SABBATICAL REPORT

Iraj B. Nejad

Department of Chemistry
Fall 2000 - Spring 2001

"It is mandatory for Community Colleges to stay current with the technological innovations."

ED net, September 1999

"Teaching Science, like Science itself, seems always to produce more questions, than answers."

John W. Moore, Chief Editor, J. Chem. Ed. October 1999

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Acess, Alliance/NCSA, Fall 2001

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Molecular Modeling

in

General and Organic Chemistry

Sabbatical Project

Iraj Behbahani
Department of Chemistry

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OVERVIEW

The concepts of molecular bonding, electronic structure, molecular orbitals, inter- and intermolecular interactions, are fundamental to all areas of chemistry. Although these topics are covered at several levels of sophistication in various chemistry courses, they are not well understood by the majority of students. The problem which students have with understanding these concepts arises from the difficult task of visualizing these abstract ideas on a submicroscopic level. Unfortunately, the typical general chemistry textbook presentation of electronic structure theory, set as it is in the language of molecular orbitals, is very abstract and it does not seem to be relevant to the educational needs and interest of the students. Many of the quantum mechanical aspects of molecular orbitals are too difficult for most beginning science major students to appreciate, much less master.

Recent advances in molecular modeling, PC-based computational chemistry, and three-dimensional visualization software, coupled with low-priced computers and workstations equipped with relatively high computing power and ***superb*** graphic capability, provide an exciting opportunity to teach the critical electronic structure and reactivity concepts in a powerful and ***innovative*** way. SPARTAN is a unique software tool that can be used <u>by ***students at all levels***</u> to enhance their comprehension of the these topics. The goal of my sabbatical project is to develop numbers of SPARTAN-based molecular modeling activities to introduce molecular modeling into the departmental curriculum beginning with General Chemistry (CHEM 1A, 1B) and progressing with increasing degrees of sophistication in Organic Chemistry courses (CHEM 12A, 12B).

THE PROJECT

Curricular Need/ Molecular Modeling

Why is it important to introduce molecular modeling in the beginning chemistry courses? With so many new concepts already essential to the understanding of the subject, how can introduction of yet another dimension to the course be justified? Would it not be better to postpone consideration of molecular modeling to more advanced courses? The answer is not. Because, molecular modeling enables the students to think more clearly about topics which are fundamental to the study of chemistry, e.g., structure, stability and reactivity of organic and inorganic compounds.

In studying chemistry, it is extremely important to explore the fundamental relationship between molecular structure and chemical and physical properties. In nearly every college chemistry course, whether introductory or advanced, students are first taught about the structure of a molecule and then taught to relate structure to a substance's properties. This so-called structure-reactivity relationship is central to the success of understanding the structural concepts in chemistry. Three-dimensional (3D) visualization is extremely important and critical for this purpose, something that the majority of students find difficult to comprehend, particularly, in the submicroscopic world of atoms and molecules. To facilitate this understanding, textbook authors utilize various strategies such as structural formulas, two-dimensional line figures, ball-and-stick models, and space-filling models to depict the molecular structure of compounds. Often, for students, the 2D drawings do not look at all like the molecules they are supposed to depict. The "low-tech" model building experiments using molecular model kits have also been utilized in the beginning courses labs to help students visualize and manipulate the structural models. Although experiments using molecular model kits have helped to an extent, they have unfortunately failed to provide a clear understanding of molecular structure and bonding. Furthermore, they provide no information at all about the chemical reactivity of a compound.

The rapid improvement and ready availability of molecular modeling software are providing an attractive alternative, to traditional drawings in displaying the 3D structure

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of molecules. There are a number of reasons that molecular modeling is superior to traditional drawings. First, the model displayed with animation on a computer screen looks and behaves more like a real molecule than a drawing does. The computer model can be viewed in 3D from different angles, and different formats can be used to show atomic positions, bond lengths, bond angles, atomic volumes and other features of interest. Second, calculated structural information such as dipole moment, bond lengths and bond angles can be obtained for comparison with the experimental data. Third, molecular modeling can be used to *predict* and *display* a variety of chemical and physical properties such as energy, dipole moment, and electron density distribution within a molecule. Fourth, many molecules that cannot be represented by a simple drawing, e.g., resonance structure, electron delocalization can be treated and studied by molecular modeling. Fifth, not only reactivity but also the reactive site(s) on a molecule can be graphically represented and studied.

In short, introduction of molecular modeling very early into the chemistry curriculum does not complicate the learning of chemistry, but rather assists the student in visualizing the structure and reactivity of the compounds. The modeling tools; *Visualization, Graphics, Animation,* allow students to comprehend concepts that are virtually impossible to understand in a traditional setting. Equipped with these tools, students can explore vast new range of chemical information and reasoning.

Molecular Modeling Facility

Over the past few years, the Department of Chemistry has been very actively involved in using state-of-the-art technological innovations to deliver the chemistry curriculum. The Department is part of the "Molecular Science Consortium" along with UCLA and CSU, Fullerton. The consortium established by a $3.4 million grant in 1996 from the National Science Foundation (NSF), aims to transform educational methods by integrating modern telecommunication and information technology into the curriculum. Funds from this consortium permitted the Chemistry Department to purchase 24 Pentium computers for use in delivering the Molecular Science curriculum. As an active participant in the preparation and submission of the consortium proposal to NSF, I

became very interested in incorporating molecular modeling into the departmental curriculum. This interest resulted in preparation and submission of two proposals (I. Behbahani, PI, Eileen DiMauro, Co-PI) to NSF and the Department of Defense (DOD). Both proposals were successful (funded for a total of $192,438 dollars). Funds from these two grants were used to purchase 16 additional Pentium II computers, an SGI workstation, and a unique COMWEB *multimodal* communication system. Together with the computers from the Molecular Science consortium, the Chemistry Department has now established the Molecular Science and Modeling Learning Center (MSMLC, 7-135). This facility is networked with broadband fiber optic cabling (provided by Mt. SAC) to facilitate student access to the Internet and it contains enough computers for students to work individually or to collaborate on group and class projects.

Software

The crux of molecular modeling, naturally, is the software; its versatility, ease of use and speed are the most important considerations. Based on extensive searching and faculty input from other local institutions, I selected SPARTAN molecular modeling software as the basis for modeling in the Department's curriculum. SPARTAN was selected because of its computational flexibility, low cost, superb graphic capability and ease of use by students. It is widely used in chemical education and chemical research and by major pharmaceutical companies everywhere. This software program combines state-of-art computational tools and exceptional visualization into one affordable package. Beyond that, SPARTAN is extraordinarily *user-friendly*. The program graphics can display structural models, orbitals, electron densities, bonding parameters and animated molecular vibrations. These capabilities coupled with ease in performing various types of molecular calculations at several levels of sophistication make SPARTAN a unique tool that can be used by *students at all levels to* enhance their comprehension of the structural topics. A recent issue of *J. Chem. Ed.* stated that "SPARTAN should be in every chemistry department in the country". Using funds from my NSF and DOD grants, 28 copies of SPARTAN were purchased and installed on computers in the MSMLC facility last year. With appropriate assignments to be

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developed in this sabbatical project, molecular modeling can be used by our students within a year.

Project Activities/Timeline

I envision molecular modeling in two places in our curriculum. In General Chemistry, it will be used primarily as a method for building and visualizing molecules, for obtaining structural information about atoms and molecules and for exploring important trends (electronegativity, polarity, bond lengths, bond angles, etc.) among molecules. More advanced applications dealing with structure and reactivity will be gradually introduced in the Organic Chemistry sequence. It is my goal that students slowly and incrementally become familiar with the various capabilities of molecular modeling, starting with relatively easy tasks in the first year and then progressing to more advanced problems in the second year as they gain experience and confidence. The ideas in this sabbatical project have been discussed with my full-time colleagues. They unanimously support this project.

(i) Activities

1. ***Competency with SPARTAN:*** Although I am familiar with the SPARTAN modeling program, I must achieve competency with the various types of calculational methods and knowledge of the limitations of each method before developing any modeling assignments.

2. ***Assignments /Activities for General Chemistry:*** Research available resources and compile a list of structural concepts essential in General Chemistry around which modeling activities can be designed and developed.

3. ***Modeling Activity Development :*** Use SPARTAN to develop an activity or activities for each concept listed in item 2. This involves choosing an appropriate optimizing method, building molecule(s), minimizing structures and creating appropriate outputs for visualization.

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4. *Writing:* Once assured of reproducibility, write assignments complete with questions for the investigated concept.

5. *Modeling Activity Manual:* Compile a manual of assignments for General Chemistry courses.

6. *Assignment/Activities for Organic Chemistry:* Research resources and compile a list of concepts, structural and reactivity related, appropriate for Organic Chemistry around which modeling assignments will be designed and developed.

7. *Modeling Activity Development:* Repeat activities 3, 4 & 5 for the identified concepts of Organic Chemistry courses.

9. *Sabbatical Report:* Write and submit a sabbatical report, detailing the progress and results of the project.

(ii) Project Timeline (Academic Year F'00-SP'01)

August – September:	Activities 1 & 2
September – November:	Activities 2, 3 & 4
December:	Activities 4 & 5
January – February:	Activities 5 & 6
March – April:	Activities 6 & 7
May:	Activities 8 & 9

ANTICIPATED BENEFITS

Merit/Value to the College

This project is in alignment with the 1997-2000 Breakthrough Goals for the College. It helps Chemistry Department faculty to improve curriculum and instructional delivery and to continue to provide quality instruction in Chemistry. Students will use state-of-the-art technology in learning molecular modeling and will comprehend the

critical bonding concepts in an innovative way. A 1990 survey by the American Chemical Society rated "knowledge of computers, experimental design and molecular modeling highest in importance for those who will be hired during the next several years. The envisioned integration of molecular modeling into our curriculum addresses this need and will help faculty to produce far more knowledgeable, enthusiastic and creative students for the future. In addition, students transferring to 4-year institutions will be well prepared for their upper-division courses and research. Integration and implementation of molecular modeling across our curriculum will prove as a model for other community colleges, illustrating utilization of the latest technology to improve the student learning process. Additionally, this advancement enhances Mt. SAC's reputation as a leader in educational technology.

Merit/ Value to the Chemistry Department

The pedagogy and the curriculum of chemistry are undergoing a tremendous change with the rapid advances in technology. As stated earlier, through several years of individual and joint collaborative work (with UCLA and CSU, Fullerton), the Chemistry Department has established the MSMLC that utilizes the latest technology in teaching and learning. Because chemical education is changing rapidly, new applications of the latest technology are necessities in the new millenium. In light of the rapid pace of computer software and hardware development, molecular modeling today has become part of the tool kit of every modern chemistry and biochemistry lab in industry and academia. Molecular modeling enables students to *visualize* a number of abstract concepts, allows them to explore and discover, and encourages them to be *creative*. This sabbatical project helps the Chemistry Department to improve and expand its curriculum, stay current with new technological advances, and make molecular modeling accessible to individual students. It is anticipated that the result of this project will lead to the development of manuals that will be used to integrate molecular modeling and computational experiments in the Department's curriculum.

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Merit/Value to Me

Since I became a chemical educator, it has always been my goal to continuously learn and utilize innovative curriculum-delivery strategies into my teaching. To accomplish my goal, I have participated in a number of NSF supported workshops (Instrumentation in Undergraduate Chemistry Curriculum, Molecular Modeling, Molecular Science, Workshop Chemistry Project, MC^2 project, to name a few) aimed at improving the teaching of chemistry at the undergraduate level. I have learned and gained a lot from these workshops and I have already incorporated a number of ideas from these workshops into my teaching. The opportunity to participate in the Molecular Science Project allowed the Department and me to initiate creation of the MSMLC facility. Since 1996, I have received funding (Project Director) in excess of $200,000 from the State (VATEA), DOD and NSF to develop an Introductory Chemistry course for Health Science majors and to incorporate molecular modeling in General and Organic Chemistry courses. As stated earlier, the funds from NSF and DOD were used to establish the MSMLC facility. I taught CHEM 1A and CHEM 1B in the MSMLC last year where traditional lecture was replaced by student-centered, computer-delivered instruction. I truly enjoyed the experience and I am currently teaching organic chemistry (CHEM 12A) in this facility for the very first time (CHEM 12B in spring 2000). Although challenging, these experiences have been very enriching to me. With the MSMLC facility complete, as a new challenge and an opportunity to further grow in my technological and teaching skills, I now look forward to developing and integrating molecular modeling into our General and Organic Chemistry courses. I strongly believe that molecular modeling exercises provide an excellent opportunity for collaborative projects, class projects and discovery-based learning. Once developed, I would be more than willing to show my colleagues in the Department how to utilize these exercises in their courses.

BACKGROUND AND STATEMENT OF PURPOSE

The purpose of this sabbatical project was to develop and incorporate molecular modeling exercises into the General and Organic Chemistry curriculum at Mt. San Antonio College. The overall goal of the project was to enable students to think with clarity and greater detail about many abstract molecular structure concepts which are fundamental to the study of chemistry.

Over the past few years, the Mt. San Antonio College Department of Chemistry has been a leader in using state-of-the-art technological innovations to deliver the chemistry curriculum. The Department has been an active participant in the "Molecular Science Consortium" together with UCLA and CSU Fullerton. The consortium, established by a $3.4 million grant in 1996 from the National Science Foundation (NSF), has allowed the chemistry faculty at Mt. SAC to integrate modern telecommunication and information technology into the curriculum. The Department also updated its general chemistry laboratory curriculum last year. The obsolete IBM PS-2 computers were replaced with Calculator-Based-Laboratory (CBL) data acquisition systems and several guided-inquiry experiments were added to the laboratory curriculum. As an active participant in the preparation and submission of the Molecular Science Consortium proposal to NSF, I became very interested in integrating molecular modeling into the chemistry curriculum. My interest in the subject has stemmed from two observations. First, that molecular modeling is a very powerful tool which has been used successfully by researchers in industry and in many chemistry and biochemistry departments for many years. While attending the Biennial Conference in Chemical Education in August 2000 at the University of Michigan, I participated in a tour to the Upjohn Company in Kalamazoo, Michigan. As we toured the facility, a senior research scientist at the company who was leading the group stated that the company's approach to the synthesis of a new drug now starts with molecular modeling. He explained that the research team first uses molecular modeling to investigate some very important factors such as the drug's stability, its solubility in blood, etc. in advance. They will then use modeling to

design an efficient synthesis pathway for the drug. All this work is done before actually working on the synthesis of the drug in the laboratory. The Fall 2001 issue of "Halicize", a publication of the National Computation Science Alliance (NCSA), reports about Stanford University researchers who are using molecular modeling to explore the behavior of organic and inorganic molecules on semiconductor's silicon surfaces. The use of molecular modeling in research is indeed ever-expanding.

The second observation which stimulated my interest in molecular modeling came from recognizing the capabilities of this "new" tool in *predicting* and *displaying* a variety of physical and chemical properties which are too difficult for most beginning science students to fully comprehend, but yet are very critical to the study of chemistry. For these stated reasons, I felt the need to incorporate molecular modeling into Mt. SAC's departmental curriculum. Based on an extensive search for a suitable molecular modeling software, I selected **Spartan** modeling software as the basis for molecular modeling in the Department's curriculum. I found the program to be very suitable, relatively low cost, with superb graphic capability and easy to use by **students at all levels.** To acquire the computers and the Spartan software for the department's curriculum, I wrote and submitted (with my colleague Eileen DiMauro as Co-PI) two grant proposals to the NSF and the Department of Defense (DoD) in 1997. Both proposals were funded for a total of $192,438 (including Mt. SAC matching funds). Monies from these two grants together with those from the Molecular Science Project allowed the department to create the Molecular Science and Modeling Learning Center (MSMLC). Department faculty have used MSMLC to deliver technology-based student-centered lectures/activities for the past four years. In order to effectively incorporate molecular modeling into the curriculum, I needed the sabbatical leave to design, develop and write modeling activities for our general and organic chemistry courses (Chem 1A, 1B, 12A, 12B).

PROJECT ACTIVITIES

A. GAINING COMPETENCE WITH SPARTAN

The first month of my sabbatical leave was spent learning the new Spartan-*Plus* 2.0 and Spartan-*Pro* modeling software. Although I was familiar with the first version of the software, I had to learn the two new Spartan software programs because the old Spartan was being phased out by Wavefunction (the publisher). We had already purchased with funds from my two grants, 28 copies of Spartan and had installed them on computers in the MSMLC facility. But because I still had funds left in the grants, I was planning to upgrade the software and also purchase a few copies of Spartan-*Pro*, a more advanced version of the program. This plan necessitated spending a good portion of the first two months of my leave on learning the new programs. During this time I ran into compatibility problems involving the new Spartan software and the Windows NT 4.0 operating system which is installed on all computers in the MSMLC facility. Once these problems were corrected a new problem arose. I was unable to print anything from the new Spartan on our network printers. Print jobs were getting lost without any error messages. However, with the help of David Pyle and the staff at Wavefunction, I was finally able to solve all the problems and have the new software installed and ready to use.

B. RESEARCHING THE RESOURCES

With the new Spartan software installed and ready to use, I began to search the literature, contact experts in the field and gather resources in order to compile a list of concepts essential in General and Organic Chemistry around which I could design and develop modeling activities. My overall goal of the project was to develop activities by which students can:

- gradually and incrementally become familiar with molecular modeling

- become able to better visualize the 3-dimensional structures of molecules

- visualize and gain a deeper understanding of the abstract structural concepts such as the electron density, polarity, molecular orbitals, etc.

- be encouraged to think, predict, explore, discover and be creative

- learn from peers by working as a team on activities

Following is a list of scientific concepts that were used to develop modeling activities for the general and organic chemistry curricula.

GENERAL CHEMISTRY

- Atomic Structure and Periodicity

- Molecular Geometry and Polarity

- Electronegativity and Polarity

- Nonequivalent Lewis Structures

- Resonance

- Expanded Octets

- Lewis Structures and Molecular Geometry

- Molecular Orbitals

- Molecular Vibrations

- Acid Strength

- Chemical Kinetics

- Coordination Compounds

- Exploratory Activities*

* This includes a collection of 17 short exercises which students have to design and carry out on their own with minimal information provided for each exercise. These exercises are included to encourage students to work as a team, be creative and apply their modeling skills from the previous activities to solving new problems.

ORGANIC CHEMISTRY

- Chemical Bonds

- Bond Lengths, Hybridization and Molecular Orbitals

- Multiple Bonds and Lone Pairs

- Resonance

- Conformational Analysis (Open-Chain Alkanes)

- Conformational Analysis (Cycloalkanes)

- Ring Strain in Cycloalkanes

- Vibrational Spectra

- Carbonyl Group Frequency

- Electronic Spectra

- Carbocation Stability

- Regioselectivity of Electrophilic Additions to C = C

- Stereospecific Reactions

- Aromatic Compounds

- Heterocyclic Aromaticity

- Electrophilic Aromatic Substitutions

- The S_N2 Reaction*

- Radical Chlorination of 1 – Chlorobutane*

- Diels – Alder Reaction*

- Synthesis of Dibenzalacetone*

* These are modeling exercises which supplement experiments the students do in the laboratory.

C. DEVELOPING ACTIVITIES FOR GENERAL CHEMISTRY

A total of 16 complete activities and an additional 17 "exploratory" activities illustrating the concepts identified in the previous section of this report were developed for general chemistry. These activities parallel the core topics commonly discussed in the yearlong general chemistry courses. They can be performed individually or to be carried out by students as a team. For the

most part, the complete activities are post-calculation analysis, meaning that I have already built and optimized the molecules and have saved the output files. To perform each activity, the students access the optimized structures in the files, measure the numerical data requested in the activity and display a number of 3-dimensional surfaces. They will examine these surfaces to obtain additional information about the molecule and, in conjunction with the numerical data, use the information to interpret the results and answer the questions. A number of the activities require students to actually build and optimize molecular geometries on their own. Detailed procedures on how to proceed are provided for each activity. The "exploratory" activities are rather short exercises which require students to think, design and perform a modeling computation on a specific chemistry concept. Only a recommended computational model is proposed but no procedure is provided for these exercises. The goal of these exercises is to encourage students to apply what they have learned to solving new problems.

D. DEVELOPING ACTIVITIES FOR ORGANIC CHEMISTRY

A total of 22 activities around the concepts identified in the previous section were developed for organic chemistry. Unlike the general chemistry activities, the majority of the organic exercises require students to actually build and optimize their own structures. Because there are typically several molecules to study in each activity, the students are strongly encouraged to work as a team on most of the activities. Four activities were developed which supplement the experiments students do in the organic laboratory. A brief introduction on the concepts being studied in each activity is provided, however, students must have a clear understanding of the topic before they can attempt the activity. Most of the questions in the activities are not simple. The students must have a good understanding of the topic and think in great detail about the activity in order to be able to answer the questions. It is hoped that the very interactive and visual nature of these activities will encourage students to work together, learn from peers in the same class and ultimately gain a deeper understanding of organic chemistry.

E. WRITING THE ACTIVITIES

There were several challenges that I had to overcome while writing the activities. First and foremost, I needed to develop a suitable template to write the activities. I certainly wanted to avoid writing repetitive procedures from one activity to the next and design unnecessarily long and tedious activities. Second, the training of students about Spartan software and its various computational models and display features had to be addressed. Third, conceptual discussion of the various computational methods and terms used in molecular modeling, at a level understandable by beginning science major students, had to be written. Molecular modeling involves rather complicated quantum mechanical calculations, the details of which were not long ago left for advanced courses in physical chemistry. Discussing the mathematical details would not only have been inappropriate, but would also have undoubtedly been a major barrier for students. After much thinking and examining several ideas and approaches, I finally decided on the following approach for writing the activities.

1. Wrote a section titled "General Operating Features" of Spartan. This section provides an overview of the general operating features of Spartan and is included in both modeling manuals.

2. Developed three tutorials. The tutorials are self-guided and together they familiarize the student with all features (computation, display, measurements, etc.) of the program. A student completing the three tutorials should be reasonably familiar with the software and be ready to work the exercises. These tutorials are included in both manuals.

3. Developed seven appendices (A – G). Each appendix focuses on a specific topic and associated terms related to molecular modeling. Conceptual descriptions of the various computational models are provided but the mathematical discussions are intentionally left out. Quite a large number of graphics generated by Spartan are included in the appendices to

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help students understand the topics. These appendices are also included in both manuals.

4. Modeling activities were written for both general and organic chemistry courses. Each activity in general chemistry is presented in five sections: Introduction, Background, Computational Procedure, Data Collection and Data Interpretation & Questions. The organic activities are presented in four sections: Introduction, Procedure, Data Collection and Data Interpretation & Questions. The two manuals developed are included in this report.

CONCLUSION

I feel that I have achieved the goals proposed when I began this sabbatical project. I have developed two molecular modeling manuals that truly reflect what I envisioned when I thought about this project. The manuals are ready to be used in our general and organic chemistry curricula. Once again I would like to extend my appreciation to Mt. SAC leadership and the members of the Salary and Leaves Committee for granting me the extension to submit my sabbatical report. I hope that I have met their expectations for a quality sabbatical report. I received continuous support from my departmental colleagues as I developed the activities and I would like to take this opportunity to thank them again.

A. PERSONAL BENEFITS

The most rewarding benefit to me is learning about a superb and exciting new teaching tool, namely Spartan, that occurred during my sabbatical leave. I feel that I have become quite competent with the software and I am ready to use it with ease in my classes. Although challenging and frustrating at times, the experience has been very enriching to me. I get satisfaction and feel very proud of being able to complete my project, having developed the products that I envisioned when I proposed the project, and being able to balance my time between writing my sabbatical report and serving as a Program Director with the National Science Foundation. I truly believe

that the exercises I have developed will provide an excellent opportunity to engage students in their own learning and provide for a discovery-based and collaborative rather than a competitive learning environment. I feel wonderful, reenergized, refreshed and eager to tryout these activities.

B. BENEFITS TO STUDENTS

The immediate benefit to students is learning to use a new discovery-based tool in their own learning. Through molecular modeling, the students will be able to visualize a number of abstract structural concepts that are fundamental to the study of chemistry. The activities will allow them to explore, discover, and interpret structural data and encourages them to be creative. I believe that the activities will encourage them to work as a team, bond together, learn from one another and polish their communication, writing, and critical thinking skills. In the Spring 2000 Semester before my sabbatical leave I tried a number of preliminary Spartan activities from scratch and handouts in my organic chemistry class. The goal was to get some student feedback prior to starting my sabbatical project. The students simply loved Spartan and felt that it greatly impacted their learning of organic chemistry. To my surprise, I found not even one single negative comment about Spartan. This only reassured and made me more determined to move forward with my project. Direct excerpts from student comments are included. The stated comments were the most frequently echoed responses by the students.

## C. BENEFITS TO THE CHEMISTRY PROGRAM

The Chemistry Department faculty have been actively engaged in delivering innovative and technology-based curriculum over the past ten years. In light of the rapid pace of technology, the department has been able to regularly upgrade its lecture and laboratory curriculum. The molecular modeling activities will definitely help the department to improve and expand its curriculum. We, the faculty, feel very proud that the Chemistry Department is regarded on a local, regional, and national level as a leader in the innovative use of technology in the classroom. The integration of molecular modeling in our curriculum to improve student learning should

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serve as a model for other community colleges and enhance the department's and Mt. SAC's reputation as a leader in educational technology and curriculum development.

STUDENT COMMENTS

- ... glad that I was exposed to this "high-tech" learning tool. It made Organic Chemistry fun.

- I loved SPARTAN and the Molecular Modeling Workbook. I can now visualize the molecular structures.

- I feel that my chemistry learning is dynamic with SPARTAN.

- Spartan helped me to develop critical thinking skills in chemistry to a great extent.

- I liked SPARTAN because we often had to work as a team in the class. We felt like a family.

- It was during the first experiment when I realized that SPARTAN activities could make concepts of Organic Chemistry much easier to comprehend.

- ... too bad we did not have enough time to do more SPARTAN activities.

- I was able to relate the textbook explanations to practical applications. That made me more interested and as a result I learned more.

- SPARTAN played such a big role in every aspect of our studying Organic Chemistry.

- ... 3-D structures coupled with display options such as electron density; HOMO and LUMO shed light on some proposed mechanisms.

Molecular
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in

General
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Contents

ACTIVITIES

   (17 Additional Short Activities)

The Art of Molecular Modeling

Molecular modeling is a major new learning tool that, for many years, has played a significant role in chemical and pharmaceutical designs and in chemical research. More recently, with the advent of many user-friendly modeling software programs coupled with low-cost computers capable of performing a wide range of calculations and simulations, molecular modeling more and more is finding its way into the general and organic chemistry curricula.

Chemistry has a reputation for being a difficult subject. In particular, the abstract concepts of molecular bonding, electronic structure, and molecular orbitals (which are fundamental to all areas of chemistry) are not well understood by a majority of the students. The problem seems to arise from the difficult task of visualizing these concepts in the 3-dimensional microscopic world of atoms and molecules. Traditionally, these molecular properties are predicted using simple Lewis structures. To help in "visualizing" these abstract concepts, various "molecular kits" such as ball-and-stick models have been widely used. Although these kits have helped to an extent, they have some serious shortcomings. For instance, electron distribution in molecules, molecular vibrations, hybridization, and dipole moment cannot be adequately illustrated with molecular kits. Now though, the availability of fast and low-priced computers equipped with user-friendly modeling software offers a unique alternative to carry out many creative and exciting "molecular modeling" experiments in order to reinforce and visualize these abstract bonding concepts in chemistry.

What exactly is meant by the term "molecular modeling?" For our purpose here, it represents commercial software which allows for molecule building, optimization (finding the best geometry for a molecule), visualization and more advanced applications involving molecular orbital calculations. The most useful information that a modeling experiment provides is a molecule's three-dimensional structure and energy. Structure tells us what the molecule looks like, while energy tells us something about the type of chemical reactions the molecule undergoes, i.e., the chemistry of the molecule. This so-called structure-reactivity relationship is a fundamental concept that is discussed and explained in nearly every college chemistry course. Molecular modeling software equipped with visual capabilities is an invaluable tool to use for this purpose. *Spartan* modeling software is one such excellent program. This program, developed by Warren G. Hehre, Professor of Chemistry at the University of California, Irvine and the president of Wavefunction, Inc., combines state-of-the-art computational tools with exceptional visualization into one complete package. Spartan is computationally flexible, offers superb graphic capabilities and above all is extraordinarily user-friendly. Once a molecule is built and optimized by Spartan, the graphic capabilities of the program provide an exceptional insight into the structure of the molecule and enable one to measure a number of interesting properties of the molecule. For instance, the molecule can be viewed in various models such as space-filling, ball-and-stick, etc. Electron distribution in the molecule can be displayed, single and multiple bonds, molecular polarity and the reaction site of a molecule can be shown and the "actual vibrations" of a molecule can superbly be animated. A very important point about Spartan is worth mentioning here. Although, optimization of a molecule involves performing complicated quantum mechanical

General Operating Features

This section provides an overview of the general operating features of PC Spartan-*Plus* 2.0 molecular modeling program. Some of the features, e.g., *File* and *Edit* should be familiar to the PC users while others are specific to the program. No detailed discussion of any features are provided, rather brief explanations to familiarize the student with function and operation of the program are presented. The descriptions in this section are best learned if you are actually sitting down and following the directions using the program. Some of the details, like the setup of a computation, are left out for later times during work on the various exercises.

START

To start PC Spartan-*Plus* (hereafter referred to Spartan for brevity), *double click* on the PC-Spartan-*Plus* icon in the window. A menu bar across the top of the screen appears. You are now in the main menu of Spartan.

MENUS

You will interact with the program almost exclusively through these menus. Pull down menus under the headings in the menu bar are used for this purpose.

BUILD

Allows you to take the currently displayed structure on the screen back into the **Builder** mode for modification or vice versa. The options under this menu are also accessible from the toolbar.

SETUP

Allows you to setup the type of calculation you want to do and specify the properties and features of the structure to be determined. It also permits you to setup and calculate various types of surfaces of an optimized structure for display purpose. The options of this menu and the **Builder** are discussed in further detail later in this section and also in appendix B at the end of the manual.

DISPLAY

Used to display the type of output that you select. The choices depend on how you setup the calculation in the first place.

Output

Allows you to scroll through the numerical output of your calculation.

Properties

Allows you to measure the energy, weight, volume and dipole moment of the molecule.

Surfaces

Selects and displays any surface you want to see assuming you have requested that surface be calculated in the "setup" part of the calculation.

Vibrations

Allows you to animate the vibrational modes of the molecule assuming you have selected "Frequencies" in the "setup" part of the calculation.

Building a Structure

To create a structure you need to start the program and then enter the molecule **Builder** by selecting **New** from the **File** menu. A new menu including a model kit appears on the screen:

You may now build your structure using the mouse to select from a palette of pre-built fragments in either the **Entry** or **Expert** *model kits*. Simply *click* (left mouse button) on the fragment of choice from the model kit and bring the cursor anywhere onto the screen and *click*. You may now select other fragments and append them to the existing fragment on screen by clicking on the fragments' free valences. It is that simple and it is best learned while you are actually sitting at the computer. As an example, lets build the molecule HClCO using the instruction provided (write Lewis structure of the molecule first):

1. *Click* on the SP² hybridized carbon ⟩c= from the kit, bring the cursor anywhere onto the screen and *click*. Rotate to your visual need.

Setup a Calculation

A. OPTIMIZATION

When done creating your molecule, you will want to take it back into the main program window to set up a computation. This is simply done by going directly to the **Setup** menu, or by first pressing [E] to refine your structure and then going to the **Setup** menu.

The most basic goal of a molecular modeling computation is to calculate the "Equilibrium Geometry" of the molecule. Where are the atoms in the space of the molecule? What are the distances from each other? What is the overall shape of the molecule? etc. How a program such as Spartan accomplishes this goal is conceptually discussed in appendix B. The computational process is referred to as "minimization" or "optimization" method.

The **Setup** menu provides access to the optimization process by selecting Calculations and then Equilibrium Geometry in the Setup submenu:

Electron Density Surface (with Ball-and-Spoke displayed inside)

Besides the electron density surface, a number of other interesting properties are also well represented by drawing surfaces in Spartan. Among them are:

Bond Density

Useful for investigating bonding characteristics (single vs. multiple) inside a molecule.

Slice

Useful for investigating the variation in electron density in the molecule.

Potential Surface

Useful for determining the regions of positive and negative charge in the structure. Color-coded based on the visual spectrum to show the regions.

Molecular Orbitals

Useful for investigating the reactive sites of the molecule (used more often in organic chemistry).

Brief discussion of each type of surfaces together with graphical examples produced by Spartan are given in appendices C-E for your reference. The practice for setup, calculation, display, and manipulation of these surfaces will be gradually introduced in the tutorials and exercises.

Introduction to Spartan | TUTORIAL 1

This self-guided tutorial exercise is intended to familiarize the student with the basic manipulation (display, measurements, display surfaces and molecular vibrations) of a typical output file generated by Spartan. No molecule building and calculation will be done in this tutorial. You should be familiar with the basic concepts of structure and chemical bonding before starting this exercise. In addition, read about surfaces in appendices B and C to become familiar with the type of properties displayed by each surface and be prepared to ask questions. Two molecules, C_4H_8 and H_2O, will be examined in this exercise. Write their Lewis structures first.

PROCEDURE:

A. C_4H_8 MOLECULE

1. *Double click* on the Spartan-Plus icon to **open** the program.

2. Select **open** from the **File** menu.

3. *Double click* on the **1AB - Tutorial** folder and then select and open C_4H_8 molecule on the screen.

4. Go to **Model** Menu. Select **Wire, Ball and Wire, Tube, Ball and Spoke**, and finally **Space Filling** from the menu. These render the structure in a variety of representations available in Spartan.


Ball-and-Wire

Tube

Ball-and-Spoke

Space Filling

13

What other molecular properties familiar to you appears in the dialog?

12. *Click* on the X to close the dialog. Select **surfaces** from the **Display** menu. Select **density** (isovalue 0.002) surface from the surface list by clicking on the yellow box adjacent to it. This is the total electron density surface for the molecule (~ 98% of   the total electron density is included in this surface).

13. *Click* anywhere on the surface. A **style** menu appears on the lower right part of the screen. Display the surface in **Transparent, Dots, Solid,** and **Mesh** styles available in the menu.

Transparent   Dots

Mesh   Solid

Note that you can simultaneouskly display the molecule *inside* the surface using any representation in the **Model** menu. You may want to check and convince yourself that the CPK (Space-Filling) model reasonably reproduces the total electron density of the molecule, i.e., it effectively represents the size of the molecule.

14. Select **Ball-and-Wire** from the **Model** menu. Go to **Surfaces** in the **Display** menu again, deselect the density surface (by clicking on the check-marked yellow box) and select the **density/potential** surface from the surface list. A color-coded surface appears on the screen.

Click on other parts on the surface to measure the potential in the same fashion. Note the sign of the potential .Identify the most "electron-rich" and "electron-poor" regions of the molecule.

16. Go to **Surfaces** in the **Display** menu, deslect the elpot surface and select the **density** (isovalue 0.32) surface. Higher electron density surfaces (isovalue 0.32 here as opposed to 0.002 in step 12) provide information about the bonding pattern in the molecule. This is because the highest electron density is found near the positively charged nuclei inside the molecule. Examining higher electron density surfaces (isovalue > 0.002) is analogus to"zooming" in the molecule to observe the subtle differneces in electron density among the various bonds and nuclei in the molecule. Describe the differences in electron density around carbon and hydrogen atoms and for C-H, C-C, and C=C bonds. Check your answer with your instructor.

17. Deselect the density surface and select the **density/potential** (isovalue 0.32) surface. What does this surface tell you about the nature of the bonds (covalent, polar or nonpolar) in the molecule. Again, describe in terms of electron density.

18. Close the file. Answer No to "Save Changes."

B. H_2O MOLECULE

Open the H_2O file from 1AB-Tutorial folder and carry out the procedure just described for C_4H_8 to practice your skills with a new molecule.

ADDITIONAL TASKS

1. Select **Ball-and-Wire** and **Diplole** from the **Model** menu to display the dipole moment for water. Ammonia, NH_3, is also present in the same folder. Open NH_3 folder as well and display its dipole moment. Which molecule is more polar? Record the numerical value of each dipole moment (**Properties** from **Display** menu).

2. *Click* on the **Dipole** in the **Model** menu to remove the dipoles (done one at a time by clicking on the molecule to select it).

3. Select **Surfaces** from the **Display** menu. Select and display the **Potential** surface from the "Surface List" for each molecule. This surface is different than the "elpot" surface examined in step 14 of C_4H_8 molecule (see appendices C and D). The **Potential** surfaces are very useful in providing information about "locations" of lone pair electrons; electrons that are associated with a single atom and are not as tightly held as bonding electrons.

(3n-5 for linear molecules). These vibrations are *quantized* (each has a unique frequency) and they are extremely useful for elucidating the structure of a molecule. Spartan can calculate and animate these frequencies. The calculated frequencies are commonly used for comparison with the experimental frequencies to detemine the structure of the molecule. The three experimental vibrations of the nonlinear triatomic water occur at 1596 cm^{-1}, 3652 cm^{-1}, and 3756 cm^{-1}

To animate the individual vibrational motions, *click* on the yellow box to the left of the frequency. Experiment with different structure models for best results. Do the calculated frequencies compare well with the experimental ones? Are the calculated frequencies consistently larger or smaller than the experimental values? If so, by what percentage? How do you describe each vibration (use terms such as "stretching," "bending" together with symmetric or asymmetric, for example symmetric stretching, etc.). When finished, unselect all frequencies and close the "Vibrations List" dialog. *Close* the H_2O file and Spartan. You have successfully completed the first tutorial. The next tutorial will guide you through creating a molecule and submitting a computational job.

Molecule Building and Calculation by Spartan (1)

This tutorial is designed to help you learn how to create, setup, and submit a computational job in Spartan. Building of a structure is initiated by first selecting **New** from the **File** menu followed by piecing together the molecule from "atomic fragments" present in either of Spartan's Entry or Expert "*Model Kits.*" A relatively few fragments in the Entry Kit allow construction of a wide variety of molecules. The Expert Kit offers more options for construction. Once created, editing of the structure can be done using the functions available in the **Build** menu. Nitrous Acid, HNO_2, will be built and studied in this tutorial. Carbon dioxide, CO_2, will be tried in the next tutorial. Together, these two exercises will describe the various construction and computational features of the program. Again, write the Lewis structure of Nitrous acid first and make sure you have completed the first tutorial before you begin to work on this one. You may also want to read appendix B to become somewhat famliar with the process of finding the equilibrium geometry (optimization) and the different levels of calculations that can be done on a molecule.

PROCEDURE:

Note: Refer to "Building a Structure" in the "Basic Operating Features" if you run into a problem while building the molecule.

Build HNO_2. Select **New** from the **File** menu, select $\boxed{\diagdown N=}$ from the entry *Model Kit* and *click* anywhere on screen. Select sp^2 hypridized oxygen $\boxed{=O}$ and *click* onto the tip of the double free valence of the nitrogen. Select the sp^3 hybridized oxygen $\boxed{\diagdown O-}$ and *click* on the single free valence of nitrogen. There is no need to connect hydrogens. The free valences are automatically converted to hydrogens upon exiting the builder. Click on **View** to exit the builder. Select **Ball-and-Wire** to display the molecule.

You have now setup the calculation of HNO_2 molecular geometry using a molecular mechanic level of calculation. The next step is to submit the job to actually do the calculation.

2. Submit the job (**Submit** under the **Setup** menu). You will be asked to supply a name and save the job. Save it as "HNO_2-SYBYL." *Click* on **OK** on the PcPlus dialog that appears.

3. When completed, *click* on **OK** to remove the dialog that appears. Measure and record all bond lengths and bond angles in the molecule.

(ii) Semi-Emperical Calculation

4. When all measurements are done, select **View** mode and re-enter the **Calculation** dialog. Setup the following operations:

You have now setup optimization of molecular geometry using the AM1 Semi-Empiracal model. Three different semi-empiracal computational models; AM1, PM3, and MNDO are included in Spartan. This is a higher level calculation compared to molecular mechanics.

5. *Click* on **OK** to close the dialog. Save the job as "HNO_2-AM1" and **Submit** the job. When completed, measure all bond lengths and bond angles in the molecule again.

(iv) Setting Up Surfaces

We will now build and examine four different surfaces, namely: **density surface** (total electron density), **bond-density surface, elpot** (electrostatic potential mapped on the electron density) and **potential surface** in this part of the exercise.

1. Select **Surfaces** from the **Setup** menu.

2. *Click* on **Add** from the "Surface List" dialog that appears.

3. *Click* on **density** from the Surface pull-down menu in the "Add Surface" list and then *click* on **OK**. This requests calculation of the "density surface."

4. *Click* on **Add** from the "Surface List" dialog again, *click* on **density (bond)** from the Surface pull-down menu and then *click* on **OK**. This requests calculation of the "bond-density" surfaces.

5. Repeat step 4 again and add calculation of the **potential** surface to the list.

6. *Click* on **Add** again. Select "density" from the surface pull-down menu **and** "potential" from the "Property" pull-down menu. This operation maps the electrostatic potential on the electron density surface to generate the **elpot** surface. *Click* on **OK**.

You shall now see on the screen a "Surface List" dialog showing the four requested surfaces with their status as "pending," meaning that they have not yet been submitted for calculation.

Surfaces List

| Surface	Property	Status	IsoValue	Res.	Label
density		Pending	0.002	med	Surface1
density		Pending	0.08	med	Surface2
potential		Pending	-20	med	Surface3
density	potential	Pending	0.002	med	Surface4

Add...   Delete

7. Select **Submit** from the **Setup** menu. This submits the job for calculation. *Click* on **OK** from the PCPlus dialog that appears. *Click* on **OK** again when the job is completed. The boxes to the left of the surfaces in the "Surface List" dialog will turn yellow and the job's status as completed. You are now ready to examine the surfaces. Proceed to "Data Interpretation" and when finished close all dialogs and exit the program. Answer NO to all "Save Changes" along the way.

b. Describe the difference between N-O and N=O bonds in terms of observed electron density for each bond.

5. Display the **Potential** surface. What information does this surface provide about the structure of HNO_2? What information is provided by the "size" and the "location" of the observed electron densities?

6. Display the **elpot** surface. Where is the most positive region of the molecule? Does it agree with the fact HNO_2 is an acid? Explain.

7. Change the isovalue to a higher number as in question 4. Describe the bond polarities (polar or nonpolar) in terms of the observed potential densities.

8. Close all dialogs, remove surfaces and exit the program.

Molecule Building and Calculation by Spartan (2)

This tutorial is designed to familiarize the student with additional building features in Spartan; namely imposing **Constrain** on some key parameters in the structure (e.g. bond length and bond angles) and calculating **Vibrations** of a molecule. Three different structures for carbon dioxide, CO_2, will be investigated in this exercise:

1.12 A° 1.43 A° O≡C——O	1.22 A° 1.22 A° O═C═O	1.22 A° C 1.22 A° O O
(1)	(2)	(3)

The best structure for CO_2 will be determined from the data. Write Lewis structure for carbon dioxide and predict its geometry and polarity from VSEPR theory before starting to work on this exercise.

CONSTRAIN IN GEOMETRY

It is desired, sometimes, to constraint (restrict or prohibit from changing) the values of some key structural parameters during geometry optimization of a molecule. As an example, consider the three structures of carbon dioxide. Building CO_2 with a single and a triple bond can be done by constraining the bond distances in the molecule. Bent carbon dioxide can be built by constraining the bond angle in the molecule to less than 180°. Holding these constraints during the optimization process would allow one to search for the best geometry (the one with the least energy) of the molecule. As another example consider the intramolecular "hydrogen bond" present in some molecules. Hydrogen bonds are "unusual" very long bonds and, if present, one may want to constraint their values during the geometry optimization of the molecule. Long bonds are also present in the "transition state" of a chemical reaction and may need to be constrained during "transition state" optimization process. There are other situations where constraining one or more parameters are essential for the geometry optimization purpose. **In brief, geometrical constraints of any kind (bond, angle, dihedral) specify conditions which Spartan must satisfy *in addition to* the usual criteria used during optimization procedure.**

You have now setup calculation of equilibrium geometry of structure (1) using AM1 Semi-Empirical method **with** the constraints specified in the build mode. ***Note that the "Constraints" box is check-marked in the dialog.*** *Remove the check-mark from the symmetry box and click* on **OK**.

7. Submit the job. Save it as "CO_2-one."

8. Close the file when finished. Build the second structure (two double-bonds, linear). Introduce proper constraints and perform a similar AM1 Semi-Empirical calculation. Save the job as "CO_2-two."

9. Repeat step 8 with the third structure (two double bonds, bond angle 120°). Save the job as "CO_2-three."

OPTIMIZING CO₂ / CALCULATING VIBRATIONS

10. Build CO_2 anyway you desire using either Entry or Expert model kits. Apply no Constraints and setup the following operations:

This setup will calculate the equilibrium geometry of CO_2 with no constraints imposed on the molecule. In addition, the vibrational frequencies for carbon dioxide will be calculated as requested by check-marking the "Frequencies" box in the "Compute" section of the Calculation dialog.

11. Save the job as "CO_2-optiom" and submit it for calculation.

Atomic Structure & Periodicity

INTRODUCTION

This exercise is intended to reinforce the concepts of atomic structure and periodicity. You should study the Aufbau principle, the Hund's rule, the atomic orbitals and the trend in Ionization Energy (IE) in your textbook before doing this exercise. Also, have your text available for reference as you do the exercise. By completing this exercise you should have a better understanding of the atomic structure, a better visual picture of the atomic orbitals and the changes that atom undergoes when it loses or gains electrons.

BACKGROUND

What is an atom? How small is it? Does it have parts? Review the classical picture of the atom from the suggestion of Democritus to Dalton's atomic theory to Bohr's model of hydrogen atom in your textbook (~20 centuries of development). Only a brief discussion of the quantum mechanical (QM) model of the atom is provided here.

By the mid-1920s it had become clear that the Bohr model of hydrogen atom could not be adapted to other atoms and a totally new approach was needed. Erwin Schrödinger (1887-1961), an Austrian physicist, along with other physicists at the time proposed a new approach which emphasized the wave properties of the electron. According to this approach, commonly called QM approach or model, the electrons in the atom behave like a standing wave and occupy some number of quantized energy levels. The position of an electron within the atom is described in terms of "electron probability" or "electron density" or simply the **atomic orbital**. An atomic orbital is generally represented by a surface that encloses 90% of the total electron density. That is, nine times out of ten an electron will be somewhere inside such a surface. For hydrogen atom, these electron density surfaces are the famous s, p, d . . . atomic orbitals. For other atoms, the same quantum mechanical model is used to show the arrangement of the electrons in the various atomic orbitals (Aufbau principle) and to successfully account for the organization of the elements within the periodic table. For obvious reasons, the details are omitted here but they can be found in the relevant sections of your textbook. Spartan, although a molecular modeling software (applied to molecules), can be applied to single atoms and ions to calculate the atomic orbitals and to explore the trends in atomic properties. This is what you will do in this exercise. Note that we will use *Spartan Pro* (not plus) in this exercise, however, the display features in both software are identical.

DATA INTERPRETATION & QUESTIONS

1. Describe any differences in the surfaces of Mg, Be, Li, Na and F atoms and their ions. What information do they reveal? Where are the greatest observed changes? Explain your answer by refering to the numerical and graphical data in the print-outs.

2. Compare the sizes of Li, Na, Be, Mg and F atoms. Do they agree with the trend of atomic radii? If not, why?

3. Compare the sizes of Na^+, Mg^{2+} and F^- ions. What trend do you predict for the radii of these ions? Do the sizes agree with your prediction.

4. Examine the *slice* surfaces for Li atom and Li^+ ion (3rd print out) What information do they reveal? Describe in terms of the electron density differences you observe. Write an equation which describes the observed difference.

5. Recall from appendix D that HOMO stand for the Highest Occupied Molecular Orbital and LUMO stands for the Lowest Unoccupied Molecular Orbital. For atoms and ions, we can take them to represent "atomic" rather than "molecular" orbitals. Similarly, "HOMO-1" represents the next orbital just below HOMO and "LUMO+1" represents the one just above LUMO, etc. A number of these HOMO and LUMO surfaces have been calculated (by Spartan) and stored in the same files for your examination. Display as many of them as you wish and see whether their shapes correlate with the electron configuration of the atom predicted by the Aufbau principle. Tag each of these orbitals as a S-type or P-type atomic orbital and correlate them with the atoms electron configuration. Do you see any degenerate orbitals? If yes, for which atoms or ions? (Hint: Examine all those for Mg^{2+} to get and idea).

6. The calculated HOMO energies (in electron volts) are:

Atom/ion	E(ev)	Atom/ion	E(ev)
Mg	-6.87	Be	-8.21
Mg^+	-14.7	Be^+	-18.12
Mg^{2+}	-81.86	Be^{2+}	-154.20

The negative value of these energies is proportional to the ionization energy (IE) of the atom or the ion (why?) Describe the observed trends. Justify the significant increases in IEs where observed.   Obtain the experimental values of the ionization energies from your textbook. Calculate the experimental and the Spartan-Calculated IE ratios such as Mg^+/Mg, Be^{2+}/Be^+, etc. Do the two ratios compare? What conclusions can you draw from this comparison?

7. Close all files, the folder and exit the program.

Molecular Geometry & Polarity I

(Bonding Pairs)

INTRODUCTION

This exercise is intended to reinforce the concepts of structure, molecular geometry and molecular polarity. You should review and study the relevant sections of your textbook prior to doing the activity and have the text available for reference as you do the exercise. By completing these exercise you should be able to better visualize the geometry of molecules and understand the implications for polarity and chemical bonding.

BACKGROUND

VSEPR provides a reliable procedure for predicting the molecular geometries of covalent compounds and ions from their Lewis structures. The basic premise of the theory is that the electron pairs (bonding and lone pairs) in the valence shell of an atom (central atom in simple molecules) minimize mutual repulsions by occupying positions in space as far from one another as possible. VSEPR theory allows easy prediction of "ideal" bond angles ($109.5°$ for tetrahedral CH_4, $120°$ for trigonal planar BF_3, etc.). The theory can also be used to predict the distortion of ideal bond angles resulting from **unequal repulsions** in the molecule. Examples are the H–O–H and H–N–H bond angles in H_2O and NH_3, respectively, where lone pairs are present in the tetrahedral frame of the molecule, and the H–C–H angle in CH_3F where a different ligand (outside atom) is present in the molecule. Generally, the direction of this distortion of ideal bond angles can be predicted by considering the *space requirements* of the lone pairs and different bonding pairs in the molecule. In this activity you will investigate the effects resulting from the presence of different ligands (outside atoms with different electronegativities) on the structure and polarity of a series of tetrahedral molecules. The effects arising from the presence of lone pairs and those from multiple bonds will be explored in the following two exercises.

COMPUTATIONAL PROCEDURE

This activity is a post-calculation exercise. Six tetrahedral molecules; CH_4, CF_4, CH_3Br, CH_3Cl, CH_3F and CH_2F_2 have already been optimized using *ab initio* 3-21G* method and the output files are saved in 1AB-Folder 2 folder. A number of **Potential** and **elpot** surfaces for the molecules have also been constructed and saved for your investigation. You need to open the files in Spartan, extract the numerical data and manipulate the surfaces as needed to answer the questions and complete the exercise.

Molecular Geometry & Polarity II

(Lone Pairs)

INTRODUCTION

This exercise is intended to reinforce the concepts of structure, molecular geometry and molecular polarity. You should review and study the relevant sections of your textbook prior to doing the activity and have the text available for reference as you do the exercise. By completing these exercise you should be able to better visualize the geometry of molecules and understand the implications for polarity and chemical bonding.

BACKGROUND

VSEPR provides a reliable procedure for predicting the molecular geometries of covalent compounds and ions from their Lewis structures. The basic premise of the theory is that the electron pairs (bonding and lone pairs) in the valence shell of an atom (central atom in simple molecules) minimize mutual repulsions by occupying positions in space as far from one another as possible. VSEPR theory allows easy prediction of "ideal" bond angles (109.5° for tetrahedral CH_4, 120° for trigonal planar BF_3, etc.). The theory can also be used to predict the distortion of ideal bond angles resulting from **unequal repulsions** in the molecule. Examples are the H–O–H and H–N–H bond angles in H_2O and NH_3, respectively, where lone pairs are present in the tetrahedral frame of the molecule, and the H–C–H angle in CH_3F where a different ligand (outside atom) is present in the molecule. Generally, the direction of this distortion of ideal bond angles can be predicted by considering the *space requirements* of the lone pairs and different bonding pairs in the molecule. In this activity you will investigate how the presence of different central atoms as well as the existence of one or more lone pairs on the central atom would affect the geometry of simple molecules. You will also explore the effects on the structure when a larger group (such as -CH_3) replaces hydrogen atom in molecules.

COMPUTATIONAL PROCEDURE

This activity is a post calculation exercise. Eight molecules; CH_4, H_2O, H_2S, H_2Se, H_3O^+, NH_3, CH_3OH and CH_3OCH_3 have already been optimized and the output fields are saved in ⌐1AB-Folder 3⌐ folder. **Potential** and **elpot** surfaces for H_2O, NH_3 and H_3O^+ have also been constructed and saved for your examination. Open the files in the folder, do your measurements and examine the surfaces as needed.

Molecular Geometry & Polarity III

(Multiple bonds)

INTRODUCTION

This exercise is intended to reinforce the concepts of structure, molecular geometry and molecular polarity. You should review and study the relevant sections of your textbook prior to doing the activity and have the text available for reference as you do the exercise. By completing these exercise you should be able to better visualize the geometry of molecules and understand the implications for polarity and chemical bonding.

BACKGROUND

VSEPR provides a reliable procedure for predicting the molecular geometries of covalent compounds and ions from their Lewis structures. The basic premise of the theory is that the electron pairs (bonding and lone pairs) in the valence shell of an atom (central atom in simple molecules) minimize mutual repulsions by occupying positions in space as far from one another as possible. VSEPR theory allows easy prediction of "ideal" bond angles ($109.5°$ for tetrahedral CH_4, $120°$ for trigonal planar BF_3, etc.). The theory can also be used to predict the distortion of ideal bond angles resulting from unequal repulsions in the molecule. Examples are the H–O–H and H–N–H bond angles in H_2O and NH_3, respectively, where lone pairs are present in the tetrahedral frame of the molecule, and the H–C–H angle in CH_3F where a different ligand (outside atom) is present in the molecule. Generally, the direction of this distortion of ideal bond angels can be predicted by considering the space requirements of the lone pairs and different bonding pairs in the molecule. In this activity you will investigate the effects on the molecular structure resulting from the presence of multiple bonds (double) different ligands (Cl_2CO vs. F_2CO), and different central atoms (F_2SO vs. F_2CO) in the molecule.

COMPUTATIONAL PROCEDURE

Like the previous activities, this is a post-calculation exercise. Four molecules: H_2CO, Cl_2CO, F_2CO and F_2SO have already been built and optimized (with *ab initio* 3-21G* model). The outputs are saved in 1AB-Folder 5 folder. **Potential** and **elpot** surfaces have also been calculated and stored in the same folder.

DATA COLLECTION

1. Draw the Lewis structures of the four molecules and predict the X–C–X (X = H, Cl, F) and

Molecular Geometry & Polarity IV

(Conclusion)

This exercise is a short wrap-up summary to activities 2–4 on the concepts of structure, chemical bonding and polarity. In these activities you explored a few parameters which significantly effect the geometry and the polarity of molecules. Briefly, the effects resulting from the presence of different ligands were explored in Activity #2. Activity #3 explored the effects on the structure and polarity arising from the presence of lone pairs on the central atom. And, in activity #4 the effects resulting from the presence of multiple bonds (double) were investigated. The resulting effects (distorted bond angles, polarities, etc.) could be explained adequately in terms of the space requirements (or the size) of either a bonding electron pair vs. a lone pair of electrons or a bonding electron pair (s-electron density) vs. a double bond (p-electron density). But what about the space requirements of a double bond vs. a lone pair of electrons? Which one needs more space? In this activity you will attempt to answer this question. When finished, you will write a one-page conclusion which explains the results of these four activities on molecular geometry.

COMPUTATIONAL PROCEDURE

This is an opportunity for you to apply what you have learned in the preceding activities to solve a new problem. So purposely, specific directions are not provided. You should design an appropriate computational job in order to answer the following question. Suggestions for molecules are provide. Other examples (approved by instructor) may also be used.

Question: Which, a lone pair of electrons or a double bond, requires more space in a molecule?

Try: (1) Cl_2CO vs. O_3 (2) H_2SO_4 vs. H_2SO_3

Method: Semi-Empirical **AM1** is sufficient.

Start with writing the Lewis structures of the molecules. See why these are good choices for answering this question. You may indeed come up with other possible choices. Think of what piece of information about the molecule would help you answer the question. Share your thoughts with your instructor and get his/her approval before actually doing the exercise.

CONCLUSION

Write a one-page conclusion which describes the results of activities 2 – 5 on the concepts of molecular geometry and polarity. Use bullet format for clarity. Cite relevant data (bond angles,

Electronegativity & Molecular Polarity

INTRODUCTION

This exercise is intended to reinforce the concept of *electronegativity* of atoms and how it varies across a period or down a column of the periodic table. Review the relevant sections of your textbook. In this exercise you will use Spartan to **build** and **optimize** a series of molecules in order to explore periodic trends in the electronegativity of atoms.

BACKGROUND

The ability of an atom in a molecule to attract shared electrons (bonding electron pairs) to itself is called the **electronegativity** of the atom. Linus Pauling (1901-1985), an American scientist who won the Nobel Prizes for both chemistry and peace first proposed the concept of electronegativity based on an analysis of bond energies of diatomic molecules (read your text for details). Using Pauling's method, electronegativity values have been determined for virtually all the elements and the results, values relative to an arbitrary value of 4.0 assigned to fluorine (the most electronegative element), have been tabulized (see your textbook). Electronegativity values can be used to predict the polarity of covalent bonds. With the exception of those between identical atoms, all covalent bonds are polar to some extent. The difference in electronegativity values of the bonded atoms reflects the degree of bond polarity ranging from nonpolar bonds (F – F), to slightly polar bonds (C – H), to highly polar bonds (O – H) and to ionic bonds (Na – Cl). Commonly, the degree of bond polarity is indicated by placing a partial positive charge (δ^+) on the end where the electron density is depleted, and a partial negative charge (δ^-) on the opposite end of the bond where the electron density is concentrated.

A molecule that has polar bonds may or may not be polar. The determining factor is the 3D-structure of the molecule. If the polar bonds within the molecule are oriented so that their polarities cancel one another, the result is a *nonpolar molecule*. However, if the electron density is concentrated on one end of the molecule, a *polar molecule* (one with a permanent dipole) results. The degree of polarity of a molecule is determined by measuring experimentally the molecule's *dipole moment* (read your text for further details). Molecular polarities (or dipole moments) can also be calculated by applying computational QM calculations to the molecule. The latter is the objective of this exercise. You will perform a series of QM calculations on a series of simple molecules in order to investigate periodic trends in the electronegativity and the rate of molecular geometry on the polarity of the molecule.

4. Describe the differences in the calculated dipole moments for O_2, NO and CO molecules. Use the corresponding **elpot** surfaces to support your answer.

5. Display the **elpot** surfaces for CO_2 and SO_2 on the same screen (use transparent style). Carefully examine the electron densities of the C – O and S – O bonds. (Hint: Change "**isoval**" to a larger value, see Tutorial 2) Which bond appears to be more polar?

6. Offer an explanation for the observed differences in the calculated bond angles and the dipole moments of CO_2 and SO_2. Use the **elpot** surfaces to justify your answer.

7. Close all files, the folder and exit the program.

Nonequivalent Lewis Structures

INTRODUCTION

This activity is intended to reinforce the concepts of nonequivalent Lewis Structures and the formal charge. Review the relevant sections of your textbook before starting the exercise.

BACKGROUND

The structure of molecules play a significant role in determining their chemical properties. From experiments on thousands of molecules chemists have learned that to form a stable compound, the atoms when bonded together, must achieve nobel gas electron configurations. Using this fact, G.N. Lewis proposed the concept of writing the Lewis structure for molecules. The Lewis structure of a molecule shows how the valence electrons are arranged among the atoms in the molecule. Writing Lewis structures for molecules is relatively simple (it is assumed that you are familiar with writing these structures). Often though, more than one valid Lewis structure is possible for a given molecule. If so, then which of the many possible Lewis structures best represents the actual bonding in the molecule? Of course, the true structure is always determined by experiments. However, the **formal charge**, the apparent charge of an atom in a molecule, can be used to evaluate the many possible Lewis structures and determine the structure that best represents the true structure of the molecule. In this activity Spartan will be used to evaluate the many possible Lewis structures for CO_2 and N_2O molecules and determine the best Lewis structures for the two molecules.

COMPUTATIONAL PROCEDURE

1. Each molecule (CO_2 and N_2O) has four nonequivalent Lewis structures. Draw all eight structures and determine the formal charges on all atoms within each structure.

2. The eight structures have been built and optimized using Semi-Empirical PM3 method. The outputs are stored in $\boxed{\text{1AB-Folder 6}}$ folder for your examination.

3. The optimized structures of CO_2 and N_2O are in $\boxed{\text{1AB-Pro-Fold1}}$ folder. You need "Spartan Pro" (not Plus) to view these structures.

Resonance

INTRODUCTION

This activity is intended to reinforce the concept of resonance. Study the relevant section in your textbook before starting the exercise.

BACKGROUND

Resonance occur when more than one valid Lewis structure can be written for a given molecule. Lewis structures that differ only in the arrangement of electron pair positions but not atom positions are referred to as the *resonance structures* of the molecule. Consider the Lewis structure for the cyanate ion (NCO-) which has 16 valence electrons. To achieve an octet of electrons around each atom, three Lewis structures are possible:

$$\left[\ddot{N} \equiv C - \ddot{O} : \right]^{-} \longleftrightarrow \left[:\ddot{N} = C = \ddot{O} : \right]^{-} \longleftrightarrow \left[:\ddot{N} - C \equiv \ddot{O} \right]^{-}$$
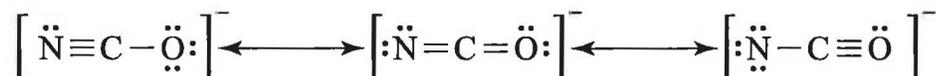
These resonance structures are continually changing back and forth and the actual structure is proposed to be an average of the three resonance structures. The actual structure is also known as the *hybrid* structure. The hybrid structure is drawn with dotted lines representing the electrons that are delocalized (spread) over the bonds in the molecule.

$$\text{Hybrid Structure:} \quad \left[\text{N} \text{=====} \text{C} \text{=====} \text{O} \right]^{-}$$
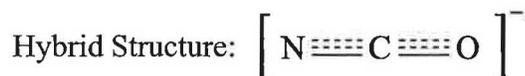
In this activity you will use Spartan to investigate whether H_2CO_3, HCO_3^- or CO_3^{2-} display any resonance.

COMPUTATIONAL PROCEDURE

1. Build and optimize, using semi-Empirical PM3 method, H_2CO_3, HCO_3^- and CO_3^{2-} molecules. Make sure to correctly identify the charges on the HCO_3^- and CO_3^{2-} ions in the calculation setup.

2. Once optimized, calculate the **elpot** surfaces for the three molecules.

Expanded Octets

INTRODUCTION

This exercise emphasizes the concept of expanded octets, a situation where the valence shell of the central atom can accommodate more than eight electrons. For some molecules this situation gives rise to different possible Lewis structures. Review the relevant section of your textbook before starting the exercise.

BACKGROUND

In writing Lewis structures, exceptions to octet rule are most common among molecules or ions where the central atom can accommodate more than eight electrons. This is commonly the case when the central atom is from the third or higher periods of the periodic table. Sulfure and phosphorous are two such examples. By engaging their 3rd orbitals in chemical bonding, they commonly form stable molecules or ions in which S and P are surrounded by more than eight valence electrons. This situation sometimes raises some interesting possibilities. Consider sulfric acid, H_2SO_4 with 32 valence electrons, as an example. Two different Lewis structures can be drawn for the molecule.

In structure **1** sulfur is an octet. In structure **2** sulfur is an expanded octet. Structure **2** is also known as the *hyperconjugated* structure. The question is which of the two structures best represents the bonding in the true sulfuric acid? The concept of formal charge can be used to *predict* the most likely structure, but does it always work? This case is an interesting and easy job for Spartan. By optimizing the two structures Spartan arrives at the correct answer.

COMPUTATIONAL PROCEDURE

The output files are stored in 1AB-Pro-Fold2 folder. You need Spartan *Pro* program.

1. Open "H_2SO_4 – Two – E"(Structure 1) and "H_2SO_4 – One – E"(Structure 2) on the same screen. Use Wire and Ball model to see the bonds. Size up the molecules and get a printout.

6. Close the acid file and open the optimized SO_4^{2-} anion. Do the same exploration for the anion as you did for the acid in the previous question. What information do you get? Are the S – O bonds in the anion identical or different? Single or double bonds? Write the Lewis structure for the anion.

7. Close the file, the folder, and exit the program.

Lewis Structure & Molecular Geometry

(Octets & Expanded Octets)

INTRODUCTION

This exercise is intended to reinforce the concepts of Lewis structure and Molecular geometry. Study the relevant sections of your textbook and have the text available for reference as you do the exercise. There are quite a number of molecules (16) to examine in this exercise, so you may want to work with another student and divide the work. However, you are strongly encouraged to work <u>together</u> on the exercise.

BACKGROUND

Lewis structures represent how valence electrons are distributed in a molecule or ion. **Octet rule** is employed to arrive at the Lewis structure of molecules. For some molecules or ions, more than one Lewis structure can be written, each of which obeys the octet rule. In these instances *formal charge* is often used to decide between the structures (Activity #7). Exceptions to the octet rule are common and are most observed among molecules or ions containing a central atom from the third or higher periods of the periodic table. Sulfure, phosphorous, and chlorine are three such examples. Making use of their 3d orbitals in bonding, these atoms can hold more than eight valence electrons in their valence shells leading to molecules with "expanded octet" (Activity #9). Other exceptions such as BF_3 also exist where the central atom has less than an octet of electrons in its valance shell. Lewis structures in conjunction with the **VSEPR** model are successfully used to predict the **electron pair geometry** (arrangement of electron pairs around the central atom) and the **molecular geometry** (3D structure or arrangement of atoms) of many molecules or ions. Review the relevant sections of your textbook for further details on these subjects. In this activity Spartan is used to: (i) investigate the geometry of molecules or ions containing a central atom with 2-6 electron pairs (bonding and lone pairs), (ii) observe the positions of the lone pairs on central atom and, (iii) determine the most stable molecular geometry where more than one is possible (e.g. SF_4, SF_5, ClF_3, etc.).

COMPUTATIONAL PROCEDURE

Note: All molecules and ions for this activity have already been optimized and stored in 1AB-Folder 9 folder. A number of surfaces (not for all molecules) have also been calculated. Semi-Empirical PM3 and *ab initio* 3-21G* methods have been used to optimize the geometries. Consequently, some of the energies are in kcal unit (PM3) while others are in **au** unit (*ab initio*). The absolute values of energies for molecules, by themselves, are not very useful. However, the *difference* in the values of energies

DATA INTERPRETATION & QUESTIONS

1. Describe any differences in the calculated bond angles for CH_4, NH_3, and H_2O molecules. Open the three molecules on the same screen and display the "potential surfaces" to draw conclusion and justify your answer.

2. Open BH_3 and BF_3 on the same screen and display their **elpot** surfaces. Explain any differences between the two surfaces. Which bonds are more polar?

3. Open CH_2O molecule and display its **elpot** surface. Use Ball and Wire model and "transparent" style display. Also display the dipole for the molecule. Describe the observed variations in the electron densities around each bond. Are the calculated bond angles identical to your predicted values? Explain any differences.

4. Open HCN on the same screen and display its elpot surface. Explain the observed electron densities around each bond. How does the multiple bond affect HCN molecular geometry?

5. Which of the three structures for the ClF_2^- ion is the most stable? By how much (kcal) over the other two structures? Does your choice agree with your prediction in Table 2 for the same ion?

6. A critical factor in the relative stabilities of the molecules containing lone pairs on their central atom involves both the *number* and the *closeness* (angle) of the l.p. – l.p. (lone pair – lone pair) and the l.p. – b.p. (lone pair – bonding pair) repulsions within the molecule. The closer the lone pairs or the bonding pairs are the stronger the repulsions and the less stable the molecule is. Identify the type of repulsions within the three structures for the ClF_2^- ion (e.g., 90° l.p. – b.p. repulsions, 180° l.p. – l.p. repulsions, etc). Are the l.p. – l.p. or the l.p. – b.p. (same angles) repulsions stronger? How did you decide?

7. Using only the 90° repulsions (strongest) in your comparison, justify the relative stabilities of the three structures for the ClF_2^- ion.

8. Which of the two structures for SF_4, SF_4-*axial* or SF_4-*eq*, is more stable? By how much (kcal)? Does it agree with your prediction?

9. Does the more stable structure for SF_4 match the optimized structure of the molecule (file SF_4 with no suffix)? If not, what is the difference in energies (kcal)? Explain the observed difference between the two structures (Hint: Display the "potential" surface for the optimized molecule in transparent style).

10. Experiments have shown that the axial S-F bonds in SF_4 molecule (and in other similar structures) are longer than the equatorial S-F bonds. Does Spartan provide the same

Molecular Orbitals

INTRODUCTION

This exercise is intended to reinforce the concepts of *Molecular Orbital Theory, bonding molecular orbitals, antibonding molecular orbitals,* and the *magnetic properties* of simple diatomic molecules. By completing this exercise you should have a better grasp of the **MO** theory and be able to better visualize the common bonding and antibonding molecular orbitals (Sigma and Pi bonds).

BACKGROUND

You should thoroughly review the MO theory, the energy level diagram associated with the theory, paramagnetism, the bond order for diatomic species and the MO electron configurations in the relevant sections of your textbook. In addition, you are strongly encouraged to review Appendix D in this manual in order to become familiar with the shapes and identification of HOMO and LUMO bonding and antibonding molecular orbitals. Have both the text and the Appendix available for references as you do the exercise. A brief discussion now follows.

As previously discussed in a few of the exercises, the electron-pair model used to arrive at the Lewis structure of molecules, reasonably explains covalent bonding in the molecule. Also, VSEPR theory does an adequate job predicting the geometry of many simple inorganic and organic molecules. Models, however, have their limitations. One major weakness of the VSEPR model is that it does not always predict the correct magnetic properties of the molecule. Experiments have shown that N_2 is **diamagnetic** (not attracted by a magnetic field) but O_2 is **paramagnetic**. The Lewis structures for N_2 and O_2 predict that both should be diamagnetic (because both have even number of electrons and the octet rule predicts that all of these electrons are paired). This discrepancy in paramagnetism for O_2 and many other molecules is resolved by using a different model, namely **MO** theory, to describe covalent bonding. MO theory treats bonding in terms of *molecular orbitals* that can extend over an entire molecule. Molecular orbitals to a molecule are what atomic orbitals are to an atom. Molecular orbitals are formed when atomic orbitals of the atoms in the molecule combine to produce a new set of orbitals (MOs). The number of MOs formed is equal to the number of atomic orbitals combined. MOs of a molecule fall into two classes: *bonding* and *antibonding*. A bonding MO is lower in energy (negative) than the atomic orbitals of which it is composed. Electrons in this type of MO favor bonding. An antibonding MO is higher in energy (positive) than the atomic orbitals of which it is composed. Electrons in this type of MO favor the separated atoms.

Considering the relative energies of the atomic orbitals involved in forming MOs, the MO theory predicts the following relative order of filling molecular orbitals:

$$\sigma_{1s} \quad \sigma_{1s}^* \quad \sigma_{2s} \quad \sigma_{2s}^* \quad \sigma_{2p} \quad \pi_{2p} \quad \pi_{2p} \quad \pi_{2p}^* \quad \pi_{2p}^* \quad \sigma_{2p}^*$$
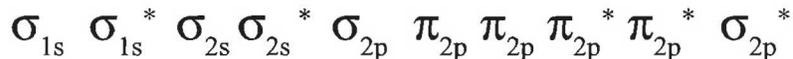
MO Energies (ev)

Molecule	Energy/Type	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
H_2	Energy	-	-	-	-16.295	6.561	-	-
	Type							
O_2	Energy			-12.181	-12.181	6.240	-	-
	Type	π_{2p}			π_{2p}^*			

2. Complete the table with the data for the five molecules. Again, you need to display the MO surfaces one at a time and examine them to determine the "Type" of MOs they represent.

DATA INTERPRETATION & QUESTIONS

1. On the basis of your data, write MO electron configuration for the five molecules. Which of the molecules do you predict to be paramagnetic? Why?

2. Which of the molecules display p – s mixing? Diatomic boron, B_2, does undergo p – s mixing. Do you predict it to be paramagnetic or diamagnetic? Explain.

3. Display the "HOMO-4" surfaces for F_2 and O_2. Do they validate their electron configurations? How?

4. On the basis of your configurations, calculate the bond order for each species. Arrange the molecules in decreasing bond order. Explain the trend by correlating the bond orders to experimental bond energies for the molecules (from your textbook).

5. On the basis of your results, predict the positions of O_2^-, O_2^+ and B_2^+ ions in the series (in question 4). Which of the ions do you predict to be paramagnetic? Which is the least stable and why?

6. Close all files, the folder and exit the program.

Molecular Vibrations

INTRODUCTION

This exercise is intended to reinforce the concepts of *molecular vibrations* and infrared (IR) Spectroscopy. Your textbook has probably nothing on this subject. However, appendix G provides an introduction to the subject and an overview of the IR Spectrascopy in some details. Review this appendix before starting this exercise. By completing this activity, you should have a reasonable understanding of IR spectroscopy and the relationship between the CO_2, H_2O and N_2O (molecules studied in this activity) molecular vibrations and the phenomenon known as the *greenhouse effect*.

BACKGROUND

As stated above, the background for this exercise is provided in some detail in appendix G. You should read the materials in this appendix before starting the exercise. Two other resources are also used for additional information.

1. **"IR Tutor"**, a multimedia program available on all computers in the MSMLC facility.

2. **"Global Warming CD"**, a multimedia CD containing a wealth of information on global warming. Limited number of the CDs are available in MSMLC. Check one out from your instructor and return it when finished with the activity.

In this activity you will use Spartan to calculate the frequencies of molecular vibrations in CO_2, H_2O and N_2O, three so-called greenhouse gases. You will then animate each vibration in order to identify its *type* (symmetric stretching, bending, etc.) and predict whether or not the vibration absorbs infrared radiation (IR active). Finally, by comparing the calculated frequencies with the corresponding experimental values, you will be able to predict how well Spartan calculates the frequencies of molecular vibrations in molecules.

COMPUTATIONAL PROCEDURE

(It is assumed that you have already studied the materials in appendix G).

A. IR TUTOR

1. Double-click on the **"IR Tutor"** icon to open the program and click on the *Continue* in the window that opens. Click on the *Introduction* and then the *Definition of Spectroscopy*. Go through the program and review the materials on the introduction to IR spectroscopy (13 screens with some very helpful simulations). Take some notes.

Molecule	Vibration IR active?	Type	Spartan Freq. (cm⁻¹)	Exp. Freq. (cm⁻¹)	Diff (Calc-expt)	%Diff
H_2O	 IR active	In plane bending	1740	1600	140	9%
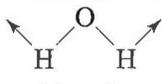
DATA INTERPRETATION & QUESTIONS

1. The first two vibrations of CO_2 and N_2O have identical frequencies. What is the difference between them? These types of vibrations are said to be "_____"?

2. The vibration at ~ 1440 cm⁻¹ for CO_2 is IR inactive but the vibration for N_2O at about the same frequency (~1450 cm⁻¹) is IR active. Why?

3. Combined together, N_2 and O_2 make up around 99% of the air we breathe. The vibrational frequencies of N_2 and O_2 are at 2540 cm⁻¹ and 2100 cm⁻¹, respectively. N_2 and O_2 are considered as greenhouse gases although their frequencies are in the IR region. On the other hand, N_2O, CO_2 and CH_4 make collectively up less than 1% of the air, yet their presence in the atmosphere is a major environmental concern . How do you explain this observation?

4. How do you explain the observed difference between the frequencies of N_2 and O_2 molecules? (Hint: The answer is somewhere in the IR tutor). On the basis of your answer, do you predict that the $C \equiv C$ or $C = C$ bond to have a higher frequency? Why?

5. Explain why the CO_2 frequency at 1388 cm⁻¹ is hidden in the molecule's IR spectrum?

6. Do you observe additional vibrations in the experimental IR spectra of CO_2, N_2O and H_2O that Spartan did NOT calculate? If yes, what kind of vibrations do they represent?

Acid Strength I

<div style="float:right">**ACTIVITY 13**</div>

INTRODUCTION

This exercise is intended to reinforce the concept of relative acidities for some common inorganic acids. You should study the sections of your textbook on the Arrhenius and the Bronsted-Lowery model of an acid before starting this exercise.

BACKGROUND

Arrhenuis model defines an acid as a species that produces hydrogen ions (H^+) in aqueous solutions. In terms of Bronsted-Lowry model, an acid is a proton (H^+) donor species. The Bronsted model is a more general definition of an acid because it is NOT limited to only aqueous solutions. But for aqueous solutions, the two definitions are identical. Different acids produce H^+ ions to different degrees and the extent to which they produce hydrogen ions forms the basis for the relative strengths of the acids.

The strength of an acid (in aqueous solutions) is defined by the equilibrium position of its ionization in water:

$$HA_{(aq)} + H_2O \leftrightharpoons H_3O^+_{(aq)} + A^- \qquad\qquad K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

A **strong acid** is one for which this equilibrium lies far to the right (more products, larger K_a). This means that a larger portion of the original acid (HA) is dissociated at equilibrium. A **weak acid** is one for which the equilibrium lies far to the left (less products, lower K_a). This indicates that only a small portion of the original acid is dissociated at equilibrium.

What are the factors important to the relative dissociation of an acid? The general answer to this question is the *structure* of the acid. More specifically, the *strength* of the bond between the hydrogen atom and the atom to which hydrogen is bond (X-H), and the *polarity* of the bond are two determining factors. In this activity and the following one you will use Spartan to study the roles these factors play in the relative acidities of a series of oxyacids. I recommend that you work in teams of two to do this exercise (purely a time consideration). If working as a team, each member should do hydrogen halides plus one series of the oxyacids in part A and the team together should do part B. If not, just do the halogen halides and halo-oxyacids (HOX) in part A and do part B.

COMPUTATIONAL PROCEDURE

All optimizations should be done using *Semi-Empirical AM1* method.

DATA INTERPRETATION & QUESTIONS

1. Where in a halo-oxyacid is the most positive potential area located? Is there a correlation between this potential and the electronegativity of the halogen in these acids? If yes, describe it. What is the factor responsible for the observed relative acidities of halo-oxyacids?

2. Answer question 1 for the hydrogen halide series.

3. Answer question 1 for the chlorine oxyacids (if done).

4. Answer question 1 for the acetic acid series in part B.

5. Based on your data, arrange the acids in each series according to the decreasing order of relative acidities.

6. Write a one to two paragraph conclusion which summarizes your observations in this activity.

7. Close all files and exit the program.

Acid Strength II

INTRODUCTION

This exercise is intended to further explore and reinforce the concepts of relative acidities, acid dissociation constants, energetics of an acid dissociation reaction (ΔH_{rxn}) and the Bronsted-Lowery model of acids. Furthermore, it is intended to display the application of different computational methods in Spartan to solving a problem.

BACKGROUND

Review the background in the previous exercise. As stated, the acid dissociation constant, K_a, is a measure of the dissociation of the acid (or the relative strength of the acid) and represents the equilibrium position of its ionization reaction in water:

$$\underset{\text{Acid}}{HA_{(aq)}} + \underset{\text{Base}}{H_2O} \leftrightarrows \underset{\text{Conjugate acid}}{H_3O^+_{(aq)}} + \underset{\text{Conjugate base}}{A^-_{(aq)}} \qquad K_a = \frac{[H_3O^+]\,[A^-]}{[H_3O^+]}$$
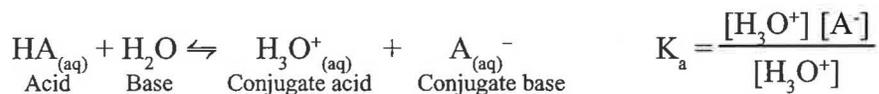
Commonly the PK_a values ($-\log K_a$) are used to compare relative acidities. For strong acids such as HNO_3 and $HClO_4$, the above equilibrium lies far to the right (very large K_a values). This means that these two acids are nearly 100% dissociated into H_3O^+ and NO_3^- or ClO_4^- ions. In other words, these two acids are stronger than the hydronium ion, H_3O^+. For acids weaker than H_3O^+, only a portion of the original acid placed in water dissociates and a smaller K_a value results.

Energetically, the equilibrium position of a reaction is determined by the difference between the equilibrium free energies of the products and the reactants:

$$\Delta G° = G°_{prod} - G°_{react} \qquad (1)$$

This difference is related to the equilibrium constant for the reaction by:

$$\Delta G° = -RT\ln K \qquad (K = K_a \text{ for the acid dissociation reaction}) \qquad (2)$$

The value of $\Delta G°$ for a reaction depends on the enthalpy change, $\Delta H°$, and the entropy change, $\Delta S°$, for the reaction according to:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (3)$$

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1. Build and optimize (AM1) each acid and its conjugate base pair (14 total). **Make sure that the "E. Solvation" in the Compute section of the "Setup Calculations" dialog is check-marked.** This will ask Spartan to calculate the energy of the optimized structure in *aqueous* solutions.

DATA COLLECTION

1. Obtain the PK_a values for the six acids from your textbook.

2. Make two data tables as follows:

Table 1:   **AM1 and 6-31G* Energies**

Structure	E_{aq}(AM1), kcal	E_{aq}(6-31G*), au
H_2O	-68.32	-76.0247430

Notes: (1) The energies are those for the molecules in *aqueous* solutions. To get them, do the usual procedure. Go to **Display** and then **Properties** from the pull-down menu. The values are written just to the right of *"Energy + SM 5.4/A:"* in the "Molecule Properties" dialog.

(2) The energies obtained by the 6-31G* method are in au (atomic unit, also known as hartree). Record **all** digits. The value for water is written as an example. Those by AM1 method are in kcal.

Obtain all of the aqueous energies from 1AB-Folder 15 folder (6-31G*) and also all of the AM1 energies (you did). Complete the table.

Table 2:   **$\Delta H_{(aq)}$ of Dissociations**

From your data in Table 1, calculate ΔH_{aq} (AM1) and $\Delta H_{(aq)}$(6-31G*) for the dissociation of the six acids in water and complete the table. Change ΔH_{aq} (6-31G*) from au to kcal unit (first calculate ΔH in au, then change to kcal using the relation 1 au = 627.5 kcal).

Acid	PK_a	ΔH (AM1), kcal	ΔH (6-31G*), kcal

Chemical Kinetics

INTRODUCTION

This activity is focused on Chemical Kinetics. In particular, *reaction mechanism, rate-limiting step (RLS), activated complex* or *transition state,* and the *activation energy* concepts are emphasized. You should study the relevant sections of your textbook before starting this exercise. Appendix F also includes additional material on these concepts.

BACKGROUND

Chemical reactions occur at very different rates. **Chemical Kinetics** is the area of chemistry that studies the speeds (or rates) of reactions and the molecular pathways by which molecules are transformed from reactants to products. The **reaction rate** of a chemical reaction is defined as *the change in concentration of a reactant or product per unit time.* For a hypothetical reaction the rate can be written as:

$$A + B \longrightarrow P$$

$$\text{Rate} = \frac{[C]_{t_2} - [C]_{t_1}}{t_2 - t_1} = \frac{\Delta[C]}{\Delta t}$$

where [C] is the concentration of the reactant or product being considered and Δ indicates a *change* in concentration. There are several methods for experimentally determining the rate of a chemical reaction. You should either be familiar with them or review them in your textbook. It is sufficient to say that the rate of a chemical reaction generally depends on the *concentrations* of the reactants and the *temperature* of the reaction. For reactions taking place in solutions, the solvent may also be a determining factor.

Most chemical reactions occur by a series of elementary steps called the **reaction mechanism**. These multistep reactions often have one step that is much slower than all the others. This step is referred to as the **rate-limiting step** and it determines the overall rate of the reaction. The reason is because the reactants can become products only as fast as they can get through this slowest step. Consider the hydrolysis of *tert*-butyl-halides (chloride or bromide), $(CH_3)_3CX$, the reactions which will be investigated in this activity, as an example:

$$(CH_3)_3C - X + H_2O \longrightarrow (CH_3)_3C - OH + HX \qquad (\text{X=Cl or Br})$$
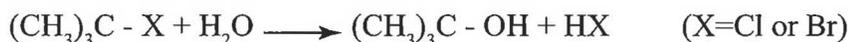
Experimental studies support the following mechanism for this reaction:

$$(CH_3)_3C - X \longrightarrow (CH_3)_3C^+ + X^- \qquad\qquad (1)$$
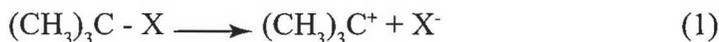
are to the right of "**Energy + SM5.4/P:**" in the dialog. Don't forget the *signs*. Also record the energies of the transition state structures. Neatly tabulize your data.

DATA INTERPRETATION & QUESTIONS

1. From your data, calculate the activation energies, $E_a(gas)$ and $E_a(aq)$, for both reactions (show calculations). Which reactions is faster in the gas phase and why? In the aqueous phase?

2. Compare the energies of t-But-Cl reactant in the gas and aqueous phases. Do the same for t-But-Br. What conclusion can you draw from this comparison?

3. Compare the energies of the t-But-Cl transition state (the file with TS suffix in the folder) in the gas and aqueous phases. Do the same for t-But-Br structure. Are there any similarities? Briefly explain.

4. Is there any difference between the activations energies (calculated in question 1) in the gas versus the aqueous phase for the t-But-Cl hydrolysis? For the t-But-Br hydrolysis? If yes, how do you explain the difference?

5. From your data, calculate the values of ΔH for the *overall* hydrolysis reactions of both halides in the gas and aqueous phases (4 values total). On the basis of these values, which reaction do you predict to be faster in the gas phase? In the aqueous phase? Why? (Show calculations).

6. Consider your answers to questions 1 and 5 together. What conclusions can you draw from these calculations? Which calculation correctly predicts the experimental observations for these hydrolysis reactions?

7. On the basis of your answer to the last question, write a generalized sentence or two that can be applied to all chemical reactions.

8. Display t-But-Cl and its corresponding transition state t-But-Cl-TS on the same screen. What is the difference between the two structures? Is there a change in the geometry? Measure and cite *two* structural parameters for both structures that can validate your answers.

9. Answer question 8 with t-But-Br and t-But-Br-TS displayed on the same screen.

10. Do your data and answers to questions 8 and 9 justify that the first step in the proposed mechanism is the RLS? Explain.

11 Display both TS-structures on the same screen and display their **elpot** surfaces. Draw

Coordination Compounds

(Transition Metals)

INTRODUCTION

This activity is intended to reinforce the concepts of transition metal coordination compounds and isomerism. The concepts of HOMO and LUMO are also emphasized. You should study the relevant chapter in your textbook and have the text available for reference as you do the exercise. You should also review appendix D to refresh your understanding of the HOMO and LUMO surfaces.

BACKGROUND

A. COORDINATION COMPOUNDS

Most transition metals (d–block elements) have the ability to form coordinate covalent bonds with neutral molecules or ions that have lone pair electrons (H_2O, NH_3, Cl^-, etc.) This is because, these metals have incompletely filled d-orbitals that can accept the lone pair of electrons. The resulting compounds which are often colored are called *Coordination Compounds*. A typical coordination compound consists of a *complex ion* (a transition metal ion with its attached ligands) and *counterions* (cations or anions) as needed to produce a neutral compound. The molecules or ions bonded to the transition metal ion are called *ligands*. Two examples are:

$[Co (H_2O)_2 (NH_3)_4]Cl_3$ Diaquatetraamminecobalt (III) chloride
$[Fe (NH_3)_3 Br]SO_4$ Triamminebromoiron (II) sulfate
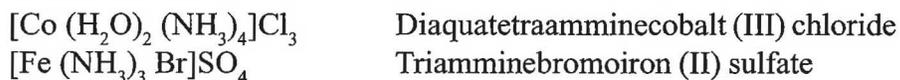
(Read about the nomenclature rules in your textbook). Ligands such as NH_3 and Cl^- that can form only one bond to the metal ion are called *monodentate* ligands (meaning one tooth). Some ligands have more than one atom with a lone pair and can form two or more bonds to a metal ion. Such ligands are referred to as *polydentate* (bidentate, tetradentate, etc.) or commonly *chelating ligands*. Ethylene diamine, $H_2NCH_2CH_2NH_2$ (abbreviated as **"en"** for simplicity) is an example of a bidentate ligand (see other examples in your textbook).

B. ISOMERISM

When two or more compounds have the same molecular formula but differ in the arrangement of their atoms, they are said to be *isomers*. Isomerism leads to different properties for the isomer molecules and is a common occurrence in many organic compounds and transition metal complexes. There are two main types of isomerism:

orbital. The ligand, however, is a molecule (or an ion) and not an atom. So, a question is from where do the electrons in the ligand contribute to bonding? Molecular Orbital (MO) theory provides the answer to this question (review appendix D). According to MO theory, the electrons come from the ligand's Highest Occupied Molecular Orbital (HOMO). Since Spartan can calculate and graphically display the *electron distribution* and the *molecular orbitals* of molecules, visual representations of these calculations (**elpot** and **HOMO** surfaces) for ligands can provide some valuable information about the nature of the metal-ligand bond formation. You will now use Spartan to examine several ligands and coordination compounds and study the concepts discussed in this section.

COMPUTATIONAL PROCEDURE

All molecules for this activity have already been optimized and can be found in **[1AB-Folder 10]** folder. Examine them as you answer the questions.

DATA COLLECTION

No numerical data collection. Proceed to the next section.

DATA INTERPRETATION

1. Open the molecule CH_2FCl and its mirror image CH_2FlCl – MI on the same screen. Use Ball and Spoke model for display. Convince yourself that they are in fact mirror images of one another (rotate). Are they superimposable? How are they related?

2. Answer question 1 for the following pairs of molecules:

    a. CHFClBr and CHFClBr – MI

    b. $Co(NH_3)_2 Cl_4$ – *cis* and $Co(NH_3)_2 Cl_4$-*cis* – MI

    c. $Co(NH_3)_2 Cl_4$ – *trans* and $Co(NH_3)_2 Cl_4$ – *trans* – MI

    d. $Co(en)_2BrF$ – *cis* and $Co(en)_2BrF$ – *cis* – MI

    e. $Co(en)_2BrF$ – *trans* and $Co(en)_2BrF$ – *trans* – MI

3. Based on your examination of the structures in questions 1 and 2, how can you predict right away whether a given structure and its mirror image are identical or enantiomers?

4. Open NH_3, $C_2O_4^{2-}$-1, $C_2O_4^{2-}$-2 and $H_2NCH_2CH_2NH_2$ (**en**) on the same screen. Display their

Exploratory Exercises

The following are a group of Spartan activities which I refer to as *exploratory* in nature. They are intended to assess the level of skills which you have acquired in working with Spartan. They are designed to be relatively short activities. If you have acquired reasonable skills in using Spartan, each activity shall take no more than one hour of your time to complete. For these activities, only an investigative question is posed and a computational method is suggested. You should first think about the kind of data (numerical and/or graphic) you would need from Spartan to answer the question, and then design an appropriate computational job in order to get the desired data. There are no questions to answer for these activities. However, once an activity is completed, you should prepare a short report which summarizes your approach to solving the problem and include conclusions you have drawn from your data. Produce hard copies of the graphics which you believe would support your conclusions and attach them to your report. If numerical data have been produced, tabulize them neatly and include them in your report as well. A few of these activities deal with organic molecules, however, they are simple enough that you should be able to do them. See your instructor if you need help with any of these activities.

Finally, there are a wide range of problems which can be tackled by Spartan and this group of activities only represent a small number of possibilities. You are strongly encouraged to think about other problems. If you come up with a burning idea about a problem, first discuss it with your instructor and seek his/her approval *before* actually attempting the problem. Afterall, this is how you can be *creative*.

Note: For brevity, abbreviations SE and HF are used to represent **Semi-Empirical** and **ab initio**, respectively, in all of these exercises (for the computational methods).

1. CHEMICAL BONDS I

Different molecules possess different types of bonds. What are the differences in bonding in the following molecules? Why LiH is used as a reducing agent but not the other two molecules?

$$H_2, HF, LiH$$

Computational Method: SE-PM3 (for numerical) and HF631-G* (for graphic)

Desired Data: Numeric and graphical

2. CHEMICAL BONDS II

Different molecules possess different types of bonds. Being as detailed as you can be, what are the differences in bonding in the following molecules? (Which molecule's carbon – carbon bond is stronger? Is $C - C$ or $C - H$ bond stronger in ethane? etc.) What do HOMO and HOMO-1 surfaces tell you about these molecules (skip benzene)?

6. MOLECULAR GEOMETRY I

The following molecules or ions are isoelectronic, meaning they all have the same number of electrons (10 electrons). Do they have identical geometries or are there any differences? Do they have the same size? Why or why not?

$$CH_3^-, H_3O^+, NH_3$$

Computational Method: HF631-G*

Desired Data: Numeric and graphical

7. MOLECULAR GEOMETRY II

Are the C_1–C_2 bond lengths identical in the following two molecules? They both appear to be single bonds in the formulas. Right?

$$
\underset{3}{CH_3} - \underset{2}{CH_2} - \underset{1}{\overset{\overset{\textstyle O}{\|}}{CH}} \quad , \quad \underset{3}{CH_2} = \underset{2}{CH} - \underset{1}{\overset{\overset{\textstyle O}{\|}}{CH}}
$$
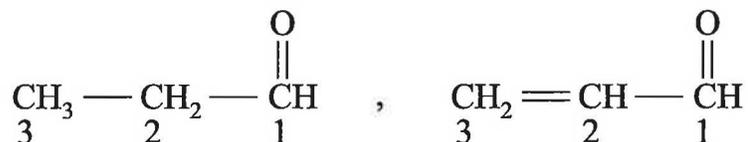
Computational Method: SE-AM1 or SE-PM3

Desired Data: Numeric and graphical

8. LEWIS STRUCTURES I

Is the correct structure for hydrocyanic acid HCN or HNC? Experimental bond lengths are (from Microwave Spectroscopy):

$$HCN\ (r_{HC} : 1.063\ A°, r_{CN} : 1.153\ A°)$$

$$HNC\ (r_{HN} : 0.986\ A°, r_{CN} : 1.172\ A°)$$

Computational Method: HF321-G*

Desired Data: Numerical

12. RELATIVE ACIDITIES I

Are ethane (C_2H_6), ethylene (C_2H_4) and acetylene (C_2H_2) really acids? The answer is yes. They are very weak organic acids. Which is the strongest acid? The weakest acid? What is the strongest conjugate base?

Computational Method: SE-PM3

Desired Data: Numeric (relative potential values on the hydrogen atoms and ΔHs for the dissociation reactions) and graphical

Tip: Display **elpot** surfaces on the same color scale and measure the relative potential values on the hydrogen atoms. For ΔH calculations assume $E_{H^+} = 0$.

13. RELATIVE ACIDITIES WITHIN A MOLECULE

Propanoic acid, an organic acid, has three types of hydrogens as seen in its formula:

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{CH_3CH_2COH}}$$
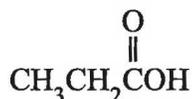
Which hydrogen is the most acidic? The least acidic? What are the formulas for the corresponding conjugate bases? Which conjugate base is the most stable and why (provide data)?

Computational Method: SE-PM3

Desired Data: Numeric and graphical (similar to the previous activity)

14. WHICH ACID IS STRONGER?

Which acid is stronger, formic (HCOOH) or acetic (CH_3COOH)? That is, which of the following reactions is more likely to occur?

$$CH_3COOH + HCOO^- \longrightarrow CH_3COO^- + HCOOH \quad (1)$$
$$\text{or}$$
$$HCOOH + CH_3COO^- \longrightarrow CH_3COOH + HCOO^- \quad (2)$$

Computational Method: SE-PM3

The product produced in the larger quantity is called the "major product" of the reaction. The first step involves addition of H^+ ion from the acid and is the slow step for the reaction (RLS). Two cations are produced by this addition:

$$CH_2 = CHCH_2\ddot{N}H_2 + H^+ \begin{cases} \nearrow CH_3\overset{+}{C}HCH_2\ddot{N}H_2 \\ + \\ \searrow CH_2 = CHCH_2\overset{+}{N}H_3 \end{cases}$$
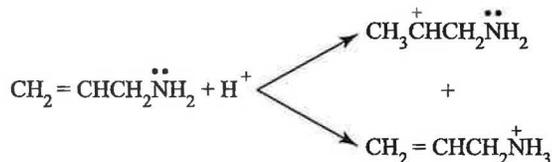
The cations then react with the Cl^- ion (from HCl) to produce the two products (fast). Which product, (1) or (2), is the major product of the reaction? Obtain both kinetic and thermodynamic data from Spartan.

Computational Method: SE-PM3

Desired Data: Numerical (kinetic and thermodynamic). Assume $E_H^+ = 0$

17. MOLECULES WITH CONFORMATIONS

Groups bonded by only a single bond can undergo rotation about that bond with respect to each other. The temporary molecular shapes that result from these rotations are called *conformations* of the molecule. An infinite number of different conformations could result from such rotations, however, not all are of equal stability. Two common conformations for ethane (C_2H_6), hydrazine (N_2H_4) and many other molecules are the *eclipsed* and *staggered* conformations.

staggered   *eclipsed*
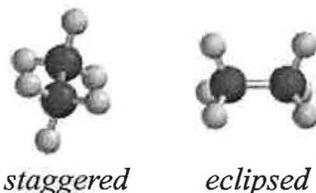
The difference in energy between the staggered and eclipsed conformations is called the **torsional barrier** of the single bond. Which is the more stable conformation (eclipsed or staggered) for ethane? For hydrazine? Why? What are the values of the two molecule's torsional barriers?

Computational Method: SE-PM3

Desired Data: Numeric and graphical (for N_2H_4 only)

Tip: You need to use the "*constraint*" feature of Spartan (see Tutorial 3. Constrain the dihedral angles).

Atoms and Molecules
An Overview

Optimization (Minimization)
Computational Methods

Electron Density Surfaces

Other Types of Surfaces

Property Maps

Reaction Pathways
Translation State

Vibrations

Atoms and Molecules An Overview

Keywords: *Conformation, Potential Energy, Global Minimum*

A simple idea of an atom was published by John Dalton, an English schoolteacher, in 1808. It states that "atoms are tiny particles that compose elements." For convenience, an atom can be viewed as a sphere with a particular radius which varies from element to element and with the charge on the atom. A molecule may be defined as a collection of atoms linked by bonds. With only two atoms, a linear molecule is possible (e.g. H_2, HCl, etc.). With more than two atoms, however, many three-dimensional structures result. Plastic model kits have been used for a long time to build simple mechanical models of molecules, and these can provide some useful information about their structure.

Bonds in the molecules are not rigid, but rather, they can bend and stretch. The time required for this bond bending and stretching is around 10^{-14} seconds. If the bending and stretching is taken to an extreme, the molecule will break. Molecules are also able to twist around their bonds, continually changing from one shape to another ($\sim 10^{-10}$ seconds). This means that a molecule which has free rotating bonds can take up many shapes (**conformations**) without breaking any of its bonds. Mechanical models are unable to represent any of these molecular behavior, but it is now possible to build such models in computers and simulate how these movements occur. If a molecule can have many conformations as stated, then what exactly is meant by the term "molecular geometry" or the "shape" of the molecule? To answer this question, we need to take a look at the "energy profile" of a molecule as the molecule is formed from its constituent elements.

ENERGY

The energy of a molecule is a very useful property for investigating the behavior of molecules. As an example, let see what happens when two hydrogen atoms at an infinite distance apart are brought together to form a bond, i.e., form the stable hydrogen molecule, H_2. Recall that a hydrogen atom is composed of a proton in its nucleus and a single electron.

how are the atoms bonded? What are their distances from each other? What is the effect of the lone pairs on the molecular structure? For molecules with more complicated shapes, few additional factors need to be considered. Among them are:

- Individual atoms within a molecule are not usually electronically neutral, although the molecule as a whole may be. As a result, atoms can attract and repel each other electrostatically even if they are not bonded together.

- A portion of the molecule may twist atound a bond (called torsional or dihedral movement) in the molecule resulting in many different conformations. What is the most stable conformation of the molecule?

- Multiple bonds (double, triple) are present within a large number of organic and inorganic molecules. What are the consequences of having such bonds on the molecular structure?

Fortunately, Mother Nature has found the actual structure of many molecules for us. These structures can be arrived at by doing experiments on the molecules as experimental chemists do. Alternatively, they can be determined by performing appropriate calculations on the molecules. The *latter* is the most basic goal of doing molecular modeling. To see how a computational modeling job finds the structure of a molecule, envision a many-dimensional potential energy surface (similar to the one discussed for hydrogen) for the molecule. *The actual structure of the molecule corresponds to the geometry the molecule posses at the very bottom of th potential energy surface* (called **glogal minimum**) This is because at this specific geometry all bond lengths, bond angles, torsions, etc. have their "ideal" values. As a result, the potential energy of the molecule is the lowest and, thus, the molecule is most stable.

Optimization (Minimization)

Keywords: *Optimized Struture, Molecular Mechanics, Molecular Orbital, Wavefunction, Semi-Empirical, ab initio, Hartree-Fock*

Optimization is the process of making small adjustments to a molecule's geometry until the "real" geometry of the molecule or one very close to it, i.e. the structure at the bottom of the potential energy surface, is obtained. As stated in appendix A, the most basic and important computational goal of a modeling software such as Spartan is to calculate this "real" geometry of the molecule. It can provide very useful information. In order to do any kind of modeling calculation, it is necessary to have a reasonable description of the molecule first. In Spartan, this is done by building a molecule using the atomic fragments in either the **Entry** or **Expert** model kit. The initial drawing is likely to have unrealistic bond lengths, bond angles and <u>dihedral</u> angles (torsions). After the initial structure is drawn, the next step is to take the constructed molecule through the optimization process. *The process of "optimizing" the structure involves first calculating the energy of the current structure and then <u>iteratively</u> making small changes to the structure's geometry(bond angles, bond lengths, torsions) to achieve a lower energy structure.* If the energy is lowered (improved), the initial geometry is forgotten, and the process is repeated with the current arrangement of atoms. The process is continued until all possible small changes will increase the energy of the system. At this point all the structural parameters are considered "optimized", the software has found the "lowest energy structure possible" and stops. Generally, the geometry of the structure found by the computer is very close to that of the actual structure found by nature, however, that is not always the case. A good initial guess at a struture rather than a random one to start the process is necessary to generate a structure which more closely resembles the "real" molecular geometry.

CALCULATIONS
COMPUTATIONAL METHODS

To start the optimization process, a modeling software makes use of some common "minimization algorithms" to treat the molecule and proceed downhill on the potential energy surface. These algorithms are mathematical models derived from applying several different levels of structure theory to molecules. There are many different algorithms available to solve a given problem, however, they can be broken down into two main classes of computational methods: 1) *Molecular mechanics* and 2) *Molecular Orbital* methods.

Within the framework of molecular mechanics calculations, there are different models to apply to the optimization task. Spartan supports two such models, namely **MMFF** and **SYBYL**, both of which are capable of providing reasonable quantitative accounts of molecular geometry and conformation. The difference between them and any other computational model presented hereafter is well beyond the scope of this discussion and will not be presented.

2. MOLECULAR ORBITAL METHODS

Molecular Orbital methods are based on Quantum Mechanics (QM) description of atoms and molecules. According to QM, atoms and molecules are made of nuclei and electrons. While nuclei are assumed to be stationary (not moving), the electrons are no longer described as point-like particles as first presented by Bohr's model of hydrogen atom. Instead, an electron is described as a "fog-like" entity or "electron cloud" that spreads over a region of space. The cloud's density varies from one point to the next and indicates the "probability" of finding the electron at each point. The electron density can be calculated using the rules of quantum mechanics and is very useful for describing the electron distribution in atoms and molecules.

The rules of quantum mechanics were developed by Erwin Schrödinger (1887-1961), an Austrian physicist who won the 1933 Nobel prize in physics for his pioneer work on the theory. Schrödinger's approach describes atoms and molecules in terms of a mathematical equation, the general form of which is:

$$\hat{H}\Psi = E\Psi$$

where, (Ψ), called the **wave function**, characterizes the electron's position in space, E is the total energy and ($\hat{H}$, called the energy operator) represents a set of complicated mathematical terms that produce the total energy of the system (atom or molecule). When this equation is analyzed, many solutions are found. Each solution is represented by a wavefunction (Ψ) that is characterized by a specific value of E. A specific wave function is often called an **Orbital**. It is postulated that the square of the wave function, (Ψ)^2, corresponds to the "probability" of finding an electron in a particular place in space.

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Electron Density Surfaces

Keywords: *Isodensity Surface, Electron Density Surface,*
Bond Density Surface

The rules of quantum mechanics state that electrons have wavelike properties and, thus, it is not possible to say where the electrons exactly are. The Heisenberg uncertainty principle also concludes that electron positions can never be known precisely. So, how do we define or visualize the position of an electron within an atom or a molecule? According to quantum mechanics the best that one can do is to say how probable it is for an electron to be at some particular location in space. Consider H atom as an example.

The graph indicates that electron density in hydrogen atom varies with distance from the nucleus. The electron density is greatest near the nucleus and, as we move away from the nucleus, the probability of finding the electron at a given position decreases rapidly. Note that there is no clear edge to the electron density; it just gets smaller and smaller with increasing distance from the nucleus. For molecules, the electron density spreads out nonuniformly over a region of space. Considering the fact that the electron density does not fall off to zero, then the problem is how to define a "boundry" for the electron density when one reaches the points of low electron densities? One way to deal with this problem is to examine each molecule's electron cloud and choose the "molecular boundry" as the point where each electron cloud has the same electron density. Constructed in this fashion the resulting skin-like surfaces, known as *isodensity surfaces* or simply *density surfaces*, provide the distribution of electrons in the molecule.

Different types of electron density surfaces can be built and displayed by Spartan following the optimization of a molecule's geometry using any *molecular orbitals* computation method. Different surfaces have specific applications. The 0.002 electron density surface (also known as the total **electron density** surface), for example, is used to define the size and shape of the molecule. Nearly all of the electron density (typically 98%) lies inside this surface. The 0.002 density surface and the space-filling model of the molecule, C_5H_6, are shown for comparison.

A third useful electron density surface can be constructed by taking a plane that slices through the molecule and map the variation in electron density in this plane. This kind of surface is called an *electron density slice*. It provides a two-dimensional contour map of the electron density.

The electron density varies considerably in this plane and a color code based on the visual spectrum is used to show this variation: blue (highest density) > green > yellow > orange > red (lowest density). The slice can be moved across the structure on screen to examine the electron density variation in the molecule.

Other Types of Surfaces

Keywords: *Molecular Orbitals, HOMO, LUMO, Spin Density, Electrostatic Potential*

Besides the electron density surfaces, Spartan provides for graphical display of other quantities resulting from molecular orbital calculations. Among the most useful quantities are the "*molecular orbitals*" themselves, the "*spin density*" (when unpaired electrons are present) and the "*electrostatic potential.*" Any of these quantities can be represented as a surface of constant value and uniqly displayed in *dot*, *mesh*, *transparent* or *solid* style. These quantities are briefly discussed in this appendix.

1. MOLECULAR ORBITALS

Molecular Orbital (MO) theory describes formation of covalent bond in terms of a mathematical combination of atomic orbitals (s, p, d....atomic orbitals or wavefunctions) to form **molecular orbitals (MOs)**. Molecular orbitals are to molecules what atomic orbitals are to atoms. Namely:

- Electrons in an atom occupy atomic orbitals. In a molecule, the electrons occupy molecular orbitals. Atomic orbitals no longer exist.

- An atomic orbital describes a region of space around an atom where an electron is likely to be found. A molecular orbital (MO) describes a region of space in a molecule where electrons are most likely to be found.

- An atomic orbital can hold two electrons with opposite spins. Each molecular orbital can hold two electrons as well and the spins have to be opposite.

- Similar to an atomic orbital, a molecular orbital has a specific size, shape and energy.

- There are occupied and unoccupied atomic orbitals for an atom. Similarly, there are occupied and unoccupied molecular orbitals in a molecule. The unoccupied MO's have higher energies.

A. H_2 MOLECULE

We know that H_2 is a very stable molecule, and is lower in energy than the separated hydrogen atoms by 432 KJ/mol. According to MO theory, combination of the *two* 1s atomic orbitals of hydrogen leads to *two* H_2 molecular orbitals. The lower energy bonding MO is filled, and the higher energy antibonding MO is unfilled. Spartan's computer-generated molecular orbitals of H_2 are shown below.

| HOMO | LUMO |

For MO_1 (HOMO), the greatest electron probability is *between* the two nuclei. This states that the electrons in this MO spend most of their time in the region between the two nuclei, thereby bonding the atoms together. We refer to this type of molecular orbital as **sigma (σ) bonding MO**. For MO_2 (LUMO), the greatest electron density is on either *side* of the nuclei and there is a node in the central region between the nuclei. We refer to this type of orbital as **sigma(σ*) antibonding MO**. The color of the two lobes in the molecular orbitals corresponds to the sign (+ or -) of the actual wavefunctions.

B.   C=C BOND

The carbon-carbon double bond is present in a large number of organic molecules. With two bonds holding the carbons together, we need *two bonding* MO's to describe the C=C bond. The Spartan's generated HOMO and LUMO together with the MO energy diagram for the C=C bond in ethylene, C_2H_4, are given below.

| HOMO | LUMO |

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HOMO is easily recognized as a lone pair on sulfur atom. The electrons in this molecular orbital are the easiest to donate by SO_2. HOMO (-1) represents the lone pairs on the two oxygen atoms. They are the next highest in energy.

D. BF$_3$

The lowest unoccupied molecular orbital (LUMO) of BF_3 is shown below. LUMO represents the place where it is easiest to *put* the next pair of electrons. In BF_3, LUMO is centered on boron. This means that if BF_3 encounters a Lewis base (also called a nucleophile) such as H-, OH-, the electron pair from the base attack boron atom of BF_3 and a chemical reaction takes place. Thus, a LUMO reveals the likely site for nucleohilic attack. Note that both sides of BF_3 are equally possible to undergo such nucleophilic attack.

2.   SPIN DENSITY

For molecules that contain a single unpaired electron (commonly called radicals), the spin density surface provides information about the location of the unpaired electron in the molecule. The Spartan calculated spin density surfaces of propyl radical ($CH_3CH_2\overset{\bullet}{C}H_2$) and allyl radical ($CH_2=CH\overset{\bullet}{C}H_2$) are shown for comparison.

For ammonia and methanol, the "electron rich" regions are represented by the lone pairs on nitrogen and oxygen, respectively. For benzene, the "electron rich" regions are above and below the plane of the ring. Electrophilic attack should occur here with equal probability on each side of the ring.

Property Maps

Keywords: *Elpot, HOMO map, LUMO map*

A property (such as HOMO, LUMO, electrostatic potential, spin) can be color encoded on an electron density surface by Spartan to give additional information beyond molecular size and shape. This so-called "mapping" is done by selecting a property from the "property" pull-down menu, and then mapping the property onto surfaces in the "Add Surface" dialog (Tutorials 1 and 2).

The above operation maps electrostatic potential (from property menu) onto the total electron density surface (from surface menu). Note that the requested property surface appears in the "Surface List" dialog. To generate this surface, Spartan first calculates the total electron density and the electrostatic potential, draws the electron density surface around the molecule, and then maps (by color encoding) the calculated potentials on the electron density surface. Those parts of the surface where the potential is most negative (electron rich) are colored red, and parts where the potential is most positive (electron poor) are colored blue. Intermediate potential values are colored according to: red<orange<yellow<green<blue. The resulting surface, commonly called the **elpot** surface conveys information about the overall charge distribution in the molecule. Generation of water's "elpot" surface is presented as an example of this process.

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map shows that the central carbon is the most electron poor site in the molecule. This is where it is easiest to put a pair of electrons and thus it is the likely site for nucleophilic attack.

D.   NITRIC ACID & NITROUS ACID

The electrostatic potential map, elpot, can reveal information useful in predicting relative acidity of molecules. However, valid comparisons require maps that use the same potential (or color) scale. The potential maps of nitrous acid (HNO_2) and nitric acid (HNO_3) on the same potential scale are shown for comparison. The maps show that the hydrogen atom in nitric acid is far more positive than hydrogen in nitrous acid. In other words, nitric acid is a stronger acid when compared to nitrous acid.

E.   LEWIS ACID-BASE REACTION

Property maps can also reveal information useful in predicting chemical reactivity of molecules. As an example, let's consider sulfur trioxide, a strong lewis acid, and its reaction with water, a lewis base, to form sulfuric acid. The elpot maps for the reaction show that sulfur atom draws in electron density from oxygen of water and that causes the water molecule to attach to sulfur trioxide. A proton shift occurs in the next step to form sulfuric acid (not shown).

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Reaction's Pathways
Transition State

Keywords: *PE Diagram, Transition State, Activation Energy,*
Kinetic Product, Thermodynamic Product

Potential energy diagrams are commonly used to describe the progress of chemical reactions. Understanding a PE diagram is important for anticipating

Reaction Progress

Energy minima correspond to the "equilibrium structures" of reactant and product. The arrangement of atoms found at the top of the potential energy barrier is called the **"transition state"** structure. The relative energies of the two minima correspond to the "relative stabilities" of the reactant and product. Here, the product is more stable because it has a lower potential energy than the reactant. In other words, this diagram represents an exothermic reaction. The energy of the maximum relative to the reactant minimum is called the **activation energy**. This is a thereshold energy that must be overcome to produce a chemical reaction. A reaction rate (speed) depends on the size of the activation energy Ea. The difference in the relative energies of the reactant and product, E, however, has no effect on the rate of the reaction.

What is the structure of the transition state? To answer this question, consider that for a chemical reaction to proceed a number of bond formation and bond breaking must take place as the reactants are converted to products. The transition state represents a *transient* arrangement of atoms in which all the bonds involved in the reaction progress are either partially formed or

Pathways 1 and 2 produce two different products and proceed via different transition state structures. Product 1 is formed faster (lower Ea) but it is less stable (more potential energy). This product is known as the **kinetic product**. Product 2, however, is more stable (less potential energy) and it is known as the **thermodynamic product**. Often, one of the two products is formed as the major product of the reaction, irrespective of barrier heights or product energies. It shall be clear from this diagram that prediction of the major product made on the basis of product stabilities alone can be wrong. Rather, relative proportions of the products depend on the relative stabilities of the products as well as the relative heights of the energy barrier (TS1 vs. TS2), and the temperature of the reaction. In general, higher temperatures favor the thermodynamic product while at lower temperatures the kinetic product is favored.

Before we leave this subject two final points should be made. First, the energy diagrams presented in this section exemplify reactions which take place in one step. A complete reaction pathway, however, may have several steps and involve several different transition states and reactive intermediates. Second, the transition state structures *can not* be determined from experiments because they are not stable. This, however, is not a difficulty for Spartan. Although there exists very little information about the geometries of the transition states from experimental data, Spartan provides ways to perform a transition state optimization when it is furnished with a reasonable "guess" of a transition state structure to start. An optimized transition state structure can provide some very useful insights into the mechanism of a chemical reaction. The transition state optimization, however, is more difficult than a typical equilibrium geometry optimization and will not discussed here.

Vibrations

Keywords: *Wavenumber, Fundemental Frequency,*
Molecular vibration

The infrared (IR) radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions (l: 7.8×10^{-5} cm to 0.01 cm). Frequencies in IR are commonly expressed in **wavenumbers** (ν) rather than in hertz, Hz. The wavenumbers, expressed in cm^{-1}, is simply the reciprocal of the wavelength in centimeter.

$$\nu = \frac{1}{\lambda(cm)}$$

Of greatest practical use to chemists is the IR midportion between 400 and 4000 cm^{-1}. Why? In reality, all molecules posses a certain amount of energy, called internal energy, distributed throughout their structure. A part of this energy causes bonds to stretch and contract (as if there were a "spring" connecting the two atoms) and the atoms to wag back and forth. Collectively, these types of motions are referred to as **molecular vibrations**. It is known that a molecule can stretch or bend (vibrate) only at specific frequencies (or energies); i.e. the frequencies are *quantized*. In other words, only certain kinds of vibrations are allowed. Some examples of allowed vibrations are shown below:

In-plane bending (scissoring)
(CO_2: 670 cm^{-1})

Out-of-plane bending (scissoring)
(CO_2: 670 cm^{-1})

In-plane bending (scissoring)
(CH_2: 1470 cm^{-1})

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Consider any one of the allowed vibrations as an example. When a molecule is irradiated with infrared radiation, energy is absorbed by the molecule *when* the frequency of the radiation matches the frequency of the vibrational motion. This absorbed radiation causes an increase in the amplitude of that specific vibration. By scanning all frequencies in the IR region (400-4000 cm^{-1}, done automatically by an IR spectrophotometer), one can determine all of the frequencies absorbed by the molecule. And since each frequency corresponds to a specific molecular motion, we can see the kind of vibrations a molecule has by measuring its so-called "IR spectrum". By analyzing those vibrations, one can find (by reference to generalized charts of characteristic bond and group frequencies) what kinds of bonds and functional groups are present in the molecule. This is the basis of IR spectroscopy.

How many different vibrations a molecule can have? A nonlinear molecule of n atoms has 3n-6 fundamental vibrational frequencies (3n-5 for linear molecules). Take ethanol, C_2H_5OH, as an example. There are nine atoms in the molecule and 21 (3x9-6) different vibrations are thus possible. The theoretical number of fundamental vibrations , however, are seldom observed in the IR spectrum of the molecule. The reasons are not discussed here. One important point, however, needs to be stated here. *Only those vibrations that result in a change in the dipole moment of the molecule are observed in IR.* These vibrations are referred to as **"IR active"** vibrations. This explains why the asymmetric stretching vibration in carbon dioxide is IR active while the corresponding symmetric stretching is IR inactive.

From the discussion above, it shall be clear that molecular vibrations are a useful tool for determining molecular structure. Fortunately, Spartan allows one to calculate and animate the vibrational modes of a molecule when *"frequency"* calculation is requested in the setup of the computation. The "Frequencies" box in the calculation setup dialog needs to be check marked (✔) for this purpose (Tutorial 3). When the calculation has completed, the individual vibrations can be animated using ball-and-spoke or any other structure models that are available in the **Model** menu. Furthermore, calculated frequencies are reported in units of cm^{-1} for easy comparison with the experimental frequencies for structural identification of the molecule.

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in

Organic Chemistry

Iraj B. Nejad

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2002

"It is mandatory for Community Colleges to stay current with the technological innovations."

ED net, September 1999

"Teaching Science, like Science itself, seems always to produce more questions, than answers."

John W. Moore, Chief Editor, J. Chem. Ed. October 1999

"Molecular Modeling is reshaping the future of chemical education."

J. Chem Ed. 1999

"SPARTAN should be in every chemistry department in the country."

J. Chem. Ed. 1995

"Molecular Modeling has bridged the worlds of theoretical and experimental chemistry."

Acess, Alliance/NCSA, Fall 2001

Contents

ACTIVITIES

The Art of Molecular Modeling

Molecular modeling is a major new learning tool that, for many years, has played a significant role in chemical and pharmaceutical designs and in chemical research. More recently, with the advent of many user-friendly modeling software programs coupled with low-cost computers capable of performing a wide range of calculations and simulations, molecular modeling more and more is finding its way into the general and organic chemistry curricula.

Chemistry has a reputation for being a difficult subject. In particular, the abstract concepts of molecular bonding, electronic structure, and molecular orbitals (which are fundamental to all areas of chemistry) are not well understood by a majority of the students. The problem seems to arise from the difficult task of visualizing these concepts in the 3-dimensional microscopic world of atoms and molecules. Traditionally, these molecular properties are predicted using simple Lewis structures. To help in "visualizing" these abstract concepts, various "molecular kits" such as ball-and-stick models have been widely used. Although these kits have helped to an extent, they have some serious shortcomings. For instance, electron distribution in molecules, molecular vibrations, hybridization, and dipole moment cannot be adequately illustrated with molecular kits. Now though, the availability of fast and low-priced computers equipped with user-friendly modeling software offers a unique alternative to carry out many creative and exciting "molecular modeling" experiments in order to reinforce and visualize these abstract bonding concepts in chemistry.

What exactly is meant by the term "molecular modeling?" For our purpose here, it represents commercial software which allows for molecule building, optimization (finding the best geometry for a molecule), visualization and more advanced applications involving molecular orbital calculations. The most useful information that a modeling experiment provides is a molecule's three-dimensional structure and energy. Structure tells us what the molecule looks like, while energy tells us something about the type of chemical reactions the molecule undergoes, i.e., the chemistry of the molecule. This so-called structure-reactivity relationship is a fundamental concept that is discussed and explained in nearly every college chemistry course. Molecular modeling software equipped with visual capabilities is an invaluable tool to use for this purpose. *Spartan* modeling software is one such excellent program. This program, developed by Warren G. Hehre, Professor of Chemistry at the University of California, Irvine and the president of Wavefunction, Inc., combines state-of-the-art computational tools with exceptional visualization into one complete package. Spartan is computationally flexible, offers superb graphic capabilities and above all is extraordinarily user-friendly. Once a molecule is built and optimized by Spartan, the graphic capabilities of the program provide an exceptional insight into the structure of the molecule and enable one to measure a number of interesting properties of the molecule. For instance, the molecule can be viewed in various models such as space-filling, ball-and-stick, etc. Electron distribution in the molecule can be displayed, single and multiple bonds, molecular polarity and the reaction site of a molecule can be shown and the "actual vibrations" of a molecule can superbly be animated. A very important point about Spartan is worth mentioning here.

1

General Operating Features

This section provides an overview of the general operating features of PC Spartan-*Plus* 2.0 molecular modeling program. Some of the features, e.g., *File* and *Edit* should be familiar to the PC users while others are specific to the program. No detailed discussion of any features are provided, rather brief explanations to familiarize the student with function and operation of the program are presented. The descriptions in this section are best learned if you are actually sitting down and following the directions using the program. Some of the details, like the setup of a computation, are left out for later times during work on the various exercises.

START

To start PC Spartan-*Plus* (hereafter referred to Spartan for brevity), *double click* on the PC-Spartan-*Plus* icon in the window. A menu bar across the top of the screen appears. You are now in the main menu of Spartan.

MENUS

You will interact with the program almost exclusively through these menus. Pull down menus under the headings in the menu bar are used for this purpose.

BUILD

Allows you to take the currently displayed structure on the screen back into the **Builder** mode for modification or vice versa. The options under this menu are also accessible from the toolbar.

SETUP

Allows you to setup the type of calculation you want to do and specify the properties and features of the structure to be determined. It also permits you to setup and calculate various types of surfaces of an optimized structure for display purpose. The options of this menu and the **Builder** are discussed in further detail later in this section and also in appendix B at the end of the manual.

DISPLAY

Used to display the type of output that you select. The choices depend on how you setup the calculation in the first place.

Output

Allows you to scroll through the numerical output of your calculation.

Properties

Allows you to measure the energy, weight, volume and dipole moment of the molecule.

Surfaces

Selects and displays any surface you want to see assuming you have requested that surface be calculated in the "setup" part of the calculation.

Vibrations

Allows you to animate the vibrational modes of the molecule assuming you have selected "Frequencies" in the "setup" part of the calculation.

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Building a Structure

To create a structure you need to start the program and then enter the molecule **Builder** by selecting **New** from the **File** menu. A new menu including a model kit appears on the screen:

You may now build your structure using the mouse to select from a palette of pre-built fragments in either the **Entry** or **Expert** *model kits*. Simply *click* (left mouse button) on the fragment of choice from the model kit and bring the cursor anywhere onto the screen and *click*. You may now select other fragments and append them to the existing fragment on screen by clicking on the fragments' free valences. It is that simple and it is best learned while you are actually sitting at the computer. As an example, lets build the molecule HClCO using the instruction provided (write Lewis structure of the molecule first):

1. *Click* on the SP² hybridized carbon ⊃C= from the kit, bring the cursor anywhere onto the screen and *click*. Rotate to your visual need.

Setup a Calculation

A. OPTIMIZATION

When done creating your molecule, you will want to take it back into the main program window to set up a computation. This is simply done by going directly to the **Setup** menu, or by first pressing [E] to refine your structure and then going to the **Setup** menu.


The most basic goal of a molecular modeling computation is to calculate the "Equilibrium Geometry" of the molecule. Where are the atoms in the space of the molecule? What are the distances from each other? What is the overall shape of the molecule? etc. How a program such as Spartan accomplishes this goal is conceptually discussed in appendix B. The computational process is referred to as "minimization" or "optimization" method.

The **Setup** menu provides access to the optimization process by selecting Calculations and then Equilibrium Geometry in the Setup submenu:

Electron Density Surface (with Ball-and-Spoke displayed inside)

Besides the electron density surface, a number of other interesting properties are also well represented by drawing surfaces in Spartan. Among them are:

Bond Density

Useful for investigating bonding characteristics (single vs. multiple) inside a molecule.

Slice

Useful for investigating the variation in electron density in the molecule.

Potential Surface

Useful for determining the regions of positive and negative charge in the structure. Color-coded based on the visual spectrum to show the regions.

Molecular Orbitals

Useful for investigating the reactive sites of the molecule (used more often in organic chemistry).

Brief discussion of each type of surfaces together with graphical examples produced by Spartan are given in appendices C-E for your reference. The practice for setup, calculation, display, and manipulation of these surfaces will be gradually introduced in the tutorials and exercises.

Introduction to Spartan ◼ TUTORIAL 1

This self-guided tutorial exercise is intended to familiarize the student with the basic manipulation (display, measurements, display surfaces and molecular vibrations) of a typical output file generated by Spartan. No molecule building and calculation will be done in this tutorial. You should be familiar with the basic concepts of structure and chemical bonding before starting this exercise. In addition, read about surfaces in appendices B and C to become familiar with the type of properties displayed by each surface and be prepared to ask questions. Two molecules, C_4H_8 and H_2O, will be examined in this exercise. Write their Lewis structures first.

PROCEDURE:

A. C_4H_8 MOLECULE

1. *Double click* on the Spartan-Plus icon to **open** the program.

2. Select **open** from the **File** menu.

3. *Double click* on the ⎡**IAB - Tutorial** ⎤older and then select and open C_4H_8 molecule on the screen.

4. Go to **Model** Menu. Select **Wire, Ball and Wire, Tube, Ball and Spoke**, and finally **Space Filling** from the menu. These render the structure in a variety of representations available in Spartan.


Ball-and-Wire

Tube

Ball-and-Spoke

Space Filling

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What other molecular properties familiar to you appears in the dialog?

12. *Click* on the X̄ to close the dialog. Select **surfaces** from the **Display** menu. Select **density** (isovalue 0.002) surface from the surface list by clicking on the yellow box adjacent to it. This is the total electron density surface for the molecule (~ 98% of   the total electron density is included in this surface).

13. *Click* anywhere on the surface. A **style** menu appears on the lower right part of the screen. Display the surface in **Transparent, Dots, Solid,** and **Mesh** styles available in the menu.

Transparent   Dots

Mesh   Solid

Note that you can simultaneouskly display the molecule *inside* the surface using any representation in the **Model** menu. You may want to check and convince yourself that the CPK (Space-Filling) model reasonably reproduces the total electron density of the molecule, i.e., it effectively represents the size of the molecule.

14. Select **Ball-and-Wire** from the **Model** menu. Go to **Surfaces** in the **Display** menu again, deselect the density surface (by clicking on the check-marked yellow box) and select the **density/potential** surface from the surface list. A color-coded surface appears on the screen.

Click on other parts on the surface to measure the potential in the same fashion. Note the sign of the potential .Identify the most "electron-rich" and "electron-poor" regions of the molecule.

16. Go to **Surfaces** in the **Display** menu, deselect the elpot surface and select the **density** (isovalue 0.32) surface. Higher electron density surfaces (isovalue 0.32 here as opposed to 0.002 in step 12) provide information about the bonding pattern in the molecule. This is because the highest electron density is found near the positively charged nuclei inside the molecule. Examining higher electron density surfaces (isovalue > 0.002) is analogus to"zooming" in the molecule to observe the subtle differneces in electron density among the various bonds and nuclei in the molecule. Describe the differences in electron density around carbon and hydrogen atoms and for C-H, C-C, and C=C bonds. Check your answer with your instructor.

17. Deselect the density surface and select the **density/potential** (isovalue 0.32) surface. What does this surface tell you about the nature of the bonds (covalent, polar or nonpolar) in the molecule. Again, describe in terms of electron density.

18. Close the file. Answer No to "Save Changes."

B. H_2O MOLECULE

Open the H_2O file from ⎡**1AB-Tutorial**⎤ folder and carry out the procedure just described for C_4H_8 to practice your skills with a new molecule.

ADDITIONAL TASKS

1. Select **Ball-and-Wire** and **Diplole** from the **Model** menu to display the dipole moment for water. Ammonia, NH_3, is also present in the same folder. Open NH_3 folder as well and display its dipole moment. Which molecule is more polar? Record the numerical value of each dipole moment (**Properties** from **Display** menu).

2. *Click* on the **Dipole** in the **Model** menu to remove the dipoles (done one at a time by clicking on the molecule to select it).

3. Select **Surfaces** from the **Display** menu. Select and display the **Potential** surface from the "Surface List" for each molecule. This surface is different than the "elpot" surface examined in step 14 of C_4H_8 molecule (see appendices C and D). The **Potential** surfaces are very useful in providing information about "locations" of lone pair electrons; electrons that are associated with a single atom and are not as tightly held as bonding electrons.

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(3n-5 for linear molecules). These vibrations are *quantized* (each has a unique frequency) and they are extremely useful for elucidating the structure of a molecule. Spartan can calculate and animate these frequencies. The calculated frequencies are commonly used for comparison with the experimental frequencies to detemine the structure of the molecule. The three experimental vibrations of the nonlinear triatomic water occur at 1596 cm^{-1}, 3652 cm^{-1}, and 3756 cm^{-1}

To animate the individual vibrational motions, *click* on the yellow box to the left of the frequency. Experiment with different structure models for best results. Do the calculated frequencies compare well with the experimental ones? Are the calculated frequencies consistently larger or smaller than the experimental values? If so, by what percentage? How do you describe each vibration (use terms such as "stretching," "bending" together with symmetric or asymmetric, for example symmetric stretching, etc.). When finished, unselect all frequencies and close the "Vibrations List" dialog. *Close* the H_2O file and Spartan. You have successfully completed the first tutorial. The next tutorial will guide you through creating a molecule and submitting a computational job.

Molecule Building and Calculation by Spartan (1)

This tutorial is designed to help you learn how to create, setup, and submit a computational job in Spartan. Building of a structure is initiated by first selecting **New** from the **File** menu followed by piecing together the molecule from "atomic fragments" present in either of Spartan's Entry or Expert "*Model Kits*." A relatively few fragments in the Entry Kit allow construction of a wide variety of molecules. The Expert Kit offers more options for construction. Once created, editing of the structure can be done using the functions available in the **Build** menu. Nitrous Acid, HNO_2, will be built and studied in this tutorial. Carbon dioxide, CO_2, will be tried in the next tutorial. Together, these two exercises will describe the various construction and computational features of the program. Again, write the Lewis structure of Nitrous acid first and make sure you have completed the first tutorial before you begin to work on this one. You may also want to read appendix B to become somewhat famliar with the process of finding the equilibrium geometry (optimization) and the different levels of calculations that can be done on a molecule.

PROCEDURE:

Note: Refer to "Building a Structure" in the "Basic Operating Features" if you run into a problem while building the molecule.

Build HNO_2. Select **New** from the **File** menu, select $\boxed{\text{N=}}$ from the entry *Model Kit* and *click* anywhere on screen. Select sp^2 hypridized oxygen $\boxed{\text{=O}}$ and *click* onto the tip of the double free valence of the nitrogen. Select the sp^3 hybridized oxygen $\boxed{\text{O–}}$ and *click* on the single free valence of nitrogen. There is no need to connect hydrogens. The free valences are automatically converted to hydrogens upon exiting the builder. Click on **View** to exit the builder. Select **Ball-and-Wire** to display the molecule.

You have now setup the calculation of HNO_2 molecular geometry using a molecular mechanic level of calculation. The next step is to submit the job to actually do the calculation.

2. Submit the job (**Submit** under the **Setup** menu). You will be asked to supply a name and save the job. Save it as "HNO_2-SYBYL." *Click* on **OK** on the PcPlus dialog that appears.

3. When completed, *click* on **OK** to remove the dialog that appears. Measure and record all bond lengths and bond angles in the molecule.

(ii) Semi-Emperical Calculation

4. When all measurements are done, select **View** mode and re-enter the **Calculation** dialog. Setup the following operations:

You have now setup optimization of molecular geometry using the AM1 Semi-Empiracal model. Three different semi-empiracal computational models; AM1, PM3, and MNDO are included in Spartan. This is a higher level calculation compared to molecular mechanics.

5. *Click* on **OK** to close the dialog. Save the job as "HNO_2-AM1" and **Submit** the job. When completed, measure all bond lengths and bond angles in the molecule again.

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(iv) Setting Up Surfaces

We will now build and examine four different surfaces, namely: **density surface** (total electron density), **bond-density surface, elpot** (electrostatic potential mapped on the electron density) and **potential surface** in this part of the exercise.

1. Select **Surfaces** from the **Setup** menu.

2. *Click* on **Add** from the "Surface List" dialog that appears.

3. *Click* on **density** from the Surface pull-down menu in the "Add Surface" list and then *click* on **OK**. This requests calculation of the "density surface."

4. *Click* on **Add** from the "Surface List" dialog again, *click* on **density (bond)** from the Surface pull-down menu and then *click* on **OK**. This requests calculation of the "bond-density" surfaces.

5. Repeat step 4 again and add calculation of the **potential** surface to the list.

6. *Click* on **Add** again. Select "density" from the surface pull-down menu **and** "potential" from the "Property" pull-down menu. This operation maps the electrostatic potential on the electron density surface to generate the **elpot** surface. *Click* on **OK**.

You shall now see on the screen a "Surface List" dialog showing the four requested surfaces with their status as "pending," meaning that they have not yet been submitted for calculation.

| Surface	Property	Status	IsoValue	Res.	Label
density		Pending	0.002	med	Surface1
density		Pending	0.08	med	Surface2
potential		Pending	-20	med	Surface3
density	potential	Pending	0.002	med	Surface4

Add...   Delete

7. Select **Submit** from the **Setup** menu. This submits the job for calculation. *Click* on **OK** from the PCPlus dialog that appears. *Click* on **OK** again when the job is completed. The boxes to the left of the surfaces in the "Surface List" dialog will turn yellow and the job's status as completed. You are now ready to examine the surfaces. Proceed to "Data Interpretation" and when finished close all dialogs and exit the program. Answer NO to all "Save Changes" along the way.

b. Describe the difference between N-O and N=O bonds in terms of observed electron density for each bond.

5. Display the **Potential** surface. What information does this surface provide about the structure of HNO_2? What information is provided by the "size" and the "location" of the observed electron densities?

6. Display the **elpot** surface. Where is the most positive region of the molecule? Does it agree with the fact HNO_2 is an acid? Explain.

7. Change the isovalue to a higher number as in question 4. Describe the bond polarities (polar or nonpolar) in terms of the observed potential densities.

8. Close all dialogs, remove surfaces and exit the program.

Molecule Building and Calculation by Spartan (2)

This tutorial is designed to familiarize the student with additional building features in Spartan; namely imposing **Constrain** on some key parameters in the structure (e.g. bond length and bond angles) and calculating **Vibrations** of a molecule. Three different structures for carbon dioxide, CO_2, will be investigated in this exercise:

The best structure for CO_2 will be determined from the data. Write Lewis structure for carbon dioxide and predict its geometry and polarity from VSEPR theory before starting to work on this exercise.

CONSTRAIN IN GEOMETRY

It is desired, sometimes, to constraint (restrict or prohibit from changing) the values of some key structural parameters during geometry optimization of a molecule. As an example, consider the three structures of carbon dioxide. Building CO_2 with a single and a triple bond can be done by constraining the bond distances in the molecule. Bent carbon dioxide can be built by constraining the bond angle in the molecule to less than 180°. Holding these constraints during the optimization process would allow one to search for the best geometry (the one with the least energy) of the molecule. As another example consider the intramolecular "hydrogen bond" present in some molecules. Hydrogen bonds are "unusual" very long bonds and, if present, one may want to constraint their values during the geometry optimization of the molecule. Long bonds are also present in the "transition state" of a chemical reaction and may need to be constrained during "transition state" optimization process. There are other situations where constraining one or more parameters are essential for the geometry optimization purpose. **In brief, geometrical constraints of any kind (bond, angle, dihedral) specify conditions which Spartan must satisfy *in addition to* the usual criteria used during optimization procedure.**

You have now setup calculation of equilibrium geometry of structure (1) using AM1 Semi-Empirical method **with** the constraints specified in the build mode. *Note that the "Constraints" box is check-marked in the dialog. Remove the check-mark from the symmetry box and click on* **OK**.

7. Submit the job. Save it as "CO_2-one."

8. Close the file when finished. Build the second structure (two double-bonds, linear). Introduce proper constraints and perform a similar AM1 Semi-Empirical calculation. Save the job as "CO_2-two."

9. Repeat step 8 with the third structure (two double bonds, bond angle 120°). Save the job as "CO_2-three."

OPTIMIZING CO_2 / CALCULATING VIBRATIONS

10. Build CO_2 anyway you desire using either Entry or Expert model kits. Apply no Constraints and setup the following operations:

This setup will calculate the equilibrium geometry of CO_2 with no constraints imposed on the molecule. In addition, the vibrational frequencies for carbon dioxide will be calculated as requested by check-marking the "Frequencies" box in the "Compute" section of the Calculation dialog.

11. Save the job as "CO_2-optiom" and submit it for calculation.

Chemical Bonds

The forces that hold atoms together in compounds are called chemical bonds. The resulting collection of atoms which function as a unit are called a molecule. There are three possible types of bonds: *covalent, polar covalent* and *ionic*. The difference between them is primarily due to the distribution of the electrons involved in the bond and how that distribution is affected by electronegativity. In this activity you will use Spartan to explore the type of chemical bonds in two sets of molecules: (a) H_2, HF, LiH and (b) $HC \equiv CLi$, $HC \equiv CNa$, $HC \equiv CK$. You will use the software to generate the *"total electron density"* surface and the *"electrostatic potential map*, or **elpot**" surface. Recall that the former is a surface which is drawn to include almost all of the electron density (~98%) of the molecule (conveys the molecule's size) and the latter shows the charge distribution in the molecule (Appendix D).

PROCEDURE

1. Build and optimize H_2, HF and LiH molecules. To build LiH you will need to go into "**Expert**" mode in the **Builder**. Use *ab initio* (Hartree-Fock) will 3-21G* for geometry optimization. Once optimized, set up and calculate the "total electron density" and the **elpot** surfaces for the molecule.

2. Build and optimize $HC \equiv CLi$, $HC \equiv CNa$ and $HC \equiv CK$ molecules in the same fashion. Again use HF321-G* for optimization and build the same surfaces.

DATA COLLECTION

Open all three molecules on the screen next to each other so that you can compare the results visually. It is best to use *Ball and Wire* model and display the surfaces in *transparent* style (Tutorial 1). If you want to display more than one surface at once on a molecule, display the smaller inner surface as a *solid*, and outer surface as a *mesh* or *dots* style. Use this method of display for all future activities, if needed.

DATA INTERPRETATION & QUESTIONS

1. Examine the total electron density surfaces for H_2, HF and LiH. Briefly explain (one to three sentences) the shapes of this surface using the concept of electronegativity.

2. For which molecule is the size of electron density on hydrogen the smallest? For which is it the largest? Is there a correlation between this size and the electronegativity of the atom to which hydrogen is bonded? Briefly explain.

3. Examine the **elpot** surfaces for the three molecules. For which molecule is the potential

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Bond Lengths, Hybridization and Molecular Orbitals

The goal of this activity is to explore how hybridization and resonance affect carbon – carbon and carbon – hydrogen bond lengths, and to get you thinking about molecular orbitals (MOs) and the electrons which occupy them. Carbon – carbon bond lengths in organic compounds depend both on the bond order (single, double, triple) and on the chemical environment in the vicinity of the bond. Carbon – hydrogen bond lengths depend on the hybridization of the carbon atom to which the hydrogen is bonded. A molecular orbital, just like an atomic orbital, represents a region in space occupied by, at most, two electrons. Molecular orbitals are extremely useful in describing the bonding and the reactivity of organic compounds. Two of the molecular orbitals, HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Occupied Molecular Orbital), are particularly useful for this purpose. For any molecule, HOMO is the bonding orbital which is energetically the highest orbital occupied by electrons. If the molecule is to donate an electron or a pair of electrons (meaning the molecule acts as a Lewis base) in a chemical reaction, it will most readily come from the HOMO. On the other hand, LUMO is the antibonding lowest energy orbital which is not occupied. If you were to add an electron or a pair of electrons to the molecule (meaning the molecule acts as a Lewis acid), the easiest place to put it is in the LUMO (see Appendix D). Spartan has a powerful capability to generate a variety of surfaces, including HOMO and LUMO, for the molecule. Graphical representation of these surfaces provides visual insights into the types of bonds and the reactivity (reactive sites) of the molecule.

PROCEDURE

1. Build and optimize H_2, C_2H_2, C_2H_4 and C_2H_6 molecules using Semi-Empirical AM1 model. Once optimized, generate the following surfaces for each molecule:

   H_2 (HOMO and LUMO, total electron density)

   C_2H_2 (HOMO, HOMO-1, HOMO-2, LUMO, LUMO+1, LUMO+2)

   C_2H_4 (HOMO, LUMO, total electron density)

2. Build and optimize, using Semi-Empirical AM1 model, benzene (C_6H_6) and 1, 3–butadiene ($CH_2 = CH – CH = CH_2$), Once optimized, calculate their **elpot** surfaces.

5. What information do the shapes of HOMO, HOMO-1 and HOMO-2 surfaces provide about the nature of the bonds present in ethyne? What type of orbitals do LUMO, LUMO+1 and LUMO+2 represent in the molecule?

6. What information do the relative energies of the HOMO and HOMO-2 orbitals provide about the bonds in ethyne? Extend your answer to explain bonding in ethene.

7. Display hydrogen and ethene on the same screen . For each molecule display the "total electron density" surface (in *Transparent, Dots* or *Mesh*), and the HOMO surface (in solid) at once. How does the size and shape of the total electron density surface in hydrogen compare to that of its HOMO? Do you find the same correspondence in ethene? Explain.

Multiple Bonds and Lone Pairs

Many organic compounds possess multiple bonds (double, triple) and lone pairs of electrons. Multiple bonds and lone pairs affect both the geometry and the polarity of molecules. This activity is designed to help you explore and learn these features of molecular structure.

PROCEDURE

1. Build and optimize methane (CH_4) and boron trifluoride (BF_3). Use Semi-Empirical AM1 model for geometry optimization. The angles in these molecules will serve as "standards" for sp^3 and sp^2 bond angles, respectively.

2. Build and optimize, using SE-AM1 model, H_2CO, F_2CO and O_3 molecules. The central atom in these molecules utilizes sp^2 hybridization. Once optimized, calculate the "total electron density" and **elpot** surfaces for the molecules.

3. Build and optimize, using SE-AM1 model, H_2O, CH_3OH and dimethyl ether, CH_3OCH_3. The central atom in these molecules utilizes sp^3 hybridization. Once optimized, calculate the "potential" surface for each molecule.

DATA COLLECTION

Draw neat and fairly large 3D–representation of the optimized structures. Measure the *different* bond angles within each structure and write the values (to ± 0.1 A°) in your diagrams. Also, record the value of the dipole moment for each molecule.

DATA INTERPRETATION & QUESTIONS

1. Are there any angle deviations from the "ideal" bond angle in H_2CO, F_2CO and O_3 molecules? If yes, explain the deviation in terms of the space requirements of a double bond or a lone pair of electrons as opposed to a single bonding pair of electrons. Use the shape of total electron density surfaces and/or the **elpot** surfaces to justify your answer.

2. Are there any angle deviations from the "ideal" bond angle in H_2O, CH_3OH and CH_3OCH_3 molecules? If yes, briefly explain using the same rationale as in the previous question. Use the shape of potential surfaces to justify your answer.

Resonance I

Most molecules can be represented without difficulty by a single Lewis structure. But, in many instances, more than one Lewis structure is needed to properly represent the molecule. Lewis structures that differ only in the arrangement of electron pair positions (π and nonbonding valence electrons) but not atom positions are referred to as *resonance structures*. Consider formate anion as an example:
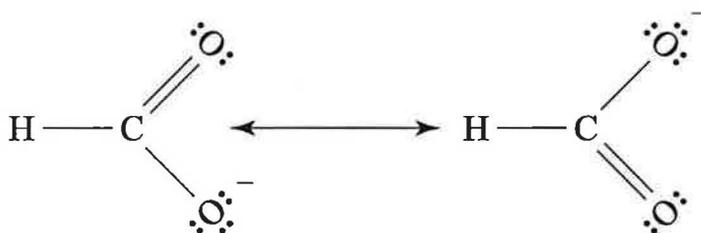
As can be seen, the atoms themselves occupy exactly the same place in both resonance forms but the placement of the π and nonbonding electrons are different. For substances which exhibit resonance, the true structure for the molecule is a **resonance hybrid** of all individual resonance forms. Resonance is an extremely useful concept and has important implications in bonding when it is present in the molecule. For this activity you will build and optimize several molecules which exhibit resonance, and will analyze optimized geometry and surface data to see what they tell you about the molecular structures.

PROCEDURE

Do all optimizations at the Semi-Empirical AM1 level.

1. Build and optimize 1, 3 – pentadiene ($CH_2 = CH – CH = CHCH_3$) and 1, 4 – pentadiene ($CH_2 = CH – CH –CH = CH_2$). Once optimized, construct their **elpot** surfaces.

2. Build and optimize acetic acid and acetate ion. Once optimized, calculate their **elpot** surfaces.

3. Build and optimize allyl cation ($CH_2 = CH – \overset{+}{C}H_2$), allyl anion ($CH_2 = CH – \overset{-}{C}H_2$) and $CH_3CH = CH\overset{+}{C}HCH_3$ cation. Once optimized, calculate the LUMO surfaces for the two cations and the HOMO surface for allyl anion (make sure to correctly indicate the charge in the "Calculation Setup").

4. Again build the allyl cation (or you may put the previous one in the **Builder** mode by opening the molecule and clicking on the "**+**" icon). Constrain a proper dihedral angle so that you get a flat structure for the ion (see Tutorial 3). Save under a different name and

Resonance II

This activity is intended to further explore the concept of resonance and its implications in the stability of molecules and ions. Generally speaking, the larger the number of resonance forms, the more spread (delocalized) the charge (or the π electrons) is, and the more stable a substance is.

PROCEDURE

1. Build and optimize benzene and $1, 3, 5$ – cyclohexatriene using Semi-Empirical PM3 model. For the latter you need to **constrain** the CC double bonds to $1.32A°$ and the CC single bonds to $1.55A°$ and check-mark the "*Constrain*" box in the "Calculation Setup" dialog (see Tutorial 3). Once optimized, calculate the "bond density" and the **elpot** surfaces for benzene.

2. Build and optimize (again using PM3 model) $2, 4$ – pentandione:

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{}} \quad \overset{\displaystyle O}{\overset{\displaystyle \|}{}}$$
$$CH_3CCH_2CCH_3$$
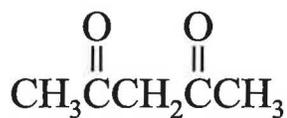
3. There are two types of hydrogen in $2, 4$ – pentanedione. An anion of the molecule can be produced when a H^+ is removed from the molecule by reaction with a strong base. Naturally, two different anions may be produced:

$$\overset{\displaystyle O}{\overset{\displaystyle \|}{}} \quad \overset{\displaystyle O}{\overset{\displaystyle \|}{}} \qquad\qquad \overset{\displaystyle O}{\overset{\displaystyle \|}{}} \quad \overset{\displaystyle O}{\overset{\displaystyle \|}{}}$$
$$\overset{..}{\overset{..}{C}}H_2CCH_2CCH_3 \quad \text{and} \quad CH_3C\overset{..}{C}HCCH_3$$
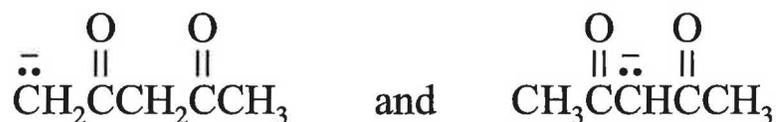
Build and optimize (PM3) the two anions. Once optimized, calculate their HOMO surfaces.

4. Build and optimize $2, 4$ – pentadienyl radical:

$$CH_2 = CH - CH = CH - CH_2$$

For optimization use Hartree-Fock 321-G* model. Furthermore, you should do the following when setting up the calculation:

<u>Multiplicity:</u>   Doublet (case when there is an unpaired electron)

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Conformational Analysis

(Open-Chain Alkanes)

Rotation occurs freely around the carbon – carbon single bonds in open-chain alkanes and haloalkanes. The different arrangements of atoms that result from this rotation are called *conformations* or conformational isomers of the molecule. Unlike constitutional isomers, different conformational isomers have the *same* connections of atoms and cannot be isolated because they interconvert rapidly. Generally speaking, it has been observed that molecules with tetrahedral carbons, like ethane, prefer a *staggered* conformation. In this activity you will use Spartan to work through the conformational analysis of *1, 2 – dichloroethane* and *2 – methylbutane*. The goal is to become familiar with all aspects of conformational analysis: creating 3D conformations on screen, representing them on paper with Newman Projections, generating a conformational energy diagram, etc. I recommend that you team-up with another student, each do one of the molecules and then share the results.

PROCEDURE

Review Tutorial 3 on constraining parameters (dihedral angle in this activity) during optimization. Do all geometry optimizations at the Semi-Empirical **PM3** level.

1. Build 1, 2 – dichloroethane. Constrain the Cl – C – C –Cl dihedral (or torsional) angle to 0.0° (eclipsed conformation). Optimize the geometry while maintaining the constraint (check-mark the "*Constrain*" box in the "Calculation Setup" dialog).

2. To build the next conformation, *click* on "**+**" icon to get in the **Builder** mode. Change the value of the dihedral angle to 60° and then constrain the angle to the new value (see Tutorial 3 or your instructor if you have questions). Save the molecule under a different name (try names like dichloroethane – 0, dichloroethane – 60, etc.) Optimize the molecule while maintaining the constraint.

3. Repeat step 2 adjusting the angle sequentially from 60° to 120°, 180°, 240° and 300° each time optimizing the structure while maintaining the angle constraint.

4. (Student 2) carry out the above procedure with 2–methylbutane:

2–methylbutane? (Use terms like Gauche, eclipsed, etc.) Why? Describe in terms of "Torsional Strain" and "Steric Strain" factors.

2. Build the "total electron density" surfaces for the most and the least stable conformations of each molecule. What does the shape of these surfaces tell you about the relative stabilities of the two conforms? Do they support your answer to question 1?

3. Display the most and least stable conformations of each molecule using the Space-Filling (CPK) model. What information about the relative stabilities of the two conformers does this representation provide?

4. Have the least stable conformation of your molecule on the screen. Remove the check-mark of the constrain box in the **Calculation Setup** and reoptimize. What happens? Explain.

Conformational Analysis

(Cyclohexanes)

Experimental combustion data show that cyclohexane is strain-free. It contains neither angle strain nor torsional strain. This is because, unlike cyclobutane, cyclohexane adopts a strain-free *chair conformation* in which all CCC bond angles reach a near ideal tetrahedral value, and all neighboring C – H bonds are staggered. This chair conformation results in two kinds of positions for the substituents on the ring: *axial* positions (perpendicular to the ring) and *equatorial* positions (in plane of the ring):
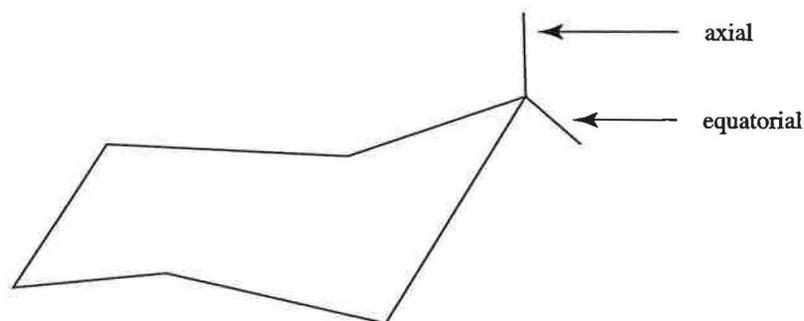
Like free rotation around the carbon – carbon single bonds in alkanes, cyclohexane rings are mobile at room temperature. Different chair conformations rapidly interconvert, resulting in the exchange of equatorial and axial positions. This phenomenon is known as the **ring-flip**.

Substituted cyclohexanes are the most common cycloalkanes in nature. Monosubstituted cyclohexanes exist as a mixture of equatorial and axial conformers, and although cyclohexane rings readily undergo ring-flip, the two conformers are not equally stable (steric effect). The relative ratio (or percentages) of the two isomers at equilibrium can be estimated using the equation:

$$\frac{N_1}{N_2} = e^{-\Delta E/RT} \qquad (1)$$

Where ΔE is the energy difference between isomers ($\Delta E = E_1 - E_2$). In disubstituted cyclohexanes, the steric effects of both substituents are determining factors in which conformation is favored at equilibrium.

DATA INTERPRETATION & QUESTIONS

1. Using equation (1) calculate the percentages of the two isomers at equilibrium for the three monosubstituted cyclohexanes at 298K. Show your work for methylcyclohexane and just tabulize the results for the others.

2. Which conformer of each monosubstituted molecule is more stable? Why? Which molecule shows a larger preference? Why? Which molecule shows a smaller preference? (Hint: display conformers in Space-Filling model to help with your answer.)

3. Why does an axial cyano substituent cause very little 1, 3 – diaxial steric strain? Again, display the conformer to help with your answer.

4. When the two methyls on trans – 1, 4 – dimethylcyclohexane go from being equatorial to axial, the energy difference is just about twice that for methylcyclohexane (check your numbers), meaning that the effect is additive. Why is the effect no longer additive for *cis* – 1, 3 – or *cis* – 1, 2 – dimethylcyclohexane? Support your answer with citing specific structural features and drawings.

5. What do your calculated energy data for the monosubstituted cyclohexanes and those for 1, 2 – and 1, 4 – dimethylcyclohexane tell you in general about the steric strain in cyclohexanes?

6. Consider the effect of ring-flip on the energies of *trans* – 1, 3 – dimethylcyclohexane and *trans* – 1 – methyl – 3 – *tert* – butylcyclohexane. Explain and justify the differences you observe.

7. Visualize the two chair conformations of the following molecule (you may use molecular models to help with your answer):
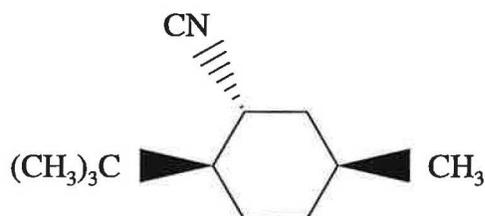
Based on your data from the cyclohexanes, which conformer do you suppose is preferred? Why? Use Spartan and calculate the energies of the two conformers. Do they agree with your prediction?

Ring Strain in Cycloalkanes

Cycloalkanes do not all have the same relative stability and reactivity. Experimental heats of combustion show that cyclohexane is the most stable while cyclopropane is the least stable cycloalkane. Experiments also show that cyclopropane and cyclobutane are more reactive in ring-breaking reactions. The relative instability of cyclopropane and other less stable (compared to cyclohexane) cycloalkanes is a direct result of their cyclic structures. For this reason their molecules are said to be *strained*, meaning that they have distorted geometries. To measure the amount of strain in a cycloalkane, known as *ring strain*, one needs to measure the potential energy of the cycloalkane and the corresponding strain-free acyclic alkane. The difference between the two energy values represents the amount of extra energy in the molecule due to strain.

One simple way to determine experimentally the cycloalkane strain energies is to measure their *heats of hydrogenation* according to the following reaction:

$$\underset{CH_2 \overline{\quad\quad} CH_2}{\overset{(CH_2)_n}{\bigwedge}} + H_2 \longrightarrow CH_3\,(CH_2)_n\,CH_3 + Heat$$
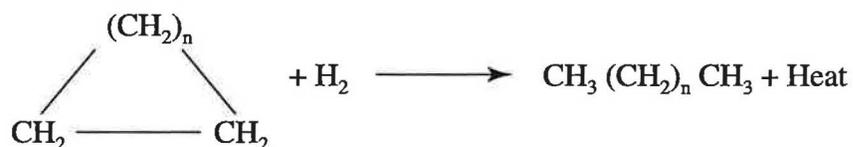
The more energy (strain) a cycloalkane contains, the more heat is released on hydrogenation. Heats of combustion data are also used for the same purpose (in textbooks). Because the cycloalkanes vary in ring size, their heats of hydrogenation (or combustion) cannot be compared directly. However, the amount of heat evolved *per CH_2 unit* can be used to compare the stabilities of the cycloalkanes.

In this activity you will use Spartan to build and optimize the series of cycloalkanes from cyclopropane to cyclooctane. You will also build and optimize their analogous n – alkanes and calculate *all* heat heats of formation. From the data you will calculate the energies of their hydrogenation reaction and the amount of ring strain in these cycloalkanes.

PROCEDURE

Use Semi-Empirical **AM1** model for all optimizations. The AM1 heat of formation for hydrogen is $E(H_2) = -5.18$ kcal/mol. Use this value in your calculations.

1. Build and optimize cyclopropane to cyclooctane. Record their energies and the ring bond angles.

5. Examine the cyclopentane structure. Is it planar? Each H – H eclipsing interaction (torsional strain) in ethane costs about 4.0 KJ/mol. Explain how this information supports the fact that cyclopentane is not planar.

6. Using the ethane torsional information provided in the previous question, calculate what fractions of the cyclopropane and cyclobutane strain energies are due to torsional strain in the molecules. What specific information in regard to the stability of the cycloalkanes does this calculation provide?

7. Optimize the structures of n–propane and cyclopropane using Hartree-Fock 321-G* model. When completed, calculate their electrostatic potential (**elpot**) maps. Display both maps on the same screen in *transparent* style and Ball-and-Wire model. Change the **isoval** from the default 0.002 to larger values (try 0.09 or 0.1) to see the electron densities around the bonds in the molecules. Focus on the electron densities around the CC bonds in the molecules. Explain and analyze any differences you observe. Be detailed. (Hint: is the electron density symmetrical around the CC bonds or displaced somewhat in one or both of the molecules?) Print a copy of the screen and attach to your report.

Vibrational Spectra

A nonlinear molecule of N atoms can undergo 3N-6 possible modes of vibration, which means the IR Spectrum of the compound could be quite complex and contain many absorptions. These absorptions, however, often overlap so that only a few bands are observed. Furthermore, some vibrations produce only weak absorptions, and are not observed at all. Fortunately, even in very complex molecules, certain functional groups (O – H, C = O, C ≡ C, etc.) have characteristic frequencies that can easily be identified. Generally speaking, stretching vibrations in molecules, particularly those involving hydrogen (O – H), occur at higher frequencies. Bond stretches not involving hydrogen, angle-bending vibrations and deformation vibrations (complex group bending vibrations) occur at lower frequencies. (Review Appendix G for further details. Also the software **IR Tutor**, available at MSMLC and on the CD accompanying your textbook, contains extensive discussion on the subject.)

The goal of this activity is to calculate the vibrational spectrum of a polyatomic molecule by Spartan, and to correlate the calculated frequencies to specific absorptions in the experimentally measured IR spectrum of the compound. By doing this activity you will be able to better visualize vibrational motions in molecules and see the ability of Spartan in predicting the vibrational frequencies of molecules.

PROCEDURE

1. Obtain a known liquid from the stockroom. Acetic acid, ethyl acetate, p-methoxy-benzaldehyde are recommended, however, other organic liquids with one or more specific functional groups can also be used. I recommend one with a carbonyl group in the molecule.

2. Use the FTIR instrument and measure the IR spectrum of your liquid as a thin film held between two salt plates. It is helpful to have the instrument measure the peak values for you. Tabulate your peak values (> 1400 cm⁻¹).

3. Build and optimize your molecule using Semi-Empirical **PM3** method. Check-mark the *Frequencies* box in the "Setup Calculation" dialog to calculate the frequencies (Tutorial 3).

DATA COLLECTION

1. Tabulize your data as follows. Record all frequencies (only > 1400 cm⁻¹) to ±1 cm⁻¹. Tabulize your data in the order of decreasing frequencies.

Carbonyl Group Frequency

The generally strong $C = O$ infrared absorption in carbonyl compounds occur at $1670 - 1780$ cm^{-1}. The exact band position (frequency) depends on the environment of the $C = O$ group in the compound. A group, G, bonded to the carbonyl can affect the characteristic frequency of the $C = O$ group by either an *inductive* effect or a *resonance* effect as displayed below:
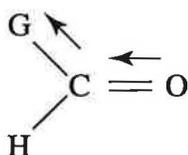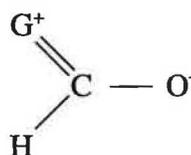
Inductive Effect   Resonance Effect

As you learned in the previous activity, Spartan can calculate the vibrational frequencies in molecules. The goal of this activity is to calculate the characteristic $C = O$ frequency in several carbonyl compounds by both Semi-Empirical (AM1 and PM3) and *ab initio* (3-21G* and 6-31G*) methods in order to see the suitability and limitations of the various computational methods. The second goal is to learn about how a group like G affects the $C = O$ stretching frequency in carbonyl compounds.

PROCEDURE

Work as a team of 2-3 and divide the work.

1. Build and optimize the following carbonyl compunds and calculate their vibrational frequencies (previous activity and Tutorial 1). Optimize each molecule by AM1 and PM3 (Semi-Empirical) and by 321-G* and 6-31G* (Hartree-Fock) methods.

    HCOOH, HCONH$_2$, CH$_3$CHO, HCOCl, HCOF

2. Build and optimize using PM3 model:

$$CH_3CH = CH\overset{\overset{\displaystyle O}{\|}}{C}H \quad \text{and} \quad C_6H_5 - CHO$$

1705 cm^{-1} 1705 cm^{-1} (experimental)

59
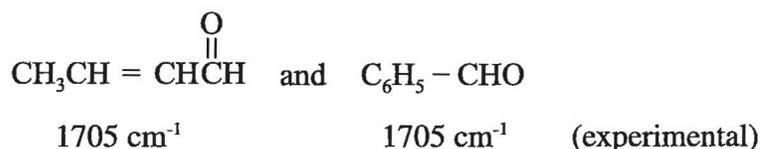
Electronic Spectra

Ultraviolet (UV) spectroscopy provides information about electronic transitions within molecules. Alkenes, conjugated alkenes and aromatic compounds absorb UV radiation in the wavelength region of 200 to 400 nm. The absorbed energy causes an electron to excite from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The most important electronic transition in alkenes and conjugated alkenes is the one in which the electron is excited from a bonding π molecular orbital to an antibonding π^* molecular orbital, a so-called $\pi \longrightarrow \pi^*$ transition:
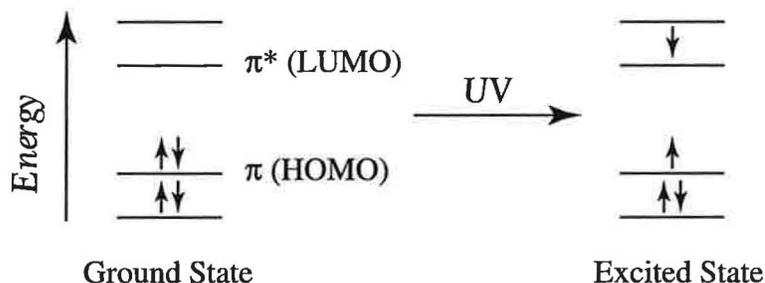
The wavelength of maximum absorption, λ_{max}, depends on the energy gap between the HOMO and the LUMO ($\Delta E = E_{LUMO} - E_{HOMO}$) and provides information about the nature of conjugated π electron system in the molecule.

In this activity you will use Spartan to calculate the HOMO and LUMO energies for several alkenes and conjugated systems. From the data you will uncover: (i) the effect the conjugation has on the HOMO – LUMO energy gap and on absorption maxima (λ_{max}), and (ii) the effects on absorption maxima when nonbonding electrons are present in the molecule.

PROCEDURE

You may want to team-up with another student and divide the work. Use Semi-Empirical **PM3** method for all optimizations.

1. Build and optimize the following molecules (PM3). The numbers in parantheses are the experimental λ_{max} in nanometers (nm).

   a) Ethene (165)   d) 1, 3 – butadiene (217)
   b) 1 – octene (177)   e) 1, 3 – cyclopentadiene (239)
   c) trans – 3 – hexene (184)   f) trans – 1, 3, 5 – hexatriene (253)

4. What effect does "conjugation" have on:

   a) the HOMO energy?

   b) the LUMO energy?

   c) the HOMO – LUMO energy gap?

   d) the absorption maxima, λ_{max}?

Cite specific data to justify your answer.

5. Compare the experimental and the calculated λ_{max} values for vanillin and the vanillin anion. Do the same for aniline and the anilinium cation. Does Spartan predict the same shift in λ_{max} values as the experiment? What is the reason for this shift? Be as detailed and as concise as you can. Display and compare the HOMO surfaces to help you arrive at your answer (Hint: where is the major difference in the HOMO maps for the neutral molecule and its anion or cation?).

6. Do you expect benzaldehye to have a smaller or larger λ_{max} than benzene? Why? Build and optimize the two molecules and use the data to validate your answer.

Carbocation Stability   **ACTIVITY 12**

Electrophilic addition reactions involving alkenes first yield *carbocation* intermediates. The relative stabilities of carbocations (1°, 2°, 3°) determine the products of the reaction. Often, a less stable carbocation *rearranges* to a more stable ion before the final products are formed. In this activity you will use Spartan to explore the relative stabilities of carbocations, the structure/ stability relationship of carbocations and the factors which influence the stability of these ions. Review the relevant sections of your textbook before starting this activity. Pay particular attention to the concept of "hyperconjugation" and how it stabilizes a carbocation.

PROCEDURE

Team-up with another student and divide the work. Use Semi-Empirical **AM1** model for *all* optimizations.

1. Build and optimize the following simple carbocations. Calculate their **elpot** surfaces (can add it while optimizing the molecule). Calculate the LUMO surface for the *tert*–butyl carbocation.

$$CH_3^+, CH_3CH_2^+, (CH_3)_2CH^+, (CH_3)_3C^+$$

2. There are other more complex carbocations to build and optimize in this activity. However, you need to figure them out on your own while answering the questions (questions 5 and beyond).

DATA COLLECTION

1. Measure the energies of the four carbocations. Display all four carbocations on the same screen and add their **elpot** surfaces in *solid* style. Obtain the color range for each of the surfaces (**Display ⟶ Properties ⟶** click on the surface). Tabulize your data (structure, energy, color range).

2. With all four **elpot** surfaces displayed on screen, change the color (property) range so that they are all on the same scale (identify the minimum and the maximum values from your data in step 1 above). Make sure to press the **Enter** key after you type each value. Print a copy and attach to your report.

3. Make a duplicate copy of the *tert*–butyl carbocation (open the molecule and save it under a different name). Have both copies open on the screen. Display the **elpot** surface in *transparent* style with **tube** model on one and the LUMO map on the other molecule. Print a copy and attach to your report.

Why in equal amounts? Again, do appropriate calculations and use the data (numerical) to validate the experimental results.

8. Consider the following two 2° carbocations:

$$\overset{+}{CH_3CCH} = CHCH_3 \text{ and } CH_2 = CH\overset{+}{C}HCH_2CH_3$$

Which ion do you predict to be more stable and why? Use Spartan to arrive at your answer (Hint: look at LUMO maps).

9. Using the results from the molecules investigated in this activity, list three (3) factors that you consider to be significantly important in the carbocation stability. Cite specific results to validate your answer.

Regioselectivity of Electrophilic Additions to C = C

Electrophilic addition of an unsymmetrical reagent such as HX to unsymmetrical alkenes can potentially produce two products. However, the reaction often yields only one product. Such reactions are said to be *regioselective* and Markovnikov's rule is used to predict the product of these addition reactions. The rule states that the positive portion of the adding reagent (H^+ in HX) bonds to the less substituted alkene carbon to yield the more stable carbocation as an intermediate. In this activity you will use Spartan to predict the products of HCl addition to the following alkenes:

1) Ethene
2) Propene
3) 2–Methylpropene
4) 1–Methylcyclohexene

PROCEDURE

Work as a team of two and divide the work. Do all optimizations using Semi-Empirical **AM1** method.

1. Build and optimize the four alkenes shown above. Calculate their **elpot** and HOMO surfaces.

2. Build and optimize the potential *pairs* of carbocations for each molecule (only one for ethene). Calculate their **elpot** surfaces. Don't forget to indicate the charge on the ions.

3. Build and optimize the two potential products for the 1–methylcyclohexene addition reaction.

DATA COLLECTION

No numerical data collected.

DATA INTERPRETATION & QUESTIONS

1. Open the four optimized alkenes on the same screen and display their **elpot** surfaces (use *transparent* style and Ball and Wire model). Carefully examine the maps. Can you tell whether one end of the π bond is more electron-rich than the other end? Answer the same question with HOMO maps displayed.

Stereospecific Reactions ACTIVITY 14

Chlorine and bromine rapidly react with alkenes to form vicinal dihalides:

$$\ce{>C=C<} + Br_2 \longrightarrow \ce{-C-C-}$$
$$\qquad\qquad\qquad\qquad\qquad Br \quad Br$$
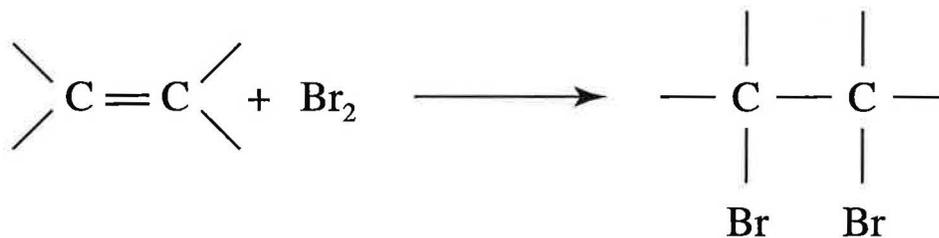
The addition reaction proceeds exclusively with *anti* stereochemistry, meaning that a specific stereoisomeric form of the product (anti product) is formed. To explain the observed product, an ionic mechanism involving a cyclic *bromonium ion* intermediate has been proposed.

$$Br^+$$
$$\ce{>C----C<}$$
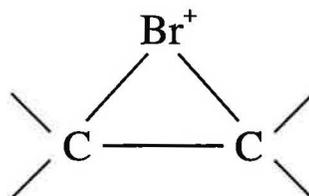
A nucleophilic attack by Br⁻ ion produces the final product of the reaction. In this activity you will use Spartan to study the **bromonium** ions formed from ethene, propene, 2–methylpropene and cyclopentene. From the ion's charge distributions (**elpot** surfaces), bond lengths and the shape of their LUMO maps, you will uncover the factors that support the stereospecificity of the reaction.

PROCEDURE

The bromonium ion optimizations have to be done using *ab initio* 3-21G* method and that takes time. For this reason, I have already optimized and saved these ions in **12AB-Three** folder. You may use them and go directly to data collection or optimize the ions on your own. If you choose to do so, follow the procedure below. You will have to build the ions in the **Expert** mode since you need a divalent bromine to make the bromonium ions.

1. Build and optimize the bromonium ions from ethene, propene, 2–methylpropene and cyclopentene. Calculate their **elpot** and LUMO surfaces. Don't forget to indicate the ion's charge in the "Calculation Setup".

From which side will the Br⁻ attack? Why? Will this attack lead to formation of *syn* or *anti* product? Is the attack an S_N1 or S_N2 reaction? Is the product optically active? Why or why not? Use the shape of the LUMO to justify your answer.

8. Is the major product formed in the previous question also the thermodynamic product of the reaction? Do the syn and anti products of cyclopentene differ greatly in stability? If not, why is the syn product not formed? How is your explanation supported by Spartan?

Aromatic Compounds   ACTIVITY 15

The word **aromatic** refers to a class of organic compounds that contain *benzene* and its relatives in their structures. Many compounds from natural sources such as benzene and toluene as well as many synthetic drugs such as Morphine are aromatic in part. Aromatic compounds are typically much more stable than alkenes, and unlike them, do not readily undergo typical alkene reactions such as electrophilic additions. In this activity you will use Spartan to study the structure, energy, charge distribution and resonance stabilization of benzene and cyclopentadiene.

benzene   cyclopentadiene
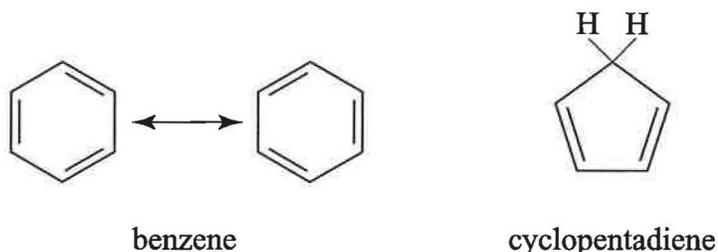
PROCEDURE

You may work individually or as a team of two. Do all optimizations using Semi-Empirical **PM3** model. Do not forget the charge when you are optimizing ions.

1. Build and optimize benzene. Calculate its **elpot** surface. Also build and optimize the hydrogen molecule.

2. Build and optimize 1, 3 – cyclohexadiene and cyclohexene.

3. Build and optimize 1, 3, 5 – cyclohexatriene. To build this molecule start with a cyclohexane ring, make the three double bonds, and *constrain* the CC single and double bonds to 1.54 and 1.32 A°, respectively. Check mark the "Constraints" box in the "Calculation Setup" dialog. *Click* on the ▼E in the toolbar to roughly optimize the molecule's geometry and then setup and submit the PM3 job. Calculate the **elpot** surface for the molecule.

4. Build and optimize cyclopentadiene, cyclopentadienyl cation and cyclopentadienyl anion. Calculate their **elpot** surfaces.

5. Build and optimize cyclopentene and cyclopentyl anion, the hydrogenation products of cyclopentadiene and cyclopentadienyl anion.

5. Calculate the "resonance energy" of benzene from the heats of hydrogenation in the previous question. Does this energy agree with that calculated in question (2)? Is it any closer to the experimental value? If not, how can we improve it?

6. Close benzene and cyclohexatriene. Open cyclopentadiene, cyclopentadienyl cation and cyclopentadienyl anion on screen. Display their **elpot** surfaces. Describe the differences you see in the electron densities of the three surfaces. Can you tell which species is aromatic? Use CC bond lengths to justify your answer. Does your choice agree with the Hückel's rule? Briefly explain.

7. Examine the energies of cyclopentadiene, the cyclopentadienyl cation and the cyclopentadienyl anion. Draw conclusion. Does your conclusion support your choice of the aromatic compound in the previous question?

8. Calculate the heats of hydrogenation for cyclopentadiene and the cyclopentadienyl anion. Are the reactions endothermic or exothermic? What does each heat specifically represent? from these data calculate the "resonance energy" for cyclopentadienyl anion. Is the anion as aromatic as benzene?

Heterocyclic Aromaticity ACTIVITY 16

Heterocyclic organic compounds contain one or more atoms other than carbon in their rings. Nitrogen, oxygen and sulfur are the most common heteroatoms. Many biologically important compound such as saccharin (sweetener) and penicillin have heterocyclic rings. Few examples of simple heterocyclic compounds are shown below.

furan   Pyrrole   dihydropyrrole   Pyridine
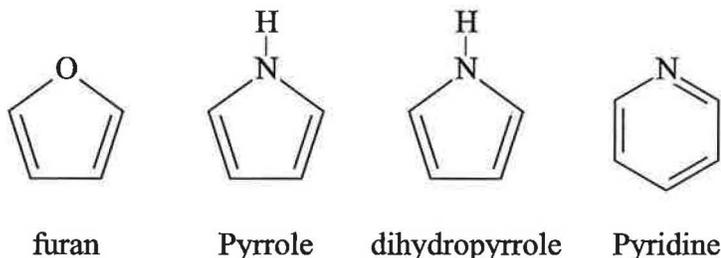
In this activity you will use Spartan to examine the energy, the charge distribution and the reactivity of several heterocyclic compounds.

PROCEDURE

Work as a team. Use Semi-Empirical **AM1** model for all optimizations. Besides the molecules to be optimized in the procedure, there will be a few more optimizations to do when you are answering the questions. Use AM1 model for them as well.

1. Build and optimize the molecules in the two series (three compounds each) stated below. Calculate their **elpot** maps as well (write their Lewis structures first).

   a) Furan, Dihydrofuran, Tetrahydrofuran

   b) Pyrrole, Dihydropyrrole, Pyrrolidine (tetrahydropyrrole)

2. Build and optimize benzene and pyridine. Calculate their **elpot** surfaces.

DATA COLLECTION

1. Open all six structures of step (1) on screen. Use *Ball-and-Wire* model. Arrange the molecules in two rows (furan row and pyrrole row). Maximize their size on screen (press and hold the **Shift** key while right clicking and moving the mouse). Label the carbons and the heteroatoms (labels in the **Model** menu). Hide the hydrogens. Also display the dipole moments (Dipole in the Model menu). Print a copy. Measure the carbon – carbon and the carbon – heteroatom

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9. Build and optimize the two potential cation intermediates in the electrophilic nitration of pyrrole. Calculate the LUMO surfaces of the two ions. Carefully examine the shape of the LUMO maps on the ring. Write resonance structures to justify your answer. How do these maps support the formation of the major product?

10. Is pyridine a stronger or weaker base than pyrrole? How do you decide from your data?

11. Unlike benzene the pyridine ring undergoes electrophilic aromatic substitutions with great difficulty. Use the two molecule's elpot maps and dipole moments (magnitude and direction) to explain this observed difference in reactivities.

Electrophilic Aromatic Substitution

I. Reactivity Effects of Substituents

Only one product forms when an electrophilic substitution occurs on benzene. When substituted benzenes undergo electrophilic attack, however, groups already on the ring affect both the **rate** of the reaction and the **site (orientation)** of the second substitution. The substituents are divided into two groups according to their influence on the *reactivity* of the ring:

A. **Activating groups,** also known as electron-donor groups are those substituents that make the ring *more* reactive than benzene itself (faster rate).
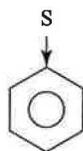
B. **Deactivating groups,** also know as electron-withdrawing groups, are those substituents that make the ring *less* reactive than benzene itself (slower rate).
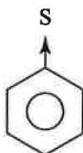
In this activity you will use Spartan to study the *reactivity* effects of a few substituents in electrophilic aromatic substitution reactions. Substituent effects on the *orientation* of the reaction will be studied in the next activity. Review the relevant chapter in your textbook before starting the activity. Pay particular attention to the proposed mechanism for the reaction as you will need to build a number of **benzenium** ion intermediates in doing this exercise.

PROCEDURE

The reactivity effects arising from the following substituents will be studied in this activity:

$$S = -Cl, \ -NO_2, \ -NH_2$$
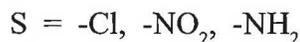
You may work as a team or individually. Use Semi-Empirical **AM1** model for all optimizations.

DATA INTERPRETATION & QUESTIONS

1. Examine the electrostatic potential surfaces for benzene, chlorobenzene, nitrobenzene and aniline (on the same scale as stated above). For which ring is the electrostatic potential more negative? For which is more positive? Rank the substituents in order of decreasing reactivity of the ring.

2. Display the HOMO surfaces for all four molecules. Focus on the shape of the HOMO on the ring carbons. Where do you expect the electrophilic attack to occur in each molecule (you can change the **isoval** to better to see the subtle differences)?

3. Calculate the energy changes for the slow step (carbocation formation) in the chlorination of the four molecules from your data. Which benzenium ion is more stable and why? Are the results consistent with your predictions based on the electrostatic potential surfaces in question (1)? Explain.

4. Write the reactions for the slow steps of the first and the second nitration of benzene. Do you predict the second nitration step to be easier or more difficult than the initial nitration of benzene? Use results from Spartan to validate your answer. (Hint: you need to build and optimize *two* more benzenium ions.)

Electrophilic Aromatic Substitution　　**ACTIVITY 18**

II. Directing Effects of Substituents

Only one product forms when an electrophilic substitution occurs on benzene. When substituted benzenes undergo electrophilic attack, however, groups already on the ring affect both the *rate* of the reaction and the *orientation* of the second substitution. The substituents are divided into two groups according to the way they affect the *orientation* of the incoming electrophile:

A. **Ortho-Para** directors, are those substituents that direct the incoming electrophilic, E^+, into the *ortho* and *para* positions.
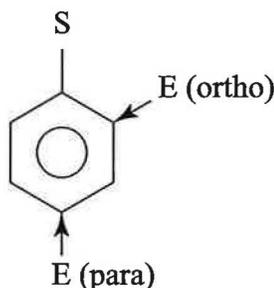
B. **Meta** directors, are those substituents that direct the incoming electrophile, E^+, into the *meta* position.
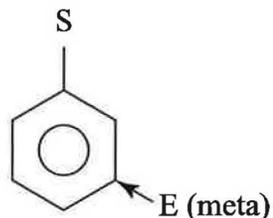
In this activity you will use Spartan to study the directing effects of a few substituents in electrophilic aromatic substitution reactions. Review the relevant chapter in your textbook before starting this activity. Pay particular attention to the proposed mechanism for the reaction as you will need to build a number of **benzenium** ion intermediates to carry out this exercise.

Make C_1, the carbon atom with the substituent (S) and number in the clockwise direction. Draw **a** resonance structure for each configuration that is consistent with your data (6 structures total). Position of the positive charge on the resonance structure should be obvious from the last column of your tables (atom with the greatest LUMO density!)

3. Arrange your data in the following manner for your report:

    a. The energy table from step 1 (one page)

    b. The bond-length data table plus the three resonance structures for the chlorination of aniline (one page).

    c. The same data and structures as in (b) for the chlorination of nitrobenzene (one page).

    d. The ortho, para, and meta LUMO maps for the chlorination of aniline (one page).

    e. The same data as in (d) for the chlorination of nitrobenzene (one page).

DATA INTERPRETATION & QUESTIONS

1. Examine the energies of the benzenium ion intermediates in table (1). Decide whether each substituent is an ortho – para or a meta director. Briefly explain the basis for your decision.

2. Use your energy data in table (1) to compare and contrast the directing effects of $-NH_2$ and $-CH_3$ substituents. What is the difference between them and what is it due to?

3. Are there any significant differences between the results for the chlorination and those for the nitration of toluene? Do you expect any difference? Why or why not?

4. Carefully draw resonance structures for the benzenium ions in the chlorination of aniline that are consistent with their LUMO maps. Based on the LUMO shapes only, which benzenium ion(s) is(are) most stable and why? How do these LUMOs provide information about the directing effect of the $-NH_2$ substituent?

5. Answer question (4) for the chlorination of nitrobenzene.

6. What do the six resonance structures drawn from the CC bond lengths specifically represent? Are they related to any of the resonance structures drawn from the corresponding LUMO maps? Briefly explain.

The S$_N$2 Reaction

This activity is a computational supplement to the synthesis of 1 – bromobutane from 1 – butanol experiment that you do in the laboratory (Williamson, 3rd ed., chapter 16).

$$CH_3CH_2CH_2CH_2OH \xrightarrow[S_N^2]{NaBr, H_2SO_4} CH_3CH_2CH_2CH_2Br$$
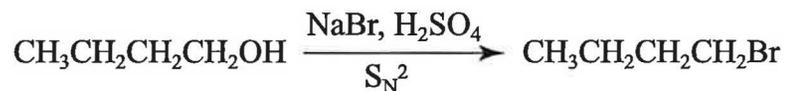
PROCEDURE

Build and optimize, using Semi-Empirical PM3 model, 1 – butanol and 1 – bromobutane. Calculate the **Vibrations** of each molecule (Activity 9). Animate and describe the characteristic vibrations in the two molecules. Use the calculated vibrations to "assign the spectrum" of each molecule. Locate the specific vibrations arising from the C – O and C – Br bonds and use them to justify the purity of your product. Recall that Spartan calculated frequencies are on the average about 10 – 12% larger than experimental frequencies.

Radical Chlorination of
1 – Chlorobutane

This activity is a computational supplement to the radical initiated chlorination of 1 – chlorobutane experiment that you do in the laboratory (Williamson, 3rd ed., chapter 18). The reaction produces four dichloroproducts in disproportionate amounts:

$$CH_3CH_2CH_2CH_2Cl \xrightarrow{\quad R^\bullet \quad}$$

$$CH_3CH_2CH_2CHCl_2$$
(1, 1 – product)

$$CH_3CH_2CHClCH_2Cl$$
(1, 2 – product)

$$CH_3CHClCH_2CH_2Cl$$
(1, 3 – product)

$$CH_2ClCH_2CH_2CH_2Cl$$
(1, 4 – product)
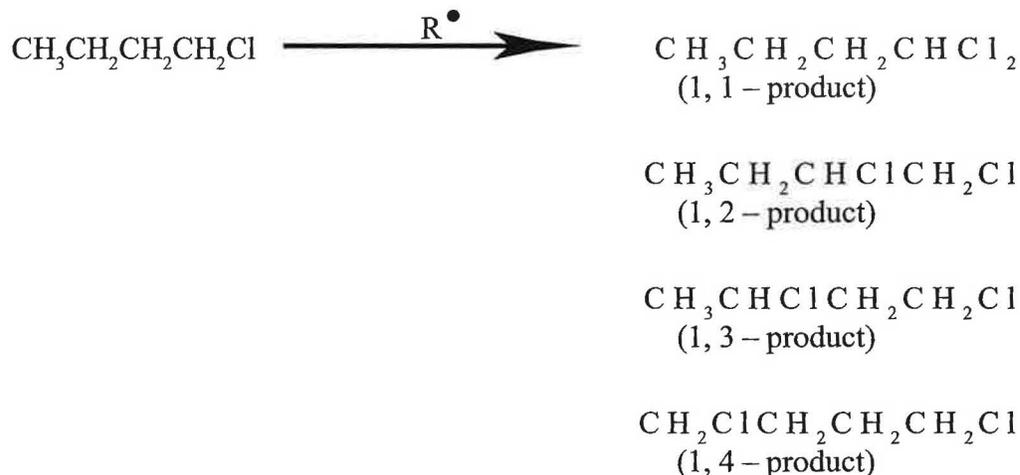
In the laboratory, the product distribution in the reaction mixture is determined by the gas chromatography (GC) analysis and is used to calculate the relative reactivities of the various hydrogens (1°, two 2° and 1° with a Cl attached) of 1 – chlorobutane. In this activity you will use Spartan to calculate: (i) the *steric* energies of the four products, (ii) the *heat of formation* of each product, and (iii) the energies of the *radical* intermediates leading to the formation of the four dichlorobutanes. You will then use these energies to get some information regarding the mechanism of the reaction.

PROCEDURE

The steric energy of a molecule can be calculated using a *Molecular Mechanics* program (see Appendix B for additional details). You will use the Spartan's **SYBYL**, a molecular mechanics optimization program, in this activity.

1. One by one construct the four dichlorobutanes. For each molecule first *press* ⊥ to do a very rough molecular mechanics optimization. Next setup a **Molecular Mechanics** with **SYBYL** job and submit for calculation. Record the steric energies (the usual way). For the products other than the 1, 1 – product (only one conformer) you should obtain and compare steric energies for the different conformers to determine if the *minimum* energy for each one has been found (6 conformers for the 1, 2 – and the 1, 3 – products each and 9 for the

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5. Answer question (4) with regard to the 1, 2 – and 1, 3 – products.

6. What information do the relative radical energies provide regarding the mechanism of the reaction?

7. Based on your experimental and calculated data, rank the three different calculated energies in an order of decreasing importance on the yield of the reaction. Provide a clear reasoning for your order.

Diels – Alder Reaction   ACTIVITY 21

This activity is a rather short computational supplement to the reverse Diels – Alder reaction that you do in the laboratory (Williamson, 3rd ed., chapter 49). Read the details of the experiment in your lab book. Briefly, when a cyclic diene (such as cyclopentadiene) and a cyclic dienophile (such as dicyclopentadiene or maleic anyhydride) react with each other, two *stereoisomers* may be formed. The two stereoisomers for the reaction between cyclopentadiene and maleic anyhydride are shown.
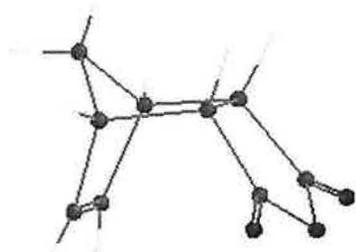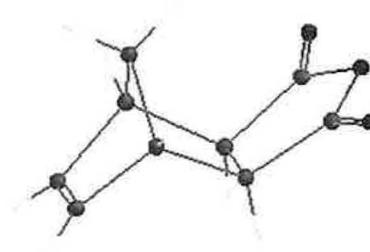
        endo isomer   *exo* isomer

Experimental data indicate that the *endo* isomer is the predominant product. To explain this observation, Otto Diels and his student Kurt Alder suggested a mechanism which involves overlap of the π electrons of the diene and the dienophile in the transition state. According to their proposed mechanism, the transition state for the formation of the *endo* isomer involves a sandwich where the diene lies directly above the dienophile. They suggested that this arrangement leads to a maximum overlap of the π electrons of the diene and dienophile resulting in a more stable transition state for the *endo* isomer (see page 574, Williamson). In this activity you will use Spartan to examine the validity of this mechanism.

PROCEDURE

The energetics of the two Diels – Alder reactions written below will be examined in this activity:

(1) $2\,C_5H_6$ ⟶ $C_{10}H_{12}$
                Cyclopentadiene   Dicyclopentadiene
                                  (endo + exo isomers)

(2) C_5H_6 + $C_4H_2O_3$ ⟶ $C_9H_8O_3$
            Cyclopentadiene   Maleic anyhydride   Diels – Alder adduct
                                          (endo + exo isomers)
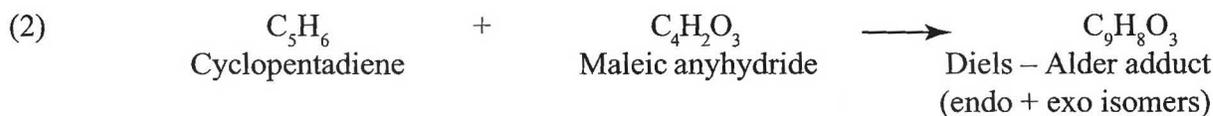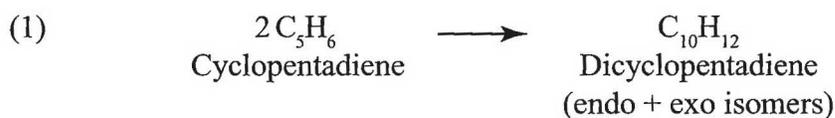
1. One by one build the *endo* and the *exo* isomers of the two products and calculate their *steric* energies using Spartan's *Molecular Mechanics* with **SYBYL** model (see previous activity).

Synthesis of Dibenzalacetone

This activity is a computational supplement to the synthesis of dibenzalacetone by the Aldol condensation that you do in the laboratory (Williamson, 3rd ed., chapter 37). Dibenzalacetone is prepared by condensation of acetone with two equivalents of benzaldehyde in basic solution

$$2\ C_6H_5CH + CH_3CCH_3 \xrightarrow{\ OH^-\ } C_6H_5 - CH = CHCCH = CH - C_6H_5$$

(with carbonyl O's above the CH, CCH₃, and CCH groups)
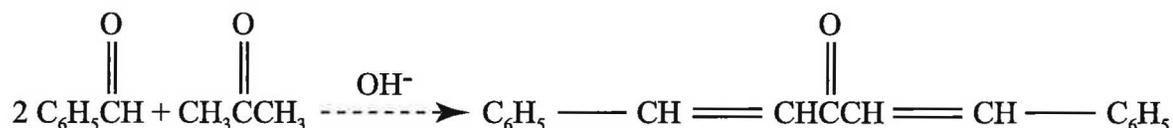
There are three geometric isomers of dibenzalacetone: *cis – cis, cis – trans, trans – trans* isomers. In the three isomers the alkene hydrogen atoms are either *cis* or *trans* to each other. In addition to the double-bond *cis – trans* isomers, single-bond *cis* and *trans* isomers for each of the three geometric isomers of dibenzalacetone also exist. There are a total of ten such isomers. The structure of one of these isomers (one of the three possible for the *trans – trans* isomer) is shown below:
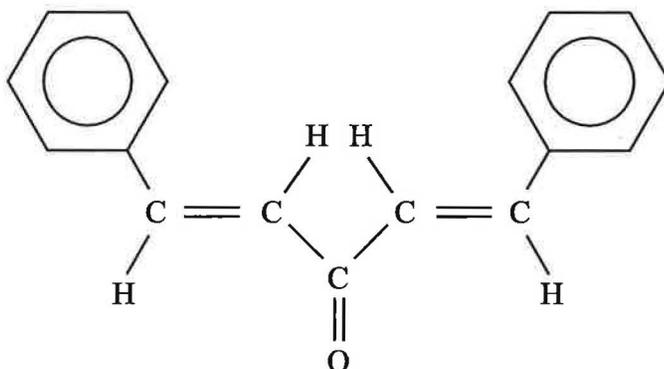
trans, s–cis, s–cis, trans

In this activity you will use Spartan to calculate the steric energies and/or heats of formation for as many of the ten possible isomeric dibenzalacetones as possible (some optimizations may not converge!) From the data you will uncover the relative stabilities of the isomers of dibenzalacetone.

Atoms and Molecules
An Overview

Appendix

A

Optimization (Minimization)
Computational Methods

Appendix

B

Electron Density Surfaces

Appendix

C

Other Types of Surfaces

Appendix

D

Property Maps

Appendix

E

Reaction Pathways
Translation State

Appendix

F

Vibrations

Appendix

G

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Atoms and Molecules An Overview

Keywords: *Conformation, Potential Energy, Global Minimum*

A simple idea of an atom was published by John Dalton, an English schoolteacher, in 1808. It states that "atoms are tiny particles that compose elements." For convenience, an atom can be viewed as a sphere with a particular radius which varies from element to element and with the charge on the atom. A molecule may be defined as a collection of atoms linked by bonds. With only two atoms, a linear molecule is possible (e.g. H_2, HCl, etc.). With more than two atoms, however, many three-dimensional structures result. Plastic model kits have been used for a long time to build simple mechanical models of molecules, and these can provide some useful information about their structure.

Bonds in the molecules are not rigid, but rather, they can bend and stretch. The time required for this bond bending and stretching is around 10^{-14} seconds. If the bending and stretching is taken to an extreme, the molecule will break. Molecules are also able to twist around their bonds, continually changing from one shape to another (~10^{-10} seconds). This means that a molecule which has free rotating bonds can take up many shapes (**conformations**) without breaking any of its bonds. Mechanical models are unable to represent any of these molecular behavior, but it is now possible to build such models in computers and simulate how these movements occur. If a molecule can have many conformations as stated, then what exactly is meant by the term "molecular geometry" or the "shape" of the molecule? To answer this question, we need to take a look at the "energy profile" of a molecule as the molecule is formed from its constituent elements.

ENERGY

The energy of a molecule is a very useful property for investigating the behavior of molecules. As an example, let see what happens when two hydrogen atoms at an infinite distance apart are brought together to form a bond, i.e., form the stable hydrogen molecule, H_2. Recall that a hydrogen atom is composed of a proton in its nucleus and a single electron.

how are the atoms bonded? What are their distances from each other? What is the effect of the lone pairs on the molecular structure? For molecules with more complicated shapes, few additional factors need to be considered. Among them are:

- Individual atoms within a molecule are not usually electronically neutral, although the molecule as a whole may be. As a result, atoms can attract and repel each other electrostatically even if they are not bonded together.

- A portion of the molecule may twist atound a bond (called torsional or dihedral movement) in the molecule resulting in many different conformations. What is the most stable conformation of the molecule?

- Multiple bonds (double, triple) are present within a large number of organic and inorganic molecules. What are the consequences of having such bonds on the molecular structure?

Fortunately, Mother Nature has found the actual structure of many molecules for us. These structures can be arrived at by doing experiments on the molecules as experimental chemists do. Alternatively, they can be determined by performing appropriate calculations on the molecules. The *latter* is the most basic goal of doing molecular modeling. To see how a computational modeling job finds the structure of a molecule, envision a many-dimensional potential energy surface (similar to the one discussed for hydrogen) for the molecule. *The actual structure of the molecule corresponds to the geometry the molecule posses at the very bottom of th potential energy surface* (called **glogal minimum**) This is because at this specific geometry all bond lengths, bond angles, torsions, etc. have their "ideal" values. As a result, the potential energy of the molecule is the lowest and, thus, the molecule is most stable.

Optimization (Minimization)

Keywords: *Optimized Struture, Molecular Mechanics, Molecular Orbital, Wavefunction,Semi-Empirical, ab initio, Hartree-Fock*

Optimization is the process of making small adjustments to a molecule's geometry until the "real" geometry of the molecule or one very close to it, i.e. the structure at the bottom of the potential energy surface, is obtained. As stated in appendix A, the most basic and important computational goal of a modeling software such as Spartan is to calculate this "real" geometry of the molecule. It can provide very useful information. In order to do any kind of modeling calculation, it is necessary to have a reasonable description of the molecule first. In Spartan, this is done by building a molecule using the atomic fragments in either the **Entry** or **Expert** model kit. The initial drawing is likely to have unrealistic bond lengths, bond angles and dihedral angles (torsions). After the initial structure is drawn, the next step is to take the constructed molecule through the optimization process. *The process of "optimizing" the structure involves first calculating the energy of the current structure and then iteratively making small changes to the structure's geometry(bond angles, bond lengths, torsions) to achieve a lower energy structure.* If the energy is lowered (improved), the initial geometry is forgotten, and the process is repeated with the current arrangement of atoms. The process is continued until all possible small changes will increase the energy of the system. At this point all the structural parameters are considered "optimized", the software has found the "lowest energy structure possible" and stops. Generally, the geometry of the structure found by the computer is very close to that of the actual structure found by nature, however, that is not always the case. A good initial guess at a struture rather than a random one to start the process is necessary to generate a structure which more closely resembles the "real" molecular geometry.

CALCULATIONS
COMPUTATIONAL METHODS

To start the optimization process, a modeling software makes use of some common "minimization algorithms" to treat the molecule and proceed downhill on the potential energy surface. These algorithms are mathematical models derived from applying several different levels of structure theory to molecules. There are many different algorithms available to solve a given problem, however, they can be broken down into two main classes of computational methods: 1) *Molecular mechanics* and 2) *Molecular Orbital* methods.

Within the framework of molecular mechanics calculations, there are different models to apply to the optimization task. Spartan supports two such models, namely **MMFF** and **SYBYL**, both of which are capable of providing reasonable quantitative accounts of molecular geometry and conformation. The difference between them and any other computational model presented hereafter is well beyond the scope of this discussion and will not be presented.

2. MOLECULAR ORBITAL METHODS

Molecular Orbital methods are based on Quantum Mechanics (QM) description of atoms and molecules. According to QM, atoms and molecules are made of nuclei and electrons. While nuclei are assumed to be stationary (not moving), the electrons are no longer described as point-like particles as first presented by Bohr's model of hydrogen atom. Instead, an electron is described as a "fog-like" entity or "electron cloud" that spreads over a region of space. The cloud's density varies from one point to the next and indicates the "probability" of finding the electron at each point. The electron density can be calculated using the rules of quantum mechanics and is very useful for describing the electron distribution in atoms and molecules.

The rules of quantum mechanics were developed by Erwin Schrödinger (1887-1961), an Austrian physicist who won the 1933 Nobel prize in physics for his pioneer work on the theory. Schrödinger's approach describes atoms and molecules in terms of a mathematical equation, the general form of which is:

$$\hat{H} \Psi = E\Psi$$

where, (Ψ), called the **wave function**, characterizes the electron's position in space, E is the total energy and ($\hat{H}$, called the energy operator) represents a set of complicated mathematical terms that produce the total energy of the system (atom or molecule). When this equation is analyzed, many solutions are found. Each solution is represented by a wavefunction (Ψ) that is characterized by a specific value of E. A specific wave function is often called an **Orbital**. It is postulated that the square of the wave function, (Ψ)^2, corresponds to the "probability" of finding an electron in a particular place in space.

Electron Density Surfaces

Keywords: *Isodensity Surface, Electron Density Surface, Bond Density Surface*

The rules of quantum mechanics state that electrons have wavelike properties and, thus, it is not possible to say where the electrons exactly are. The Heisenberg uncertainty principle also concludes that electron positions can never be known precisely. So, how do we define or visualize the position of an electron within an atom or a molecule? According to quantum mechanics the best that one can do is to say how probable it is for an electron to be at some particular location in space. Consider H atom as an example.

The graph indicates that electron density in hydrogen atom varies with distance from the nucleus. The electron density is greatest near the nucleus and, as we move away from the nucleus, the probability of finding the electron at a given position decreases rapidly. Note that there is no clear edge to the electron density; it just gets smaller and smaller with increasing distance from the nucleus. For molecules, the electron density spreads out nonuniformly over a region of space. Considering the fact that the electron density does not fall off to zero, then the problem is how to define a "boundry" for the electron density when one reaches the points of low electron densities? One way to deal with this problem is to examine each molecule's electron cloud and choose the "molecular boundry" as the point where each electron cloud has the same electron density. Constructed in this fashion the resulting skin-like surfaces, known as *isodensity surfaces* or simply *density surfaces*, provide the distribution of electrons in the molecule.

Different types of electron density surfaces can be built and displayed by Spartan following the optimization of a molecule's geometry using any *molecular orbitals* computation method. Different surfaces have specific applications. The 0.002 electron density surface (also known as the total **electron density** surface), for example, is used to define the size and shape of the molecule. Nearly all of the electron density (typically 98%) lies inside this surface. The 0.002 density surface and the space-filling model of the molecule, C_5H_6, are shown for comparison.

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A third useful electron density surface can be constructed by taking a plane that slices through the molecule and map the variation in electron density in this plane. This kind of surface is called an *electron density slice*. It provides a two-dimensional contour map of the electron density.

The electron density varies considerably in this plane and a color code based on the visual spectrum is used to show this variation: blue (highest density) > green > yellow > orange > red (lowest density). The slice can be moved across the structure on screen to examine the electron density variation in the molecule.

Other Types of Surfaces

Keywords: *Molecular Orbitals, HOMO, LUMO,*
Spin Density, Electrostatic Potential

Besides the electron density surfaces, Spartan provides for graphical display of other quantities resulting from molecular orbital calculations. Among the most useful quantities are the *"molecular orbitals"* themselves, the *"spin density"* (when unpaired electrons are present) and the *"electrostatic potential."* Any of these quantities can be represented as a surface of constant value and uniqly displayed in *dot*, *mesh*, *transparent* or *solid* style. These quantities are briefly discussed in this appendix.

1. MOLECULAR ORBITALS

Molecular Orbital (MO) theory describes formation of covalent bond in terms of a mathematical combination of atomic orbitals (s, p, d....atomic orbitals or wavefunctions) to form **molecular orbitals (MOs)**. Molecular orbitals are to molecules what atomic orbitals are to atoms. Namely:

●   Electrons in an atom occupy atomic orbitals. In a molecule, the electrons occupy molecular orbitals. Atomic orbitals no longer exist.

●   An atomic orbital describes a region of space around an atom where an electron is likely to be found. A molecular orbital (MO) describes a region of space in a molecule where electrons are most likely to be found.

●   An atomic orbital can hold two electrons with opposite spins. Each molecular orbital can hold two electrons as well and the spins have to be opposite.

●   Similar to an atomic orbital, a molecular orbital has a specific size, shape and energy.

●   There are occupied and unoccupied atomic orbitals for an atom. Similarly, there are occupied and unoccupied molecular orbitals in a molecule. The unoccupied MO's have higher energies.

A. H_2 MOLECULE

We know that H_2 is a very stable molecule, and is lower in energy than the separated hydrogen atoms by 432 KJ/mol. According to MO theory, combination of the *two* 1s atomic orbitals of hydrogen leads to *two* H_2 molecular orbitals. The lower energy bonding MO is filled, and the higher energy antibonding MO is unfilled. Spartan's computer-generated molecular orbitals of H_2 are shown below.

HOMO   LUMO

For MO_1 (HOMO), the greatest electron probability is *between* the two nuclei. This states that the electrons in this MO spend most of their time in the region between the two nuclei, thereby bonding the atoms together. We refer to this type of molecular orbital as **sigma (σ) bonding MO**. For MO_2 (LUMO), the greatest electron density is on either *side* of the nuclei and there is a node in the central region between the nuclei. We refer to this type of orbital as **sigma(σ*) antibonding MO**. The color of the two lobes in the molecular orbitals corresponds to the sign (+ or -) of the actual wavefunctions.

B.   C=C BOND

The carbon-carbon double bond is present in a large number of organic molecules. With two bonds holding the carbons together, we need *two bonding* MO's to describe the C=C bond. The Spartan's generated HOMO and LUMO together with the MO energy diagram for the C=C bond in ethylene, C_2H_4, are given below.

HOMO   LUMO

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HOMO is easily recognized as a lone pair on sulfur atom. The electrons in this molecular orbital are the easiest to donate by SO_2. HOMO (-1) represents the lone pairs on the two oxygen atoms. They are the next highest in energy.

D. BF₃

The lowest unoccupied molecular orbital (LUMO) of BF_3 is shown below. LUMO represents the place where it is easiest to *put* the next pair of electrons. In BF_3, LUMO is centered on boron. This means that if BF_3 encounters a Lewis base (also called a nucleophile) such as H-, OH-, the electron pair from the base attack boron atom of BF_3 and a chemical reaction takes place. Thus, a LUMO reveals the likely site for nucleohilic attack. Note that both sides of BF_3 are equally possible to undergo such nucleophilic attack.

2.   SPIN DENSITY

For molecules that contain a single unpaired electron (commonly called radicals), the spin density surface provides information about the location of the unpaired electron in the molecule. The Spartan calculated spin density surfaces of propyl radical ($CH_3CH_2\overset{\bullet}{C}H_2$) and allyl radical ($CH_2=CH\overset{\bullet}{C}H_2$) are shown for comparison.

For ammonia and methanol, the "electron rich" regions are represented by the lone pairs on nitrogen and oxygen, respectively. For benzene, the "electron rich" regions are above and below the plane of the ring. Electrophilic attack should occur here with equal probability on each side of the ring.

Property Maps

Keywords: *Elpot, HOMO map, LUMO map*

A property (such as HOMO, LUMO, electrostatic potential, spin) can be color encoded on an electron density surface by Spartan to give additional information beyond molecular size and shape. This so-called "mapping" is done by selecting a property from the "property" pull-down menu, and then mapping the property onto surfaces in the "Add Surface" dialog (Tutorials 1 and 2).

The above operation maps electrostatic potential (from property menu) onto the total electron density surface (from surface menu). Note that the requested property surface appears in the "Surface List" dialog. To generate this surface, Spartan first calculates the total electron density and the electrostatic potential, draws the electron density surface around the molecule, and then maps (by color encoding) the calculated potentials on the electron density surface. Those parts of the surface where the potential is most negative (electron rich) are colored red, and parts where the potential is most positive (electron poor) are colored blue. Intermediate potential values are colored according to: red<orange<yellow<green<blue. The resulting surface, commonly called the **elpot** surface conveys information about the overall charge distribution in the molecule. Generation of water's "elpot" surface is presented as an example of this process.

map shows that the central carbon is the most electron poor site in the molecule. This is where it is easiest to put a pair of electrons and thus it is the likely site for nucleophilic attack.

D.   NITRIC ACID & NITROUS ACID

The electrostatic potential map, elpot, can reveal information useful in predicting relative acidity of molecules. However, valid comparisons require maps that use the same potential (or color) scale. The potential maps of nitrous acid (HNO_2) and nitric acid (HNO_3) on the same potential scale are shown for comparison. The maps show that the hydrogen atom in nitric acid is far more positive than hydrogen in nitrous acid. In other words, nitric acid is a stronger acid when compared to nitrous acid.

E.   LEWIS ACID-BASE REACTION

Property maps can also reveal information useful in predicting chemical reactivity of molecules. As an example, let's consider sulfur trioxide, a strong lewis acid, and its reaction with water, a lewis base, to form sulfuric acid. The elpot maps for the reaction show that sulfur atom draws in electron density from oxygen of water and that causes the water molecule to attach to sulfur trioxide. A proton shift occurs in the next step to form sulfuric acid (not shown).

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Reaction's Pathways
Transition State

Keywords: *PE Diagram, Transition State, Activation Energy,*
Kinetic Product, Thermodynamic Product

Potential energy diagrams are commonly used to describe the progress of chemical reactions. Understanding a PE diagram is important for anticipating

Reaction Progress

Energy minima correspond to the "equilibrium structures" of reactant and product. The arrangement of atoms found at the top of the potential energy barrier is called the **"transition state"** structure. The relative energies of the two minima correspond to the "relative stabilities" of the reactant and product. Here, the product is more stable because it has a lower potential energy than the reactant. In other words, this diagram represents an exothermic reaction. The energy of the maximum relative to the reactant minimum is called the **activation energy**. This is a threshold energy that must be overcome to produce a chemical reaction. A reaction rate (speed) depends on the size of the activation energy Ea. The difference in the relative energies of the reactant and product, E, however, has no effect on the rate of the reaction.

What is the structure of the transition state? To answer this question, consider that for a chemical reaction to proceed a number of bond formation and bond breaking must take place as the reactants are converted to products. The transition state represents a *transient* arrangement of atoms in which all the bonds involved in the reaction progress are either partially formed or

Pathways 1 and 2 produce two different products and proceed via different transition state structures. Product 1 is formed faster (lower Ea) but it is less stable (more potential energy). This product is known as the **kinetic product**. Product 2, however, is more stable (less potential energy) and it is known as the **thermodynamic product**. Often, one of the two products is formed as the major product of the reaction, irrespective of barrier heights or product energies. It shall be clear from this diagram that prediction of the major product made on the basis of product stabilities alone can be wrong. Rather, relative proportions of the products depend on the relative stabilities of the products as well as the relative heights of the energy barrier (TS1 vs. TS2), and the temperature of the reaction. In general, higher temperatures favor the thermodynamic product while at lower temperatures the kinetic product is favored.

Before we leave this subject two final points should be made. First, the energy diagrams presented in this section exemplify reactions which take place in one step. A complete reaction pathway, however, may have several steps and involve several different transition states and reactive intermediates. Second, the transition state structures *can not* be determined from experiments because they are not stable. This, however, is not a difficulty for Spartan. Although there exists very little information about the geometries of the transition states from experimental data, Spartan provides ways to perform a transition state optimization when it is furnished with a reasonable "guess" of a transition state structure to start. An optimized transition state structure can provide some very useful insights into the mechanism of a chemical reaction. The transition state optimization, however, is more difficult than a typical equilibrium geometry optimization and will not discussed here.

Vibrations

Keywords: *Wavenumber, Fundemental Frequency, Molecular vibration*

The infrared (IR) radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions (l: 7.8×10^{-5} cm to 0.01cm). Frequencies in IR are commonly expressed in **wavenumbers** (ν) rather than in hertz, Hz. The wavenumbers, expressed in cm^{-1}, is simply the reciprocal of the wavelength in centimeter.

$$\nu = \frac{1}{\lambda(cm)}$$

Of greatest practical use to chemists is the IR midportion between 400 and 4000 cm^{-1}. Why? In reality, all molecules posses a certain amount of energy, called internal energy, distributed throughout their structure. A part of this energy causes bonds to stretch and contract (as if there were a "spring" connecting the two atoms) and the atoms to wag back and forth. Collectively, these types of motions are referred to as **molecular vibrations**. It is known that a molecule can stretch or bend (vibrate) only at specific frequencies (or energies); i.e. the frequencies are *quantized*. In other words, only certain kinds of vibrations are allowed. Some examples of allowed vibrations are shown below:

In-plane bending (scissoring)
(CO_2: 670 cm^{-1})

Out-of-plane bending (scissoring)
(CO_2: 670 cm^{-1})

In-plane bending (scissoring)
(CH_2: 1470 cm^{-1})

Consider any one of the allowed vibrations as an example. When a molecule is irradiated with infrared radiation, energy is absorbed by the molecule *when* the frequency of the radiation matches the frequency of the vibrational motion. This absorbed radiation causes an increase in the amplitude of that specific vibration. By scanning all frequencies in the IR region (400-4000 cm^{-1}, done automatically by an IR spectrophotometer), one can determine all of the frequencies absorbed by the molecule. And since each frequency corresponds to a specific molecular motion, we can see the kind of vibrations a molecule has by measuring its so-called "IR spectrum". By analyzing those vibrations, one can find (by reference to generalized charts of characteristic bond and group frequencies) what kinds of bonds and functional groups are present in the molecule. This is the basis of IR spectroscopy.

How many different vibrations a molecule can have? A nonlinear molecule of n atoms has 3n-6 fundamental vibrational frequencies (3n-5 for linear molecules). Take ethanol, C_2H_5OH, as an example. There are nine atoms in the molecule and 21 (3x9-6) different vibrations are thus possible. The theoretical number of fundamental vibrations , however, are seldom observed in the IR spectrum of the molecule. The reasons are not discussed here. One important point, however, needs to be stated here. *Only those vibrations that result in a change in the dipole moment of the molecule are observed in IR.* These vibrations are referred to as **"IR active"** vibrations. This explains why the asymmetric stretching vibration in carbon dioxide is IR active while the corresponding symmetric stretching is IR inactive.

From the discussion above, it shall be clear that molecular vibrations are a useful tool for determining molecular structure. Fortunately, Spartan allows one to calculate and animate the vibrational modes of a molecule when *"frequency"* calculation is requested in the setup of the computation. The "Frequencies" box in the calculation setup dialog needs to be check marked (✔) for this purpose (Tutorial 3). When the calculation has completed, the individual vibrations can be animated using ball-and-spoke or any other structure models that are available in the **Model** menu. Furthermore, calculated frequencies are reported in units of cm^{-1} for easy comparison with the experimental frequencies for structural identification of the molecule.

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