

Colorado State University
CHEM 372
Physical Chemistry Laboratory - 1

Notes for
Quantum Molecular Computation Methods

The following is a set of short notes to outline the experiment in question and to provide helpful guidance to those executing the experiment.

- A.** This "experiment" involves the use of ab initio Quantum Molecular (QM) computation methods. Computers are used to assist in solving Schrodinger's equation when analytic methods fail us.
- B.** In this work the commercial program named Gaussian will be used. This program is based on pioneering work performed by John Pople (British, Nobel prize in chemistry 1998, deceased). In a gross oversimplification it can be said that Gaussian uses linear combinations of a series of gaussian functions to generate wave functions for solving Schrodinger's equation. The user provides a molecular structure (in terms of atoms and atomic coordinates) to the program and the program returns a variable and user-selectable quantity of computed information.
- C.** At this time there is no single computational method that exceeds all others in computational accuracy and speed of widely varying molecular systems. As a consequence there are several (even many) variations on the basic computational theme. These variations are embodied in the so-called "Level of Theory", a term that describes both the size and qualitative nature of the "Basis Set" of functions used to form the wave function and the "Method" that describes the theoretical approach, empirical or first-principle parameterization, the approximations used (or not used), and the various electronic interactions included in the computation.
- D.** In this laboratory the Gaussian program is installed under the Unix-like OS X operating system and must be accessed (as of this writing) through the same operating system. A so-called "input file" is created using a text editor (named TextEdit and roughly comparable to the equivalent NotePad program), which is then submitted to Gaussian using a "terminal session" utilizing a CLI (Command Line Interface) and the output appears as a new text file where the desired computational information is contained. This output file is read, again with a text editor, and parsed by the user. In more advanced situations, it is possible to generate the input file using a user-created program and to parse the output file in a systematic and programmatic fashion.

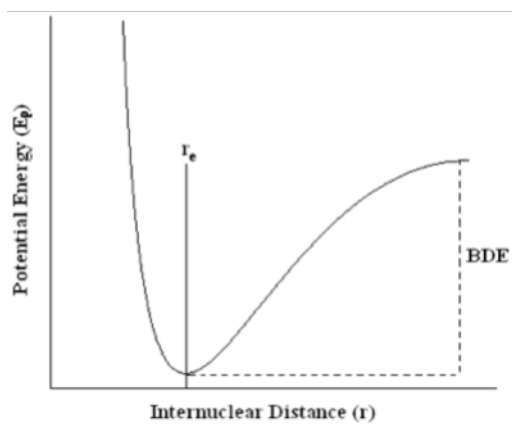


Figure 1. Example potential energy (E_p) diagram showing several key parameters including, equilibrium distance (r_e) and bond dissociation energy (BDE).

- E. In this experiment the potential energy (PE) of several diatomic molecules will be calculated as a function of interatomic distance by repeated calculation of the so-called "Single Point Energy" of the system, that is, the energy at a single molecular configuration, and a PE vs. interatomic distance diagram will be created using a modern data visualization and processing program also installed in the laboratory. A suitable number of distance-based energy calculations must be performed to characterize the important features of the PE curve including the close approach of the atoms, the region around the energy minimum and the progression to large separation of the atoms. The energy and distance units used are non-SI and must be converted to SI units. The energy corresponding to a distance where the atoms are non-bonded must be computed and set to zero so that the depth of the energy minimum can be easily read from the diagram.
- F. The first phase of this work is to compute a potential energy vs. interatomic distance diagram for a hydrogen molecule (H_2) using the Restricted Hartree-Fock (RHF) method and the 6-113G basis set. The raw data must be converted into SI units (both in energy and distance) and then presented in a quality, completed diagram, that is, properly formatted as has been repeatedly defined in this course.
- G. The energy vs. distance data can then be modeled using a classical harmonic oscillator. The region near the energy minimum is fit to a third-order polynomial with an offset x -

$$E_p(r) = a_0 + a_1(r - r_e) + a_2(r - r_e)^2 + a_3(r - r_e)^3$$

value. The value of a_2 can be converted into the force constant for this molecule and with this force constant and the reduced mass of the pair of atoms that compromise the molecule the fundamental frequency for the $v = 0 \rightarrow 1$ vibrational transition can be calculated. Perform all of these calculations. Compare the results of these calculations to literature values.

- H. Gaussian's calculation time is very sensitive to the number of electrons in the submitted structure. These calculations can be lengthy for larger and more interesting molecules. It is a Good Thing to be able to access Gaussian and its host computer remotely so that

the calculations can be performed at times of day other than the scheduled laboratory sections. For this purpose proficiency in several network-enabled tools must be acquired including an FTP (File Transfer Protocol) client, a SSH (Secure Shell) client and a VPN (Virtual Private Network) client. The web browser Firefox (<http://www.firefox.com/>) has plug-ins for the first two clients, that is, FireFTP and FireSSH. Learn to use and test out both of these clients *while in the laboratory* using the computers located there or your own personal computer *while it is in the laboratory*. After you leave the laboratory you must learn how to "tunnel" under the university's firewall using the university-supplied VPN system (see <http://acns.colostate.edu/>). Do this.

- I. Repeat this process for three additional molecules as assigned to you by teaching staff.