

Chapter 5

Mathematics for Computational Chemistry

The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved. – P.A.M. Dirac

5.1 Key Notes

5.1.1 Fundamental Mathematics:

Molecular modeling is a mathematical science. It attempts to define and describe molecules and their interactions with other molecules in mathematical terms. The computer is then used to solve the mathematical equations, which are numerous and complex. There are two broad categories of mathematics:

1. those that calculate the behavior of the nuclei of the atoms and neglect the behavior of electrons. These are known as **molecular mechanics/molecular dynamics (MM/MD) calculations**.
2. those that calculate the behavior of electrons and neglect the behavior of nuclei. These are known as **electronic structure calculations**.

The *North Carolina High School Computational Chemistry Server* (<http://chemistry.ncssm.edu>) is used to perform these calculations. This chapter, however, deals primarily with electronic structure calculations, with a very short description of MM/DD.

The fundamental mathematical equation to be solved is the **Schrödinger** equation, which looks to be able to help us predict chemical properties by calculating the behavior of electrons. The fundamental property that results from the solution of this equation is the *energy* of the molecule or molecular system.

5.1.2 Fundamental Approximations:

All of the methods use **approximations** to simplify the calculations. Although computer software and hardware are improving, and our ability to describe chemical structure and behavior is improving, we still must accept some simplifications to our models. In electronic structure calculations, there are three primary approximations:

1. the **Born-Oppenheimer approximation**: states that we ignore the motion of nuclei in molecules
2. the **Hartree-Fock (HF) approximation**: states that we can simplify our calculations by aggregating, or combining, the motion of electrons
3. the **Linear Combination of Atomic Orbitals (LCAO)**: states that we can construct molecular orbitals by a relatively straightforward addition of calculated atomic orbitals.

All of these approximations serve to give us less than a perfect solution to whatever calculation we are doing. As the famous statistician George Box declared:

All models are wrong, some are useful.

As the approximations, methods, and tools improve, so too will the accuracy of our calculations.

5.1.3 Solving the Schrodinger Equation:

Despite all of our best efforts, it is still not possible to be able to solve the Schrödinger equation. An exact solution of this equation will result in an energy value that is the lowest possible energy for a given molecular system. Any approximation will result in a higher, and more inaccurate, energy value. In other words, the choice of one or more approximations ensures that our final results will be different from that of the actual molecule. The **variation theorem** states that *the calculated energy will always be greater than the true energy*.

5.2 Fundamental Mathematics:

Molecular mechanics uses mathematics that are the most understandable to most normal human beings! In this method, we apply Newtonian mechanics to determine molecular properties. In Newtonian mechanics, atoms are modeled as if they are hard spheres connected together by flexible springs. By calculating the motion of the balls as the springs are contracted and expanded, using the spring equation (Equation 5.1), we can predict various chemical properties. F represents force, k is the spring constant, and x is the distance between the two hard spheres, representing the length of the bond between two atoms. Using a set of numbers known as a **force field**, molecules can be modeled.

$$F = -kx \quad (5.1)$$

Most molecular modeling tools look to solve the **Schrödinger Equation**. This equation can be used to calculate an approximate idea of the behavior of electrons in an atom or molecule. The equation calculates the **wavefunction** of an electron, which is a mathematical description of the probability of an electron being at some location in relation to the nucleus of the atom. When this equation is calculated, chemists can determine the energy of the atom or molecule. Chemists can also use the calculation results to derive a wide variety of other properties or characteristics of the atom or molecule.



Figure 5.1: Representation of path of electron in Bohr model. The electron follows a precise path.

In discussing the wavefunction, we are interested in the behavior of the electron, particularly its location and motion. In classical (Newtonian) mechanics, we assume that electrons are billiard balls, or particles, that move along a fixed path in the atom, as shown in Figure 5.1. As Niels Bohr postulated, these billiard balls can only exist at very well defined distances from the nucleus. This is the concept of **quantization**. Based on the level at which the electron exists, we can calculate properties such as the energy of the electron and, subsequently, the energy of the atom and of the molecule.

It turns out that the Bohr model does not accurately portray the behavior of electrons. A newer model, known as quantum chemistry, was developed (primarily in the mid-1900s) to address the limitations of the classical mechanics model. In the quantum

model, we cannot predict the specific location of the electron, only the probable location and behavior of the model.

The mathematical formula that looks to predict the probability that an electron might be at some location is known as the wavefunction. We can show this as an **electron cloud** (Figure 5.2). In this graphic, we state that there is a probability that the electron or electrons can be found somewhere inside the cloud.



The mathematical equation that represents the calculation of the wavefunction is known as Schrödinger's equation (Equation 5.2), named after the Austrian physicist Erwin Schrödinger. In its most well known format, the Schrödinger equation is represented by:

Figure 5.2: Representation of electron cloud in quantum model. The electron is somewhere in the cloud.

$$H\Psi = E\Psi \quad (5.2)$$

where H is an operator known as the Hamiltonian, Ψ (psi) is the wavefunction, and E is the energy.

This is a very simple looking, but very complicated, mathematical equation! This equation is an **eigenfunction**, a special type of mathematical equation. A short explanation of eigenfunctions follows.

Suppose you have a function such as:

$$f(x) = x^2 \quad (5.3)$$

This is a very simple function. In this case, we perform an operation on the independent value x to obtain a new value, y . In this case, the operation is squaring (raising to the 2nd power).

In calculus, we can perform an operation known as **differentiation**. If we differentiate the function shown above, we get this new result:

$$f'(x) = 2x \quad (5.4)$$

Notice that we now have a new, different function, $2x$ instead of x^2 . Since we have a new function as a result of this operation (differentiation), the function $f(x) = x^2$

is not an eigenfunction. Now lets introduce a new function:

$$f(x) = e^{2x} \quad (5.5)$$

Now lets do the same operation (differentiation) on this function. As before, we obtain a new function:

$$f'(x) = 2e^{2x} \quad (5.6)$$

Notice in this new function we have a constant (2) times the original function e^{2x} . Because we have the original function multiplied times a constant, the function $f(x) = e^{2x}$ is known as an **eigenfunction**.

Now take a look back at the Schrödinger equation. This too is an eigenfunction. We perform an operation on the wavefunction (Ψ), using the **Hamiltonian** operator (H). What comes out is a constant, in this case E , the energy of the molecule, and the original function, the wavefunction. Being able to calculate the energy of the molecule is tremendously important, and many other properties of the molecule can be derived from this calculation.

To finish out this mathematics, we should briefly explore the **Hamiltonian** operator (Equation 5.7). An operator is any mathematical action applied to a number, group of numbers, functions, etc. Addition, multiplication are both operations. Finding the square root is an operation. Finding the derivative or evaluating an integral are both operations. The Hamiltonian is also an operator, performing a complex mathematical operation on the atom or molecule.

$$H_{elec} = -\frac{1}{2} \sum^{elec} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) - \sum_i \sum_I^{elec \text{ nucl}} \left(\frac{Z_I}{R_I - r_i} \right) + \sum_i \sum_{j < i}^{elec \text{ elec}} \left(\frac{1}{r_i - r_j} \right) + \sum_J \sum_{J < I}^{nucl \text{ nucl}} \left(\frac{Z_I Z_J}{R_I - R_J} \right) \quad (5.7)$$

The Hamiltonian operator is shown in Equation 5.7. There are four parts to this equation:

1. $-\frac{1}{2} \sum^{elec} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)$: this calculates the kinetic energy of the electrons in the system. The unusual symbol ∂ is a partial differential equation that measures the change in the movement of the electron. The x , y , and z in the denominator represent the location of the electron in three dimensions. The symbol \sum says add all of these calculations together.
2. $\sum_i \sum_I^{elec \text{ nucl}} \left(\frac{Z_I}{R_I - r_i} \right)$: determines the electron-nuclear attractive energy, that energy that results because of the different charges on the electrons and the nuclei.

The Z notation is the atomic number of the atom ($Z = 1$ for hydrogen), R is the internuclear radius, and r is the interelectron radius.

3. $\sum_i^{elec} \sum_{j<i}^{elec} (\frac{1}{r_i-r_j})$: determines the repulsive forces of electron on electron.
4. $\sum_J^{nucl} \sum_{J<I}^{nucl} (\frac{Z_I Z_J}{R_I-R_J})$: determines the attractive forces of the nuclei in the molecular system

Even a general understanding of this operator should help the reader to understand why computers are necessary. This operation is done thousands, millions, and even billions of times each time a quantum calculation is performed.

5.3 Fundamental Approximations:

Most molecular modeling codes use approximations in order to perform the quantum chemical calculations in a reasonable period of time. An approximation is a mathematical shortcut or simplification of some representation of the problem. Approximations are, in essence, an inexact representation of some reality. In molecular modeling, there are several fundamental approximations:

5.3.1 Born-Oppenheimer approximation:

This approximation states that, due to the size and relative slowness of the nucleus as compared with electrons, most quantum chemical packages assume that it is stationary. In the Hamiltonian above, we only calculate the kinetic and potential energies of the electrons, not that of the nuclei. This significantly reduces the complexity of the calculations, making a calculation possible in a reasonable amount of time for molecules of reasonable size.

5.3.2 Hartree-Fock approximation:

Most chemists also describe the Hartree-Fock approximation. In this approximation we don't correlate the electrons. Suppose we have two electrons in the system, A and B. It is easy to correlate these two electrons, because we can measure the effect that A has on B and the effect that B has on A. However, as soon as we have three electrons (A, B, and C, Figure 5.3) the calculations become much more difficult. We have to measure the effect that A has on B, the effect that A has on C, the effect that B has on A, the effect that B has on C, the effect that C has on A, and the effect that C has on B.

As you can imagine, when we have more than three electrons (and most systems do!), the increase in computations increases exponentially.

In the *Hartree-Fock approximation*, we simplify the calculations by combining two or more electrons and pretending that they are a single electron, albeit a pretty big one. Returning to our three-electron system, we combine B and C now called BC as one electron. Now we first have to calculate the effect that A has on BC and the effect that BC has on A. We then have the electrons switch places. We now combine A and B, forming AB, and calculate the interaction of AB with C.

This system certainly makes the calculations simpler, but it does so at a cost to accuracy of the answer. As is shown in the graphic later in this reading, this approximation establishes a limit (the Hartree-Fock limit) to how accurate our answer can be.

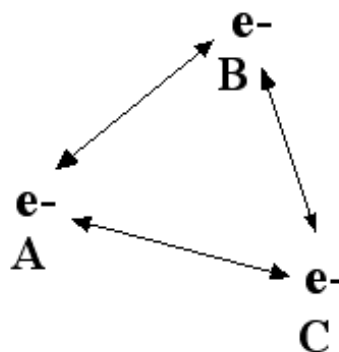


Figure 5.3: A three-electron system, showing the electron-electron interactions.

5.3.3 Linear Combination of Atomic Orbitals (LCAO):

In this approximation, we can model a molecular system by calculating the characteristics of the individual atoms in the molecule as if they are by themselves. We then simply add (**linear combination**) the results of the individual atoms to predict the molecular properties. Specifically, we calculate the wavefunction for each atom, otherwise known as the atomic orbital. For example, to calculate the molecular orbitals of water, we calculate the atomic orbital of the oxygen atom and each of the two hydrogen orbitals. Using the LCAO approximation, we then calculate the molecular orbitals of water by relatively simple addition of the atomic orbitals.

It is important to remember that the goal is to solve the Schrödinger equation as exactly as possible. Every approximation used reduces the accuracy of our calculations, and, subsequently, the accuracy of our chemical understanding.

5.4 Solving the Schrodinger Equation:

A more accurate calculation of the Schrödinger equation will always result in a lower energy value for the molecular system. The **variation theorem** states that *the calculated energy (\bar{E}) will always be greater than the true energy (E)* :

$$\bar{E} > E \quad (5.8)$$

The graphic shown looks to help visualize this reality.

For a fictitious molecular system, a typical answer results in the Hartree-Fock energy value. Assuming we apply all of the available approximations using the best possible starting numbers, the best we can do is the Hartree-Fock limit. The reader should notice that, in relative terms, this is a very long way away from the exact solution of the Schrödinger equation!

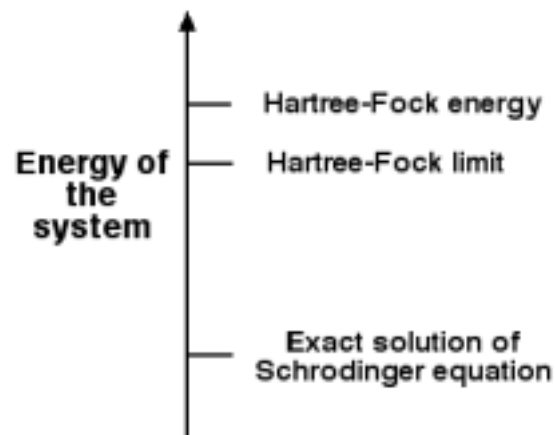


Figure 5.4: The Hartree-Fock Energy Limit