EXPERIMENT 1

INTRODUCTION TO COMPUTATIONAL CHEMISTRY

INTRODUCTION

Computational chemistry is the application of chemical, mathematical and computing skills to the solution of interesting chemical problems.[1] It uses computers to generate information such as properties of molecules or simulated experimental results. Researchers in many areas of chemistry routinely use electronic structure methods to predict molecular structures as well as physicochemical properties and even to predict the outcome of a chemical reaction. Computational chemistry has become a useful way to investigate materials that are too difficult to find or too expensive to purchase. It also helps chemists make predictions before running the actual experiments so that they can be better prepared for making observations.

Until recently accurate quantum chemical calculations were only possible for very small molecules, but developments in computer hardware and software now enable quality calculations to be performed on molecules with up to about 50–100 atoms.[2] At the beginning of the 21st century applications to molecules of biological interest actually became possible. For large, non-polymeric, molecular weight molecules it is often necessary to use semi-empirical methods, in which many of the integrals are replaced by parameters obtained from experimental measurements, in particular from thermochemical and spectroscopic data. Semi-empirical methods are usually not very reliable but can yield results, even for large molecules, within a reasonable timescale, that provide a valuable aid to the interpretation of experimental data.

Very few aspects of chemistry can be computed exactly, but almost every aspect of chemistry has been described in a qualitative or approximate quantitative computational scheme. The biggest mistake that computational chemists can make is to assume that any computed number is exact. However, just as not all spectra are perfectly resolved, often a qualitative or approximate computation can give useful insight into chemistry if you understand what it tells you and what it doesn't. While the ability to use modern quantum chemistry software packages is no longer dependent on a detailed understanding of quantum mechanics, there is, nevertheless, a considerable benefit to be gained from a basic knowledge of quantum chemistry and some familiarity with the procedures used in the computer programs.

There are a number of software packages available for electronic structure calculations and molecular visualization, the majority of which are relatively user-friendly. We will use G03W revision E.01, which is the Gaussian 03 package for the MS Windows environment (versions compatible with other computer platforms, such as Unix and Mac, are also available) and its associated visualization program GaussView4 (a Graphical User Interface, GUI). The lab exercises are meant to have you experiment with the Gaussian program. You will gain experience with how to submit jobs, how to make choices in preparing the input, how to interpret the output, and how to obtain meaningful results that can be compared to experimental quantities.

MODEL CHEMISTRIES

A model chemistry is a numerical technique used to explore chemistry on a computer.[1,2] It can be generalized into three broad categories: *ab initio* (Latin for "from scratch"), semi-empirical and molecular mechanics, as summarized in Table 1.

Table 1. Summary and important aspects of the various techniques used in computational chemistry.[1,2]

Technique	Features	Advantages	Disadvantages	Best for
Molecular Mechanics	• Uses classical physics • Relies on force-field with embedded empirical parameters • Computationally least intensive –fast and useful with limited computer resources • Can be used for molecules as large as enzymes	• Relies on potentials that have to be somehow supplied • Sometimes inaccurate because the supplied potentials are used beyond their proven range of validity	• Particular force field, applicable only for a limited class of molecules • Does not calculate electronic properties • Requires experimental data (or data from ab initio calculations)	• Large systems • (~1000 of atoms) • Systems or processes with no breaking or forming of bonds
Semi-Empirical	• Uses quantum physics • Uses experimentally derived empirical parameters • Uses many approximation	• Less demanding computationally than ab initio methods • Capable of calculating transition states and excited states	• Requires experimental data (or data from ab initio) for parameters • Less rigorous than ab initio) methods	• Medium-sized systems (hundreds of atoms) • Systems involving electronic transition
ab initio	• Uses quantum physics • Mathematically rigorous, no empirical parameters • Uses approximation extensively	• Useful for a broad range of systems does not depend on experimental data • Capable of calculating transition states and excited states	• Computationally expensive	• Small systems (tens of atoms) • Systems involving electronic transition • Molecules without available experimental data • Systems requiring rigorous accuracy

Molecular Mechanics Methods

If a molecule is too big to effectively solve the Schrodinger equation, even in a semi-empirical treatment, it is still possible to model its behavior by avoiding quantum mechanics.

This is done by constructing a simple expression for "molecular force field", i.e. the potential energy as function of all atomic positions, and using it study molecular properties without the need to compute a wave function or total electron density. The energy expression consists of simple classical equations, such as the harmonic oscillator equation, in order to describe the energy associated with bond stretching, bending, rotation and intermolecular forces, such as van der Waals interactions and hydrogen bonding. All of the constants in these equations must be obtained from experimental data or an *ab initio* calculation.

In a molecular mechanics method, the database of compounds used to parameterize the method (a set of parameters and functions is called a force field) is crucial to its success. Where as a semi-empirical method may be parameterized against a set of organic molecules, a molecular mechanics method may be parameterized against a specific class of molecules, such as proteins. Such a force field would only be expected to have any relevance to describing other proteins.

The good side of molecular mechanics is that it allows the modeling of enormous molecules, such as proteins and segments of DNA, making it the primary tool of computational biochemists. The bad side is that there are many chemical properties that are not even defined within the method, such as electronic excited states. In order to work with extremely large and complicated systems, molecular mechanics software packages often have powerful and easy-to-use graphical interfaces. Because of this, mechanics is sometimes used because it is easy, but not necessarily a good way to describe a system.

Solving the Schrodinger Equation

The other two techniques, semi-empirical and *ab initio*, rely on solving the Schrödinger equation (Equation 1.1). Solutions of the equation provide a wavefunctions, Ψ, which describe the behavior of electrons in atoms and molecules, and their associated energies, E. It is well known that exact analytical solutions can only be found for simple cases (particle in a box, harmonic oscillator, rigid rotor, hydrogen atom, hydrogen-like ions) and even simple two-electron systems, such as the helium atom, only approximate solutions can be found.[3] The

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi+\frac{8\pi^2 m}{h^2}(E-V)\Psi=0 \tag{1.1}$$

availability of powerful computers, however, means that for many-electron atoms and molecules, these calculations can now be carried out to a high level of approximation, such that excellent agreement with experimental data can be achieved in many cases.

Semi-empirical Methods

Semi-empirical calculations are set up with the same general structure as *ab initio* methods, but certain pieces of information, such as two electron integrals, are approximated or completely omitted. In order to correct the errors introduced by omitting these parts of the calculation, the method is parameterized, by curve fitting in a few parameters or numbers, in order to give the best possible agreement with experimental (empirical) data.

The good side of semi-empirical calculations is that they are much faster than *ab initio* calculations. The bad side is that the results can be erratic. If the molecule under study is similar to molecules in the database used to parameterize the method, then the results may be very good. If this molecule is significantly different from anything in the parameterization set, the answers may be poor. Semi-empirical calculations have been very successful in computational organic chemistry, where there are only a few elements used extensively and the molecules are of moderate size. More recently, semi-empirical methods devised specifically for inorganic chemistry have been developed.

ab initio Methods

In *ab initio* methods, no approximations are used other than mathematically tested ones. One very useful approximation that can be made for molecules is the Born–Oppenheimer approximation. This states that, because the mass of electrons is orders of magnitudes smaller than the mass of the nuclei, it can be assumed that the electrons will adjust instantaneously to a change in the nuclear coordinates. This means that the nuclear and electronic terms in the Schrödinger equation can be separated, enabling it to be solved for fixed positions of the nuclei, and the electronic energy can be calculated at various inter-nuclear distances.

The simplest of the *ab initio* procedures is the Hartree–Fock self-consistent field method (HF-SCF), originally developed for calculations on atoms and further developed by the Nobel Prize winner John A. Pople[4] and others for calculations on molecules. This method is well described in textbooks[3,5-7] and will be covered later in the semester.

Basis Sets

Almost all electronic structure calculations on molecules make the assumption that molecular wavefunctions can be constructed using a linear combination of atomic orbitals (LCAO).[1,2,8] The atomic orbital functions could be assumed to be the solutions of the Schrödinger equation for the hydrogen atom, known as Slater functions (or Slater-type orbitals, STOs), which have an e^{-r} dependence, where r is the distance from the nucleus. However, integration involving these functions can be difficult and it was shown in 1950[9] that these could be replaced by Gaussian functions (or Guassian-type orbitals, GTOs), which have the form e^{-r^2}, and for which there exist analytical solutions for the integrals. The shape of a Gaussian function is, however, rather different from that of a Slater function, with the absence of a cusp at the nucleus and a more rapid drop in value with the distance from the nucleus.

A linear combination of several GTOs with different α-values can look like a STO, thus several GTOs are needed in any LCAO-MO calculation. They are usually combined together so as to make them look like the usual atomic functions; that is, a single basis function is composed of one or more Gaussian functions. For example, Equation 2 describes an s-type basis function, where N is the number of Gaussian functions composing the basis function, and is called the

$$\chi_{\mu}(r) = \sum_{i}^{N} d_{i\mu} e^{-\alpha_{i\mu} f_{\mu}^{2} r^{2}} \tag{4.2}$$

degree-of-contraction of the basis function. The coefficients, $d_{i\mu}$, are called contraction coefficients, that is, the weighting of each Gaussian contribution to the function. The quantities $\alpha_{i\mu}$ are called the exponents, defining the width of the Gaussian: a large value corresponds to a sharp Gaussian whereas a small value corresponds to a broad Gaussian. The parameters f_{μ} are called the scale factors for the basis functions, most often set equal to one. Values for all of the coefficients are obtained by seeking the best fit to atomic properties, such as ionization energy.

One of the earliest of these is the STO-3G basis set, where three GTOs represent each atomic STO. This is referred to as a “minimal basis set”, as only one of each type of atomic orbital is used. Thus, for the atoms Li – Ne, the 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ STOs are each given by three GTOs. Further improvement can be found by using two 1s functions for hydrogen (different α values) and two 2s and two 2p functions for 2nd row atoms such as carbon. These are known as split-valence, or Pople style, basis sets, where the valence orbitals are represented by two sets of functions but the core orbitals are represented by a single set of functions, for example,

> carbon 3-21G: 1s combination of three Gaussians, 2s and 2p same
> two Gaussians; plus 2s′ and 2p′ same one Gaussian.
>
> carbon 6-31G: 1s combination of six Gaussians, 2s and 2p same
> three Gaussians; plus 2s′ and 2p′ same one Gaussian.

The system of notation used here is of the form i-jk, where i is the number of Gaussians representing each core basis function and j and k are the numbers of Gaussians representing the split-valence basis functions. Further improvement in calculations is obtained by the use of triple-split-valence basis sets, of which the only important one is 6-311G. Here there are 6 Gaussians for the core basis functions and the valence functions are split into three sets, comprising three, one, and one Gaussians, respectively.

In general, electronic structure calculations are often improved by adding functions corresponding to orbitals with a higher angular momentum than those that are occupied. For example p functions may be added to hydrogen, d functions to C, N, O, and so forth, and f functions to transition metals. This is denoted by an asterisk or by specifying functions, for example,

> 6-31G* or 6-31G(d): Adds d functions to 2nd row elements (C, N,
> O, etc.).
>
> 6-31G** or 6-31G(d,p): Adds d functions to 2nd row elements (C,
> N, O, etc.) and p functions to H.

For anions, and atoms with lone pairs, it may be that there is some electron density far from the nuclei. This can be handled by the addition of diffuse functions, which are broad Gaussian functions (small α coefficient) that are not readily calculated for isolated atoms, but are chosen by well-established rules of thumb. These functions are represented in the basis set specification by a + or ++ sign, for example,

> 6-31+G: Adds diffuse functions to 2nd row elements (C, N, O,
> etc.).
>
> 6-31++G: Adds diffuse functions to 2nd row elements and H.

Experience shows that the addition of polarization and diffuse functions to H atoms is not usually necessary.

Calculations involving the heavier atoms, for example, transition metals, can be very time-consuming owing to the large numbers of electrons involved and the fact that larger basis sets are not available for heavier atoms. The problem can be reduced in size by restricting the full calculation to the valence electrons only and including the core electrons simply as an effective core potential (ECP), similar to the “6” in a split-valence basis set. A number of these have been proposed, of which probably the most popular is the Los Alamos ECP. In combination with double-zeta functions for the valence electrons, the Los Alamos ECP is used in the "LanL2DZ" basis set, which is often employed in calculations on molecules involving transition metals.

In contrast to the split-valence basis sets, double zeta (DZ) and triple zeta (TZ) basis sets split all the orbitals into either two or three sets of functions, where the term "zeta" refers to the exponents. Likewise, quadruple zeta (QZ) basis sets split all orbitals into four sets of functions, and so forth. Another important difference between multiple zeta and split-valence basis functions is that different α coefficients are used for s- and p-type orbitals.

The general philosophy employed in choosing a basis set is dictated by the nature of the problem. It is appropriate to choose the biggest (and therefore the best) basis set available for the atoms contained within the molecule of interest, consistent with the need to obtain meaningful results within an acceptable timescale. What constitutes an acceptable timescale is not easy to define but for most problems a researcher would require a solution within a few weeks at most. In practice, the split-valence basis sets 6-31G and 6-311G are the most widely used but are inferior to the double and triple zeta basis sets, respectively. A further advantage of the latter is that the addition of diffuse functions is often unnecessary because these basis sets contain GTOs with small α values. For methods involving electron correlation there are some "correlation consistent"-"polarized valence n zeta" basis sets: cc-pVnZ, where n=D (double), T (triple), Q (quadruple) and 5 (quintuple). These basis sets already contain polarization functions and diffuse functions are added by using the prefix "aug-" for augmented. Software, such as Gaussian 03, contains an extensive range of basis sets but also allow for user-defined basis sets. New basis sets are constantly being developed and a compilation of all basis sets currently available can be downloaded, in program specific formats, from the Web.[10,11]

Electron Correlation Methods

The major deficiency of the HF-SCF method is that it treats each electron as moving under the influence of the average effect of all other electrons. In this approximation the probability of finding any one electron at a particular position in space is independent of the positions of the other electrons.

However, this approach fails to account completely for Coulombic interactions between electrons causing them to repel each other. In other words, the motions of the electrons are "correlated", and electron correlation causes electrons to be further apart than as described by the HF-SCF approach.[5-7] Electron correlation can be handled in quantum chemical calculations using a number of approaches, of which two of the most common are Møller–Plesset perturbation theory and density functional theory.

Møller–Plesset Perturbation Theory

Perturbation theory is a well-established method in quantum mechanics for the solution of the Schrödinger equation, where the Hamiltonian can be represented by the addition of a small perturbation to a Hamiltonian for which solutions are known. Simple examples of applications of perturbation theory are given in most introductory texts on quantum chemistry,[5-7] where it is shown that improvements can be achieved by taking the perturbation to successively higher orders. Electron correlation can be treated by a perturbation approach, since the problem that we are trying to solve is similar to the HF-SCF solution. Møller and Plesset[12] used a perturbation theory method to determine the correlation energy correction, following an HF-SCF calculation. The perturbation can be truncated at second order (MP2), third order (MP3) or even higher orders (MP4 and MP5). This procedure is computationally intensive, especially for higher orders, and even for small molecules can require several gigabytes of disk space for temporary storage of the integrals that are generated. Nevertheless, the effort is rewarded by results that give a much closer fit to experimental data than the HF-SCF method.

Density Functional Theory

Density functional theory (DFT) provides an alternative approach to electron correlation.

The basis of this theory, developed by Hohenberg and Kohn (awarded a Nobel Prize for his work on DFT in the same year that Pople was awarded the Nobel Prize) in 1964[13], is the proof that the ground-state electronic energy is determined completely by the electron density, ρ. The aim of DFT methods is to design functionals connecting electron density with the energy.

A functional equation is an equation where the unknown is a function. Thus, although a wavefunction is a function, an energy depending on a wavefunction or electron density is a functional. A generalized DFT expression is given by Equation 3, where T_S is the kinetic energy

$$E_{DFT}[\rho] = T_S[\rho] + E_{ne}[\rho] + J[\rho] + E_{XC}[\rho] \tag{4.3}$$

functional (S denotes that the kinetic energy is obtained from a Slater determinant), E_{ne} is the electron–nuclear attraction functional, J is the Coulomb part of the electron–electron repulsion functional, and E_{xc} represents the exchange correlation functional. The dependence of each of these terms on the electron density, ρ, is represented by ρ in brackets following each term. In practice, it is customary to use hybrid SCF-DFT methods, where part of the exchange energy is calculated using the HF method, as it is a defined quantity. A wide variety of hybrid methods are available, the two most frequently used are B3LYP and PBE0 (pronounced PBE nought).[14] Hybrid DFT-SCF methods, in general, are particularly attractive because they are only marginally more computationally intensive then HF-SCF, yet provide results that are comparable with those obtained using the much more demanding MP perturbation method.

EQUILIBRIUM STRUCTURES

In most quantum chemical calculations the first step requires optimization of the molecular geometry, which is finding a stationary point on the potential energy surface. Mostly this is done on an isolated molecule, assumed to be in the gas phase and not interacting with any other molecules. This is not a necessary restriction, however, since it is possible to do calculations on interacting molecules, for example, modeling hydrogen bonding or a chemical reaction. Modern software packages also provide methods for incorporating the effect of a solvent or to model the solid state using periodic boundary conditions. For simplicity we will consider only isolated molecules.

A sensible starting point for geometry optimization is to use experimental data whenever possible. For example, the geometry may have been obtained from gas-phase microwave or Raman data or in the solid state from X-ray diffraction in which case it may be convenient to provide the input as Cartesian coordinates. Many of the known crystal structures are available from Internet databases, for example, the Cambridge database. In the absence of experimental data we construct models using reasonable values for bond distances, inter-bond angles, and dihedral angles. Model building may be done using molecular visualization software, such as the Gaussian graphical interface GaussView. It is important to note that even when experimental structures are available it is still often necessary to optimize the geometry at the chosen model chemistry prior to the calculation of molecular properties.

Geometry optimization involves a mathematical procedure called nonlinear optimization, for which several algorithms have been developed.[1,2,8,15] The energy and wavefunctions (or densities) are computed for the initial guess of the geometry, which is then modified iteratively until (i) a stationary point has been identified and (ii) forces within the molecule are zero. This can often be difficult for non-rigid molecules, where several energy minima may exist in close proximity, and some effort may be required to find the global minimum (the lowest energy stationary point characterized as a minimum). Figure 1 shows a flowchart of the steps involved in a geometry optimization.

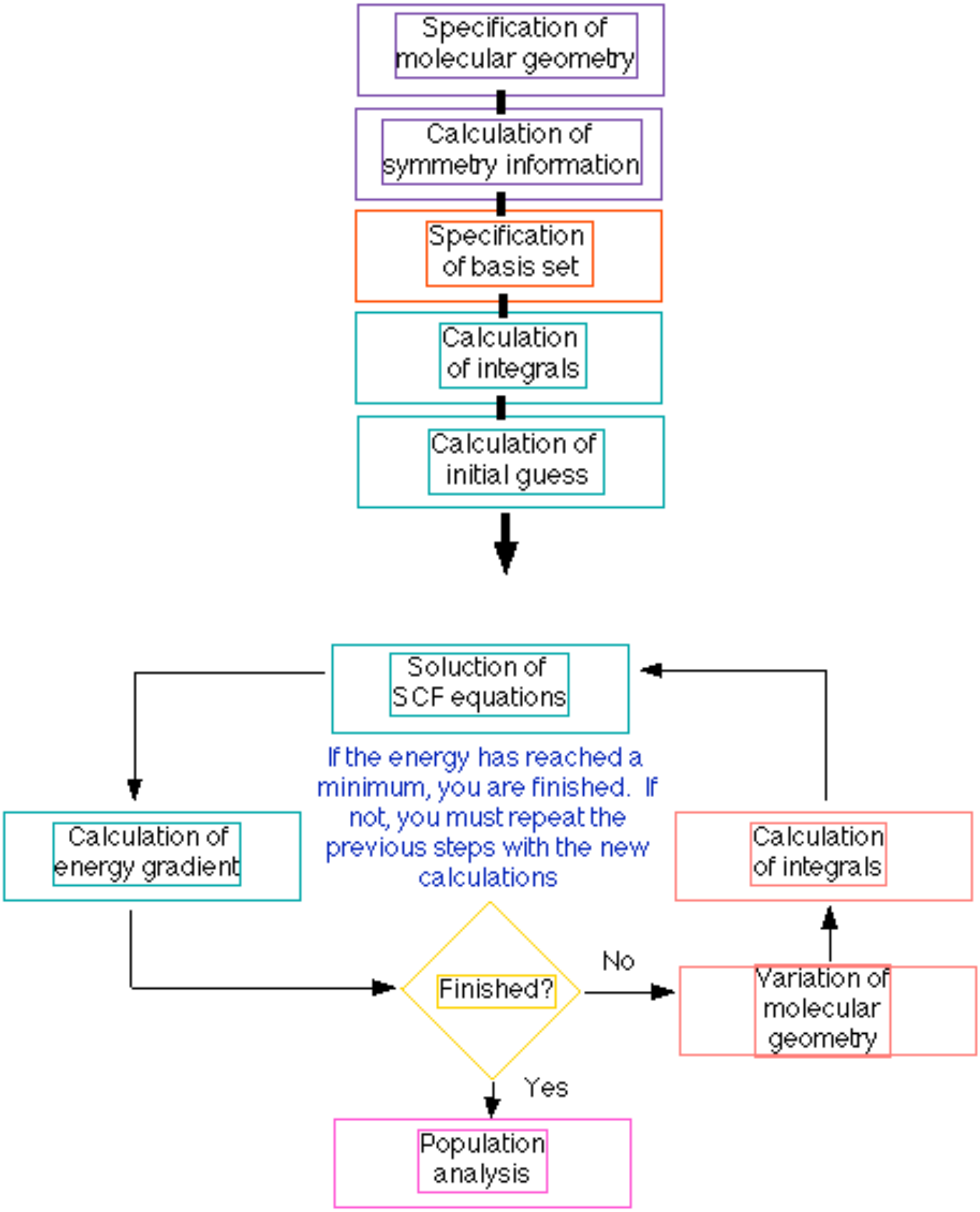

Figure 1. Generalized flowchart of the steps involved in a geometry optimization.

MOLECULAR PROPERTIES

A great many molecular properties can be obtained very easily from quantum chemical calculations, for example, dipole and multipole moments, polarizability, ionization energy, electron affinity, and so forth. Other properties may require more effort; for example, calculation of the vibrational modes involves computation of the second derivative of the energy with respect to pairs of atomic Cartesian coordinates, that is, force constants. In addition to simulation of infrared and Raman spectra, which also require computation of dipole and polarizability derivatives, the determination of force constants provides a useful check on the geometry optimization.[1,2,8,15]

Since an optimized geometry should result in zero forces within the molecule, all principal force constants should be positive and therefore not result in any imaginary vibrational frequencies. If there are one or more imaginary frequencies then the geometry optimization has ended in a transition state, or other type of stationary point, rather than an energy minimum. The eigenvectors of the imaginary frequencies will then help to point in the direction of the structure corresponding to an energy minimum. Finding transition states is, of course, a necessary part of using quantum chemical methods to model reactions.

Note that, vibrational frequency calculations are based on the assumption that vibrations may be treated as harmonic oscillators, whereas in reality vibrations are to some extent anharmonic. This is especially so for vibrations involving hydrogen atoms. Anharmoncity constants can be computed from cubic and quartic force constants (i.e., third and fourth derivatives of energy with respect to atomic Cartesian coordinates) but their calculations are very demanding and are realistic only for smaller molecules. For larger molecules, it is customary to scale the calculated vibrational wavenumbers for comparison with experimental data.

In calculations of the vibrations of larger molecules their assignments are often not straightforward. Although it is customary for organic chemists to attribute bands in infrared and Raman spectra to the stretching or deformation modes associated with specific functional groups, this is really an oversimplification. For example in amides the “C=O” stretching vibration is one which also involves CN stretching and NH in-plane deformation. The proportions of each type of motion that constitute each vibration can be expressed in terms of potential energy distributions. These may be calculated using normal coordinate analysis software, using the force constants and molecular geometry from an *ab initio* calculation. Alternatively, vibrational modes can be shown pictorially, and as animations, using visualization software capable of reading the output from quantum chemical programs.

PROCEDURE

There are many types of calculations you can run. For this lab you will run Energy, Geometry Optimization and Frequency Analysis.

Setting up a calculation

Because you will be running *ab initio* type calculations (recall this is Latin for "from scratch"), you will be required to give the program very specific information so that it has a place to start from.

Molecular structure

Prior to running a calculation, you will need to provide the program with information about what nuclei are present and where they are relative to one another. There are two main options here: (i) providing a z-matrix, whereby you start with a central atom and then define where all other atoms in the molecule are using distances and angles (involving both 3 and 4 atoms) relative to the central atom; (ii) using a Cartesian coordinate system. The former is used when a GUI is unavailable while the latter is straightforwardly obtained using a GUI.

Theory and Basis Set

Each time you run Gaussian, you as a computational chemist must make choices in terms of what approximate model to use in constructing the Hamiltonian for the system. For this lab, you will use Hartree-Fock (HF), second order Møller and Plesset perturbation theory (MP2), and DFT (B3LYP and PBE0, the latter goes by the keyword PBE1PBE in Gaussian) along with several basis sets.

Charge and Multiplicity

These choices depend on your molecule and the electronic state of interest. Specifying the charge simply tells Gaussian how many electrons are in the system relative to the number of protons, which you specified using the molecular structure. Declaring a multiplicity restricts these electrons to certain spin cases.

EXERCISES

1. Calculate the energy of the H-like atoms (H, He^{+}, C^{+5}) using the Hartree-Fock method and the cc-pVnZ basis set series (n=D,T) – you will need to choose custom under basis set and add cc-pVnZ to the extra keyword section, making sure to also include the scf=tight keyword. Tabulate the energy (in Hartree) and number of basis functions for each calculation. Compare your energy results with the exact value and discuss the effect of the number of basis functions. Discuss the effect of increasing nuclear charge on the energy. (16 marks)

2. Perform a geometry optimization followed by a frequency assessment (opt+freq keyword) using the B3LYP method and 6-31-G(d) basis set on two small molecules: BH_3, CH_4. Tabulate the bond lengths, nuclear-nuclear repulsion energy, rotational constants and occupied orbital energies at both the starting geometry and the final optimized geometry. Calculate the HOMO-LUMO gap (in eV), provide the molecules electron configuration (e.g., $\sigma^2\sigma^{*2}\sigma^2\pi^4\sigma^2$), and record the wavenumber for the highest three molecular vibrations and describe their nuclear motions. (39 marks)
3. Is molecular oxygen diamagnetic or paramagnetic? Decide this based on two calculations: one for the triplet state and one for the singlet state. Make sure to optimize the geometry in each case. Tabulate the values from HF, MP2, B3LYP and PBE0 (choose PBE1PBE) using the 6-311+G(d) basis set. Determine ΔE_{S-T} (the energy difference between the singlet and triplet state) in kJ/mol. Discuss whether your results agree with qualitative MO theory? . (14 marks)
4. What is the energy change for the reaction of CH_3^- (methyl anion) and H^+ (hydrogen cation) to form methane (CH_4)? Only use B3LYP, but try it at two different basis sets: 6-31G(d) and 6-311+G(2d,p). Hint: no need to calculate H+ (its electronic energy is zero). Compare your results to the accepted value of -1785 kJ/mol (taken from W1BD calculations which are consistent with the best experimental estimates). When comparing results to an accepted value, you should always compute a percent error. Discuss the relative accuracy of these two basis sets. (10 marks)

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