



Computational Chemistry Workshops
West Ridge Research Building-UAF Campus
9:00am-4:00pm, Room 009

Electronic Structure - July 19-21, 2016
Molecular Dynamics - July 26-28, 2016

Aspects of Computational Chemistry

Why Computational Chemistry?

Chemistry is an experimental science which provides insights concerning the behavior of matter, including the properties of molecules and their interaction with each other. Experiments are studied using a broad variety of experimental techniques, and new molecules are synthesized using a mixture of rational strategies and trial and error procedures. At all stages of a chemical investigation, the same basic questions arise, which pose the framework for the discipline of Computational Chemistry:

1. How are the results of a chemical experiment or a physical measurement analyzed?

This question is concerned with the correct interpretation of physical measurements with respect to the behavior of the molecular system under investigation. This could possibly be an NMR or IR spectrum, the measurement of a pK_a value, or a kinetic or thermochemical measurement. In very many cases, the analysis of the experiment immediately rules out several possibilities but allows other alternatives.

Computational Chemistry can help to discern between alternatives, and may be able to reliably predict the outcome of the experiment from all possible alternatives.

2. Can one exclude several possibilities from consideration by predicting the outcome of the experiment beforehand?

This question is concerned with predictive power. For example, if there is a model or that reliably indicates what is and what is not possible, it may save a great deal of time in the laboratory by avoiding the possible synthesis of compounds that may never exist, or by running reactions that may never provide the desired result.

A truly predictive model based on Computational Chemistry can thus save much time from trial and error by guiding the experimental work.

3. What are the underlying principles that govern the behavior of classes of substances?

This question is concerned with the degree of qualitative insight that chemists very often need, in order to understand the behavior of classes of substances, such as the ability to categorize a large body of experimental evidence in terms of the properties of functional groups or structural motives.

Thus, a good theory should not only provide results that pertain to individual molecules, but also provide a framework and language in which the results obtained for related substances can be phrased.

Fortunately, there exists an excellent theory based on Quantum Mechanics, which to some extent, satisfies all of the criteria mentioned above. Quantum Mechanics applied to chemistry defines the field of Quantum Chemistry, which is based on theoretical physics, but the areas studied are mostly of a chemical nature. Quantum Chemistry is a sub-discipline of theoretical chemistry which contains many other branches that are not directly related to Quantum Mechanics, such as Molecular Dynamics, for example.

This workshop is concerned with Quantum Chemistry in its practical realization, Computational Chemistry, and is intended to show with an absolute minimum of theoretical

background, how to approach chemical problems with the aid of computers. Despite the usefulness and sophistication of the theoretical approaches, it is important to be critical, and to seek close ties with the experimental results. This process will ultimately also enable one to perform better calculations, as well as an ability to judge their strengths and weaknesses.

Chemical Intuition versus Rigorous Calculations

Chemical Intuition

Closely related to the desire for qualitative understanding is the nature of developing models of reality based on chemical intuition. A chemical model aims at providing a conceptual framework in which a restricted part of reality can be understood and discussed on the basis of a minimum number of preferably simple rules. Typical examples for models that have deeply invaded chemical thinking are the Hückel model of aromatic molecules and the Ligand Field Theory of inorganic chemistry. Both are qualitative models and do not have strong theoretical underpinnings. Yet, after the introduction of a minimum number of parameters, e.g. resonance integrals, ligand-field strengths, Racah parameters, a tremendous amount of insight is provided into the behavior of very large classes of compounds.

Thus, chemical models imbedded in concepts derived from chemical intuition are qualitative, if one defines rigorous first principles of physics as the ultimate target. However, with a good model, based on chemical intuition, the parameters have a direct connection to those first principles. In this sense, the Hückel theory and Ligand Field Theory are relatively qualitative models where neither the ligand-field strength nor the resonance integrals have any rigorous theoretical definition. However, the spin-Hamiltonian model, used to interpret NMR and ESR spectra is a very good chemical model, since the parameters used with it, including chemical shifts, spin-spin couplings, g-factors, and hyperfine coupling constants can be rigorously related to first principles of physics.

Rigorous Calculations

On the opposite extreme are high-accuracy calculations that can presently be performed with sophisticated computer programs and large-scale computational facilities. The outcomes of such calculations are highly accurate numbers that refer to individual molecules, in particular electronic states. One could argue that the only properties of interest are physical observables such as the molecular structure, or the energy change during a chemical reaction or spectroscopic transition. Thus, each molecule is a completely separate physical entity, whose particular property is calculated to high precision.

The usefulness of a given theoretical method is then judged by statistical means where the average and maximum errors for a large collection of molecules are studied. Using this approach, one basically discards the much of the chemical regularity that is close to the heart of the vast majority of experimentally working chemists.

Both the model and rigorous calculational approaches have much to recommend themselves. It is indisputable that models are of great importance for the past, present, and future of chemistry. Equally important is the development of theories that make ever more precise predictions in ever shorter turnaround times. Yet, it is important to attempt a qualitative approach to pick out the chemical concepts inside the complicated computations.

Molecular States and Total Energies

Quantum mechanics is centered around the Schrödinger equation, which exists in both time-dependent and time-independent forms. For a given molecular system with N -electrons and M -nuclei, the time-independent Schrödinger equation has an infinite number of solutions which define the states of definite energy that the system can adopt. Associated with each state is a:

- Total Energy: $E_I(I = 0, 1, \dots)$, and a
- N-electron Wave function: $\Psi_I(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$

where \mathbf{x}_i denotes the space and spin-coordinates of a single electron. The square of the many-electron wave function evaluated at the point $\mathbf{x} \equiv \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N$ corresponds to the probability density associated with the probability of finding N electrons in an infinitesimal volume element $d\mathbf{x}$ around point \mathbf{x} . Transitions between such states are observed in spectroscopic experiments. Dynamics of evolving systems can be studied by solving the time-dependent Schrödinger equation. This workshop is mainly concerned with molecules in stationary states and, in particular, in their lowest energy state, E_0 , which is called the electronic ground state. However, the energies of excited states will be studied as well.

The Born-Oppenheimer Approximation

In addition to the total energy E and the many-electron wavefunction Ψ , the Schrödinger equation contains the Hamiltonian Operator (HO), H , which corresponds to the total energy of the system. Fortunately, for the vast majority of chemical applications, the HO contains only a few terms, namely those that describe the kinetic energy of the particles (electrons, nuclei) and their electrostatic (coulombic) interactions which is inversely proportional to the interparticle distance. All other terms that contribute to the total energy are much smaller, and can be well treated using the methods of perturbation theory. Despite this deceptive simplicity, the Schrödinger equation for a molecule is still far too complex to be solved either analytically or numerically and therefore approximations are necessary. The refinement of such approximations represents a major research goal of Quantum Chemistry.

The first approximation that is central to Quantum Chemistry is the Born-Oppenheimer (BO) approximation which allows for the separate, independent treatment of electrons and nuclei. It rests on the fact that nuclei are much heavier than electrons, and consequently move much more slowly. Thus, the fast electrons are always in equilibrium with the slow nuclei.

All Computational Chemistry rests on the fundamental assumption of the Born-Oppenheimer Approximation in which the motions of the electrons and atomic nuclei can be decoupled and treated separately:

$$\Psi(\mathbf{R}, \mathbf{r}) = \Psi^{nucl}(\mathbf{R}) \times \Psi^{elec}(\mathbf{R}, \mathbf{r})$$

This is an enormously simplifying feature for the equations used in modeling and simulation and leads to two major fields of simulation with many subfields.

Potential Energy Surfaces

The electronic wave function above depends parametrically on the nuclear configuration (\mathbf{R}), and is the solution of the electronic Schrödinger equation.

$$H^{elec}\Psi^{elec}(\mathbf{R}, \mathbf{r}) = E(\mathbf{R})\Psi^{elec}(\mathbf{R}, \mathbf{r})$$

where H^{elec} is the electronic Hamiltonian and corresponds to the motion of electrons (\mathbf{r}) in the field of fixed nuclei (\mathbf{R}).

- The potential energy surfaces (PES) are generated by the solution of the electronic part of the Schrödinger equation which provides an energy for each fixed position of the nuclei, yielding a $3N - 6$ dimensional surface.
- Each electronic state has its own PES.
- On this PES, the motion of the nuclei can be treated either classically or quantum mechanically.

As a consequence of the Born-Oppenheimer approximation, the nuclei can be assumed to be at rest from the point of view of the electronic system, and the Schrödinger equation needs to only be solved for the electrons at fixed nuclear positions. The total energies and many-electron wave functions then become parametric functions of the nuclear coordinates

$$E_I(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_M) \equiv E_I(\mathbf{R}), \text{ wavefunction } \Psi_I(\mathbf{x}|\mathbf{R})$$

The function $E_I(\mathbf{R})$ is called a potential energy surface (PES), and it can be obtained by calculating the energy, $E_I(\mathbf{R})$, the electronic energy, at different points \mathbf{R} . Unfortunately, the variation of the energy with respect to \mathbf{R} can be visualized graphically only for, at most, two coordinates which represents two-dimensional cuts through very complicated energy landscapes.

Particular points on a given potential energy surface deserve special attention. These are the stationary points, $\bar{\mathbf{R}}$, and are characterized by a vanishing first derivative:

$$\frac{\partial E_I(\mathbf{R})}{\partial R_A} = 0 \quad \text{for all } A$$

Such points can be minima, maxima, or saddle points of varying order. The nature of a stationary point can be determined by calculating the Hessian matrix:

$$H_{AB} = \frac{\partial^2 E_I(\mathbf{R})}{\partial R_A \partial R_B}$$

Either six eigenvalues or five eigenvalues for linear molecules of the Hessian matrix are precisely zero, and correspond to nuclear motions that describe the molecular translations and rotations. For minima, all remaining eigenvalues of the Hessian matrix must be positive. A single negative eigenvalue corresponds to a transition state in a chemical reaction. Higher order saddle points are not of chemical interest. Note, that for a given electronic state, say the ground state, the function, $E_0(\mathbf{R})$, may have many minima which correspond to different isomers or conformations of a molecular system. Each stationary point is associated with a different total energy, and the lowest of such energies represents the most stable of the possible isomers.

Wave Function Theory (WFT)

Unfortunately, even within the Born-Oppenheimer approximation, the properties of N -electron molecules cannot be solved exactly except for 1- and 2-electron systems, since the task is still far too complex. Over the decades, the community of theoretical chemists and physicists has studied this problem extensively and developed many different approximations to the problem. Presently, the most popular of these methods will be discussed below.

Semiempirical Methods

Such methods include Hückel, Extended Hückel, CNDO, ZINDO, and others, are designed as inexpensive substitutes for either Hartree-Fock (HF) or Density Functional Theory (DFT) based methods. In contrast to the latter methods, they contain many adjustable parameters that are used to compensate for the drastic neglect of certain integrals that are time-consuming to calculate in the more precise methods. Semiempirical methods can be used for much larger molecular systems than either the HF or DFT methods. However, these methods are also much less reliable.

Extended Hückel Molecular Theory (EHT)

The Hückel theory is the simplest semi-empirical method for the description of molecular systems, and will be discussed a little later on. It was developed in 1931 by Erich Hückel for the calculation of planar conjugated hydrocarbons.

Later, Hoffmann generalized this very successful concept, termed Extended Hückel Theory (EHT), to all molecules, and applied it with great success to many areas of chemistry. The appeal of the Hückel and EHT methods is that they can provide many qualitative insights into the behavior of molecules, in particular of molecules that are closely related. It is always a good idea to perform a few simple EHT calculations at the beginning of a project in order to gain familiarity with the systems investigated and to use the results to determine what factors might be worthwhile examining with more rigorous electronic structure methods.

EHT theory might be thought of as an essentially very simple, semiempirical approximation of Hartree-Fock (HF) theory. In HF theory, a single Slater determinant is taken as the wavefunction for the description of the N -electron system.

The single determinant is composed of one-particle molecular orbitals (MOs) that are found as solutions to a pseudo-eigenvalue problem of the form:

$$\hat{F}\psi_i = \varepsilon_i\psi_i \quad (1)$$

where \hat{F} is the Fock operator, which describes the motion of a single electron in the field of the nuclei and the remaining electrons.

The MOs are written as a linear combination of atomic orbitals (LCAO):

$$\psi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i} \varphi_{\mu}(\mathbf{r}) \quad (2)$$

after which the calculation boils down to the solution of a generalized eigenvalue problem for the determination of the unknown MO coefficients, $c_{\mu i}$, and the orbital energies, ε_i :

$$\mathbf{F}\mathbf{c} = \varepsilon\mathbf{S}\mathbf{c} \quad (3)$$

Where ε is a diagonal matrix with orbital energies and the matrix elements of the Fock matrix, \mathbf{F} , and overlap matrix, \mathbf{S} , are defined by:

$$\begin{aligned} F_{\mu\nu} &= \langle \varphi_{\mu} | \hat{F} | \varphi_{\nu} \rangle \\ S_{\mu\nu} &= \langle \varphi_{\mu} | \varphi_{\nu} \rangle \end{aligned} \quad (4)$$

As will be discussed, more quantitative methods, such as HF or Density Functional Theory (DFT) calculations, require the use of large basis sets and iterative cycles for the optimization of the MOs. In EHT theory, one focuses on the qualitative shape of the valence orbitals and usually pays attention to those orbitals that are located near the highest occupied molecular orbital (HOMO) - lowest unoccupied molecular orbital (LUMO) gap.

According to qualitative molecular orbital arguments, the highest and lowest molecular orbitals are the most important for determining the reactivity of the system. In order to obtain an idea of what these orbitals may look like, it is not necessary to solve the rather laborious Hartree-Fock equations. In fact, this was a major challenge for all but the smallest molecules in the 1960s, when EHT theory was suggested. The assumptions involve replacing the Fock operator by a semiempirical effective one-electron operator, \hat{h}_{eff} , and including a minimal set of valence orbitals, φ_i .

For example, a carbon atom includes $2s, 2p_x, 2p_y, 2p_z$ orbitals, while for titanium atom, $3d_{xy}, 3d_{xz}, 3d_{yz}, 3d_{x^2-y^2}, d_{z^2}$, and $4s, 4p_x, 4p_y, 4p_z$ orbitals are employed. It is not necessary to specify the operator \hat{h}_{eff} precisely. In order to solve [Equation 1](#), it is necessary to specify only the matrix elements of this operator which are given by:

$$h_{\mu\nu}^{\text{eff}} = \begin{cases} \alpha_{\mu\mu}, & \text{if } \mu = \nu \\ \beta_{\mu\nu}, & \text{if } \mu \neq \nu \end{cases} \quad (5)$$

The diagonal elements $\alpha_{\mu\mu}$ represent the energy of atomic orbital, φ_{μ} , in the free atom, and are approximated by the valence shell ionization energies (VOIP), which can be determined from atomic spectroscopy. These numbers are negative and represent the average energy required to remove an electron from the given orbital ($2s, 2p, 3d, \dots$). The lower these energies, the higher the electron attracting ability of the atom. The off-diagonal matrix elements are called resonance integrals which measure the strength of interaction between two atomic orbitals. Intuitively, it is reasonable to expect that these integrals are related to the overlap integrals, and in EHT, are given by:

$$\beta_{\mu\nu} = \frac{1}{2}KS_{\mu\nu}(\alpha_{\mu} + \alpha_{\nu}) \quad (6)$$

The constant, $K = 1.75$, is an empirical parameter which is used for adjusting the resonance integrals to reasonable values given that the form of Equation 6 is an approximation. Values of α parameters for atoms H – F are given in Table 1

Element	α_{1s}	α_{2s}	α_{2p}
H	-13.60	-	-
Li	-	-5.40	-3.50
Be	-	-10.00	-6.00
B	-	-15.20	-8.50
C	-	-21.40	-11.40
N	-	-26.00	-13.40
O	-	-32.30	-14.80
F	-	-40.00	-18.10

Table 1: Values of α (eV) Used in EHT Calculations.

Following the solution of the generalized eigenvalue problem in Equation 3 with the approximations described above, the resulting MOs are filled in order of increasing energy with the available electrons to find the electronic ground state. The total energy is simply the sum of orbital energies:

$$E^{\text{EHT}} = \sum_i n_i \varepsilon_i \quad (7)$$

where n_i ($= 0, 1$ or 2) is the occupation number of the i^{th} orbital. In connection with

Hückel Molecular Orbital Theory (HMO) for π -Electron Systems

Although it existed prior to EHT theory, the HMO theory of planar aromatic π -systems might be thought of as a further simplification of the EHT method. In this case, one considers only the π -electrons in p_z orbitals of planar molecules. Substituent effects are included in an approximate mannerr, by modifying the π -parameters of the atoms to which the substituents are attached.

In Hückel theory only resonance integrals between atoms that are nearest neighbours are kept and assigned a constant value.

$$h_{\mu\nu}^{\text{eff}} = \begin{cases} \alpha_{\mu\mu}, & \text{if } \mu = \nu \text{ orbitals are on the same atom} \\ \beta_{\mu\nu}, & \text{if } \mu \neq \nu \text{ orbitals are on different atoms and bonded to each other} \\ 0, & \text{if } \mu \neq \nu \text{ orbitals are on different atoms and **not** bonded to each other} \end{cases} \quad (8)$$

Furthermore, in HMO theory, the off-diagonal elements of the overlap matrix are neglected:

$$S_{\mu\nu} = \begin{cases} 1 & \text{if } \mu = \nu \\ 0 & \text{otherwise} \end{cases} \quad (9)$$

Thus, the calculations become geometry independent, and the only construct required to perform an HMO calculation is molecular connectivity.

The final eigenvalue problem to be solved is:

$$\mathbf{h}^{\text{eff}} \mathbf{c} = \varepsilon \mathbf{c} \quad (10)$$

Although these approximations clearly represent a gross oversimplification of the molecular electronic structure problem, it can hardly be overemphasized how much HMO theory has shaped chemical thinking about aromatic molecules and their properties. However, HMO theory will not be pursued, but the framework of the EHT method will be seen in Walsh Diagrams.

Limitations of Semiempirical Molecular Orbital Methods

Qualitative approaches to molecular orbital methods can be limited because of its approximate nature. From a quantum chemical point of view, the use of atomic charges, HOMO/LUMO energies and shapes that make this simple approach questionable. Atomic charges are not observables and strongly depend on analysis and the basis set. In addition, the shape of the orbitals depends on the method and basis set used. As seen in the analysis above, the MOs employed are obtained from minimal basis sets in the extended Hückel framework.

Nowadays, one is able to go beyond qualitative theory, and employ more quantitative methods, such as Hartree (HF) or Density Functional Theory (DFT) calculations, as a basis for the analysis of chemical reactivity. Nevertheless, semiempirical methods are extremely valuable for providing a fundamental understanding of chemical problems.

Slater Determinants and Molecular Orbitals

The simplest reasonable guess that one can make for $\Psi(\mathbf{x}|\mathbf{R})$ that satisfies the fundamental physical requirements for a valid N -electron wavefunction is the form of a single Slater-determinant.

$$\Psi(\mathbf{x}|\mathbf{R}) = \frac{1}{\sqrt{N!}} = \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix}$$

The quantities (ψ) appearing inside the determinant depend only on a single set of electronic coordinates. Such single-electron wavefunction are called orbitals, and the square of the integral over all space must exist in order for them to be physically acceptable.

Loosely speaking, orbitals describe the motion of individual electrons. The Slater determinant is the antisymmetrized product of such single-particle wave functions built from the coordinates of the electrons. It is often abbreviated as: $\Psi(\mathbf{x}|\mathbf{R}) = |\psi_1\psi_2\cdots\psi_N|$. Such a single N -electron Slater determinant describes the uncorrelated motion of N electrons. Since $|\psi_i(\mathbf{x})|^2$ describes the probability distribution for a single electron, it is not surprising that the total electron density described by a single Slater determinant is simply:

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_{i=1}^N \int |\psi_i(\mathbf{r}, s)|^2 ds \\ &= \sum_{i=1}^N |\psi_i^\alpha(\mathbf{r})|^2 + \sum_{i=1}^N |\psi_i^\beta(\mathbf{r})|^2 \\ \rho(\mathbf{r}) &= \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r})\end{aligned}$$

The integral in the first line is taken over the spin degree of freedom only. Since electrons carry either a spin-up or a spin-down intrinsic angular momentum, the second and third lines describe the decomposition of the total electron density into the separate densities of the spin-up and spin-down electrons. It now becomes obvious how each orbital contributes to the total electron density.

In chemistry, orbitals are used to explain many observations. However, since electrons repel each other, the single-determinant wavefunction, is a drastic, however useful, simplification, and one-electron functions cannot provide a completely accurate description of the N -electron state. Orbitals are used in different contexts as will be seen below.

Hartree-Fock Theory

A full understanding of Hartree-Fock theory would require more extensive discussion, but the aim here is to provide only a rough idea of the concepts. Actually, a few things about Hartree-Fock theory are already known, although it hasn't yet been discussed. Molecular orbital (MO) theory, or the linear combination of atomic orbitals molecular orbital (LCAO-MO) theory is something that is quite familiar, and is actually the same as Hartree-Fock theory. The basic idea is that the motion of each electron is described by a molecular orbital (MO). Each MO is constructed as a linear combination of atom-centered basis functions. The Hartree-Fock procedure simply solves for the linear expansion coefficients.

The variables in the Hartree-Fock equations, unfortunately, implicitly depend on themselves, so they must be solved in an iterative manner. In typical cases, the Hartree-Fock solutions can be obtained in several iterations. For tricky cases, convergence may be improved by changing the form of the initial guess. Since the equations are solved self-consistently, Hartree-Fock is an example of a self-consistent field (SCF) method.

The Mean Field Approximation

However, molecular orbitals are not real, except for the special case of the hydrogen atom. Molecular orbitals are the product of Hartree-Fock theory, which is not an exact theory, but an approximation to the electronic Schrödinger equation. The approximation is that each electron feels only the average Coulomb repulsion of all the other electrons which makes Hartree-Fock theory much simpler than the full N -body problem. Unfortunately, in many cases, this approximation is rather serious and can lead to serious errors. It can be corrected by explicitly accounting for electron correlation by density functional theory (DFT), many-body perturbation theory (MBPT), configuration interaction (CI), and other means.

Wave function methods try to compute an-accurate-as-possible many-electron wavefunction which then automatically leads to an accurate total energy. These treatments are almost invariably built upon the Hartree-Fock (HF) method, which is a variant of a mean-field theory. Because of its mean-field nature, the HF method is also called independent particle model. The HF approach is probably the simplest possible model that takes proper account of the required antisymmetry of the N -electron wavefunction, because it satisfies the Pauli principle.

Minimization of the energy of a single Slater determinant with respect to the shapes of the orbitals yields a set of optimum occupied orbitals of a given system. Such orbitals are called Hartree-Fock orbitals. The Slater Determinant, composed of the occupied Hartree-Fock orbitals, forms the total Hartree-Fock wavefunction, and is a simple 0th-order approximation to the N -electron eigenfunction of the BO operator.

Electron Correlation

The errors that remain in the HF method are called correlation errors, and they can be reduced by using various *correlated ab initio* methods. Impressive progress has been made along these lines, and there are now many close-to-exact solutions available. The large-scale use of such methods in chemistry is presently still prevented by the high computational cost which scales as $O(N^5)$ and $O(N^7)$ with molecular size, where N is a measure of the system size (e.g. the number of electrons or nuclei), and O means that the leading term of the computational effort requires a time that is proportional to the indicated power of N .

In post-Hartree-Fock methods, such as MP2, excited determinants are formed by replacing 1, 2, 3,... occupied orbitals of the Hartree-Fock determinant with empty orbitals. The resulting correlated wavefunction is then determined as a linear or nonlinear combination of the Hartree-Fock determinant and the set of excited determinants. One can think of the admixture of excited determinants as describing the effect of electrons jumping briefly out of their occupied orbitals into virtual orbitals, in order to minimize their repulsion with the other electrons in the system. Note, that the excited determinants do not describe genuine excited states of the molecule, but are merely used as building blocks for the improvement of the HF wavefunction.

The Pauli Exclusion Principle and Electron Spin

The Pauli Exclusion Principle states that a maximum of two electrons can reside in each orbital, and are distinguished by means of a spin quantum number. Two electrons in one orbital must then have different spin quantum numbers which can have one of two values, α and β . The physical basis for electron spin is that it has an intrinsic magnetic moment. The two spin functions corresponding to α and β spin are normalized and orthogonal to each other:

$$\int \alpha^2 d\tau = \int \beta^2 d\tau = 1; \quad \int \alpha\beta d\tau = 0$$

The total wavefunction for an electron is, therefore, a product of a spatial component and a spin component:

$$\psi(\text{spatial}) \times \psi(\text{spin})$$

*The following postulate applies to systems of identical spin $\frac{1}{2}$ particles (fermions): the wavefunction of a system of identical electrons must be **antisymmetric** with respect to the interchange of any two electrons.*

Multiplicity (Spin Multiplicity)

The number of possible orientations of the spin angular momentum, corresponding to a given total spin quantum number (S), is calculated as $2S + 1$ for the same spatial electronic wavefunction. Thus, a singlet state has an overall spin ($S = 0$) and multiplicity ($2S + 1 = 1$), and a doublet state has a net spin ($S = \frac{1}{2}$), and multiplicity ($2S + 1 = 2$), etc ...

Charge and Multiplicity for Computational Chemistry Applications

Most applications need to know how many electrons are in a molecule, provided through the charge, as well as the spin multiplicity. For instance, a calculation on methane (CH_4), would require input for neutral methane (charge = 0, $S = 1$) or methane cation (charge = +1, $S = 2$). As discussed above, the multiplicity can be computed from the total spin as $(2S + 1)$. As another example, a calculation on a neutral nitrogen atom would have a charge = 0, and a multiplicity of 4. That's because there are three unpaired electrons in nitrogen $S = \frac{3}{2}$ and multiplicity = $2 \times \frac{3}{2} = 4$.

Example: The Helium Atom

The helium atom can be considered from the standpoint of electron spin by multiplying a spatial function, a spin function, and the antisymmetric requirement. The spatial component of the wavefunction for the ground state is $1s(1)1s(2)$, and to take spin into account, it must be multiplied by a spin eigenfunction for two electrons. The notation $\alpha(1)\alpha(2)$ indicates a state where electron 1 has spin up and electron 2 has spin up.

The four normalized two-electron spin eigenfunctions with the correct exchange properties are

$$\begin{aligned} \text{symmetric} : & \begin{cases} \alpha(1)\alpha(2) \\ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ \beta(1)\beta(2) \end{cases} \\ \text{antisymmetric} : & \begin{cases} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \end{cases} \end{aligned}$$

Now a spin component from above for the He ground-state is included with the spatial component, $1s(1)1s(2)$, which is symmetric with respect to exchange. The overall electronic wavefunction including spin must be antisymmetric. Hence, the symmetric spatial function is multiplied by an antisymmetric spin function from above to yield:

$$\Psi_{\text{GS}}(\text{He}) = 1s(1)1s(2) \cdot \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Example: The Hydrogen Molecule (H_2)

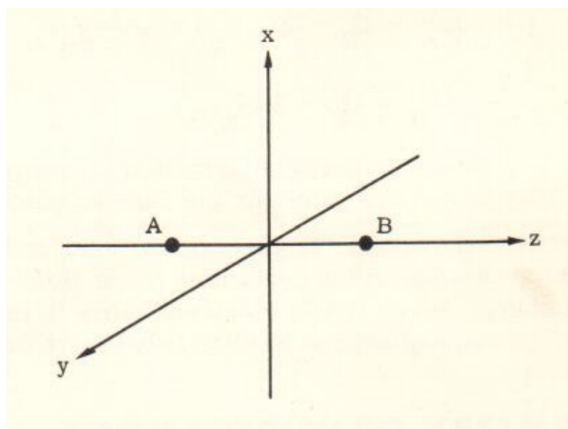


Figure 1: The H_2 diatomic molecule showing the origin of the coordinate system halfway between the two H nuclei, A and B. The molecule is aligned along the z -axis.

Assuming that there is an s orbital on each H atom, one can take a linear combination of atomic orbitals (LCAO)

$$\psi_i = \sum_{\mu=1}^k c_{\mu i} \phi_{\mu}(\mathbf{r})$$

to construct the following bonding and antibonding molecular orbitals (MO):

$$\begin{aligned} \psi_1 &= \sqrt{\frac{1}{2+2S}} (s_A + s_B) \\ \psi_2 &= \sqrt{\frac{1}{2-2S}} (s_A - s_B) \end{aligned}$$

H₂ Ground State

The orbital configuration the ground state of H₂ is given as $(\psi_1)^2$, and symmetry operations are performed ψ_1 to determine the symmetry of this molecular orbital::

Symmetry Operation	Comment
$\hat{E} \cdot (s_A + s_B) = +1 \cdot (s_A + s_B)$	Identity Operation
$\hat{C}_\varphi \cdot (s_A + s_B) = +1 \cdot (s_A + s_B)$	Arbitrary rotation about z axis $\rightarrow \sigma$
$\hat{\sigma}_v \cdot (s_A + s_B) = +1 \cdot (s_A + s_B)$	Reflection in either the xz or yz planes $\rightarrow \sigma^+$
$\hat{C}_2 \cdot (s_A + s_B) = +1 \cdot (s_B + s_A)$	Two-fold rotation about x or y axes $\rightarrow \sigma^+$
$\hat{i} \cdot (s_A + s_B) = +1 \cdot (s_B + s_A)$	Inversion about center of symmetry $\rightarrow \sigma_g^+$
$\psi_1 = 1\sigma_g^+ \approx (s_A + s_B)$	

The following notation, $1\sigma_g^+(1) = 1\sigma_g^+(1)\alpha(1)$, is called a **Spin Orbital**, the product of a spatial component and spin component, which can be used in a Slater Determinant to construct the appropriate antisymmetric wavefunction. The Slater Determinant for the singlet ground state of the H₂ molecule can be written as

$${}^1\Psi_{\text{GS}} = \left| \begin{matrix} 1\sigma_g^+(1) & 1\sigma_g^+(1) \\ 1\sigma_g^+(2) & 1\sigma_g^+(2) \end{matrix} \right| = \frac{1}{\sqrt{2}} \begin{vmatrix} 1\sigma_g^+(1) & 1\sigma_g^+(1) \\ 1\sigma_g^+(2) & 1\sigma_g^+(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left(1\sigma_g^+(1)1\sigma_g^+(2) - 1\sigma_g^+(2)1\sigma_g^+(1) \right)$$

$${}^1\Psi_{\text{GS}} = 1\sigma_g^+(1)1\sigma_g^+(2) \cdot (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

Expanding the above equation into atomic orbitals yields the following:

$${}^1\Psi_{\text{GS}} = \left\{ \overbrace{[s_A(1)s_A(2) + s_B(1)s_B(2)]}^{\text{Ionic Terms}} + [s_A(1)s_B(2) + s_A(2)s_B(1)] \right\} \{ \alpha(1)\beta(2) - \alpha(2)\beta(1) \}$$

which points out that the Hartree-Fock method does not fully take into account electron correlation, because both electrons on the H₂ molecule can be on either H_A or H_B.

H₂ Excited States

The Orbital configuration for the low-lying excited states are obtained by promoting one electron into the $1\sigma_u^+$ orbital to yield the $(1\sigma_g^+)^1(1\sigma_u^+)^1$ configuration has the following properties:

Symmetry Operation	Comment
$\hat{E} \cdot (s_A - s_B) = +1 \cdot (s_A - s_B)$	Identity Operation
$\hat{C}_\varphi \cdot (s_A - s_B) = +1 \cdot (s_A - s_B)$	Arbitrary rotation about z axis $\rightarrow \sigma$
$\hat{\sigma}_v \cdot (s_A - s_B) = +1 \cdot (s_A - s_B)$	Reflection in either the xz or yz planes $\rightarrow \sigma^+$
$\hat{C}_2 \cdot (s_A - s_B) = -1 \cdot (s_A - s_B)$	Two-fold rotation about x or y axes $\rightarrow \sigma^+$
$\hat{i} \cdot (s_A - s_B) = -1 \cdot (s_A - s_B)$	Inversion about center of symmetry $\rightarrow \sigma_u^+$
$\psi_2 = 1\sigma_u^+ \approx (s_A - s_B)$	

$$^3\Psi_{\text{ES}} = \left\{ \begin{array}{ll} \left| \begin{array}{c} \alpha \\ (1\sigma_g^+)(1\sigma_u^+) \end{array} \right| & M_S = +1 \\ \frac{1}{\sqrt{2}} \left[\left| \begin{array}{c} \alpha \\ (1\sigma_g^+)(1\sigma_u^+) \end{array} \right| + \left| \begin{array}{c} \beta \\ (1\sigma_g^+)(1\sigma_u^+) \end{array} \right| \right] & M_S = 0 \\ \left| \begin{array}{c} \beta \\ (1\sigma_g^+)(1\sigma_u^+) \end{array} \right| & M_S = -1 \end{array} \right\} S = 1$$

The $M_S = +1$ component of the excited triplet state can be expanded to yield the following:

$$^3\Psi_{\text{ES}(M_S=+1)} = \left| \begin{array}{c} \alpha \\ (1\sigma_g^+)(1\sigma_u^+) \end{array} \right| = \left| \begin{array}{cc} 1\sigma_g^+(1) & 1\sigma_g^+(1) \\ \alpha & \alpha \\ 1\sigma_u^+(2) & 1\sigma_u^+(2) \end{array} \right| = 1\sigma_g^+(1)1\sigma_u^+(2) - 1\sigma_g^+(2)1\sigma_u^+(1)$$

$$^3\Psi_{\text{ES}(M_S=+1)} = (1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)) \cdot \alpha(1)\alpha(2)$$

Notice, how the first excited state, an open-shell singlet state, cannot be represented by a single Slater Determinant:

$$^1\Psi_{\text{ES}_1} = \frac{1}{\sqrt{2}} \left[\left| \begin{array}{c} \alpha \\ (1\sigma_g^+)(1\sigma_u^+) \end{array} \right| - \left| \begin{array}{c} \beta \\ (1\sigma_g^+)(1\sigma_u^+) \end{array} \right| \right]$$

Finally, exciting two electrons into the $1\sigma_u^+$ orbital yields the configuration $(1\sigma_u^+)^2$, the second excited-state singlet, which can be represented by one Slater Determinant, analogous to the ground state:

$$^1\Psi_{\text{ES}_2} = \left| \begin{array}{c} \alpha \\ (1\sigma_u^+)(1\sigma_u^+) \end{array} \right| = \frac{1}{\sqrt{2}} \left| \begin{array}{cc} 1\sigma_u^+(1) & 1\sigma_u^+(1) \\ \beta & \beta \\ 1\sigma_u^+(2) & 1\sigma_u^+(2) \end{array} \right| = \frac{1}{\sqrt{2}} \left(1\sigma_u^+(1)1\sigma_u^+(2) - 1\sigma_u^+(2)1\sigma_u^+(1) \right)$$

$$^1\Psi_{\text{ES}_2} = 1\sigma_u^+(1)1\sigma_u^+(2) \cdot (\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

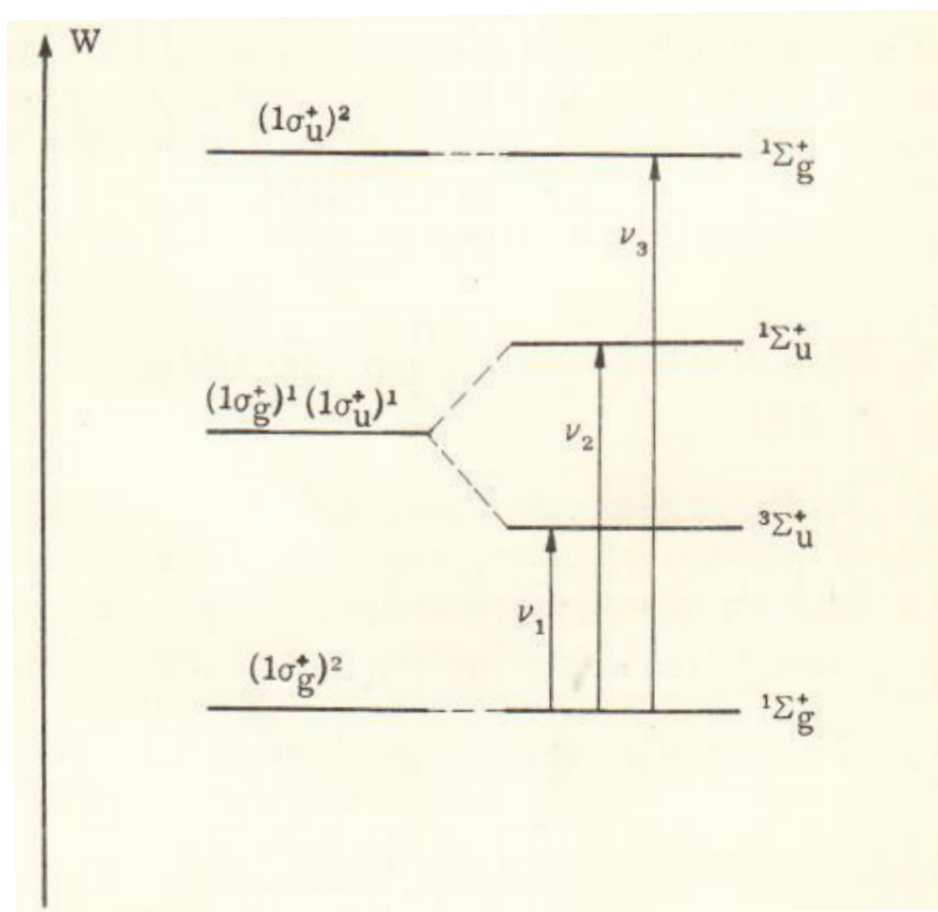


Figure 2: Lowest electronic states for H_2 . On the left, the electronic configurations are indicated, while on the right, the corresponding electronic states are given. The symbol, ν , shows the frequency of light absorbed.

Density Functional Theory (DFT)

Walter Kohn and John Pople shared the 1998 Nobel Prize in Chemistry for their work in Density Functional Theory (DFT). The computer programs that actually solve the DFT equations have a lot in common with Hartree-Fock programs. Quite frequently theorists simply adapt their Hartree-Fock program to do DFT computations. Like Hartree-Fock, the DFT equations must be solved self-consistently, making DFT another type of SCF method.

Instead of focusing on wave functions and orbitals, DFT focuses on the electron density, although it usually employs orbitals to obtain the density. It includes an approximate treatment of electron correlation, and therefore should be more accurate than Hartree-Fock theory. There are actually very many different DFT methods, depending on the particular treatment of correlation or *exchange*.

The drawback of DFT is that exact density functional is unknown, and a DFT computation is difficult to improve. This contrasts with all other *ab initio methods*, where a better basis, better trial wavefunction, or enhanced correction can improve the results, until the electronic Schrödinger equation is solved exactly. The advantage of using DFT is that it tends to give very accurate results much more cheaply than some competing methods.

Within density functional theory, a Slater determinant is used in a completely different context, and provides the decomposition of the total electron density that is necessary to apply the Kohn-Sham scheme. They proposed to work instead with a system of non-interacting electrons. In general, the wavefunction of the non-interacting electrons is different from that of the interacting ones and so is the density. However in the Kohn-Sham approach, a fictitious non-interacting system is constructed, in such a way, that its density is the same as that of the interacting electrons

The challenge is then shifted from finding a universal density functional to finding the fictitious system of non-interacting electrons which has the same density as the real one with the interacting electrons. This allows one to set up more accurate DFT calculations as the expression for the kinetic energy of non-interacting electrons is known, so there is no need for approximate kinetic energy functionals of the density. Thus, the exact system, and the non-interacting reference system simply share the same electron density which is formally used to calculate the exact ground-state energy. In practice, it is not known how to go from the exact electron density to the exact energy, and, therefore, all practical DFT is approximate.

Many-electron wavefunctions contain much more information than is strictly necessary, since the Born-Oppenheimer Hamiltonian does not contain more than two-body interactions. In fact, the only difficult term is the electron-electron interaction ($\frac{1}{r_{ij}}$). Thus, in principle, the problem is fully solved, if one could know the electron-pair distribution function, $\Gamma(\mathbf{x}_1, \mathbf{x}_2)$, which is closely related to the probability of finding a pair of electrons at points \mathbf{x}_1 and \mathbf{x}_2 respectively. Unfortunately, it has been found to be impossible, so far, to calculate this function without approximating the many-electron wavefunction.

However, the Hohenberg-Kohn theorem states that one does not need to know the pair distribution function, but that the knowledge of the electron density $\rho(\mathbf{x})$ is *in principle* enough to deduce the exact total energy of the electronic ground state. Unfortunately, the

exact recipe that describes how to deduce the exact energy from the electron density is unknown. Nevertheless, over the years, many highly intelligent guesses to this universal functional have been made, and each of these constitutes a different density functional. The practical realization of DFT is the Kohn-Sham method which is essentially at the same level of complexity as Hartree-Fock theory, but almost invariably provides better results.

Because of very good performance performance capability, DFT is presently the methodology of choice for most chemical applications, and can be applied to molecules with 100-200 atoms using standard computational hardware.

Perspective on Orbitals from WFT and DFT

No matter to what end orbitals are used, they help in building molecular wave functions or densities, but they are not fundamental objects of theory. In fact, the entire discipline of Quantum Chemistry can be carried to high-precision without any recourse to orbitals whatsoever. This necessarily means that individual orbitals do not have a fundamental physical or chemical reality or relevance. Nevertheless, orbital pictures are so prevalent in chemistry, and will be used throughout this workshop. It is, however, important to point out that the theoretical justification of the orbital-based pictures can be unambiguous, and should be used carefully.

Quantative methods, such as WFT and DFT, also involve ambiguities, since the filled orbitals converge to definite properties, while the unoccupied orbitals do not. The occupied orbitals, derived from a Slater determinant, used in HF theory or the calculation of electron density in DFT, are optimized by the variation procedure. But, the only criterion for unoccupied orbitals is their orthogonality to the occupied orbitals. In the limit of a complete basis set, the unoccupied orbitals form a continuum, and the lowest unoccupied orbitals (LUMOs) are not really defined.

In HF theory, the energies of unoccupied MOs are fundamentally incorrect, because the fictitious electrons in the unoccupied orbitals experience the repulsive field of all N electrons of the system, whereas the occupied orbitals experience the correct $N - 1$ electron potential. The energies of occupied orbitals can be related to physical properties, such as ionization energies by invoking the Koopman's theorem.

The situation in DFT is also problematical, because the virtual MOs experience the correct $N - 1$ electron repulsive field, but the energies of the occupied MOs are incorrect due to artificial self-interaction of the electrons, which is caused by the approximate description of electron exchange in DFT. As a workaround for the shortcomings of both HF and DFT, hybrid methods have been developed where the electron exchange is described by a mixture of the exact single determinant expression provided by HF theory and a density functional. The mixing coefficient is usually treated as an empirical parameter, and the value is determined by optimal reproduction of experimental properties, such as ionization energies and optical spectra. In this way, one can take advantage of the cancellation of inherent errors in both approaches.

Basis Sets

It is necessary to use an approximate decomposition of the orbitals on the atoms in terms of a finite set of L known functions, φ :

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^L c_{\mu i} \varphi(\mathbf{r})$$

This set of basis functions, φ , constitutes the basis set for a given calculation. Only in the limit that the set is complete in the mathematical sense can the orbital be exactly expanded in the basis set. For any incomplete set, the results of our calculations will depend on the nature and size of the basis set that we use. In general, larger basis sets (if properly designed) are more accurate than smaller basis sets but will also lead to longer computation times. Thus, there is always a cost-versus-accuracy trade-off to be made in choosing a specific basis set for a given computational task.

The basis set problem has been thoroughly studied by quantum chemists. As a consequence, there are many different standard basis sets available. Each basis set has a different name and a different range of elements that is supported. Broadly speaking, basis sets can be categorized by their construction rules.

Atomic Orbitals

From the qualitative discussions that are commonly found in textbooks one could get the impression that there is a carbon $2s$ orbital and three carbon $2p$ orbitals that entirely determine the chemical and spectroscopic behavior of any carbon atom in any molecule. From this point of view it may be rather confusing to be pulled into the subject of basis sets in quantum chemical calculations.

The suggestion that, in principle, only a single $2s$ and three $2p$ orbitals on a carbon center are necessary to describe the molecular environment remains valid even in Quantum Chemistry. However, the important point is that the atomic orbitals become distorted from the shapes they have in the neutral atom upon bonding with other atoms in a molecule. Furthermore, the shape of orbitals also changes for each state of a neutral carbon atom, if it becomes a cation or an anion. The state of a carbon atom in a molecule may also be a mixture of several atomic states, and the carbon center might have a partial charge. In molecules, a combination of all of these effects need to be taken into account.

Radial and Angular Distortion

The symmetry around a given carbon center, for example, in a molecule is less than spherical, and, therefore, there will be an additional distortion of the shape of the basic orbitals that is due to this symmetry lowering. Basically, there are two major types of distortions that are taken into account in basis set design: radial and angular distortion.

Radial Distortion

Radial distortion is characterized by the expectation value of $\langle r \rangle$, the average radius, for a given atomic orbital. Atomic orbitals will tend to contract the more they are involved in bonding, and the more positive the charge on the center where they are located. Importantly, the contraction or expansion can be different for different MOs. Thus, for a σ -bonding p -AO, the distortion is generally different compared to a π -bonding MO, a non-bonding σ -MO, an anti-bonding σ^* , or an anti-bonding π^* MO.

In general, chemical core orbitals, e.g. a carbon $1s$ orbital, distort very little, since they are held very tightly by the nuclear charge. Generally, it is sufficient to represent such orbitals by a single basis function. The radial distortion is represented in calculations by supplying several types of the principal atomic orbitals, but with different spatial extent. Thus, if there is a single set of $2s$ -type orbitals and $2p$ type on a carbon atom, this is considered a single-zeta basis set. Two sets of $2s, 2p$ functions constitute a double-zeta basis set, and three sets of functions, a triple-zeta basis set. In most cases, a triple-zeta basis sets allows for an adequate modelling of the radial distortion effects that arise in molecules.

A double-zeta basis should be a minimum requirement. Calculations with single-zeta basis sets are not reliable. Higher accuracy can be reached with quadruple-zeta or pentuple-zeta basis sets, but such calculations become very time consuming. In calculations with anions, the charge density will tend to become very diffuse, and, in such cases, it is advisable to add a set of particularly diffuse basis functions in order to describe the additional expansion of the electron cloud.

Angular Distortion and Basis Functions With Higher Angular Momentum

Depending on the local symmetry and bonding interaction, in which an orbital may be involved, an inequivalency may arise. For example, the two lobes of a p -orbital may become inequivalent, or an s -orbital becomes polarized deviating from spherical symmetry.

The angular distortion effects are modelled by including in the basis sets orbitals with higher angular momentum quantum numbers, and these are called polarization functions, since they describe an angular distortion of the atomic orbitals which is brought about by the anisotropic molecular environment. Thus, for carbon atoms, d -functions and, perhaps, f -functions are included in the basis sets. These basis functions are by no means representations of the atomic $3d$ and $4f$ orbitals. On the contrary, they have similar spatial extent as the $2s$ and $2p$ functions, but mainly help these these orbitals, through small admixtures, to depart from pure s or p shapes.

In general, one set of polarization functions on non-hydrogen atoms is a minimum requirement for obtaining a reasonably accurate calculation. A single set of p -polarization functions should also be included on the hydrogen atoms. Two sets of polarization functions provide better results, and three sets on non-hydrogen atoms ($2d, 1f$) and hydrogen atoms ($2p, 1d$) provide very good results. However, calculations with these basis sets become rather time consuming.

Accuracy of Basis Sets

In this workshop, a small number of standard basis sets will be used, including the SVP (Split-Valence-Polarisation) basis set, a double-zeta basis with one set of polarization functions on all atoms. The more accurate TZVP basis set is a triple-zeta basis with one set of polarization functions. The TZVPP basis set of triple-zeta quality, consisting of two sets of polarization functions, which yields results that are fairly good, i.e close enough to the basis set limit, properly reflects the theoretical method used and avoids limitations of the basis set truncation. All of the basis sets mentioned above were developed by the Karlsruhe quantum chemistry group, and are particularly efficient. Other basis sets can be obtained from the EMSL library: <http://www.emsl.pnl.gov/forms/basisform.html>.

Gaussian Functions

In general, for practical reasons, the individual basis functions are almost universally taken as a linear combination of Gaussian functions decay as e^{-r^2} . Such functions show behavior at both short and long distances from the nucleus that is incorrect, if compared to the known limiting behavior of exact atomic Hartree-Fock orbitals. In addition, Gaussian functions have important calculational advantages that can be exploited very efficiently in sophisticated quantum chemical program packages used in this workshop.

Model Chemistries

The task of Computational Chemistry can now be defined more clearly:

- a) Choose an initial set of atomic coordinates that represents the system of interest.
- b) Choose a theoretical method (e.g. HF, MP2, CASSCF, DFT, TDDFT, ...) that is appropriate for the problem to be solved.
- c) Choose a basis set.
- d) Carry out the calculation of molecular structure, energy, and molecular properties.

The combination of a given theoretical method with a specific basis set defines a model chemistry, which will determine the achievable accuracy in a given study. Accurate model chemistries take up significant computer resources, while less accurate model chemistries yield necessarily predictions of lower reliability. The choice of model chemistry is, therefore, an important aspect of a theoretical study, and is dictated by experience and available computational resources. Model chemistries of unknown accuracy need to be calibrated before they can be applied in chemical application studies. The process of calibration consists of testing the predictions of the model chemistry for a range of molecular systems and the properties of interest. A proper calibration yields a solid confidence level (or error interval) for predicting model chemistry with respect to the chosen property.

In this workshop, the concern is not to utilize all the various methods of computational quantum chemistry, but instead, to focus on a few successful standard methods, including the Hartree-Fock method, the simplest correlated ab initio methods, as well as the DFT method, both of which will be used to address various chemical problems. However, one should always be aware, that every quantum chemical method provides only an approximate solution which can fail in some instances. There is no substitute for seeking careful feedback from experiments in judging the quality and reliability of a given quantum chemical calculation.