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# Preliminary results in working with molecular modeling software

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Abstract--In order to help facilitate the growing need for an understanding of periodic trends in molecules, an attempt was made to use a molecular modeling software package (ChemCad) to make a series of ab initio calculations of various properties of diatomic molecules. Limitations of the package precluded calculations for strictly diatomic molecules, as well as precluding consecutive substitution of a large series of atoms into a larger molecule. This attempt does have significance in that it has allowed the physics department at Southern College to more effectively communicate with molecular modeling software developers and users.

## I. INTRODUCTION

There is a growing interest in the classification of molecules coinciding with the increasing level of sophistication and accuracy of experiments. Bergman notes that "trends of behavior in series of atoms or molecules are today very effectively used by theorists to uncover, among the unsuspected variety of measured phenomena, what one might call primitive patterns of understanding . . . of atomic and molecular forces at play in chemical reactions, energy losses in surface scattering, astrophysical processes, plasma chemistry and other apparently quite unrelated areas."[1] We are helping in this process by analyzing and comparing the values for various molecular properties among diatomic molecules, in order to help establish that the trends are periodic in diatomic molecules.[2-5] Since there are so many molecules for which there is no existing experimental or theoretical data,[2] we undertook the project discussed in this paper -- an attempt to make *ab initio* calculations for some of the molecular properties for a large number of molecules using a computer-assisted drawing package with interfaces to minimum energy, geometry-optimizing programs.

Originally our plan was to "construct" diatomic molecules, optimize their geometry and electron structure, and use the calculations to get values for some interesting molecular properties. These values would then be plotted using other programs developed for the research work. After working with the software package for awhile, we realized that a somewhat different approach would be necessary; starting with a larger molecule, we would consecutively replace one of its atoms with each atom from a series of atoms and perform a similar analysis on it. This approach would hopefully help us get around some of the limitations of the package and let us demonstrate existing periodicity.

## II. THEORY

There are several properties which collectively give an accurate description of a given molecule. One type, the Potential-Surface properties, includes such things as internuclear separation, dissociation energy, and vibrational frequency. It is this type of property which the program was designed to calculate. One approach to demonstrating periodic trends in diatomic molecules involves constructing a three dimensional graph for each of the molecular properties to be studied, using a series of atoms for the x and y axes. The position along the z axis at any point (x,y) is determined by the value of the property for the diatomic molecule obtained by joining the atoms at the x and y coordinates. Valleys, ridges and hills in the resulting surface show the periodic trends.[5,6]

This method can be extended to more dimensions for larger molecules, but the computation and interpretation processes quickly become very complicated. However, as an alternate method when working with larger molecules (cyclobutane in our case), all but one of the atoms can remain constant, leaving just one as a variable. A graph can be constructed by plotting the data values versus the one atom.[2,5]

## III. The Software

The software package used in our attempt at making global calculations consisted of ChemCad, a menu-driven molecular drawing program, with interfaces to two optimization programs. ChemCad itself can be used to design molecules from a choice of 72 different atoms, display them in 3-D if so desired, and view them from any angle statically or dynamically. It has an extensive library of pre-optimized rings and substituents commonly used in organic chemistry. Bond lengths and angles can be determined from within this program, although it appears to adjust values in order to keep the molecules on a "good drawing scale." To get precise determinations it is necessary to use one or both of the auxiliary programs.

The one we used more frequently, MM2, uses reiterative techniques to lower the total energy of the molecule, putting it in its most stable state. It calculates values for bond lengths and stretching energy, bond and dihedral angles, and final steric energies, as well as dipole moments, compression energies and other properties.

The other program, Modified Neglect of Diatomic Overlap (MNDO) is a semiempirically parameterized version of Neglect of Diatomic Differential Overlap (NDDO), which assumes zero differential overlap between atomic orbitals of different atoms. Using the eigenvalues of appropriate matrices, which it builds, it yields values for heats of formation, ionization potentials and dipole moments, as well as interatomic separations.

## IV. RESULTS

### A. Diatomic molecules

At the very onset of this project we made some calculations, using ChemCad alone, for bond lengths of some diatomic molecules. The program appeared to be using a value close to the sum of the covalent radii of the two atoms, except in the case of the rare gases for which it yielded significantly shorter lengths than the sum of the covalent radius and van der Waals radius, or the sum of the two van der Waals radii. (See Table I).

**TABLE I.** ChemCad values for radius for four diatomic molecules compared with existing molecular data for internuclear separation and covalent radii.

| Mol. | ChemCad (Å) | Mol. data[a] (Å) | sum of covalent radii[b] (Å) |
|---|---|---|---|
| $O_2$ | 1.46 | 1.2075 | 0.74 + 0.74 = 1.48 |
| $Ar_2$ | 1.96 | 3.758 | 1.54 + 1.54 = 3.08 |
| $H_2$ | 0.64 | 0.74144 | 0.37065 + 0.37065 = 0.7413 |
| ZnC | 2.020003 | . . . | 1.333 + 0.77226 = 2.10526 |

[a] K.P. Huber and G. Herzberg, *Constants of Diatomic Molecules*, (Van Nostrand, Reinhold, New York, 1979).

[b] J.A. Campbell, *Chemical Systems--Energetics, Dynamics, Structure*, (W.H. Freeman, San Fransisco, Calif., 1970), p. 313.

The next step was to construct diatomic molecules with ChemCad and to optimize them using MM2. After looking at the results for $B_2$ and $O_2$ (with single, double, and triple bonds), it became apparent that ChemCad was not giving MM2 all the information necessary to complete meaningful calculations for these molecules. Although the resulting values for bond lengths were not too far from the known values (See Table II), with the exception of singly and doubly bonded $B_2$, MM2 also yielded error messages stating that constants for bond types and angles would have to be read in by the user. This situation was not too helpful, since the whole point was to determine the constants theoretically, so we moved into a new stage of the project.

**TABLE II.** MM2 values for internuclear separation of $B_2$ and $O_2$ compared with known values.

| Source | $B_2$ (Å) | $O_2$ (Å) |
|---|---|---|
| ChemCad | | |
| single bond | 2.330 | 1.460* |
| double bond | 1.640 | 1.460* |
| triple bond | 1.909* | 1.460* |
| Huber & Herzberg[a] | 1.590 | 1.20752 |

*Accompanied by error message--"Read in bond lengths and angles."

[a] See Table I.

## B. Larger molecules

Our next goal was to substitute various atoms into a larger molecule (on which MM2 could perform calculations) and analyze the results. We chose to use cyclobutane from ChemCad's pre-optimized ring library for this molecule. This particular choice was made basically because cyclobutane is a fairly simple molecule, yet large enough, we hoped, to allow us to substitute a large variety of atoms without running into the difficulties faced in dealing with diatomic molecules.

In the first set of substitutions, all four $sp^3$ carbon atoms were replaced with $sp$ hybrids and then with $sp^3$ hybrid nitrogen atoms. MM2 greeted both trials with the same error messages it gave for the diatomic case.

For the next set of substitutions, only one carbon atom one the cyclobutane was treated as a variable. The results from this study did yield some error message free calculations (See Table III), but, perhaps more importantly, it directed us to one of ChemCad's fundamental restrictions -- in order for a molecule to optimized by MM2, it must obey the octet rule. This is demonstrated by the fact that of the list of possible substitution atoms used by ChemCad, the only ones which did not yield error messages were Si, the $sp^2$ hybrid C and a cyclopropyl type Carbon, each of which has four valence electron which can combine with the other

Carbons in such a way that all will have a full octet.

**TABLE III.** MM2 values for energy and dipole moment of optimized cyclobutane with one C atom replaced with a substituent atom.

| | Substituent atom | | |
|---|---|---|---|
| | C($sp^2$) | C(cyclopropyl) | Si |
| Final Steric Energy (Kcal) | 36.5150 | 43.4067 | 26.3447 |
| Compression | 1.1483 | 1.4413 | 4.5528 |
| Bending | 23.1983 | 31.1812 | 23.3699 |
| Stretch-bend | -1.4747 | -2.0094 | -8.6285 |
| Vanderwaals | | | |
| 1,4 energy | 2.4812 | 2.1967 | .5165 |
| Other | -.2826 | -.2709 | -.1695 |
| Torsional | 11.4445 | 10.8678 | 6.7036 |
| Dipole Moment (D) | .422 | .213 | .936 |

## V. CONCLUSIONS

Although it would seem at first that this whole experiment was fruitless, it actually has had, and hopefully will continue to have, some very positive results.

(Obviously the actual numbers are not one of them.) First of all, the experience has given us an opportunity to familiarize ourselves with molecular modeling software. This, in turn, has allowed us to communicate more effectively with people who develop and market similar packages, making them aware of possible modifications which would allow them to make global molecular calculations, similar to the set of atomic calculations made by Fraga.[7] We are in the process of negotiating with molecular modeling software developers about future involvement with global calculations of values for various properties. At the least this communication has increased the level of awareness of a need for such calculations.

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**Endnotes**

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