Advanced Chemistry Classroom and Laboratory ———————

Computational Chemistry Using Modern Electronic Structure Methods

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The undergraduate chemistry curriculum in the 21st century is, in many ways, radically different from that of a generation ago. Indeed it is ironic to note that when the authors were students a great deal of quantum mechanics was taught although there was very little practical use for the knowledge gained, owing to the lack of sufficiently powerful computers. (Nowadays, debatably perhaps, much less quantum chemistry is taught, largely because fewer undergraduates have sufficient mathematical background and there are fewer lecturers capable of teaching the subject adequately.) However, the power of modern computers, even that of a PC of modest specification, means that high-level calculations on molecules of medium size are possible. 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. At the beginning of the 21st century applications to molecules of biological interest are now beginning to be possible.

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. 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. The purpose of this article is to provide background to the methods employed in quantum chemistry, illustrated by some simple examples. There are a number of software packages available for electronic structure calculations and molecular visualization, the majority of which are user-friendly and suitable for class use.[1] We use the Gaussian package, which can be run either in the Unix or MS Windows environments. This program is especially suitable for undergraduate use; the latest version is Gaussian 03 (1).

The Schrödinger equation is the cornerstone of quantum mechanics:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}\left(E - V\right)\psi = 0 \quad (1)$$

Solution of the equation provides the wavefunctions, Ψ, which describe the behavior of electrons in atoms and molecules, as well as the eigenvalues, *viz* their associated energies, E. It is well-known, however, that exact analytical solutions can only be found for simple cases such as the particle in a box, harmonic oscillator, rigid rotor, and the hydrogen atom or hydrogen-like ions. Even for a simple two-electron system such as the helium atom, only approximate solutions can be found. However, the availability of powerful computers means that for polyelectronic 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. The input for such calculation requires the definition of *a basis set, the molecular geometry, charge, and spin multiplicity*.

For large (non-polymeric) molecular weight molecules it is often necessary to use semiempirical methods, in which many of the integrals required to be solved are replaced by parameters that have been obtained from experimental measurements, in particular from thermochemical and spectroscopic data. Semiempirical 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. These methods are also particularly attractive for computational chemistry workshop exercises in an undergraduate chemistry course.

Ab Initio Calculations

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 motion of electrons in a molecule is much faster than that of the nuclei, the positions of nuclei may be assumed to be fixed. 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 internuclear distances.

The simplest of the ab initio procedures is the Hartree–Fock self-consistent field method (HF-SCF) (2), which was originally developed for calculations on atoms and later further developed by the Nobel Prize winner Pople (3) and oth-

ers for calculations on molecules. This method is well-described in textbooks and will not be discussed further.

Basis Sets

All electronic structure calculations on molecules make the assumption that molecular wavefunctions can be represented as the linear combination of atomic orbitals (LCAO). The atomic orbital functions could be assumed to be the solutions of the Schrödinger equation for the hydrogen atom, which have an $\exp(-r)$ dependence, where r is the distance from the nucleus. Nevertheless, integration involving these functions can be difficult and it was shown in 1950 *(4)* that these could be replaced by Gaussian functions, which have the form $\exp(-r^2)$, and for which there exist analytical solutions for the integrals. The shape of a Gaussian function is, however, rather different from that of a $\exp(-r)$ function, as shown in Figure 1, since there is no cusp at the nucleus and it tails off more rapidly with distance from the nucleus.

However, the combination of several Gaussian functions with different bandwidths does give a closer match to real atomic functions. A linear combination of several Gaussian functions with different α values (half-bandwidths) can look like the atomic functions 1s and so forth but many are needed in any LCAO-MO. 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, an s-type basis function is

$$\Psi_\mu(r) \;=\; \sum_i^N d_{i\mu} \exp\!\left(-\alpha_{i\mu} f_\mu^2\, r^2\right) \tag{2}$$

where N is the number of Gaussian functions composing the basis function, and is called the degree-of-contraction of the basis function. The coefficients d_i 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, but are 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, for example,

> STO-3G: This is called a "minimal basis set", 1s is given by **three** Gaussians and 2s, $2p_x$, $2p_y$, $2p_z$ *each* by another **three**.

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 basis sets, in which 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.
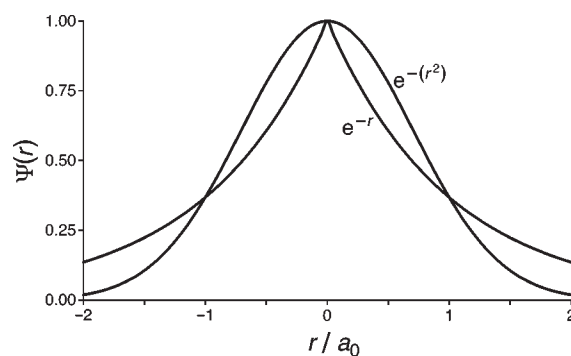

Figure 1. Comparison of $\exp(-r)$ and $\exp(-r^2)$ functions.

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 contrast to the split-valence basis sets the 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 orbitals.

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. These are denoted by adding an asterisk to the basis set or specifying p, d functions, and so forth, 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. Experience shows that the addition of polarization and diffuse functions to H atoms is not usually necessary, 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.

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). 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.

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 Gaussian functions with small α values. For methods involving electron correlation there are some "correlation consistent" basis sets: cc-pVNZ, where N = D (double), T(triple), Q (quadruple) and 5 (quintuple) zeta. These basis sets also contain polarization functions; diffuse functions are added by using the prefix "AUG-". Software such as Gaussian 03 contains an extensive range of basis sets but also enables the use of user-defined basis sets. A full compilation of all the basis sets that are currently available can be downloaded from the Web.[2]

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 motion of the electrons are said to be correlated, and electron correlation causes electrons to be further apart than as described by the HF-SCF approach. Electron correlation can be handled in quantum chemical calculations using Møller–Plesset perturbation theory or 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 one for which solutions are known. Simple examples of applications of perturbation theory are given in most introductory texts on quantum chemistry, 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 (5) 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 also awarded a Nobel Prize) in 1964 (6), 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

$$E_{DFT}[\rho] = T_S[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \quad (3)$$

where T_S is the kinetic energy 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 in which the exchange energy is calculated by the HF method. A wide variety of hybrid methods are available, the one used most frequently is B3-LYP, which incorporates Becke's three parameter exchange functional (B3) (7) with the Lee, Yang, and Parr correlation functional (LYP) (8). 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.

Geometry Optimization

In any quantum chemical calculation the first step requires optimization of the molecular geometry. 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, in the United Kingdom using the Cambridge database accessible via CrystalWeb.[3] In the absence of experimental data we construct models using reasonable values for bond distances, interbond angles, and dihedral angles. Model building may

be done using molecular visualization software, such as the Gaussian graphical interface GaussView, or by the Z-matrix method (Box 1).

It is important to note that even when experimental structures are available it is still necessary to optimize the geometry at the level of theory we are using before attempting calculations of molecular properties. Geometry optimization involves the mathematical procedure called nonlinear optimization, for which several algorithms have been developed.

The energy and wavefunctions are computed for the initial guess of the geometry, which is then modified iteratively until (i) an energy minimum has been identified and (ii) forces within the molecule are zero. This can often be difficult for nonrigid molecules, where there may be several energy minima, and some effort may be required to find the global minimum. Figure 2 shows a flowchart for the steps involved in geometry optimization.

The Z-matrix effectively provides a "road map" specifying the structure of a molecule in terms of internal coordinates, which are of three types: bond distances, interbond angles, and dihedral angles. Each line of a Z-matrix specifies the internal coordinates for an atom within the molecule, in the following manner:

Atom 1, Atom 2, bond distance, Atom 3, interbond angle, Atom 4, dihedral angle

Note that the first atom to be defined is the starting point and requires no coordinates, the second atom requires only a bond distance, the third atom only a bond distance and interbond angle, but the fourth and subsequent atoms require all three coordinates

The following Z-matrix could be used for hydrogen peroxide, H_2O_2, where the atom numbers and coordinates are defined in the diagram.
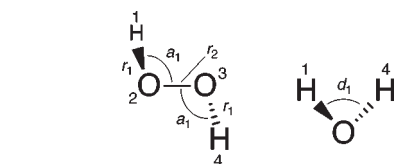

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H1
O2   H1   r1
O3   O2   r2   H1   a1
H4   O3   r1   O2   a1   H1   d1
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Bond distances are given in Å and angles in degrees. The dihedral angle is that between the planes formed by atoms 1-2-3 and 2-3-4. It is positive if, viewing along bond 2-3, with atom 2 nearer to the observer than 3, the angle from the projection of 2-1 to the projection of 3-4 is traced in a clockwise direction.

By using the same variables for the two OH distances and the two OOH angles we ensure that the geometry optimization proceeds with the correct symmetry, i.e., C_2. Coordinates may be specified as constants instead of variables, by using the actual values rather than symbols in the Z-matrix. This is useful when exploring different conformers of a molecule by, for example, using constant values of a dihedral angle to specify eclipsed or staggered conformers.

The advantage of the Z-matrix method, with respect to Cartesian coordinates, is that it is straightforward, although often time-consuming, for large molecules, since no three-dimensional trigonometry is required. Although using model building software with a graphical user interface is much easier, the Z-matrix offers a greater degree of control, especially when exploring different conformers.

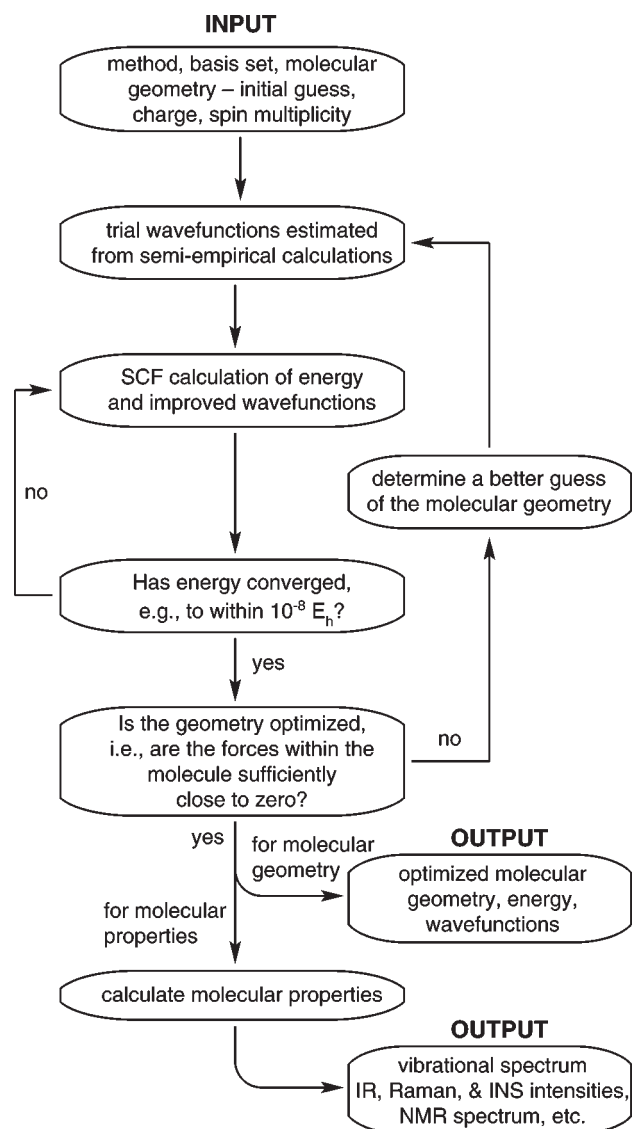Box 1. The Z-matrix method.

Figure 2. Flowchart illustrating the steps involved in quantum chemical calculations of molecular structures and properties.

Table 1. HF-SCF Calculations on H₂O

Basis Set	No. of Functions	E/E_h	r/Å	θ/deg
STO-3G	7	−74.9659	0.989	100.0
3-21G	13	−75.5860	0.967	107.6
3-21+G	17	−75.6193	0.965	111.0
3-21G**	19	−75.6180	0.941	105.8
3-21+G**	23	−75.6523	0.939	108.8
6-31G	13	−75.9854	0.950	111.6
6-31G*	19	−76.0108	0.947	105.5
6-31+G*	23	−76.0177	0.948	106.5
6-31G**	25	−76.0236	0.943	106.0
6-31+G**	29	−76.0312	0.943	107.1
6-31++G**	31	−76.0313	0.943	107.1
6-311G	19	−76.0110	0.946	111.9
6-311G*	24	−76.0324	0.939	107.5
6-311+G*	28	−76.0378	0.940	108.1
6-311++G*	30	−76.0380	0.940	108.1
6-311++G**	36	−76.0534	0.941	106.2
DZ	14	−76.0110	0.951	112.5
DZ*	20	−76.0352	0.947	106.4
DZ+*	24	−76.0377	0.947	106.7
DZ**	26	−76.0470	0.944	106.6
DZ++**	32	−76.0498	0.945	106.8

Table 2. MP2 Calculations on H₂O

Basis set	No. of Functions	E/E_h	r/Å	θ/deg
STO-3G	7	−75.00604	1.014	97.3
3-21G	13	−75.70780	0.989	105.1
6-31G	13	−76.11318	0.975	109.3
6-31+G*	23	−76.20978	0.971	105.5
6-311+G*	28	−76.24471	0.959	107.6
DZ	14	−76.13639	0.979	110.6
DZ+*	24	−76.22614	0.971	105.6
DZ++**	32	−76.24964	0.965	104.7
cc-pVDZ	24	−76.22867	0.965	101.9
AUG-cc-pVDZ	41	−76.26091	0.966	103.8
cc-pVTZ	58	−76.31866	0.959	103.5
AUG-cc-pVTZ	92	−76.32899	0.962	104.2

Table 3. B3-LYP Calculations on H₂O

Basis set	No. of Functions	E/E_h	r/Å	θ/deg
STO-3G	7	−75.32277	1.027	97.2
3-21G	13	−75.97397	0.997	103.9
6-31G	13	−76.38612	0.976	108.3
6-31+G*	23	−76.42257	0.969	105.5
6-311+G*	28	−76.44381	0.963	107.0
DZ	14	−76.41439	0.977	110.0
DZ+*	24	−76.44280	0.970	105.7
DZ++**	32	−76.45272	0.967	105.4
cc-pVDZ	24	−76.42063	0.969	102.8
AUG-cc-pVDZ	41	−76.44464	0.965	104.7
cc-pVTZ	58	−76.45984	0.961	104.4
AUG-cc-pVTZ	92	−76.46620	0.962	105.1

Table 1 shows the results of HF-SCF calculations on H₂O with a variety of basis sets, giving the energy and molecular geometry. There is a general trend towards lower energy with increasing number of basis functions, although the double zeta basis set (DZ) gives lower energies than the split-valence basis sets 6-31G and 6-311G with fewer functions. Larger basis sets have not been included in this tabulation because they do not yield any significant improvement compared to the HF-SCF method. The energies are given in Hartrees (1 E_h = 4.3597×10^{-18} J and is equivalent to 2625.5 kJ mol⁻¹).

The molecular geometry can be compared with the experimental values r = 0.958 Å and θ = 104.5°. Small basis sets yield a bond length that is too large, whereas the larger basis sets make the bond length too short. A wide variety of bond angles are obtained, which are mostly larger than the experimental value. A closer fit to experimental data is achieved using electron correlation methods, as illustrated in Tables 2 and 3, which shows the results of MP2 and B3-LYP calculations on H₂O. Clearly, the MP2 and B3-LYP methods yield results that are much closer to experimental data than the HF-SCF method. In Figure 3 we compare the cal-
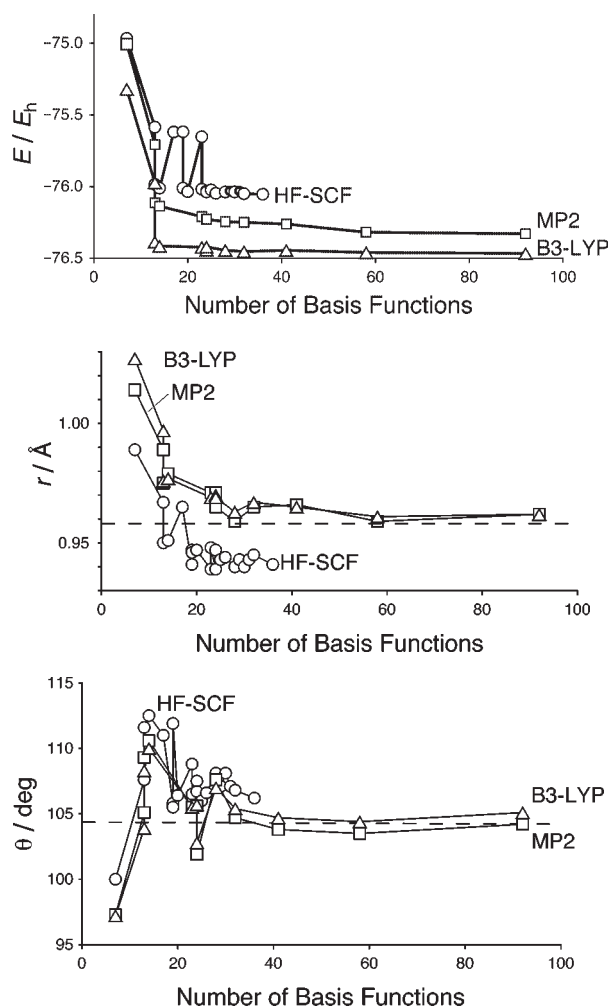

Figure 3. Comparison of the calculated energy, bond distance, and interbond angle for H₂O using the HF-SCF, MP2, and B3-LYP methods with different basis sets. The dotted line represents the experimental value.

culation of energies, bond distance, and bond angle for H_2O using the three methods.

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. 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 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.

As examples, Tables 4 and 5 show some HF-SCF, MP2, and B3-LYP calculations of the vibrational spectra of two simple molecules: methane and methanal. These examples have been chosen because the calculations are sufficiently small that they could be done as exercises within a workshop on quantum chemistry. In both cases the calculated vibrations are compared with the experimental values of the harmonic, $\tilde{\nu}$, and anharmonic, $\tilde{\omega}$, wavenumbers. As we would expect the electron correlation methods give far superior results to the HF-SCF method. Although the calculated band wavenumbers differ somewhat from their observed positions (i.e., anharmonic values), the MP2 and B3-LYP calculations give a good fit to the harmonic band wavenumbers. This is because the 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, as is made evident in the tables. 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 (molecular weight) molecules. For larger molecules, it is customary to scale the calculated vibrational wavenumbers for comparison with the (anharmonic) experimental data.

For the examples given here the assignments of the molecular vibrations are well-established. 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 that is capable of reading the output of quantum chemical programs such as Gaussian. The freeware program Moldaw (9) is ideal for such purposes since, in addition to the capability of displaying molecular structures from a variety of file formats (including the popular pdb format), it can also extract the molecular geometry and vibrational modes from a Gaussian output file. For the visualization of molecular orbitals the authors recommend the freeware programs Molekel (10) and gOpenMol (11).

Table 4. Calculations of the Molecular Vibrations of CH$_4$

Vibration	$\nu_1(a_1)$	$\nu_2(e)$	$\nu_3(t_2)$	$\nu_4(t_2)$
Description	sym str	sym def	antisym str	antisym def
Expt. $\tilde{\omega}$	3025.5	1367.4	3156.8	1582.7
$\tilde{\nu}$	2918.0	1310.8	3019.2	1533.7
HF/6-31G(d,p)	3174.4	1469.0	3285.2	1685.5
HF/6-311+G(3df,2p)	3148.4	1454.6	3246.3	1666.9
MP2/6-31G(d,p)	3132.6	1404.5	3273.6	1624.1
MP2/6-311+G(3df,2p)	3077.1	1357.5	3211.4	1588.2
B3-LYP/6-31G(d,p)	3047.4	1356.4	3163.8	1579.3
B3-LYP/6-311+G(3df,2p)	3026.5	1342.6	3128.9	1560.2

Table 5. Calculations of the Molecular Vibrations of H$_2$CO

Vibration	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(a_1)$	$\nu_4(b_1)$	$\nu_5(b_1)$	$\nu_6(b_1)$
Description	$\nu_s(CH_2)$	$\nu(CO)$	$\delta(CH_2)$	δ_{op}	$\nu_{as}(CH_2)$	$\delta(HCO)$
Expt. $\tilde{\omega}$	2977.9	1778.3	1529.0	1191.0	2997.0	1298.1
$\tilde{\nu}$	2782.5	1746.0	1500.2	1167.3	2843.3	1249.1
HF/6-31G(d,p)	3120.5	2025.3	1668.3	1335.6	3195.4	1376.7
HF/6-311+G(3df,2p)	3088.6	1989.8	1649.3	1333.9	3157.5	1367.3
MP2/6-31G(d,p)	3026.1	1791.6	1586.5	1218.3	3103.8	1296.4
MP2/6-311+G(3df,2p)	2974.9	1769.5	1547.9	1200.8	3050.5	1275.4
B3-LYP/6-31G(d,p)	2898.9	1846.5	1554.7	1200.3	2955.6	1274.4
B3-LYP/6-311+G(3df,2p)	2883.3	1812.6	1531.1	1196.1	2940.6	1264.5

Further Reading

As the next step from this article we thoroughly recommend the companion to the Gaussian software *Exploring Chemistry with Electronic Structure Methods (12)*. This book provides a more detailed description of the topics covered here and contains abundant examples. We also recommend the textbook by Simons *(13)* and his web site *(14)*, which contains a wealth of information and useful links, and the books by Jensen *(15)* and Cremer *(16)*.

Notes

1. Access to the Web sites for most of the available software can be gained from *http://www.chem.swin.edu.au/chem_ref.html* (accessed May 2007).

2. A full compilation of all the basis sets that are currently available can be downloaded from *http://www.emsl.pnl.gov/forms/basisform.html* (accessed May 2007).

3. Many of the known crystal structures are available from *http://cds.dl.ac.uk* (accessed May 2007).

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