like." This is why ionic and polar compounds either dissolve or are miscible in water (a very polar solvent) and relatively non-polar compounds (oils and fats) do not dissolve or mix with water. Students also learn that polar compounds have associated with them a non-zero dipole moment while non-polar compounds possess very low dipole moments that approach zero. Based on these simple and general principles, we can perform an analytical separation of a mixture of several different compounds based on their relative attraction to or solubility in a liquid stationary phase. An experiment often performed in analytical chemistry courses is the separation of caffeine and aspirin contained in analgesic tablets. The particular experiment we perform is a liquid chromatographic separation that employs a polar mobile phase to carry the solutes through a closed column. The column is packed with a very non-polar stationary phase. Therefore, the less polar of the two solutes will be attracted to the non-polar stationary phase and exit the column at a later time while the more polar of the two solutes will travel with the mobile phase and exit the column at an early time. In this particular example, we use an electronic structure computational program to calculate the dipole moments of the aspirin and caffeine molecules, use these calculated dipole moments to predict their relative polarities, and thereby predict their elution order. Our prediction can be correlated with the actual experimental observations made in the laboratory. The results from this specific calculation indicate that caffeine is the most polar molecule, and students predict that it will exit the column first. However, this prediction may or may not be accurate based on the identity and pH of the mobile phase. Specifically, the elution order is caffeine first followed by aspirin when the pH of the mobile phase is 3. At pH 4, however, this prediction does not fit the experimental observations. However, this prompts students to consider in what forms aspirin and caffeine exist at the two different pH values. Based on initial experiences with acids and pK_a values in organic chemistry, students ultimately realize that aspirin is deprotonated (*i.e.*, charged) at pH 4. The charged character of aspirin at this pH makes it very polar, and this is enough to reverse the elution order of caffeine and aspirin. Recalculating the dipole moment for aspirin in its deprotonated form gives numbers (and a predicted elution order) consistent with the experimental results.

4.2 Spectroscopy

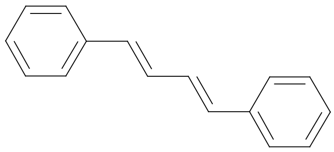
Another important topic in analytical chemistry is spectroscopy, the study of the interaction of light with matter. Spectroscopic analysis is very important in analytical chemistry, and electronic structure computational programs like *PC-Spartan +* can be employed as very effective tools for teaching fundamental concepts. It is often difficult for student to visualize what actually takes place when a molecule interacts with light. We have employed electronic structure computational programs to aid in their understanding of molecular absorption spectroscopy. In the case where a molecule absorbs ultraviolet or visible light, electrons in the molecule are promoted to higher energy levels. This is difficult for students to visualize conceptually. However, if a student can see a picture of electron density in a molecule (electrostatic potential) before and after it absorbs light, his or her fundamental understanding of this process will become more clear. Most electronic structure computational programs allow the user to construct a molecule and calculate and visualize the ground state or HOMO (Highest Occupied Molecular Orbital) and the excited state or LUMO (Lowest Unoccupied Molecular Orbital). Depending on the molecule and functionalities, one can observe differences in the electron densities of specific functional groups that give rise to absorption signals in the ultraviolet or visible regions of the electromagnetic spectrum.

4.3 Predicting Trends

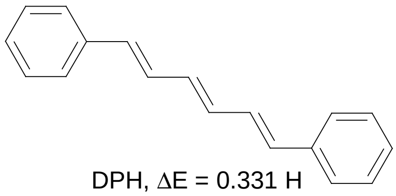
In advanced analytical chemistry courses it is possible to enhance understanding of spectroscopic trends by performing calculations for a particular family of molecules. As an example, we use the family of α, ω-diphenylpolyenes to explain the experimental observation that absorption maxima shift to longer wavelengths when the number of conjugated double bonds is increased. The explanation is based upon the actual energy gap (ΔE) between the HOMO and LUMO. An electronic structure computational program can be used to calculate molecular orbital energies for each of the molecules in the series. We choose *trans*-stilbene (*t*S), 1,4-diphenyl-1,3-butadiene (DPB), 1,6-diphenyl, 1,3,5-hexatriene (DPH), and 1,8-diphenyl-1,3,5,7-octatetraene (DPO), and perform *ab initio* calculations employing the 3-21G$^{(*)}$ basis set. Although the absolute orbital energies may have quite a significant error, we are merely interested in the trend exhibited by a family of similar molecules. The trend itself is self-consistent, so it is possible to draw some useful conclusions from the data. From these calculations, students conclude that the HOMO energies increase as the number of conjugated double bonds increases while the LUMO energies exhibit a systematic decrease with increasing conjugation. The end result is that the energy gap between the HOMO and LUMO decreases as the number of conjugated double bonds increases, giving rise to a red shift in absorption spectra with increasing conjugation [see Fig. 1].



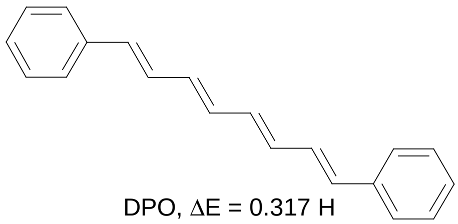
*t*S, ΔE = 0.366 H



DPB, ΔE = 0.343 H



DPH, ΔE = 0.331 H



DPO, ΔE = 0.317 H

Figure 1: Structures of diphenylpolyenes and the energy difference (ΔE) between the HOMO and LUMO in Hartrees (H).

4.4 Vibrational Spectroscopy

At this point we wish to address briefly the applications of electronic structure computations in advanced analytical spectroscopy courses and their potential overlap with advanced inorganic courses. Programs like *PC-Spartan +* allow the user to build molecules, calculate the fundamental vibrational frequencies of these molecules, and animate the vibrations. This is particularly useful in helping students understand selection rules for vibrational spectra and their correlation with symmetry. Many programs label each calculated frequency with symmetry notation. Students can also use calculated vibrational frequencies to make band assignments in an experimental spectrum. While there is a finite difference between the experimental and calculated energies, students are expected to make use of their chemical intuition and knowledge of symmetry as they assign the vibrational modes.

5 Conclusion

The use of electronic structure computations in the undergraduate chemistry curriculum has endless possibilities. We have presented some of the ways we have used this type of software in our courses; however, this is not to suggest the limit to which this software can be used in the instruction of these courses. We have found that the use of such software, though an important *addition* to the curriculum, *does not require the removal* of any significant content from these courses. These types of computations enhance student learning through better visualization and expose students to modern research tools in chemistry.

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