

# Chemistry 4681 Module: Electronic Structure of Small Molecules Background Handout

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## 1 Computational Chemistry

The term “computational chemistry” is used to mean many different things. It could mean, for example, the use of computers to analyze data obtained in complicated experiments. However, more frequently this term means the use of computers to make *chemical predictions*. Sometimes computational chemistry is used to predict new molecules or new reactions which are later investigated experimentally. Other times, computational chemistry is used to supplement experimental studies by providing data which are hard to probe experimentally (for example, transition state structures and energies). Since its modest beginnings in the 1950’s and 1960’s, advances in theoretical techniques and in computer power have dramatically increased the usefulness and importance of computational chemistry.

There are two main branches of computational chemistry: one is based on classical mechanics, and the other is based on quantum mechanics. Molecules are sufficiently small objects that, strictly speaking, the laws of quantum mechanics must be used to describe them. However, under the right conditions, it is still sometimes useful (and much faster computationally) to approximate the molecule using classical mechanics. This approach is sometimes called the “molecular mechanics” (MM) or “force-field” method [1]. All molecular mechanics methods are *empirical* in the sense that the parameters in the model are obtained by fitting to known experimental data.

Quantum mechanical methods can usually be classified either as *ab initio* or *semi-empirical*. The first label, *ab initio*, means “from the beginning” and implies an approach which contains *no empirical parameters*. This category includes Hartree-Fock (HF), configuration interaction (CI), many-body perturbation theory (MBPT), coupled-cluster (CC) theory, and other approaches [2]. These methods, particularly Hartree-Fock theory, will be the focus of this lab. The second category, *semi-empirical*, includes methods which make serious approximations to the quantum mechanical laws and then employ a few empirical parameters to (hopefully) patch things up. These methods include the modified neglect of differential overlap (MNDO), Austin Model 1 (AM1), and many others. Density functional theory (DFT) [3] methods are quantum mechanical approaches which are hard to categorize as *ab initio* or *semi-empirical*. Some DFT methods are free from empirical

parameters, while others rely heavily on calibration with experiment. The current trend in DFT research is to employ increasing numbers of empirical factors, making recent DFT techniques semi-empirical.

One of the postulates of quantum mechanics is that the wave function contains all information which is known *or can be known* about a molecule. Hence, quantum mechanical methods provide all possible information about a system, in principle at least. In practice, theoretical chemists have to figure out how to extract the property from the wave function, and then they have to write computer programs to perform the analysis. However, it is now fairly routine to compute the following molecular properties:

### Properties Obtainable From Quantum Mechanical Methods

- Geometrical structures (rotational spectra)
- Rovibrational energy levels (infrared and Raman spectra)
- Electronic energy levels (UV and visible spectra)
- Quantum Mechanics + Statistical Mechanics  $\rightarrow$  Thermochemistry ( $\Delta H$ ,  $\Delta S$ ,  $\Delta G$ ,  $C_v$ ,  $C_p$ ), primarily gas phase.
- Potential energy surfaces (barrier heights, transition states); with a treatment of dynamics, this leads to reaction rates and mechanisms.
- Ionization potentials (photoelectron and X-ray spectra)
- Electron affinities
- Franck-Condon factors (transition probabilities, vibronic intensities)
- IR and Raman intensities
- Dipole moments
- Polarizabilities
- Electron density maps and population analyses
- Magnetic shielding tensors  $\rightarrow$  NMR spectra

## 2 Electronic Structure Theory

### 2.1 Born-Oppenheimer Approximation

One of the central approximations in the application of quantum mechanics to chemistry (“quantum chemistry”) is the Born-Oppenheimer approximation, which states that the electronic and nuclear degrees of freedom are nearly separable. This is a good approximation because the electrons are much lighter than the nuclei, so they move much faster and can rearrange themselves to a stable configuration almost as soon as the nuclei move. Hence, to a good approximation, one can fix the nuclei at a given set of coordinates and solve for the probability distribution of the electrons; this is called the “electronic structure” problem. If one obtains the electronic energy for a series of nuclear arrangements, one can map out the potential energy surface (PES) of the molecule. Since the electronic energy is independent of the orientation or translation of the molecule (assuming no external electromagnetic fields), the PES of a molecule has dimension  $3N-6$ , where  $N$  is the number of nuclei ( $3N-5$  for a linear molecule). To get a really complete model of a molecule, one would have to obtain the PES and *then* simulate the motion of the nuclei on that PES; this procedure is called *dynamics* and is necessary for a complete understanding of reaction mechanisms and other properties. However, quite a lot of information can be obtained considering only electronic structure, and that is the focus of this lab.

### 2.2 Levels of Theory

In electronic structure theory, the “level of theory” has two degrees of freedom: one is the treatment of “electron correlation,” and the other is the basis set. Electron correlation simply refers to the fact that the motion of each electron influences the motion of all other electrons (due to the Coulomb repulsion between each pair of electrons). For more than two electrons, this is an  $N$ -body problem which cannot be solved exactly by analytic techniques. It can be solved exactly using numerical methods, but the computational cost is enormous, scaling as the factorial of  $N$ . Hence, various approximations must be used; some of these are described below.

The other variable is the basis set; here, we refer to a basis set of one-electron functions (or orbitals), usually centered on the atoms. The electronic Schrödinger equation becomes greatly simplified once we solve it using such a basis. The larger the basis set (the more orbitals it contains), the more accurately we model the Schrödinger equation *for the given correlation method*. However, even an infinite basis set can give incorrect answers when paired with an approximate treatment of electron correlation. Likewise, even an exact treatment of electron correlation can give terrible answers when paired with a very small basis set. Better and better results can be obtained when one increases the basis set *and* improves the treatment of correlation. In the limit

of an infinite basis set and an exact treatment of electron correlation, the electronic Schrödinger equation would be solved exactly.

## 2.3 Basis Sets

*Ab initio* electronic structure computations are almost always carried out numerically using a *basis set* of orbitals. It is important to choose a basis set large enough to give a good description of the molecular wave function. Typically, the basis functions are centered on the atoms, and so sometimes they are called “atomic orbitals.” However, it is important to note that this does *not* imply that they are actually solutions to the electronic Schrödinger equation for the atom. In modern practice, these atom-centered basis functions are usually chosen to be Gaussian-type orbitals (GTO’s), which have the form

$$\Psi_{GTO}(x, y, z) = x^l y^m z^n e^{-\zeta r^2}, \quad (1)$$

where  $x, y, z$  are the local (atom-centered) Cartesian coordinates,  $l, m, n$  are positive integers which more or less describe the angular momentum of the orbital, and  $r$  is the radial distance to the atomic center. Spherical orbitals are usually given by  $l = m = n = 0$ , a  $p_x$  orbital is given by  $l = 1, m = n = 0$ , a  $d_{xy}$  orbital is given by  $l = m = 1, n = 0$ , etc. Unlike hydrogen atom orbitals, GTO’s do not have radial nodes; however, radial nodes can be obtained by *combining* different GTO’s. Quite frequently, an atomic basis function is actually a fixed linear combination of GTO’s; this is called a *contracted Gaussian basis function*.

The smallest possible basis set is called the *minimal basis set*, and it contains one orbital (which may be contracted) for every orbital we usually think of for an atom (including unoccupied orbitals). For example, hydrogen has just one orbital, but carbon has 5 (1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub>) even though one of the p orbitals for carbon atom will be unoccupied. The STO-3G basis is a very well-known minimal basis set which contracts 3 Gaussian functions to approximate the more accurate (but more difficult to compute) Slater type orbitals. Although a contracted GTO might give a good approximation to an atomic orbital, it lacks any flexibility to expand or shrink in the presence of other atoms in a molecule. Hence, a minimal basis set such as STO-3G is not capable of giving highly accurate results.

The solution is to add extra basis functions *beyond* the minimum number required to describe each atom. Then, the Hartree-Fock procedure (below) can weight each atomic orbital basis function more or less to get a better description of the wave function. If we have *twice* as many basis functions as in a minimum basis, this is called a “double zeta” basis set (the zeta,  $\zeta$ , comes from the exponent in the GTO). Hence, a double-zeta basis set for hydrogen would have two functions, and a true double-zeta basis set for carbon would have 10 functions. However, sometimes people “cheat” and use only a single orbital for the core (1s), giving 9 functions for carbon. Such

basis sets are said to be “double-zeta *in the valence*” space; they are also called “split-valence” basis sets. Double-zeta basis sets are often denoted DZ. Often additional flexibility is built in by adding higher-angular momentum basis functions. Since the highest angular momentum orbital for carbon is a p orbital, the “polarization” of the atom can be described by adding a set of d functions. A hydrogen atom would use a set of 3 p functions as polarization functions. A double-zeta plus polarization basis set might be designated DZP. The most famous example of a split-valence double-zeta plus polarization basis set is Pople’s so-called 6-31G\* basis. This obscure notation means that the core orbital is described by a contraction of 6 Gaussian orbitals, while the valence is described by two orbitals, one made of a contraction of 3 Gaussians, and one a single Gaussian function. Just to confuse you, the star (\*) indicates polarization functions on non-hydrogen atoms. If polarization was added to hydrogen atoms also, this basis would be called 6-31G\*\*. The confusing nature of this nomenclature has caused some chemists to start switching to slightly improved notation such as 6-31G(d,p), where the polarization functions are listed explicitly.

This lab will not investigate the nuances of basis set design, but you need to have a basic grasp of what basis sets are, since you’ll be using them!

## 2.4 Hartree-Fock Theory

A full understanding of Hartree-Fock theory would require a few weeks of study. Here, we will aim for only a rough idea of what is going on. Actually, you already know a few things about Hartree-Fock theory, even if you haven’t heard the term before. You almost certainly have heard about molecular orbital (MO) theory, or the linear combination of atomic orbitals molecular orbital (LCAO-MO) theory. This is actually the same as Hartree-Fock theory, which is named after the two physicists who invented it. The basic idea is that we will describe the motion of each electron by a molecular orbital. The mathematics behind it is that each MO is made of a linear combination of atom-centered basis functions. The Hartree-Fock procedure simply solves for what the linear expansion coefficients actually are.

The variables in the Hartree-Fock equations unfortunately depend on themselves, so they must be solved in an iterative manner. You will see these iterations in the outputs you run in the lab. In typical cases, the Hartree-Fock solutions can be obtained in roughly 10 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.

Unfortunately, you are probably under the illusion that molecular orbitals are somehow “real” or “true.” Except for the special case of the hydrogen atom, this is completely false. Molecular orbitals are the product of Hartree-Fock theory, and Hartree-Fock is *not* an exact theory: it is an approximation to the electronic Schrödinger equation. The approximation is that we pretend that each electron feels only the *average* Coulomb repulsion of all the other electrons. This

approximation makes Hartree-Fock theory *much* simpler than the real problem, which is an  $N$ -body problem. Unfortunately, in many cases this approximation is rather serious and can give bad answers. 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.

## 2.5 Density Functional Theory

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. In the Q-Chem program [4], both Hartree-Fock and DFT are done using a module called `scfman`.

Instead of focusing on wave functions and orbitals, DFT focuses on the electron density (although it usually employs orbitals to get 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” (which we will unfortunately leave undefined for this lab). Feel free to experiment with some of the different DFT approaches in the lab.

The drawback of DFT is that nobody knows how to take a given DFT computation and improve it. This contrasts with all other *ab initio* methods, where an expert can always tell how to keep improving the results until the electronic Schrödinger equation is solved exactly. The reason anyone uses DFT is that it tends to give very accurate results much more cheaply than some competing methods.

## 2.6 Many-Body Perturbation Theory

Very simply put, many-body perturbation theory (MBPT) is a way to account for electron correlation by treating it as a perturbation to the Hartree-Fock wave function. It is a rather straightforward application of simple perturbation theory. Usually, one computes corrections to the energy using second-order perturbation theory, which is abbreviated MBPT(2). This is usually also called second-order Møller-Plesset perturbation theory, or MP2. For some problems, MP2 is more reliable than DFT. It is virtually always an improvement on Hartree-Fock.

In principle, one could go up to higher orders of perturbation theory (MP3, MP4, etc), but the computer programs become too hard to write, and the results (perhaps surprisingly) don't

necessarily get any better.

### 3 Theoretical Predictions of Molecular Properties

When we discuss molecular properties, we are usually referring to the properties of a molecule when it is at equilibrium: i.e., when the nuclei are in their minimum-energy configuration on the potential energy surface. It is important to keep this in mind, since computational chemistry programs often report properties (energy, dipole moment, etc) for *any* geometry at which they are run. So, if you are trying to report the equilibrium properties, you need to first *optimize* the molecule to get the nuclei at the minimum on the PES. Only then should you attempt to determine the equilibrium molecular properties. In particular, be careful that you don't accidentally reset the geometry to the Hyperchem "guess" geometry by hitting "Model Build" after the geometry optimization. If you do this, your results will all be for the wrong geometry!

A special comment should be made about theoretically determined vibrational frequencies. Every computational chemistry program defaults to predicting the *harmonic* vibrational frequencies, which are the frequencies determined from the second-derivative of the potential energy surface according to the harmonic oscillator approximation:

$$\omega_i = \sqrt{\frac{k_i}{m}} \quad (2)$$

for each normal mode  $i$ . However, the potential energy surface is of course not exactly harmonic, and the true vibrational frequencies will have contributions from third, fourth, and higher derivatives of the PES. Thus, theoretical harmonic frequencies are almost always too high compared to experimentally measured *fundamental* frequencies.

That said, it is still sometimes possible to make correct comparisons between theory and experiment. One way is to compute the fundamental frequencies using theory. This is very involved and far beyond the scope of this lab. The other way is for experimentalists to do enough experiments to extract out the harmonic frequency. These are usually available for diatomic molecules and some polyatomic molecules. If experimentally deduced harmonic frequencies are available for your molecule, please report them. If not, please note that you have fundamental frequencies, and be aware that there will be a small discrepancy due to anharmonicity (often about 2-3%).

## 4 Walsh Diagrams

Walsh diagrams are very useful in making quick predictions about the geometries of small molecules. Introduced in 1953 [5], these are ranked among the great achievements of molecular orbital theory. Walsh constructed his diagrams by plotting “orbital binding energies” against bond angles. The basic idea is that the total energy is the sum of all the orbital binding energies; therefore, by considering the stabilization or destabilization of all the orbitals by a change in the angle, one can predict (roughly) the equilibrium bond angle for a given state of a molecule.

Today, we usually use orbital energies (also called orbital eigenvalues) in Walsh diagrams. The truth is that nobody really knows exactly what Walsh’s “orbital binding energies” were! However, whatever Walsh plotted, his diagrams are very helpful. In this lab, you will construct your own Walsh diagram for a particular molecule using the Hartree-Fock orbital energies.

Here we will briefly discuss how Walsh diagrams are interpreted. Usually, core orbitals (1s for B, C, N, O, F, Ne) are not included in Walsh diagrams, since they are very low in energy and not changed much by bond angle bending. Only valence orbitals are included. Note that some of the valence orbitals are usually unoccupied. Figure 1 presents the Walsh diagram for  $AH_2$  molecules. Let us consider a simple molecule,  $H_2O$ . The electronic configuration of  $H_2O$  is  $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1$ , as you could determine by hand (if you knew how) or by running a program like Q-Chem.

From the Walsh diagram, we can see that if we doubly occupied the  $2a_1$ ,  $1b_2$ ,  $3a_1$ , and  $1b_1$  orbitals (remember, the core orbital doesn’t enter into the diagram), the lowest energy would come at roughly  $100^\circ$ . Although the  $2a_1$  and  $1b_2$  orbitals go up in energy as the molecule is bent from  $180^\circ$  towards  $90^\circ$ , their energies do not increase nearly as rapidly as the energy of the  $3a_1$  orbital decreases. Hence, the molecule is stabilized by bending. Note that the  $1b_1$  orbital energy is basically flat and doesn’t care whether the molecule is linear or bent. As you can see from the diagram, the energies of  $1b_2$  and  $2a_1$  start to rise more rapidly just before  $90^\circ$ , which is why the equilibrium geometry is a little larger, around  $100^\circ$ . Although one could get out a ruler to determine more exactly the minimum energy angle, there would be little point, since the Walsh diagram is capable only of approximate results (and can even make totally wrong predictions in some cases). In this case, the diagram works well, since the equilibrium bond angle for water is  $104.52^\circ$ .

What if an electron was promoted from the  $1b_1$  orbital to the  $4a_1$  orbital? This would give us a  $^3B_1$  or  $^1B_1$  state of  $H_2O$ , depending on whether the unpaired electrons were singlet or triplet coupled. What would the geometry of this excited electronic state be? From the Walsh diagram, we can see that the  $1b_1$  orbital doesn’t care if the molecule is linear or bent. Therefore, it has no influence on the equilibrium geometry. However, we now have one electron in the  $4a_1$  orbital. Since there is only one electron in this orbital, instead of two, the influence of this orbital will only be half as much as the doubly occupied orbitals. We can see that the  $4a_1$  orbital prefers linear

Figure 1: Walsh diagram for  $\text{XH}_2$  molecules from Herzberg [6].

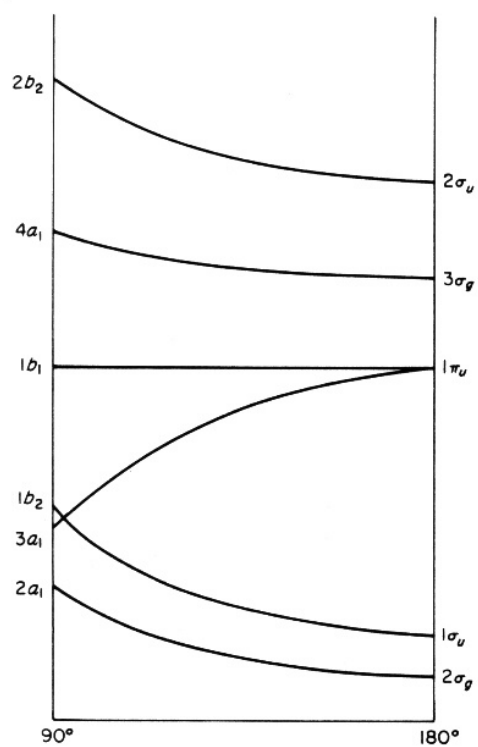


FIG. 125. Walsh diagram for  $\text{XH}_2$  molecules. The variation of orbital energies in going from a bent ( $90^\circ$ ) to a linear conformation is shown. The  $1s$  orbital of X is not included.

geometries, but only very slightly. Therefore, we predict the equilibrium geometry for this excited state to be very similar to the ground state, but slightly closer to linear (if the ground state is  $104.52^\circ$ , maybe the excited state is  $107^\circ$ ?). I have not yet been able to find an experimental value for the bond angle of the  $^3B_1$  or  $^1B_1$  states of  $H_2O$ .

## References

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