Example Applications of Molecular Orbital Methods – Part 1

The following examples provide illustrations of how molecular orbital methods can be used to obtain a variety of properties of molecular systems and information about chemical reactions. This set of examples is by no means complete—many other types of information also can be obtained.

Properties Related to Electron Density

One of the drawbacks of molecular mechanics methods is that properties involving electrons cannot be calculated since molecular mechanics force fields do not treat electrons explicitly. Molecular orbital methods can calculate properties involving electrons, including electron densities, electrostatic potentials, atomic charges, and dipole moments.

As an example of the calculation of electron densities, Figure 1 presents electron density surfaces calculated for carbonic acid (H$_2$CO$_3$), bicarbonate ion (HCO$_3^-$), and carbonate ion (CO$_3^{2-}$). The surfaces plotted have constant electron density, and they clearly show the differences in electron density for single bonds, double bonds, and the equivalence in bonds as a result of resonance structures.

![Figure 1](image1.png)

**Figure 1.** Electron density surfaces (isodensity value = 0.2 a.u.) for carbonic acid, bicarbonate ion, and carbonate ion, illustrating variations in density for single and double bonds, as well as resonance effects.

Another property that may be obtained using molecular orbital methods is an electrostatic potential map. This property provides a measure of the electrostatic potential that a small test charge would feel if brought in the vicinity of the electron distribution of the molecule. The electrostatic potential is generally mapped onto an electron density surface. Examples of electrostatic potential maps are provided for the simple diatomic molecules LiH, H$_2$, and HF in Figure 2.

![Figure 2](image2.png)
Figure 2. Electrostatic potential maps (plotted on an isodensity surface = 0.002 a.u.) for LiH, H₂, and HF. The blue color indicates positive, green is neutral, and red is negative.

It is also possible with molecular orbital methods to partition the electron density and assign charges to each of the atoms in a molecule. There are a variety of ways of doing the partitioning; two of the most common methods are known as Mulliken population analysis and Natural population analysis. Results of the determination of atomic charges for LiH and HF using Mulliken population analysis are shown in Figure 3. (Of course the charges on the H atoms of H₂ are equal to 0.)

Figure 3. Atomic charges calculated using Mulliken population analysis for LiH and HF.

Vibrational Frequencies and Infrared Spectra
Molecular orbital methods can be employed to determine vibrational frequencies and predict infrared spectra. To account for anharmonic effects, the calculated frequencies often are scaled by an empirical factor of 0.9. Table 1 presents some example results for formaldehyde calculated at a relatively low level of theory. Even with a modest calculation, the scaled frequencies are in reasonably good agreement with experiment.

Table 1. Calculated and scaled vibrational frequencies of formaldehyde determined at the Hartree-Fock/6-31+G(d) level compared with experimental results.
The intensities of infrared transitions also may be computed using molecular orbital methods and a simulated infrared spectrum may be produced. An example for formaldehyde is shown in Figure 4.

![Infrared Spectrum](image)

**Figure 4.** Formaldehyde (a) calculated and (b) experimental infrared spectra. Unscaled frequencies obtained at the Hartree-Fock/6-31+G(d) level were used to generate the calculated spectrum.

**NMR Chemical Shifts**

A relatively recent development in the application of molecular orbital methods is the determination of NMR chemical shifts. It has only been in the last two decades or so that reliable methods for the calculation of NMR shifts have been available. As an example, consider the calculation of $^{13}$C NMR chemical shifts of ethyl crotonate. The structure of this molecule optimized using molecular orbital methods (the Hartree-Fock method with a 6-31G(d) basis set) is shown in Figure 5. Atoms 7 and 8 correspond to oxygen atoms, and atoms 2, 3, 4, 5, 9, and 10 are carbon atoms.

![Ethyl Crotonate](image)

**Figure 5.** Sketch of ethyl crotonate along with HF/6-31G(d) optimized structure.
The experimental $^{13}\text{C}$ NMR spectrum of ethyl crotonate is shown in Figure 6. Note that although molecular orbital methods can be used to determine proton NMR chemical shifts, they are generally more sensitive to the environment and require a little more care to accurately compute using molecular orbital methods.

Figure 6. Experimental $^{13}\text{C}$ NMR spectrum of 20% ethyl crotonate in CDCl$_3$ with TMS as standard [from S. Braun, H.-O. Kalinowski, and S. Berger, 100 and More Basic NMR Experiments, VCH Publishers, Weinheim, Germany, 1996, p. 42].

The experimental and calculated $^{13}\text{C}$ chemical shifts are listed in Table 2. The numbering of the carbon atoms correlates to the numbers shown in Figure 2. The chemical shifts are measured relative to TMS.

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Experimental Chemical Shift (ppm)</th>
<th>HF/6-31G(d) Chemical Shift (ppm)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>144</td>
<td>145.8</td>
<td>1.3</td>
</tr>
<tr>
<td>3</td>
<td>123</td>
<td>117.3</td>
<td>4.6</td>
</tr>
<tr>
<td>4</td>
<td>18</td>
<td>18.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>167</td>
<td>159.0</td>
<td>4.8</td>
</tr>
<tr>
<td>9</td>
<td>60</td>
<td>53.0</td>
<td>11.7</td>
</tr>
<tr>
<td>10</td>
<td>14</td>
<td>15.2</td>
<td>8.6</td>
</tr>
</tbody>
</table>

As the results in Table 2 illustrate, the agreement between the calculated and experimental chemical shifts is good. Note that perfect quantitative agreement cannot be expected. For one reason, the calculated results come from gas phase structures with no solvent interaction while the experimental results were determined in solution. In addition, deviations between experiment and calculations may be observed due to the use of small basis sets or inadequate levels of theory for the system being studied.
**Reaction Paths**

Molecular orbital methods can be employed not only to determine the reactants, products, and transition state of a chemical reaction, but also to calculate the complete reaction path. One type of calculation to determine reaction paths is called the Intrinsic Reaction Coordinate (IRC) calculation. An example will be presented for the isomerization reaction of HCN to produce HNC.

To begin an IRC calculation, the reactants and products (HCN and HNC, respectively) were optimized at the HF/6-31G(d) level. Next, the transition state was optimized and verified to be a saddle point by the presence of one imaginary frequency (1146.5i cm\(^{-1}\), in this case). The optimized structures are shown in Figure 7.

![Image of optimized structures](image)

**Figure 7.** Optimized structures at the HF/6-31G(d) level of HCN, the transition state for isomerization, and HNC.

Beginning from the transition state, the IRC calculation attempts to find the lowest energy path from the transition state to the reactants and to the products. An example of an IRC calculation for the isomerization of HCN, determined at the HF/6-31+G(d) level, is shown in Figure 8.

![Image of IRC energy diagram](image)

**Figure 8.** IRC energy diagram for isomerization of HCN to HNC at HF/6-31+G(d) level.

The points on the graph indicate that structures were obtained for every point shown along the reaction path. Note that the IRC calculation in this case did not go all the way to the fully-optimized reactants and products. Both HCN and HNC are linear molecules. As the slope of the reaction path approaches zero, it becomes more difficult for the IRC calculation to go all the way to the reactants and products; however, it is clear from this IRC what the reactants and products should be. In fact, IRC calculations are commonly employed to verify that the transition state obtained really does connect the reactants and products in a reaction.