Quantum Mechanical Calculations Laboratory

**Objective:** The transition energy for one of the dye molecules used in the “Particle in the Box” experiment will be calculated by several different methods available in the Spartan program. The accuracy of the results will be compared to experiment.

**Quantum Mechanical Calculation Methods Available in Spartan**

All of the methods available within the Spartan program are attempts to approximate the solution to the Schrödinger equation for a multi-electron case. The Schrödinger equation can only be exactly solved for the one-electron “hydrogen-like” case. All multi-electron cases can only be solved through approximate methods.

The difficulty of solving the multi-electron case is an example of what is called the “Three Body Problem”. In the one electron case we account for the interactions between the single electron and the nucleus. In the two-electron case there are now three pairs of interactions: between the first electron and the nucleus, between the second electron and the nucleus and between the two electrons. These interactions are considered one at a time. The nuclear attraction of the first electron can be determined, however this interaction will then have effects on the repulsion between the two electrons as the first electron changes position as it is attracted by the nucleus. The change in repulsion between the first and second electrons will cause a change in the position of the second electron that will result in changes in the attraction to the nucleus of the second electron and this will result in a perturbation of the attraction of the first electron to the nucleus, the interaction that we started the process with. This becomes an infinite series of perturbations that is impossible to solve and difficult to approximate mathematically.

In Quantum Mechanics two important approximations that are applied to this problem are the Born-Oppenheimer Approximation and the Linear Combination of Atomic Orbitals (LCAO) Approximation. The Born-Oppenheimer Approximation is based on the fact that nuclei are heavy and move much slower than electrons. The Born-Oppenheimer Approximation treats the nuclei as stationary, the kinetic energy of the nuclei is zero and the nuclear-nuclear repulsion energy is a constant. This removes two sets of terms from the calculation of the molecular Hamiltonian. The LCAO Approximation assumes that a multi-electron solution will resemble a sum of one-electron solutions. The one-electron solutions are called a basis set of atomic orbitals.

The Hartree-Fock or *Ab Initio* model is based on the Born-Oppenheimer and LCAO approximations. The Hartree-Fock model uses only one-electron solutions and it does not take into account electron correlation. Electron correlation is the electrons interacting or coupling to one another through repulsive forces. The correlation energy is defined as the difference between the experimental energy of the system and the energy calculated by the Hartree-Fock model.

Semi-empirical methods (AM1, PM3) use one-electron solutions and have limited corrections for electron correlation effects. Semi-empirical methods simplify the calculations by treating the core electrons as fixed charges (causing other distortions) and only using molecular orbital functions for the valence electrons.
The Møller-Plesset (MP2) method Hamiltonian expresses the perturbation caused by electron correlation as an integral of overlap between empty and filled molecular orbitals to account for changes in electron-electron interactions as a result of electron orbital promotions. Higher order perturbations (MP3, MP4,…) can be included in the method.

Density Functional methods are based on a theorem that states that the minimum energy of a set of electrons in a Coulombic Field (a set of nuclei) is a unique functional (function of a function) of the electron density. In most models the functional takes into account corrections for electron correlation.

The accuracy of the calculated results will vary with the nature of the basis set (one-electron or hydrogen-like functions) used. The basis sets vary in the number of Gaussian functions that are used to represent the radial wavefunction of the atom. The angular wavefunctions of the atom are given by the spherical harmonics. The basis sets have names like STO-3G, which stands for “Slater Type Orbital – 3 Gaussians”, and is considered the minimal basis set.

More sophisticated basis sets use more Gaussian functions. Separate sets of Gaussian functions are used to represent core orbitals and valence orbitals, and the valence orbitals have Gaussian functions that are allowed to vary independently during the calculation. The STO6-31G basis set uses 6 Gaussian functions for the core orbitals and two sets of 3 and 1 Gaussian functions that can change independently of each other for the valence electrons. Some basis sets add p-type Gaussians to s orbitals, d-type Gaussians to p orbitals, etc. in order to represent the polarization that can occur to atomic orbitals in a molecule. An asterisk in the basis set name indicates the addition of polarization functions to a basis set. The downside of adding more functions to a basis set is an increase in the time required for computation.

**Using Spartan**

Spartan can only be used on the computer that has the “dongle” inserted into the printer port. The “dongle” contains a code that is required to run the program. Click on the Spartan icon and when the program window opens click on “new” under the “file” menu. This should open up the atom palette on the right hand side of the window.

Left click in the window to the left of atom palette and the selected atom will appear. Left clicking a second time on one of the yellow open valences of the atom will create a second atom bonded to the first. Clicking on the yellow “make bond” icon at the top of the window and then selecting two yellow open valences can also form bonds. To remove a bond left click on the “break bond” icon to the right of the “make bond” icon and then select a bond to break. To the left of the “make bond” icon is the “delete” icon, which can be used to remove atoms from the window. After deleting an atom make sure to click on the “add fragment” icon to the left of the “delete” icon when you want to continue building.

By clicking on the expert tab of the atom palette it is possible to build with any atom off of the periodic table in the palette and to choose the atoms hybridization. Single bonds can be changed to double bonds by clicking the appropriate icon on the bottom of the expert atom palette and then clicking on a yellow open valence in the structure to the left.
Use this procedure to build one of the three dye molecules, shown in the picture below, that were used in the “Particle in the Box” experiment. When you have finished building the molecule click on the “minimize” icon above the window that runs a molecular mechanics routine to adjust angles and bond lengths to reasonable values.

The Molecules

1,1'- Diethyl-2,2'-Cyanine Iodide

1,1'- Diethyl-2,2'-Carbocyanine Iodide

1,1'- Diethyl-2,2'-Dicarbocyanine Iodide

Only construct the cations in Spartan.

Calculations

Clicking on “calculations” under the set-up menu sets up the calculations. We will run a calculation under each of the following methods:

1) Semi-Empirical (AM1 or PM3)
2) Hartree-Fock STO-3G basis set
3) Hartree-Fock with a higher order basis set
4) MP2 with any basis set
5) Density Functional with any basis set.

The first calculation is a geometry optimization of the ground state. The top line of the calculations window should read “Equilibrium Geometry” followed by the method and basis set. Our molecule is a cation and the ground state multiplicity is a singlet as all electrons are paired. Click on the “orbitals & energies” option in the print section of the window. Click on the OK button and the calculations window closes but the calculations have not started. In order to start the calculations click on “submit” under the set-up menu. Calculations with larger basis sets will take more time to run, be patient.
We will approximate the transition energy for the lowest energy band observed in the absorptions spectrum as the HOMO-LUMO energy difference. The energy of a transition can be divided into two components, the promotion energy, which is the energy difference between the relevant orbitals, and a term which represents the change in electron-electron repulsion on going from the ground to the excited state. Recognizing that it is this second contribution to the energy that causes havoc for ground state calculations it should not be surprising that the problems are even worse for excited state calculations.

When the calculation is completed click on “output” under the display menu. This will open a window that contains the result of the calculation. Record the total energy of the molecule, the eigenvalues or energies for the HOMO and LUMO and the time required for the calculation. The energies are sometimes reported in atomic units (au) or hartrees. The necessary conversion is:

\[ 1 \text{ au} = 1 \text{ hartree} = 627.5 \text{ kcal/mol} = 2,625.5 \text{ kJ/mol} = 219,474.6 \text{ cm}^{-1} \]

**Discussion**

Compare the experimental value for the lowest energy transition in the dye absorbance spectra to the different theoretical values for the HOMO-LUMO energy. How does the accuracy improve as the level of theory increases? How does the computation time increase as the level of theory increases?

Compare the theoretical transition energy for each method with the total energy of the system calculated by that method. What percent accuracy does the calculation method need with respect to the total energy in order to make good predictions on chemically relevant quantities that would change during a reaction or spectroscopic experiment? The answer to this question is the reason why there is a continuing search for better methods of approximation with which to solve the Schrödinger equation for a molecular system.