

Chem 565 Assignment 2

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- a.) The Born-Oppenheimer approximation is a method of calculating the energy and wavefunction for some molecule which assumes that the electronic and nuclear movements within a molecule are separable, such that a molecular wavefunction can be rewritten in order to easily approximate the energies, etc. of a complicated molecule. Essentially, it allows for molecular wavefunction to be written such that $\Psi = \psi_{\text{electronic}} \times \psi_{\text{nuclear}}$. Assumptions are made, based on the large difference between nuclear and electron masses, that the nucleus is basically stationary from the standpoint of the electrons and the electron's potential is effectively "smeared out," from the standpoint of the nucleus. The molecular Hamiltonian before the approximation with M_A being the ratio of the nucleus A to the electron mass, Z_A being the atomic number of nucleus A, is

$$\hat{H} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1} \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}.$$

With the BO approximation, the wavefunction is split in two, and the Hamiltonian for the electronic energy is

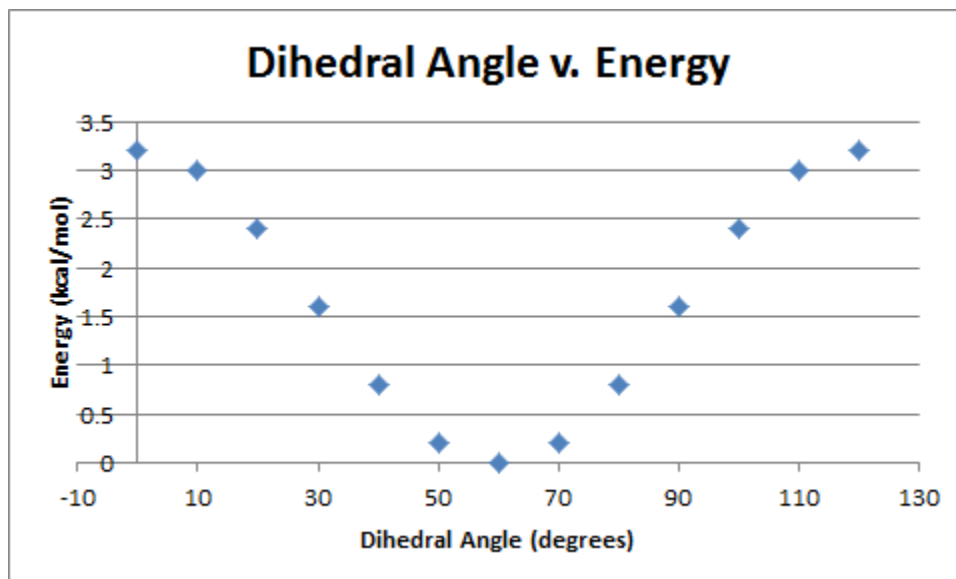
$$\hat{H}_e(R) = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N-1} \sum_{j>i}^N \frac{1}{r_{ij}},$$

and so $\hat{H}_e \phi_e(r; R) = E_e(R) \phi_e(r; R)$. The nuclear Hamiltonian is then

$$\hat{H}_n = - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + E_e(R) + \sum_{A=1}^{M-1} \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}.$$

This is far more simple than the original, exact time-independent molecular Hamiltonian because we can now replace the need for exact electronic coordinates by their averaged values (expectation values). Indeed, the new, factorized wavefunction is now actually tractable for accurate approximations, since the original Schrodinger equation is now separated into two SEs.

- b.) A potential energy surface is a construct used to describe a system's energy in terms of parameters such as positions of atoms. Essentially, an energy function which is dependent on some parameters, called $E(r)$, forms a surface where each r corresponds with some value of $E(r)$, creating an "energy landscape." These surfaces can be used for analysis of molecular structure and reactions—for instance, minima on the PES correspond to stable chemical species, and 'saddle points' correspond to transition states.
- c.) The energies have been vertically shifted such that the minimum is zero.



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- a.) The stretching frequency increases with the substituents' electronegativity, and decreases with the increase of mass. The C-O stretching frequencies are 2131.99 for F₂CO, 2023.30 for Cl₂CO, and 1915.45 for CH₂O.
- b.) The experimental value for formaldehyde's CO stretching frequency is 1745. The HF method, although fast, is extremely inaccurate. The CISD method, while providing the most accurate results, takes a lot of computing resources, for not much of an increase in accuracy when compared to the B3LYP method. Across the methods, the basis set 6-31G seems to offer the best improvement in accuracy and only requires marginally more computation time. As such, the combination of method and basis set which seems to offer the best compromise between accuracy and computational cost is B3LYP/6-31G.

Method	Calculated Frequency	Percent Error (%)	CPU Time (s)
HF/3-21G	1915.45	9.77	3
HF/6-31G	1909.77	9.44	3
HF/6-311G	1895.73	8.64	3
CISD/3-21G	1755.49	.60	45
CISD/6-31G	1744.21	.04	48
CISD/6-311G	1745.51	.03	90
B3LYP/3-21G	1760.09	.87	4
B3LYP/6-31G	1748.12	.18	5
B3LYP/6-311G	1732.32	.73	6

- c.) From the log file, the second derivative of energy with respect to the carbon-oxygen bond is $1.39157 E_h/a_0^2$, which is the "spring constant" in the harmonic oscillator model of the bond. The frequency of this oscillator is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where μ is the reduced mass, given by

$$\begin{aligned} \frac{1}{\mu} &= \frac{1}{m_A} + \frac{1}{m_B} \\ &= \frac{1}{(12.0107 \text{ u})} + \frac{1}{(15.9994 \text{ u})} \end{aligned}$$

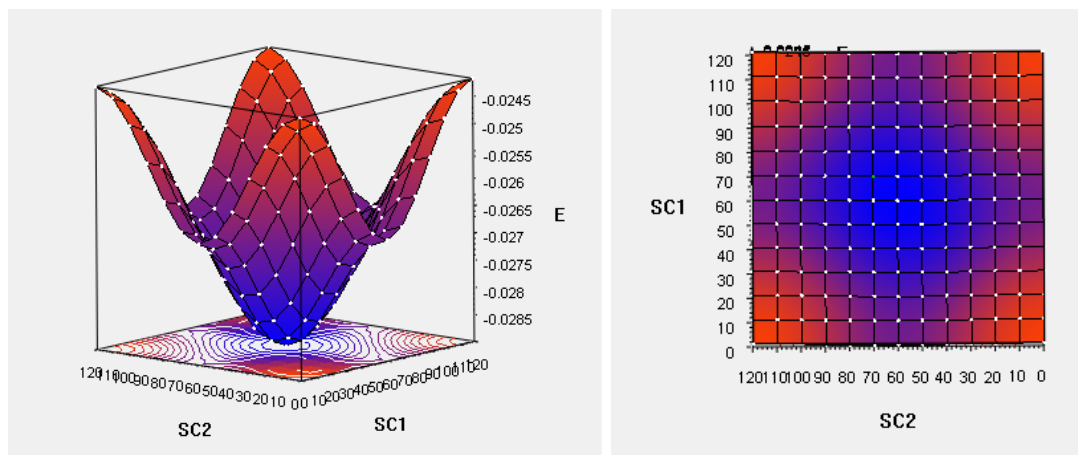
solving for μ yields $\mu = 6.8605 \text{ u}$. Plugging this into the equation for frequency, we get

$$\nu = \frac{1}{2\pi} \sqrt{\frac{1.39157 E_h/a_0^2}{1.13922 \cdot 10^{-26} \text{ kg}}} = 2315 \text{ cm}^{-1},$$

which matches with the Gaussian calculated value, which is 2315.87 /cm.

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a.)



- b.) SC1 and SC2 represent the dihedral angles $H_4-C_1-C_2-C_3$ and $H_9-C_3-C_2-C_1$.
- c.) Minimum: (60,60). Maxima: (0,0), (120,0), (120,0), (120,120). Saddle points: (0,60), (60,0), (60,120), (120,60).
- d.) The minimum corresponds to the conformation in which both the C-C bonds are staggered. The maxima correspond to the conformations in which both are eclipsed. The saddle points correspond to the conformations where one is staggered and one is eclipsed.