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Visualization of electronic properties of molecules in chemical reactions

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Modern computational methods allow for the tracking of entire chemical reactions, ranging from initial reactants, through transition states, and to the final products. They also permit the computation of a variety of properties that can change as the reaction proceeds from start to finish. Visualization of these reactions is often difficult and usually limited to static displays of specific steps along the reaction paths. This article describes a program, Reaction Viewer, that we have developed to visualize a chemical reaction dynamically. The article also describes the use of this program to see the movement of electrons and other electronic effects, as well as steric ramifications during the reaction.

INTRODUCTION

Computational chemistry has become an extremely important tool in understanding chemical reactions and mechanisms. With the vast computing capabilities now available, it is possible to utilize sophisticated theoretical approaches to "watch" chemical reactions occur. In this way, intermediates, transition states, and potential products can be, in many cases, accurately predicted. In addition, it is possible to calculate with surprising accuracy the energy of activation (ΔE_{act}), a measure of the ease or difficulty for a certain reaction to occur.

The U.S. Army Edgewood Research, Development and Engineering Center (ERDEC) is actively involved in employing many aspects of computational chemistry to solve mission-related problems. Pursuant to this, molecular orbital metrologies have been used to examine the geometry and electronic structure of chemical compounds, as well as to predict reaction mechanisms and reaction pathways.[1–10] Because molecular orbital methods deal almost exclusively (to a first approximation) with electrons, it is possible to compute and follow how a reaction would proceed. A major problem with this, however, is the sheer volume of data created by a single reaction pathway calculation. Large tables of numbers are created for each step along the path and with a minimum of 20 steps (usually much greater), the information overflow becomes unwieldy very rapidly.

Fortunately, chemistry is basically a visual science. Molecular models and pictures are very much a part of the tools in a chemist's toolbox. It is, therefore, not surprising that the enormous number of tables resulting from a calculation can be reduced to series of pictures that can be easily understood and interpreted. There are a number of programs available today that can be utilized to view ground state geometries or their stationary points.[11] These programs are not capable, however, of viewing an entire "movie" of multiple molecular orbital or molecular dynamics computations. This constraint limits their usefulness in examining chemical reactions. This article describes our efforts in developing an animation program called Reaction Viewer for the dynamic display of semiempirical molecular orbital results. We show how the immense information contained in a series of molecular orbital calculations can be simplified by real-time visualization using the Reaction Viewer.

The Reaction Viewer is also valuable in providing insight on how two reactants come together, and how and when bonding (as opposed to electrostatic attraction) occurs during a chemical reaction. In addition to visualizing the reaction, a number of properties that change during the course of a reaction can also be visualized. For example, the Reaction Viewer displays the energy distribution of the chemical reaction. This helps a chemist not only visualize the process of the reaction and identify its crucial states, but, more importantly, examine the relationship between the molecular structure and its corresponding energy value at every point during the reaction.

There are a number of other properties that change during the course of a reaction and that can be computed by molecular orbital methods. One of the most important properties in a chemical reaction is the distribution of electron density, either as bonds form and break, or as the density builds up and decreases on a particular atom (in the form of

Color Plates for this article are on pages 304–306.

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formal charge). In each of these cases, it is possible to "watch" this phenomenon using molecular orbital methods and molecular graphics. This article also describes our efforts to add the visualization of electronic properties into the dynamic reaction display.

MOLECULAR ORBITAL METHOD

There are a number of theoretical methods available for use by the practicing computational chemist today, both commercial and public domain.[12] Molecular orbital (MO) methods differ from molecular mechanics and molecular dynamics computations in a number of key areas. For the purpose of this discussion, the primary difference is the ability of MO methods to consider electrons explicitly. Although this greatly increases the time for computation, it enables us to examine in detail how bonds break and form.

Molecular orbital methods range in complexity from the relatively unsophisticated extended Huckel method, to the time-consuming ab initio approaches. Because of the need of the requirement for doing 20 to 30 computations for a single dynamic display coupled with the need for assuring that the wavefunction is fairly accurate, the NDDO (neglect of diatomic differential overlap) methods were chosen as the most appropriate for our task.[13,14] These methods, found within the MOPAC and AMPAC program suites, provide the capability to carry out calculations on fairly large structures, but still retain confidence in geometry and in electronic configuration.[15]

DEVELOPMENT OF REACTION VIEWER

The Application Visualization System (AVS) is an industry standard visualization application software and development environment.[16] AVS users can construct their own visualization applications by combining software components into executable flow networks. The components, called modules, enable users to extend the base capabilities of AVS for a specific application.

There have been previous attempts at developing modules for displaying MOPAC results, one included in the now defunct Chemistry Viewer,[17] and one developed as part of ConvexAVS.[18] The primary function of both of the modules/networks is to read a stationary geometry, and display that geometry for verification purposes. Unfortunately, there is no provision in either package to read and display a series of geometries, as one would have from a reaction (as depicted in a reaction coordinate calculation). Also, both packages were limited as to the information that could be displayed on the surface of molecule. Because of our interest in studying how reactions occur, we required a module that could dynamically display the geometries computed from a reaction calculation, as well as relevant numeric thermodynamic information and electronic information.

Because AVS has a modular architecture, developing a graphical display program for visualizing MOPAC results required only the writing of one module, that of a MOPAC reader, and the construction of an appropriate AVS network. The Read_Mopac module reads a MOPAC-generated output file, and extracts pertinent information regarding structure, formal charges, energy values, atom types, and bonding information. The major advantage of this module over similar modules is the ability to extract all structures from a reaction coordinate computation. These structures, complete with all supplementary information, are stored in sequential frames, permitting a dynamic display of the "movie."

The AVS network, Reaction Viewer, created to display MOPAC results dynamically is shown in the lower right-hand corner of Color Plate 1. This network reads the pertinent information using the Read_Mopac module, and displays the molecular structure and its properties through the AVS library modules tube, generate colormap, label, col_legend2, animated integer, geometry viewer, and graph viewer. Color Plate 1 shows a sample display of the program. The left-hand column is the control panel. A user can pick different options provided by this program using the mouse. The upper right-hand corner shows the display of a molecular structure for a particular state of the reaction of methylphosphonodifluorodate (DF) and methoxysilane. The graph of the middle column shows the simple energy distribution graph of this chemical reaction.

The detailed functions provided by the Reaction Viewer and the ways chemists can use them to enhance their studies are discussed in the following sections.

DYNAMIC VIEW OF CHEMICAL REACTION PROCESS AND ENERGY DISTRIBUTION

The basic function of Reaction Viewer is to extract the desired information directly from the output file of MOPAC and animate the change of structures of a molecule in different computations. The Reaction Viewer displays not only the structure of the molecule associated with each computation but also shows a diagram of the energy values versus computations. It allows a user to see the change of energy as the corresponding structure of the molecule changes.

For example, when an animation starts, a display of the molecular structure of the beginning state of a reaction is shown in a window. A simple energy distribution line graph with an x to indicate the energy value associated with the current displayed molecular structure is displayed in a separate window. These two pictures are shown on the first row of Color Plate 2.

As the animation processes to state 2, the display of the new molecular structure replacing the one for the previous state is illustrated at the right-hand side of the second row of Color Plate 2. The corresponding simple energy line graph with two x's indicating energy values associated with the current and previous states is shown at the left-hand side. Note that the rightmost x on the energy distribution line graph indicates the location of the energy value in the graph for the current displayed molecular structure. Thus, at each state of an animation, a user can immediately locate the energy value associated with the current displayed molecular structure from the energy distribution.

Identifying important states in a reaction through this display is also simple. This is because a user can visualize the exact position of the energy value on the graph for any state of a reaction during the animation. Therefore, when the animation proceeds to the state associated with a maximum energy value, the user can stop the animation to take

a closer look at the molecular structure for the transition state of the reaction.

Color Plate 2 shows some snapshots of molecular structures and their corresponding dynamic displays of the energy distribution for different stages of the animation. This animation helps a chemist not only visualize the process of the reaction and identify its crucial states, but more importantly, examine the relationship between the molecular structure and its corresponding energy value at every state of the reaction.

VISUALIZING FORMAL CHARGES AS THE REACTION PROCEEDS

The ability to read and display formal charge information and the ability to display atom labels are important to the computational chemist, both in understanding the chemistry behind a reaction, and in ensuring that the input structure is correct. By coloring the sphere (normally based on atom type as shown in Color Plate 1) by formal charge in the Reaction Viewer, it is possible to view how electrons migrate both within and between molecules as a reaction occurs. Labels, both numeric and atomic symbol, as shown in Color Plate 3 permit a chemist to debug structures and interpret reactions more easily.

Formal charge information is available from each computation along the reaction path. Unfortunately, it is often difficult to follow precisely how the formal charges change as the reaction occurs, and requires repeatedly flipping through the pages of the output. Color Plates 2 and 3 show that the Reaction Viewer provides the option of coloring the balls in the ball-and-stick representation based on the formal charge. The colors of balls will dynamically change as the reaction is viewed. This is extremely useful in identifying regions of partial charge in the intermediate and transition states, and in predicting how bonds will form.

VISUALIZING BOND DIPOLE INTERACTIONS THROUGH AN APPROXIMATION INVOLVING THE FORMAL CHARGES

Another important feature of the Reaction Viewer is the visualization of bond dipole strengths. This is an attempt to visualize the dipole moment for each bond, and to see how these bond dipoles change over the course of a reaction. A number of researchers have shown the importance of bond dipoles over the molecular dipole moment in describing physical and chemical properties. An option is provided by the Reaction Viewer to display the bond color based on the relative bond dipole.

To ease the computation of the bond dipole and to make the visualization possible using several molecular orbital packages, the formal charges of the atoms are used. As shown in Color Plate 4, all bonds are color coded on the basis of the difference between the formal charges of the two atoms involved in that bond. Blue indicates a small difference in the formal charges, green indicates a moderate difference, and red indicates a large difference. In this way, display of the structure with bond dipole information will immediately show which bonds have a large separation of charge and which do not. From a chemical standpoint, this sort of information is useful in identifying a bond as covalent or ionic. A small bond dipole indicates a small charge separation and therefore a covalent bond.

COLOR-CODED VISUALIZATION OF BOND STRENGTHS

The Reaction Viewer also provides the display of bond strengths. MOPAC displays (with the appropriate keyword) a bond order matrix indicating how strong each bond is in the molecule. As shown in Color Plate 5, each of the bonds has 1 of 11 colors based on the bond strength displayed in the bond order matrix. This allows us to see, by immediate inspection, how strong each bond is in the molecule.

The real power of the Reaction Viewer is not so much the display of a static structure, such as the ground state or transition state, but the ability to observe how the formal charge changes, how the bonds change their dipole, or how bonds change in strength during the course of a reaction. Because the Reaction Viewer displays a movie as opposed to frame-by-frame display, it is possible to watch how each of these phenomena change during the course of a reaction.

CHEMISTRY USING THE REACTION VIEWER

To demonstrate how the Reaction Viewer can be used to assist in the understanding of a chemical reaction, the reaction of methylphosphonodifluorodate (DF) and methoxysilane is shown as an example.[1] The reaction of these two species is shown in Figure 1.

This reaction can occur by one of two routes: (1) the attack by the phosphoryl oxygen on the silicon, followed by migration of the methoxy group to the phosphorus, resulting in the eventual loss of silyl fluoride, or (2) attack by the silyl oxygen on the phosphorus, followed by migration of the silyl group to the phosphoryl oxygen, resulting in the eventual loss of silyl fluoride. In both cases the reaction intermediate is the same, a trigonal bipyramidal phosphorus compound as shown in Figure 2.

The Reaction Viewer permits us to examine not only the reaction itself, but also how the electronics and bonding change during the reaction. The animation capability in the Reaction Viewer allows us to see how the phosphorus atom

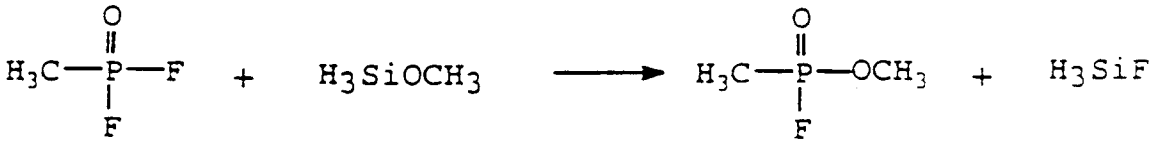

Figure 1. Reaction of DF and methoxysilane.

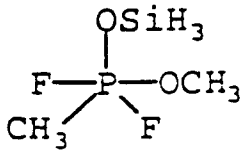

Figure 2. Trigonal bipyramidal intermediate.

changes in the formal charge during the reaction. Also, by using the bond strength option, it is possible to observe how the phosphoryl oxygen bond changes from P=O to P–O–X as the reaction proceeds to the intermediate, and then back to P=O as the reaction ends.

CONCLUSIONS

This article has shown how the Reaction Viewer can be used to not only watch a reaction occur, but also to observe how electronic properties of a molecule change during the course of a reaction. This is especially pertinent when one is interested in how electrons migrate during the process from reactants to products, or how bonds are redefined during the course of a reaction.

The examples cited here utilize gas-phase MO methods. Developments in solvent effects methodology have resulted in the incorporation of solvent effects into standard MO computations.[8–9] Although the Reaction Viewer does not specifically incorporate these new methodologies, minor modification to the Read_Mopac module should be trivial, and it will then be possible to incorporate the different solvent models.

There are a number of other fundamental descriptors normally computed by MOPAC that change or could change during the course of a reaction, and which would be amenable to graphical display. Future directions for the enhancement of the Reaction Viewer include the possibility of including polarization effects and to display how polarization volumes change, how spin density is affected, and how the HOMO and LUMO change during a reaction. Further, we will examine if the recently implemented dynamic reaction coordinate can yield useful information, and whether this information can be easily visualized.

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