1. The following problem explores the Pauli Exclusion Principle and wave function symmetry. Let $\Psi_1$ and $\Psi_2$ be the functions for a particle in a one-dimensional particle in a box with $n = 1$ and $n = 2$, respectively. If one electron are in each of these orbitals, the space part of the triplet and singlet wave functions are:

$$\Psi_A = \frac{1}{\sqrt{2}} [\Psi_1(1) \Psi_2(2) - \Psi_2(1) \Psi_1(2)] \quad \text{and} \quad \Psi_S = \frac{1}{\sqrt{2}} [\Psi_1(1) \Psi_2(2) + \Psi_2(1) \Psi_1(2)]$$

respectively. Suppose that electron 1 is in a small element of length $dx$ at $x = 0.250 \, a$ and electron 2 is in a small element of length $dx$ at $x = 0.255 \, a$. The quantity $a$ is the length of the box. Show that $\Psi_A$ has a very small value under these conditions while $\Psi_S$ is large. What happens to $\Psi_A$ if both electrons are at $x = 0.250 \, a$? This problem shows how an anti-symmetric spatial wave function keeps the electrons apart.

2. Determine the atomic terms that correspond to a $p^1f^1$ configuration. Specify the total orbital angular momentum and the spin multiplicity. Use the following steps: [Try Problem 25.28 first]

(a). Draw all possible explicit singlet states. For example, one of the explicit singlet states is:

(b). Calculate $M_L$ for each of the states.

(c). Find $L = |M_L|_{\text{max}}$. Remove the $M_L$ states from the list from part (b) corresponding to this $L$.

(d). Find $L = |M_L|_{\text{max}}$ for the remaining states. Remove the $M_L$ states from the list corresponding to this $L$.

(e). Repeat part (d) until all the $M_L$ states are accounted for. Write the term symbols for each of the different $L$ values that you have found (for example, $1D$ or $3P$).

(f). Repeat steps (a) through (e) for all possible explicit triplet states. For example, one of the explicit triplet states is:

(g). Verify that the Clebsch-Gordon series applied to the total orbital angular momentum gives the same results.

3. For the $H_2^+$ ion, show that for the bonding orbital $c_A = c_B$ using $E_+$ and for the anti-bonding orbitals $c_A = -c_B$ using $E_-$.
Michael Addition of trans-Acrolein¹

Introduction:

trans-Acrolein is:

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{O} \\
\text{H}
\end{array}
\]

Acrolein and other \(\alpha,\beta\)-unsaturated carbonyl compounds are known not only to undergo nucleophilic addition at the carbonyl carbon, but also Michael addition at the \(\beta\) olefin position.

The lowest-unoccupied molecular orbital (LUMO) of acrolein designates regions of the molecule where the next pair of electrons (the nucleophile) will likely go. Specifically, the carbon on which the LUMO has a greater amplitude will be the more reactive toward attack by a nucleophile. This exercise is designed to explore the specificity of Michael addition to trans-acrolein. You can use Spartan, WebMo with Mopac, or GaussView with Gaussian. Spartan is by far the easiest option.

Procedure-Spartan Version: In the Schupf lab log in to your account. Open the Applications folder and choose Spartan 14.

1. Click on the New Build icon (a water molecule) at the upper-left in the icon bar. Build trans-acrolein: start by clicking on the “>C=” molecular fragment and then clicking on the Builder screen. For subsequent additions click on the desired molecular fragments and then on open valences, which are yellow bond fragments. In the Builder, to rotate around a bond, highlight the bond (if necessary) and press the Option key and drag with the left-mouse button. To generate a reasonable starting structure, click on the Molecular Mechanics Minimize button. This button is the jagged green arrow icon at the lower-right of the Builder screen.

2. Submit an Equilibrium Geometry calculation at the semi-empirical PM3 level: to do this pull down the Setup menu and choose Calculations.. In the new dialog box choose “Equilibrium Geometry” at “Ground” state with a “Semi-Empirical” method at the “PM3” level. Set the Total Charge to Neutral and the Unpaired Electrons to 0. Click on the Submit button. Save the resulting file in your Documents folder with an appropriate name and the “.spardir” file extension. The calculation should be complete in a second or three.
3. Pull down the Setup menu and choose Surfaces. Click on Add, and then select LUMO from the Surface menu. When the job has completed (a second or two), in the Surfaces dialog click on the check-box on the line: “LUMO Completed 0.032”. The LUMO is then displayed. Pull the Surfaces dialog to one side so that you can see the molecule (leave the Surfaces dialog box open).

4. A much clearer representation follows by mapping the absolute value of the LUMO onto the electron density surface (a so called LUMO map). An electron density map is surface at a specific value of the electron density (e.g. $\Psi^2$). This depiction corresponds to the value of the LUMO that an approaching nucleophile would “see.” In the Surfaces dialog click on Add. Select “|LUMO| map.” The calculation is completed in a second or two.

6. First turn off the LUMO surface by clicking on the blue check-box on the line “LUMO Completed 0.032”. Next, click on the check-box on the line: “|LUMO| map Completed 0.002”. The shape of the surface displayed is that of the electron density, and the colors show the absolute value of the amplitude of the LUMO on the density surface. To see the underlying atoms, so that you can focus on the $\beta$-position, click on the surface. At the lower-right of the display in the Style pull down menu choose Transparent. The default limits for the color scheme are too broad. So next click right on the surface and choose Properties. In the Property Range dialog change the maximum (which has a default value of 0.05) to 0.013. The color red corresponds to a zero value and the color blue corresponds to a maximum value. Is the LUMO map consistent with the LUMO you displayed earlier? You can obtain quantitative values of the mapped property by left clicking on the surface at different spots. The LUMO amplitude is listed in the Properties dialog box under the “Val:” heading.

Report: See the questions at the end of the write-up.

Procedure: WebMo version:

1) Start WebMo using the link on the course home page or the URL:
   “http://schupflab.labs.keyes.colby.edu/cgi-bin/webmo/login.cgi”
   Mouse over “New Job” and click on “Create New Job.” In the WebMO Editor window, draw your molecule. As an example, the instructions below are for acrolein. You can build other molecules in a very similar fashion. In general it is best to build the skeleton of the molecule with all carbons, first, and then change the necessary carbons to heteroatoms. Usually, only the C-C skeleton is sketched, the hydrogens are added later automatically.

   i) Click on the Build icon: . Click in the Editor window to create the first atom. Then starting at the first atom drag the mouse to the right to create the second, third, and fourth atoms. Drag twice between two atoms to make the double bonds. The default element is carbon, so the next step is to change the last atom to O.

   ii) Click on the periodic table icon: . Click on O in the table and then on the atom that you want to switch in the Editor window. Pull down the Clean-Up menu and choose Add
Hydrogens. If you make a mistake, there is an Undo option under the Edit menu, or pull down the File menu and choose New to begin again.

iii) Pull down the “Clean-Up” menu and choose “Comprehensive- Mechanics” to adjust the bond lengths and angles to a reasonable guess. These guesses are derived from bond length and angle tables associated with the built-in molecular mechanics force field. This minimization is a rough guess to the molecular structure.

Then click on the blue “>” button at the bottom-right of the editor window to close the Editor window.

**Running a Molecular Orbital Calculation using WebMo:**

2) Under Choose Computational Engine, choose MOPAC and then click on the blue “>” button, to continue. Under the “Configure Mopac Job Options” page, enter a job name and choose the following options (See the figure below):
   - Calculation: Geometry Optimization
   - Theory: PM3
   - Charge: 0
   - Multiplicity: Singlet

   ![Job Options](image)

   For the multiplicity for other molecules, use Hund's rule or your Lewis dot structure to decide the number of unpaired electrons. If all the electrons are spin-paired use singlet (most molecules are diamagnetic singlets). If there is one unpaired electron, as in NO, use doublet (most radicals are doublets), if there are two unpaired electrons, as in O$_2$, use triplet.

3) Click on the blue “>” button, to start the calculation. The screen will switch back to the Job Manager screen. After a few seconds the status of your calculation should change to “Complete”. You can also click on the Refresh button to check the current status of your calculation. Click on the magnifying glass to see the results. You can rotate your model by dragging with the left mouse button. Zoom while holding down the Shift key.

4) Scroll down in the View Job window. Record the final energy, which is listed as the “PM3 Heat of Formation” and note the units.

5) Back in the Molecule Viewer, you can measure bond lengths by clicking on the Select icon, ![Select](image). Click and then shift-click on pairs of atoms to determine the distances. You can measure the bond angles by choosing the Select icon. Now click and then shift-click on the three
atoms whose bond angle you desire. To return to 3-D rotation of the molecule, click on the
Rotate icon: 🔄.

7) Modeling Options: Click on the Preferences icon, ⬤. Choose how you want to see your
model by changing the Atom Size and Bond Size values (try the different settings). Leave the
molecule in the Ball and Spoke form with the default values of 20% Atom size and 100%
Bond size. An Atom Size setting of 100% corresponds to the “space-filling” or Van der
Waals model. The space-filling model uses tabular values of the Van der Waals radii for the
atomic radii. Therefore the "sizes" of the atoms in this type of display are only suggestive of
the size and shape of the molecule, and will not vary with the true electron density around the
atom. To get a much better representation of the size of the molecular orbitals, use a density
surface as described in the Electron Density Surfaces section below.

WebMO Electron Density and Electrostatic Potential Surfaces

9) View the molecule and then click on the “New Job Using this Geometry” button. Then click
on the blue “>” button, twice to view the Configure Mopac Job Options window. Enter a job
name and choose the following options:
   Calculation: Molecular Orbitals
   Theory: PM3
   Charge: 0
   Multiplicity: Singlet

![Job Options](image)

Complete the calculation as you did before. View the new results by click on the
 corresponding magnifying glass icon.

10) Scroll down in the View Job window to the Molecular Orbitals section. Click on the
magnifying glass adjacent to the Electron Density entry (actually, clicking on any one of the
magnifying glass icons in the Molecular Orbital section gives you access to all the MO plots
and surfaces).
After a short interval, during which a Java applet will be loaded, the Molecule Viewer will switch to the Molecular Orbital Viewer mode, at the top of the page. The electron density surface should be displayed. You can reorient the surface using the mouse. Resizing is done while holding down the Shift key.

11) Click right in the MO Viewer window, slide right on Opacity and choose Transparent. Note the position of the $\alpha$ and $\beta$ carbon atom, relative to the surface. The default value for the isodensity surface corresponds to roughly a 90% contour surface. The 90% contour surface provides a visualization of the shape and size of a molecule, as seen by other nearby molecules. Iso-value electron density surfaces are more realistic than “space-filling” models. However, to see the effects of electron sharing from bond formation, we need to choose a higher iso-value so that we can focus on the high-electron density portions of the molecular orbital.

12) Click on the Preferences icon, $\mathbb{H}$. Change the Iso. Value(ED) setting to 0.05, and then click on apply. The electron density surface will be redrawn to highlight the regions of the molecular orbital with high electron density. The electron density surface with large values of the density are called “bond density” surfaces. Where are the electrons localized? What is the size of the bond density surface around each atom? What is the size of the electron density along the internuclear axis between the nuclei?

In the Preferences Dialog, click on Default to return to the default electron density Isoelectronic Value of 0.0030, before continuing.

13) **Using Electrostatic Potential Surfaces**: To see the electrostatic potential surface, click on the Electrostatic potential button in the MO Viewer. The red color corresponds to regions where the positive test charge is attracted to the surface giving a negative energy, in other words a
region of high electron density and net negative local charge. The blue regions correspond to areas with low electron density and net positive local charge. Where are the electrons localized? Is the charge distribution the same as predicted using electronegativity?

14) Viewing Molecular Orbitals: The list of molecular orbitals is displayed at the left in the MO Viewer (or also in the Molecular Orbitals section at the bottom of the output listing for Gaussian calculations). Click on the entry for the LUMO, the lowest energy unoccupied molecular orbital.

<table>
<thead>
<tr>
<th>MO</th>
<th>Occ.</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>-5999.0</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>-9999.0</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>-23987</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>-20315</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>-17133</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>-16787</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>-15011</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>-1446</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>-13266</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>-1197</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>-10694</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>-0.187</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>1.769</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>2.452</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>3.852</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>3.493</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>4.003</td>
</tr>
<tr>
<td>18</td>
<td>0</td>
<td>4.066</td>
</tr>
<tr>
<td>19</td>
<td>0</td>
<td>9999.0</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>9999.0</td>
</tr>
</tbody>
</table>

Sometimes, the applet has problems switching from density surface based displays to MO mode. If the MO or surface isn’t displayed, return to the Job Manager and then reload your results by clicking on the magnifying glass again.

15) Nucleophilic (LUMO) Density Surfaces: Click on the Nuc (LUMO) density button. The electron density surface colored by the LUMO amplitude should be displayed. Click right in the MO Viewer window, slide right on Opacity and choose Transparent. Note the position of the $\alpha$ and $\beta$ carbon atom, relative to the surface. The blue color corresponds to regions of larger LUMO amplitude.

16) Displaying the Dipole Moment: Scroll down to the Calculated Properties section and click on the magnifying glass adjacent to the dipole moment listing. The dipole moment vector will be displayed in the Molecule Viewer at the top of the page. Is the dipole in the direction that you predicted? Is the dipole in agreement with the electrostatic potential surface and the partial charges listed in the Calculated Quantities section?

17) When finished, click on the blue “>” button to return to the Job Manager.
**Questions to hand in** (One or at most two sentences are fine for answers):

1. Is the LUMO of acrolein consistent with experimental evidence for reactivity of \(\alpha,\beta\)-unsaturated carbonyl compounds with respect to Michael addition?

2. Draw the resonance structure that predicts the position of nucleophilic attack on the alpha or beta carbon of the C=C double bond, whichever is most likely according to your results. Show the shifts in the electron pairs with arrows for the nucleophilic attack.

3. Does this resonance structure agree with the LUMO map intensity distribution? Explain how you know that they agree or disagree with reference to attack at the alpha or beta carbon of the C=C double bond.

**References:**