Practical Quantum Chemistry

Richard P. Muller

May 6, 2017

Contents

Chapter 1

A Gentle Introduction to Quantum Mechanics

1.1 Introduction

> I think I can safely say that nobody understands quantum mechanics. *Richard P. Feynman*
>
> The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved. *Paul A. M. Dirac*
>
> In mathematics you don't understand things. You just get used to them. *Johann von Neumann*

The quantum mechanical world can be disorientingly different from the classical world we are familiar with. Feynman and Dirac's quotations are strong words from two men who won Nobel prizes for unraveling the mysteries of quantum mechanics. How are we to rush in where Feynman and Dirac feared to tread?

In my opinion, von Neumann summarizes the experience of learning quantum mechanics very well. Quantum mechanics is only strange when we try to put it in terms of our classical mechanics intuition; if we can treat it on its own terms it can be simple and even beautiful. And to Dirac we might suggest that the availability of inexpensive computers and 40 years' experience in quantum chemistry has gone a long way toward, if not *solving* the equations of quantum mechanics, at least intelligently approximating them.

Quantum chemistry seeks to understand the structure of the world around us. The world that we see and smell and taste, we do so because of the quantum chemistry of molecules. Grass is green and blood is red because of the absorption of light by metalloporphyrin molecules. The semiconductors that power the microchips that power our computers switch on and off because of quantum chemical interactions. Learn a little bit about quantum chemistry and you can say a lot about the world. This is

because electrons are the *glue* that hold the material world together, and the science that understands how electrons act as this glue is quantum chemistry.

Moreover, quantum chemistry is a logical stopping point as we cascade down to smaller and smaller scales. Those areas of physics that describe scales smaller than the quantum chemistry world (with lengths on the order of 1 Å$= 1 \times 10^{-10}$ meter) might be beautiful, and might offer a deeper appreciation of the symmetry of the laws of physics, but say nothing more about the nature of the material world we interact with than does quantum chemistry.

The topic of quantum chemistry is often treated almost as if one needs the dark secrets of the Rosicrurians to understand the field. Although I suspect that this misconception does a great deal to satisfy the egos of quantum chemists, it means that many students who could become seduced by the intellectual beauty of the field are afraid to take courses in it. Which is a terrible shame, because never has quantum chemistry been more important to the technical world.

And so this book seeks to present the material that a student needs to begin on the path of quantum chemistry. Whenever possible, I seek to *demystify* the process, to make things as simple as possible. I have focused on the areas and principles of quantum chemistry that all students of the field must know, and, as such, I have neglected some topics, and presented others too briefly. Throughout the book I have provided extensive citations to other material that will help the student pursue the topic further.

Although I try to make the material in the book as simple as possible, students who have not been exposed to college-level General Chemistry and Calculus courses will probably find the material difficult. Also, it will probably be beneficial for students to have had some exposure to Quantum Mechanics (for example, as it is typically presented in a sophomore-level Physics Course). For students who have not had such an introduction, the rest of this chapter presents the major features of the field as simply as possible.

1.2   How the Quantum World Differs from the Classical World

One of the first indications that something was wrong with the world of classical physics came in attempts to model *black body radiation*. Black body radiation refers to the light emitted by a hot object; it is why a poker left in the fireplace glows red. Indeed, the color of flames, including the sun, is largely due to black body radiation. The problem with black body radiation came when physicists in the late 19th century tried to predict what wave lengths of light would arise from such a hot object. The equations that Raleigh and Jeans derived predicted an enormous release of energy that was clearly wrong. This erroneous prediction was known as the *ultraviolet catastrophe* (a good name for a glam-rock band if there ever was one). A crisis arose in physics, because although everyone knew that Raleigh and Jeans' prediction was wrong, no one knew how to fix it.

Max Planck and Albert Einstein came to the rescue, fortunately. Planck found a
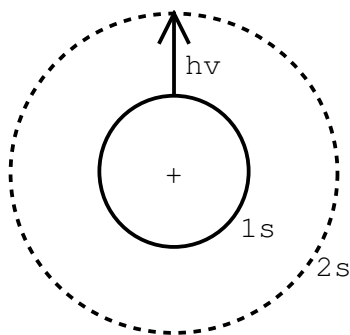
Figure 1.1: Bohr's planetary model of the hydrogen atom. The atom can absorb a photon of frequency $\nu = \frac{E_{2s} - E_{1s}}{h}$ and make a quantum leap from the ϕ_{1s} to the ϕ_{2s} orbital.

functional form

$$\rho(\nu) = \alpha\nu^3 \left(\frac{\exp(-h\nu/kT)}{1 - \exp(-h\nu/kT)} \right) \tag{1.1}$$

that approximated the energy density ρ of the light released at a given frequency ν. Einstein provided the physical interpretation. He reasoned that energy could only be absorbed or radiated in discrete packets or *quanta* of size $h\nu$. Here h is called *Planck's constant* and has the value $6.6 \times 10^{-34} Js$.

Einstein's prediction was a shocking departure. It was as if, according to Einstein, you could drive your car 55 miles per hour or 57 miles per hour, but there was no way possible that you could drive your car 56, or 56.2, or 56.3234513, miles per hour, and that you had to make a discrete jump from 55 to 57 miles per hour. Now, in reality, the size of the jump is much, much smaller than 2 miles per hour. But the fact that such a jump, no matter how small, was required ran contrary to everything the 19th century physicist knew about the world.

Another mystery at the time was the spectrum of hydrogen. When one shined light on atomic hydrogen, it would absorb only a few of the wave lengths. The other wave lengths would pass through the hydrogen untouched. Neils Bohr took Einstein's idea of energy only being absorbed or emitted in quanta and proposed a planetary model for the hydrogen atom. The electrons, he supposed, were negatively charged particles orbiting the positively charged nucleus like the planets orbit the sun. The orbits further from the nucleus represent higher energy states. When an atom absorbs light the electron makes a *quantum leap* from one of the low orbits to a higher orbit. Only certain wave lengths of light correspond to the energy difference between the two states, and only these wave lengths can be absorbed by the atom. Conversely, when an atom emits light an electron makes another quantum leap from a state of higher energy to a state of lower energy. Figure 1.2 sketches the Bohr planetary model for the hydrogen atom.

Elegant as Bohr's model of the atom was, it unfortunately failed to describe more complex properties of atoms such as why they bond together to form molecules, which is what we are mainly concerned with in this book. In 1925 Ernest Schrodinger pro-

posed what he called *wave mechanics*, and Werner Heisenberg proposed he called *matrix mechanics*. Both of these theories were later shown to be equivalent, and are now both subsumed in what is now known as *quantum mechanics*.

Quantum mechanics solves the *Schrodinger equation*

$$\hat{H}\psi = E\psi, \tag{1.2}$$

which determines everything that can be known about the atom or molecule we are considering. The Schrodinger equation is an example of an *eigenvalue equation* (*eigen* is the German word for *even*). The Schrodinger equation says that there is a function ψ when acted on by some *operator* $\hat{H}$ yields the original function ψ times some constant E. $\hat{H}$ is known as the *Hamiltonian operator*, named after W. R. Hamiltonian, the Astronomer Royal of Ireland, who came very close to discovering quantum mechanics early in the 19th century. The Hamiltonian contains all of the sources of energy in our system. We normally write this as

$$\hat{H} = \hat{T} + \hat{V} \tag{1.3}$$

where $\hat{T}$ represents the *kinetic energy*—the energy coming from the momentum of the particles in the system—and the $\hat{V}$ represents the *potential energy*—the energy (in molecules) coming from the electrostatic interactions between the particles in the system. The little hats over the letters indicate that these terms are *operators* rather than constants. Constants are just numbers that multiply functions, whereas operators tell us to do something: take a derivative, multiply it by another number, add something else to it.

The wave function ψ that is the solution to the Schrodinger equation provides everything we can know about the system we are studying. The probability of finding with its particles at the coordinates $\{x_1, x_2, \ldots x_N\}$ is given by

$$P(x_1, x2, \ldots x_N) = |\psi(x_1, x_2, \ldots x_N)|^2, \tag{1.4}$$

the square of the wave function. The momentum of the particles is given by

$$\hat{p}\psi = \left(\frac{\hbar}{i}\right)\nabla\psi \tag{1.5}$$

where

$$\nabla = \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \tag{1.6}$$

is the gradient operator—the operator that says to take the slope in all directions. $\hbar = h/2\pi$ is another form of Planck's constant.

We've just gone through a lot of mathematics. Hopefully, much of this rigor will be more understandable after we investigate a real quantum mechanical system in the next section. But before we do so, let us comment on the most revolutionary aspects of quantum mechanics. In classical mechanics, a particle's momentum was computed completely separately from its position. A car could be driving 30 miles per hour at the corner of State and Main Streets, or it could be driving 40 miles per hour at the

corner of State and Main Streets. Quantum mechanics tells us that the position and the momentum of a system are linked, because they both come from the wave function ψ.

The fact that the position and momentum of a particle are linked together means that if we know the position very exactly, we are forced to know the momentum a little less exactly, because both of these quantities come from the same wave function ψ, and a wave function that has a very well defined position has a less well defined momentum. This trade-off is the *Heisenberg uncertainty principle*

$$\delta p \delta x \geq \hbar/2, \tag{1.7}$$

which says that the uncertainty in the measurement of the momentum p multiplied by the uncertainty in the measurement of the position x must be greater than one-half Planck's constant. Recall that Planck's constant is very small, so that the Heisenberg uncertainty principle does not impose a very large restriction. What is surprising is not the size of the restriction, but the fact that there is a restriction at all. Again, like the concepts of quantum leaps, nothing that the early 20th century physicists had ever seen before could prepare them for such a development.

Equally strange was the wave nature of matter that the solutions to the Schrodinger equation implies. In classical mechanics particles are particles. In quantum mechanics particles often act like waves. Louis de Broglie distilled this relationship down to the mathematical expression

$$\lambda = h/p. \tag{1.8}$$

That is, the wave length associated with a particle is inversely proportional to its momentum. This relationship explains why we didn't notice the connection until the late 19th century: for real world objects like cars and baseballs, the momentum is so large as compared to Planck's constant h that the wave length is immeasurably short, and the objects behave as if they had no wave nature at all. But when objects become small enough, roughly the size of protons or electrons, we can start to observe their wave nature. Electrons can interfere with themselves, just as water waves form interference patterns when they overlap. When electrons pass through small enough openings, luckily the scale of the spacings in crystals, they can *diffract*, and we can understand a great deal about the crystal structure by interpreting the diffraction pattern. Electrons can also *tunnel*, seep through walls that they shouldn't be able to. The wave nature of matter tells us that there is a very small probability that your car will tunnel from your garage to your bedroom while you sleep. Because cars are large, and thus their wave lengths are very small, this probability is incredibly small. You could wait many times the age of the universe without observing it happen. However, there is some small finite probability that it could occur. Because electrons are so much smaller than cars, and their wave properties are much more substantial, we must account for tunneling when we try and predict how they behave.

One of the real advantages that we as chemists have is that we are really only concerned with the electrons and nuclei that form molecules. We will find that molecules are a wonderful arena for the wierd dance of quantum mechanics to play itself out. As soon as we can get used to the fact that electrons delocalize over large parts of the molecule, it becomes very easy to develop a new intuition regarding the behavior of electrons in molecules.
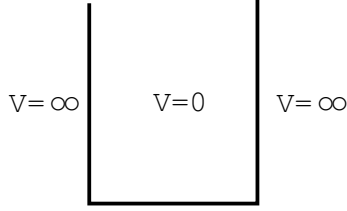
Figure 1.2: One dimensional box for an electron. The potential energy is 0 between $x = 0$ and $x = L$, and is infinite elsewhere.

1.3 The Particle in a Box: Analytical Solution

We will begin our investigation of the behavior of electrons by looking at what happens when we confine electrons in a small space. We're really interested in putting an electron in a box. But, since the math is easier, we will first look at a one-dimensional version of a box. Of course, electrons aren't one-dimensional, but in the current exercise we will pretend that they are.

Figure 1.2 shows the configuration we are going to consider. The box is L in length, and since the potential is infinite at the walls, the electron can never be there.

To describe this system we must solve the Schrodinger equation, and to do this we must first determine the Hamiltonian. Classically, the kinetic energy is given by

$$T = \frac{p^2}{2m},\tag{1.9}$$

and we can use the same formula in quantum mechanics, by inserting the expression for p from equation (1.5). The kinetic energy is then given by

$$\hat{T}\psi = -\frac{\hbar^2}{2m_e}\nabla^2\psi\tag{1.10}$$

(m_e is the mass of the electron). Since we're only doing a one dimensional problem, we have

$$\hat{T}\psi = -\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial x^2}.\tag{1.11}$$

As it turns out, we do not have any other sources of energy, and this expression is the entire Hamiltonian:

$$\hat{H}\psi = -\frac{\hbar^2}{2m_e}\frac{\partial^2\psi}{\partial x^2}.\tag{1.12}$$

Now that we know the form of the Hamiltonian, we begin trying to solve it. We are looking for a function that has a second derivative that is a constant times the original function itself. We note that both $\psi(x) = \sin(x)$ and $\psi(x) = \cos(x)$ meet this requirement.

We next look at the boundary condition. Since the potential is infinite at the walls of the box, the electron can never be there, which means that the wave function must

be zero there. We note that $\sin(0) = 0$, whereas $\cos(0) = 1$, which means that $\psi(x) = \sin(x)$ meets the boundary condition at $x = 0$. We next write the function is a slightly more general form, as the function

$$\psi(x) = A \sin(ax) \tag{1.13}$$

meets all of the requirements that have already been met by $\psi(x) = \sin(x)$. We will now determine values for A and a.

First, we have only used one of the boundary conditions. Recall that the wave function must be zero at both walls. We have used the wall at $x = 0$ to select the $\sin(x)$ function over the $\cos(x)$ function. We must now chose a value of a such that the function goes to zero at the $x = L$ wall as well. When $x = L$,

$$\psi(L) = A \sin(al) = 0. \tag{1.14}$$

Now, the function $\sin(x)$ is zero when $x = \pi, 2\pi, 3\pi, \ldots$, or generally, $x = n\pi$, where $n = 0, 1, 2, \ldots$. Thus, $al = n\pi$ and $a = \frac{n\pi}{L}$, so that our wave function is now

$$\psi(x) = A \sin\left(\frac{n\pi}{L}x\right). \tag{1.15}$$

Recall that the probability of finding an electron at x is given by $|\psi(x)|^2$. If we integrate the wave function everywhere, we know we have to find one and only one electron. This requirement is called *normalization* and leads to

$$1 = \int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = A^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right) dx. \tag{1.16}$$

From a table of integrals we can look up the identify

$$\int_0^{\pi} \sin^2(mx) dx = \frac{\pi}{2}. \tag{1.17}$$

Substituting this into equation (1.16) yields

$$1 = A^2 \frac{L}{2} \tag{1.18}$$

and thus,

$$A = \sqrt{\frac{2}{L}}. \tag{1.19}$$

Our wave function is now

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right). \tag{1.20}$$

Recalling that our Hamiltonian is given by equation (1.12), we must solve the equation

$$E\psi = -\frac{\hbar^2}{2m_e} \frac{\partial^2 \psi}{\partial x^2} \tag{1.21}$$

11
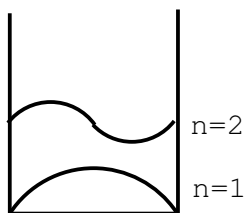
Figure 1.3: Lowest wave functions for an electron in a one-dimensional box.

Inserting equation (1.20) and working through the derivatives gives

$$E = \frac{n^2 \pi^2 \hbar^2}{2 m_e L^2}. \tag{1.22}$$

Since we worked so hard for this result, let us take some time to reflect on some interesting results from this solution. First, note that the solutions are a function of n: we didn't find merely one solution, we found an entire family of solutions. Secondly, note that the energy depends upon the square of n, which means that as n increases, the energy levels get further apart. Finally, note that the energy depends inverseley upon the square of the box length L, which means that as the box gets bigger, the energy becomes more stable, and subsequent energy levels get closer together.

Figure 1.3 shows the lowest wave functions for the electron in a one-dimensional box.

1.4   Solving the Particle in a Box with Grid Points

In general the problems we will encounter in quantum chemistry do not have analytical solutions. (When we say a solution is *analytical* we mean that it has a nice, simple one-line wave function such as $\psi(x) = A \sin(ax)$.) In fact, the electron in a box is one of only a very few Hamiltonians that we can solve analytically. This section will explore the *numerical* techniques that will let us find approximate solutions using linear algebra.

Suppose the electron in a one-dimensional box were not solvable analytically, or suppose it didn't occur to us to try $\sin(x)$ as a possible solution. We could *numerically approximate* the solution, by representing it as its value at a finite number of grid points (the approach we will pursue in this section), or expand in a finite set of *basis functions* (the approach we will use in much of the remainder of the book). As we use more points, or more basis functions, our numerical approximation becomes more and more accurate.

We will employ a principle in quantum chemistry called the *variational principle* that says that if we do such an expansion, any solution we find will be higher than the true energy, and thus the best combination is the one with the lowest energy.

We will approximate our wave function as its value at a set of points $\{x_i\}$.

$$\psi(x) \approx c_i x_i \tag{1.23}$$
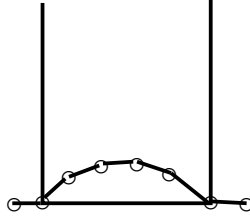
Figure 1.4: Approximation of the wave function by its value at a fixed number of points. Note that the points continue into the "forbidden region" at either side, but the wave function is zero in that region.

where c_i are the coefficients that we are going to adjust to find the lowest energy. Figure 1.4 shows roughly what our approximate wave function might look like.

In order to use such an approximation in the Schrodinger equation, we must be able to compute the second derivative that is required by the kinetic energy operator. We will use the *finite difference approximation*, whereby the first derivative is given by

$$\frac{df(x_i)}{dx} = \frac{f(x_{i+1}) - f(x_{i-1})}{\Delta x} \tag{1.24}$$

and the second derivative is given by

$$\frac{d^2 f(x_i)}{dx^2} = \frac{f(x_{i+1}) - 2f(x_i) + f(x_{i-1})}{\Delta x^2} \tag{1.25}$$

and $\Delta x = x_i - x_{i-1} = x_{i+1} - x_i$.

To solve the Schrodinger equation, we want to insure that at every point

$$-\frac{\hbar^2}{2m_e} \frac{d^2 \psi(x_i)}{dx^2} + V(x_i) = E\psi(x_i). \tag{1.26}$$

We can solve these equations by setting them up in a matrix equation. If we wish to find the eigenfunctions of the second derivative operator alone, we could solve a set of equations that look like:

$$\begin{bmatrix} -\frac{2}{\delta^2} & \frac{1}{\delta^2} & & & \\ \frac{1}{\delta^2} & -\frac{2}{\delta^2} & \frac{1}{\delta^2} & & \\ & \frac{1}{\delta^2} & -\frac{2}{\delta^2} & \frac{1}{\delta^2} & \\ & & \ddots & & \\ & & & \frac{1}{\delta^2} & -\frac{2}{\delta^2} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_n \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_n \end{bmatrix} \tag{1.27}$$

These matrix equations are known as eigenvalue equations. The correspondence between the differential equations known as eigenvalue equations (for example, equation (1.2)) and their finite matrix representation is a difficult one to get an intuitive feeling for. The next section gives a brief introduction to matrix equations.

1.5 Matrix Equations

Vectors and matrices are one- and two-dimension arrays of variables; they are useful because by manipulating matrices and vectors we can often obtain an entire family of solutions. The field of *linear algebra* deals with solving matrix and vector equations. One particularly useful result of rewriting equations in matrix/vector form is that we can then use standard linear algebra packages such as the LAPACK program library [1] to obtain solutions to the equations on a computer.

A matrix is a two-dimensional array of numbers:

$$\mathbf{A} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ A_{21} & A_{22} & A_{23} & A_{24} \\ A_{31} & A_{32} & A_{33} & A_{34} \\ A_{41} & A_{42} & A_{43} & A_{44} \\ A_{51} & A_{52} & A_{53} & A_{54} \end{bmatrix} \tag{1.28}$$

where here the matrix $\mathbf{A}$ is said to have 4 *columns* and 5 *rows*.

A vector is a matrix with only one column:

$$\mathbf{b} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \end{bmatrix}. \tag{1.29}$$

Here the vector $\mathbf{b}$ has 4 *rows*.

We can define addition and subtraction on matrices as well:

$$\mathbf{A} + \mathbf{B} = \begin{bmatrix} A_{11} + B_{11} & A_{12} + B_{12} & A_{13} + B_{13} & A_{14} + B_{14} \\ A_{21} + B_{21} & A_{22} + B_{22} & A_{23} + B_{23} & A_{24} + B_{24} \\ A_{31} + B_{31} & A_{32} + B_{32} & A_{33} + B_{33} & A_{34} + B_{34} \\ A_{41} + B_{41} & A_{42} + B_{42} & A_{43} + B_{43} & A_{44} + B_{44} \\ A_{51} + B_{51} & A_{52} + B_{52} & A_{53} + B_{53} & A_{54} + B_{54} \end{bmatrix} \tag{1.30}$$

which of course only works if $\mathbf{A}$ and $\mathbf{B}$ have the same number of rows and columns. Similarly, vector sums are given by

$$\mathbf{a} + \mathbf{b} = \begin{bmatrix} a_1 + b_1 \\ a_2 + b_2 \\ a_3 + b_3 \\ a_4 + b_4 \end{bmatrix} \tag{1.31}$$

and the vectors must have the same number of rows.

We define the product of a scalar α and a matrix $\mathbf{B}$ as

$$\alpha\mathbf{B} = \begin{bmatrix} \alpha B_{11} & \alpha B_{12} & \alpha B_{13} & \alpha B_{14} \\ \alpha B_{21} & \alpha B_{22} & \alpha B_{23} & \alpha B_{24} \\ \alpha B_{31} & \alpha B_{32} & \alpha B_{33} & \alpha B_{34} \\ \alpha B_{41} & \alpha B_{42} & \alpha B_{43} & \alpha B_{44} \\ \alpha B_{51} & \alpha B_{52} & \alpha B_{53} & \alpha B_{54} \end{bmatrix}. \tag{1.32}$$

We define the product of two matrices $\mathbf{C} = \mathbf{A} \times \mathbf{B}$ as

$$C_{ij} = \sum_k^N A_{ik} B_{kj}. \tag{1.33}$$

Here N is equal to the number of columns of $\mathbf{A}$ and the number of rows of $\mathbf{B}$; if the number of columns of the first matrix is equal to the number of rows of the second matrix we can multiply them. When we multiply a $M \times N$ matrix by a $N \times P$ matrix we obtain a $M \times P$ matrix. Since vectors are just matrices with one column, we can multiply a matrix by a vector $\mathbf{c} = \mathbf{A} \times \mathbf{b}$ if the number of columns of $\mathbf{A}$ is equal to the number of rows of $\mathbf{b}$. When we multiply a $M \times N$ matrix by a N-vector, we obtain an M vector.

Note that in general matrix multiplication does not *commute*. That is,

$$\mathbf{A} \times \mathbf{B} \neq \mathbf{B} \times \mathbf{A}. \tag{1.34}$$

In this book, we will write matrices with an uppercase emboldened letter, e.g. $\mathbf{A}$, and vectors with a lowercase emboldened letter, e.g. $\mathbf{b}$.

We define the *transpose* of a matrix with the superscript †. The transpose of a matrix is obtained by switching the rows and columns. That is,

$$\mathbf{A}^\dagger = \begin{bmatrix} A_{11} & A_{21} & A_{31} & A_{41} & A_{51} \\ A_{12} & A_{22} & A_{32} & A_{42} & A_{52} \\ A_{13} & A_{23} & A_{33} & A_{43} & A_{53} \\ A_{14} & A_{24} & A_{34} & A_{44} & A_{54} \end{bmatrix}; \tag{1.35}$$

when we take the transpose of a 5×4 matrix we obtain a 4×5 matrix. The transpose of a (column) vector is a *row vector*, and corresponds to a matrix with only one row.

Closely related to the transpose of a matrix is the *adjoint*. The adjoint of the matrix $\mathbf{A}$ is written $\mathbf{A}^*$, and the values are given by

$$\mathbf{A}^* = \begin{bmatrix} A_{11}^* & A_{21}^* & A_{31}^* & A_{41}^* & A_{51}^* \\ A_{12}^* & A_{22}^* & A_{32}^* & A_{42}^* & A_{52}^* \\ A_{13}^* & A_{23}^* & A_{33}^* & A_{43}^* & A_{53}^* \\ A_{14}^* & A_{24}^* & A_{34}^* & A_{44}^* & A_{54}^* \end{bmatrix}; \tag{1.36}$$

where A_{ij}^* represents the *complex conjugate* of A_{ij}. If A_{ij} is complex, that is, if it has both a real and imaginary part given by $A_{ij} = a + ib$, $A_{ij}^* = a - ib$. Obviously, if $\mathbf{A}$ is real, $\mathbf{A}^* = \mathbf{A}^\dagger$.

A special type of matrix we will encounter in quantum mechanics is called a *Hermitian matrix*. A Hermitian matrix is *self-adjoint*, $\mathbf{A} = \mathbf{A}^*$. If all of the values of $\mathbf{A}$ are real, the matrix is *symmetric*, $\mathbf{A} = \mathbf{A}^\dagger$.

The most common type of matrix problem we will come across in quantum mechanics is the *eigenvalue equation*, which is the linear algebra version of equation (1.2). In this format, given a matrix $\mathbf{A}$, we wish to find the family of solution vectors $\mathbf{x}$ and scalars λ where

$$\mathbf{A}\mathbf{x} = \lambda\mathbf{x}. \tag{1.37}$$

Solving an eigenvalue equation like this is often referred to as *diagonalization* because we find a transformation that will make $\mathbf{A}$ into a diagonal matrix to solve the equations. The scalar values λ are known as the *eigenvalues* of $\mathbf{A}$, and the vectors $\mathbf{x}$ are known as the *eigenfunctions* or *eigenvalues* of $\mathbf{A}$.

One interesting property of Hermitian and symmetric matrices is that all of their eigenvalues are real. Additionally, for symmetric matrices the eigenvectors are also real.

We will discuss other problems in linear algebra as we encounter them.

1.6 Solving the Matrix Equations for the Particle in a Box

We now have enough information to begin considering solutions to the numerical one-dimensional Schrodinger equation give in equation (1.26). First, let's set some parameters for the problem. We will solve for the energy levels of an electron in a box of length 1 atomic unit. *Atomic units* are chosen so that the mass of an electron ($9.1 \times 10^{-}31$ kg) is the mass unit, the electron charge (4.8×10^{-10} esu) is the charge unit, and the Bohr radius (0.529 Å) is the length unit, and the *hartree* (627.51 kcal/mol) is the energy unit. These units are convenient because in atomic units $\hbar = 1$, and the Schrodinger equation is greatly simplified.

We will space points at 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0. The points at 0.0 and 1.0 will be in the forbidden region. Technically the potential is infinite in this region. Since computers can't handle infinite numbers, we will set the potential to be 100 atomic units of energy (also known as *Hartrees*), an enormous amount of energy (it takes only $\approx 0.1 - 0.2$ Hartrees to break a typical chemical bond).

Our Hamiltonian now looks like

$$
H = \frac{1}{\delta^2}
\begin{bmatrix}
100 & -\frac{1}{2} & & & & & & & & & \\
-\frac{1}{2} & 1 & -\frac{1}{2} & & & & & & & & \\
& -\frac{1}{2} & 1 & -\frac{1}{2} & & & & & & & \\
& & -\frac{1}{2} & 1 & -\frac{1}{2} & & & & & & \\
& & & -\frac{1}{2} & 1 & -\frac{1}{2} & & & & & \\
& & & & -\frac{1}{2} & 1 & -\frac{1}{2} & & & & \\
& & & & & -\frac{1}{2} & 1 & -\frac{1}{2} & & & \\
& & & & & & -\frac{1}{2} & 1 & -\frac{1}{2} & & \\
& & & & & & & -\frac{1}{2} & 1 & -\frac{1}{2} & \\
& & & & & & & & -\frac{1}{2} & 1 & -\frac{1}{2} \\
& & & & & & & & & -\frac{1}{2} & 100
\end{bmatrix}
\tag{1.38}
$$

and the terms not listed are zero. Here we are neglecting the kinetic energy terms in the forbidden region, because we assume that the magnitude of this term will be far less than the potential term.

We solve equation (1.38) by using a computer program to compute the eigenvalues and eigenvectors of the matrix. Appendix A.1 has some simple programs to compute these values, but here we show examples of the solutions.

Table 1.1: Comparison of the numeric and analytical energies (in Hartrees) of the lowest three states of the particle in a box.

n	E_1	E_2	E_3
11	4.885	19.06	41.16
21	4.920	19.56	43.56
41	4.930	19.69	44.19
81	4.933	19.72	44.35
161	4.934	19.73	44.39
Analytical	4.935	19.74	44.41

Table 1.1 compares the analytical and numeric energies of the lowest three eigenstates of the particle in a box problem. By the time we have use 161 points we are making decent approximations to the exact results.

Figure 1.5 compares the lowest energy wave functions for the numeric and analytical techniques.

1.7 Solving Other One Dimensional Hamiltonians with Grid Points

It only took us a page to write down the analytical solution to the particle in a box, and it took us many times as long to write down the numerical solution. Why should we bother with numerical solutions?

There are only three quantum mechanical problems that we can solve analytically—the particle in a box that we already saw, the harmonic oscillator, and the Hydrogen atom. Whereas we can use the simple code that we just worked out and solve almost *any* one-dimensional problem that nature throws at us. This section will explore some of the systems that are most relevant to Chemistry.

Figure 1.6 shows the three lowest eigenvectors of the harmonic oscillator with the potential $V(x) = 50x^2$.

Figure 1.7 shows the three lowest eigenvectors of the Coulomb potential $V(x) = \frac{1}{|x|}$. This is a one-dimensional version of the electron-nuclear potential seen in the hydrogen atom. Note that, in contrast to the rounded wave functions the harmonic oscillator had at the origin, the Coulomb wave functions have cusps, a result of the singularity in the potential at the origin. Again, the same code is used to solve this potential as was used in the other one-dimensional problems.

The reader will note that the matrices we have derived for the kinetic energy, potential energy, and the total Hamiltonian are all symmetric, $\mathbf{A} = \mathbf{A}^\dagger$. This relationship isn't accident, we can show that the matrices derived from all quantum mechanical operators corresponding to observable properties are Hermitian.
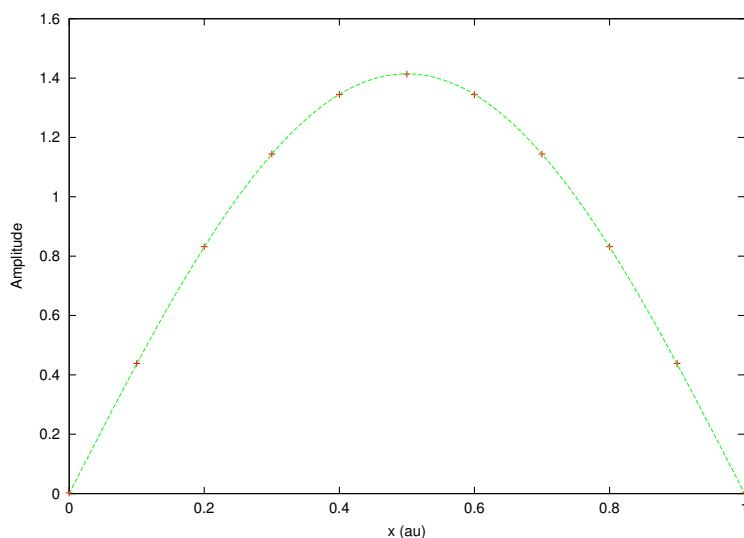
Figure 1.5: Comparison of the numeric (points) and exact (line) solutions for the most stable wave function for the particle in a box. Even with only 11 points, the functions are nearly indistinguishable.

1.8 Basis Set Expansions

In the previous section we saw the utility of expanding our wave function in some sort of a numerical approximation. In that section we approximated the wave function as its values at a number of different points. As the we use more and more points this approximation becomes more exact. This is a useful approximation for one-dimensional potentials, but becomes less effective in two and higher dimensions.

The Schrodinger equation determines the optimal shape for the wave function. By expanding the wave function in a finite set of points, the problem of optimizing the wave function shape is transformed into a matrix problem, which can be easily solved on a computer.

For molecular systems we will expand in a *basis set*. Basis functions are primitive three-dimensional shapes; when we expand the wave function in a set of basis functions we once again obtain a matrix equation that can be easily solved. Subsequent chapters will discuss basis functions and the resulting matrix equations in more detail.

The most common type of basis function used in quantum chemistry is the *Gaussian basis function*, which has the form

$$\chi(x; x_0) = N \exp\{-\alpha(x - x_0)^2\} \tag{1.39}$$

in one dimension. Here N is the normalization constant, and x_0 is the center of the function. Gaussian functions have a number of properties that make them useful for quantum chemistry. The first is that the product of two Gaussians on different centers

18

Figure 1.6: Lowest three eigenvectors of the harmonic oscillator with potential $V(x) = 50x^2$. The same code that computed the particle in a box problem can be used with a different potential to compute the new problem.
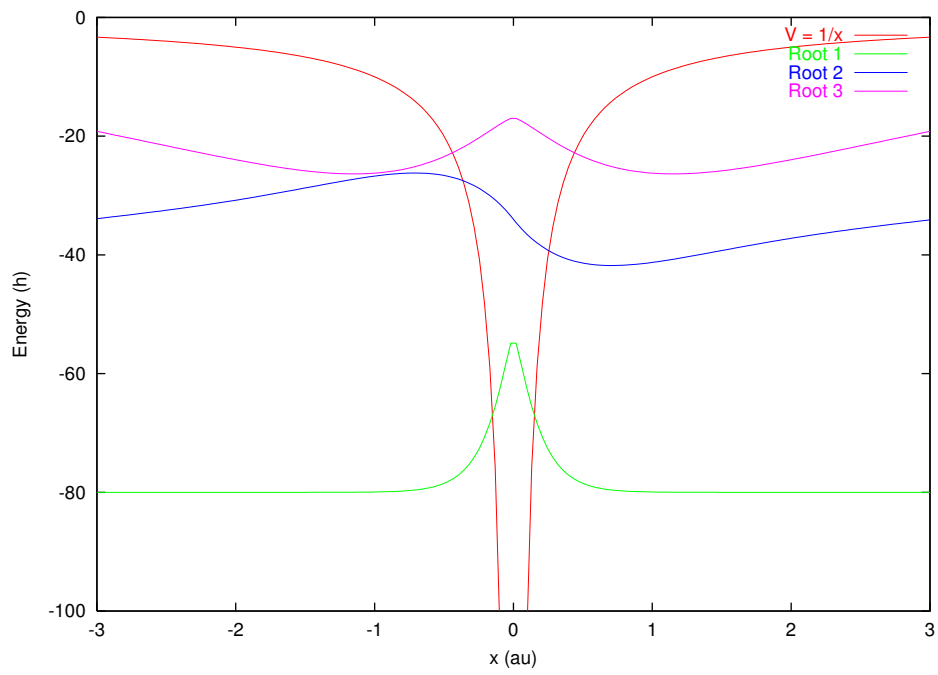
Figure 1.7: Lowest three eigenvectors of the Coulomb potential $V(x) = \frac{1}{|x|}$. The potential and the energy of the lowest eigenvector are not drawn to scale for simplicity.
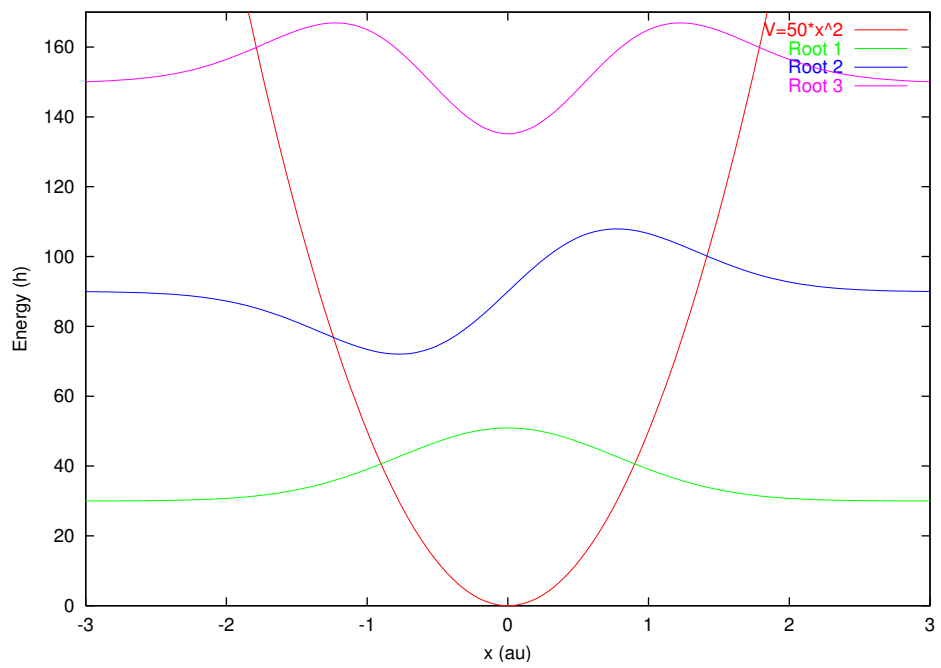
is another Gaussian centered somewhere in between. That is,

$$\exp\{-\alpha(x-x_a)^2\}\exp\{-\beta(x-x_b)^2\} = \exp\left\{\frac{-\alpha\beta(x_a-x_b)^2}{\gamma}\right\}\exp\{-\gamma(x-x_c)^2\}, \tag{1.40}$$

where

$$\gamma = \alpha + \beta, \tag{1.41}$$

$$x_c = \frac{\alpha x_a + \beta x_b}{\gamma}. \tag{1.42}$$

This property greatly simplifies the matrix elements we need to calculate.

If we want to use gaussian basis functions to solve the particle in a box, we need to work out several different types of matrix elements to go into the matrix form of the Schrodinger equation. The easiest of these elements is the overlap matrix elements

$$\begin{aligned}
S_{ij} &= \int \chi_i(x)\chi_j(x)dx \tag{1.43}\\[2mm]
&= N^2 \int \exp\{-\alpha_i(x-x_i)^2\}\exp\{-\alpha_j(x-x_j)^2\}dx \tag{1.44}\\[2mm]
&= N^2 \exp\left\{\frac{\alpha_i\alpha_j(x_i-x_j)^2}{\gamma}\right\} \int \exp\{-\gamma(x-x_c)^2\}dx \tag{1.45}\\[2mm]
&= \exp\left\{\frac{\alpha_i\alpha_j(x_i-x_j)^2}{\gamma}\right\} \tag{1.46}
\end{aligned}$$

which, if we stipulate $\alpha_i = \alpha_j = \alpha$, simplifies to

$$S_{ij} = \exp\{\alpha(x_i-x_j)^2\}. \tag{1.47}$$

The potential energy matrix elements are given by

$$\begin{aligned}
V_{ij} &= \int \chi_i(x)V(x)\chi_j(x)dx \tag{1.48}\\[2mm]
&= N^2 \int \exp\{-\alpha_i(x-x_i)^2\}V(x)\exp\{-\alpha_j(x-x_j)^2\}dx \tag{1.49}\\[2mm]
&= N^2 \exp\left\{\frac{\alpha_i\alpha_j(x_i-x_j)^2}{\gamma}\right\}V(x_c) \int \exp\{-\gamma(x-x_c)^2\}dx \tag{1.50}\\[2mm]
&= \exp\left\{\frac{\alpha_i\alpha_j(x_i-x_j)^2}{\gamma}\right\}V(x_c) \tag{1.51}\\[2mm]
&= \exp\{\alpha(x_i-x_j)^2\}V\left(\frac{x_i+x_j}{2}\right), \tag{1.52}
\end{aligned}$$

assuming that V(x) is a constant-valued function such as in the particle in a box, where it is either 0 or ∞.

The kinetic energy matrix elements are the most difficult. These are given by

$$T_{ij} = -\frac{1}{2} \int \chi_i(x)\frac{d^2}{dx^2}\chi_j(x)dx \tag{1.53}$$

21

$$= -\frac{N^2}{2} \int \exp\{-\alpha_i(x-x_i)^2\} \frac{d^2}{dx^2} \exp\{-\alpha_j(x-x_j)^2\}dx \quad (1.54)$$

$$= N^2 \int \exp\{-\alpha(x-x_i)^2\}(\alpha - 2\alpha^2(x-x_j)^2)$$
$$\times \exp\{-\alpha(x-x_j)^2\}dx \quad (1.55)$$

$$= N^2\alpha \int \exp\{-\alpha(x-x_i)^2\} \exp\{-\alpha(x-x_j)^2\}$$
$$-2N^2\alpha^2 \int \exp\{-\alpha(x-x_i)^2\}(x-x_i)^2$$
$$\times \exp\{-\alpha(x-x_j)^2\}dx \quad (1.56)$$

$$= \alpha \exp\{\alpha(x_i - x_j)^2\} - 2N^2\alpha^2 \exp\{\alpha(x_i - x_j)^2\} \times$$
$$\int (x-x_i)^2 \exp\{-\alpha(x-x_c)^2\}dx. \quad (1.57)$$

The problem with the last equation is that it is the product of functions centered about two different centers. We must expand the $(x-x_i)^2$ term in a binomial series about x_c to put the equation in a form we can integrate.

Now that we have all of the matrix elements we need for the particle in a box we can solve the equations. The form of the Schrodinger equation is

$$(\mathbf{T} + \mathbf{V})\mathbf{c} = \mathbf{S}\mathbf{c}E, \quad (1.58)$$

which, because of the presence of the overlap matrix $\mathbf{S}$, is a little more complex than the form we solved using the grid point method. With grid points we didn't have to worry about overlap, but with Gaussian functions we do. This transforms the normal matrix eigenvalue equation into a generalized eigenvalue problem. This, too, may be solved using standard routines from linear algebra packages.

1.9   Suggestions for Further Reading

Volume III of Feynman's *The Feynman Lectures on Physics* [2] presents a careful and thoughtful introduction to quantum mechanics. Pauling's *The Nature of the Chemical Bond* [3] is a magnificent introduction to quantum mechanics in chemistry. For more mathematical treatments of the subject, both Dirac's *The Principles of Quantum Mechanics* [4] and von Neumann's *Mathematical Foundations of Quantum Mechanics* [5] offer detailed discussion of the quantum mechanical theory that underpins the material in this section, and are both remarkably easy to read.

Chapter 2

Simple Hartree-Fock Theory

2.1 Introduction

The last chapter showed how we can construct and solve Hamiltonians for simple one-dimensional systems to get a feeling for how quantum mechanical systems work. The current chapter, and the rest of the book, will focus on a particular type of quantum mechanical system, the electronic structure problem, the study of which is known as quantum chemistry.

This chapter introduces *Hartree-Fock* (HF) theory. HF is a suitable place to start a discussion about practical quantum chemistry because the equations are relatively simple and yet much profound chemistry can be described by them. The problem that faces quantum chemistry is the Schrodinger equation. Typically, Schrodinger equations of more than a few particles cannot be solved exactly, and a molecule with N_A nuclei and N_e electrons has $N_p = N_A + N_e$ particles. Fortunately, the *Born-Oppenheimer approximation* (section 2.2) lets us reduce the number of particles to only the N_e electrons, and the *self-consistent field approximation* (section 2.5) reduces the problem to having to solve for one particle (which is now an *orbital* that holds two electrons) at a time. The resulting equations are the Fock equations (section 2.7), whose solutions are expressed as a linear combination of atomic orbitals (section 2.8). We conclude with a description of properties that can be obtained from HF calculations (section 2.9).

2.2 The Electronic Hamiltonian

Electronic structure theory seeks to find solutions to the non-relativistic time-independent Schrodinger equation

$$H\Psi = E\Psi \tag{2.1}$$

where H is the Hamiltonian operator for the nuclei and electrons in a molecule. For these molecular systems, H is given by

$$H = -\sum_{i=1}^{N_{el}} t_i - \sum_{A=1}^{N_{at}} t_A - \sum_{i=1}^{N_{el}} \sum_{A=1}^{N_{at}} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{N_{el}} \frac{1}{r_{ij}} + \sum_{A=1}^{N_{at}} \sum_{B=1}^{N_{at}} \frac{Z_A Z_B}{R_{AB}} \tag{2.2}$$

for a system with N_{el} electrons and N_{at} nuclei, where the quantities in H are expressed in atomic units, t_i and t_A are the kinetic energy of electron i and nuclei A, respectively, M_A is the nuclear mass of atom A in units of electron mass, Z_A is the charge on nucleus A, r_{iA} is the distance of electron i from nucleus A, r_{ij} is the distance between electrons i and j, and R_{AB} is the distance between nuclei A and B.

The molecular Hamiltonian is commonly simplified using the *Born-Oppenheimer approximation*, which derives from the observation that nuclei are much heavier than electrons (protons and neutrons are some 1800 times heavier than an electron, and most nuclei have many protons and neutrons), and consequently move much more slowly than do electrons. To a good approximation one can fix the nuclear coordinates and consider only the electronic part of the Hamiltonian. The consequence of this approximation is that the molecular Hamiltonian H now becomes H_{el}, the electronic Hamiltonian, and is given by

$$H_{el} = -\sum_{i=1}^{N_{el}} t_i - \sum_{i=1}^{N_{el}} \sum_{A=1}^{N_{at}} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{N_{el}} \frac{1}{r_{ij}} \tag{2.3}$$

For simplicity, the terms in H_{el} involving only one electron are grouped into a single term h,

$$h = -\sum_{i=1}^{N_{el}} \left(t_i + \sum_{A=1}^{N_{at}} \frac{Z_A}{r_{iA}} \right) \tag{2.4}$$

and H_{el} is given by

$$H_{el} = h + \sum_{i>j}^{N_{el}} \frac{1}{r_{ij}} \tag{2.5}$$

The nuclear repulsion energy

$$E_{nr} = \sum_{A>B}^{N_{at}} \frac{Z_A Z_B}{R_{AB}} \tag{2.6}$$

is constant for a fixed geometry and can be evaluated separately. H will hereafter refer to only the electronic Hamiltonian H_{el}.

2.3 The Molecular Wave Function

The solutions to H are in the form of a product of molecular orbitals

$$\Psi = \prod_{i}^{N_{el}} \psi_i. \tag{2.7}$$

The molecular spin orbitals ψ_i are composed of a spatial function ϕ_i and a spin function θ_i. The spatial orbital ϕ_i is a function of the position r_i of electron i. ϕ_i describes the spatial distribution of electron i such that $|\phi_i(r)|^2 dr$ is the probability of finding the

electron in the volume element dr. This probability for each orbital integrated over all space must be one, giving the normalization condition

$$\int \phi_i^*(r)\phi_i(r)dr = 1 \tag{2.8}$$

Spatial molecular orbitals can be taken to form an orthonormal set

$$\int \phi_i^*(r)\phi_j(r)dr = \delta_{ij} \tag{2.9}$$

Orbital ϕ_i also has a spin component θ_i. The spin of an electron in orbital ϕ_i is described by one of the orthogonal pair of functions α—*spin up*—and β—*spin down*. Each spatial orbital can accommodate one electron with α-spin, and one electron with β-spin. Thus, the simple product wave function has the form

$$\phi_1\alpha\phi_1\beta\phi_2\alpha\phi_2\beta\cdots\phi_{N_{occ}}\alpha\phi_{N_{occ}}\beta \tag{2.10}$$

where $N_{occ} = N_{el}/2$. The wave function for an electron that describes both the spatial and spin components is the spin orbital ψ

$$\psi_1 = \phi_1\alpha, \tag{2.11}$$

$$\psi_2 = \phi_1\beta, \tag{2.12}$$

and so on. Spin orbitals are convenient for evaluating many of the energy expressions in electronic structure theory; Appendix ??? describes techniques for evaluating matrix elements using spin orbitals.

Because each of the individual orbitals is normalized, the total probability of finding an electron anywhere in the wave function is equal to N_{el}.

$$|\Psi|^2 = \int \Psi^*(1\cdots N_{el})\Psi(1\cdots N_{el})dr_1\ldots dr_{N_{el}} \tag{2.13}$$

2.4 Antisymmetry and the Slater Determinant

The Pauli exclusion principle states that a wave function must change sign when the spatial and spin components of any two electrons are exchanged.

$$\Psi(1,2,\cdots,i,\cdots,j,\cdots,N_{el}) = -\Psi(1,2,\cdots,j,\cdots,i,\cdots,N_{el}) \tag{2.14}$$

The Pauli principle derives from the fact that electrons are indistinguishable particles, so that observable properties of the wave function cannot change upon exchange of electrons. Because these observables depend on $|\Psi|^2$, the wave function must either be symmetric (having the same sign) or anti-symmetric (having opposite sign) when electrons are exchanged. In practice only anti-symmetric wave functions are observed.

Because the wave functions must be anti-symmetric, the simple product wave function form 2.10 will not work. A convenient method of making a simple product wave function anti-symmetric is to use a Slater determinant. For the two electron simple

product wave function $\phi_1(1)\alpha(1)\phi_1(2)\beta(2)$, the anti-symmetric wave function is given by evaluating

$$\Psi(1,2) = 2^{-1/2} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) \end{vmatrix} \tag{2.15}$$

$$= 2^{-1/2}\phi_1(1)\phi_1(2)(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \tag{2.16}$$

The generalization of the Slater determinant to an arbitrary number of particles (and using spin orbitals to signify an arbitrary spin coupling) is

$$\Psi(1,2,\ldots,N) = (N!)^{-1/2} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_N(2) \\ \vdots & \vdots & & \vdots \\ \psi_1(N) & \psi_2(N) & \cdots & \psi_N(N) \end{vmatrix} \tag{2.17}$$

The $(N!)^{-1/2}$ is the normalization condition. For convenience, two shorthand notations are often used for 2.17. The first

$$\Psi(1,\ldots,N) = (N!)^{1/2}\mathcal{A}\left[\psi_1(1)\psi_2(2)\cdots\psi_N(N)\right] \tag{2.18}$$

uses the anti-symmetry operator $\mathcal{A}$ to represent the determinant and explicitly normalizes the wave function. The second notation uses Dirac bracket notation

$$\Psi(1,\ldots,N) = |\psi_1(1)\psi_2(2)\cdots\psi_N(N)\rangle \tag{2.19}$$

to represent both the Slater determinant and the normalization constant $(N!)^{-1/2}$. Both notations use only the diagonal of the Slater determinant to represent the wave function.

Because Slater determinants are so commonly used to antisymmetrize wave functions, individual configurations (as shown above) of a wave function are often referred to as determinants.

2.5 The Self Consistent Field Approximation

Even with the restrictions already made, it is not in general possible to solve 2.3 for many-electron wave functions. Consequently, we use the *self-consistent field* (SCF) approximation to replace the many-electron Hamiltonian with many one-electron Hamiltonians. In the SCF approximation, each electron no longer interacts with other electrons, but with the *average field* produced by the other electrons.

The SCF approximation has some dramatic shortcomings. Consider two electrons in a single orbital. Because the electrons only see each other's average field, a configuration where the electrons are next to each other is just as likely as a configuration where the electrons are on the other side of the molecule. The interactions excluded by the SCF approximation are known as *electron correlation*, and subsequent chapters will deal with ways of correcting for it.

Applying the SCF approximation to the exact electronic Hamiltonian given by 2.3 is commonly known as the Hartree-Fock (HF) approximation, which reduces the electronic Hamiltonian to

$$H_{HF} = h + v_{HF} \tag{2.20}$$

where v_{HF} is a two-electron operator representing the Hartree-Fock field.

2.6 The Hartree-Fock Energy Expression

Given a wave function with N doubly-occupied orbitals

$$\Psi = |\phi_1(1)\alpha(1)\phi_1(2)\beta(2)\cdots\phi_N(2N-1)\alpha(2N-1)\phi_N(2N)\beta(2N)\rangle \quad (2.21)$$

we can simplify the notation by writing

$$\Psi = |\phi_1\bar{\phi}_1\cdots\phi_N\bar{\phi}_N\rangle \quad (2.22)$$
$$= |1\bar{1}\cdots N\bar{N}\rangle \quad (2.23)$$

where a bar over an orbital signifies spin down, and no bar signifies spin up, and the order of the orbitals implies electron index. The energy of Ψ is thus given by

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad (2.24)$$
$$= \frac{\langle 1\bar{1}\cdots N\bar{N}|h + v^{HF}|1\bar{1}\cdots N\bar{N}\rangle}{\langle 1\bar{1}\cdots N\bar{N}|1\bar{1}\cdots N\bar{N}\rangle} \quad (2.25)$$

The denominator will be unity if the wave function is properly orthonormalized. The numerator can be broken into one-electron and two-electron terms, where the one-electron terms are given by

$$\langle 1\bar{1}\cdots N\bar{N}|h|1\bar{1}\cdots N\bar{N}\rangle = \sum_{i=1}^{N} 2h_{ii} \quad (2.26)$$

and the two-electron terms are given by

$$\langle 1\bar{1}\cdots N\bar{N}|v^{HF}|1\bar{1}\cdots N\bar{N}\rangle = \sum_{i,j=1}^{N} (2J_{ij} - K_{ij}) \quad (2.27)$$

The electronic energy is given by

$$E_{el} = \sum_{i}^{N} 2h_{ii} + \sum_{ij}^{N} (2J_{ij} - K_{ij}) \quad (2.28)$$

The J_{ij} terms are matrix elements of the Coulomb operator, which is the quantum mechanical operator corresponding to the macroscopic Coulombic repulsion between electrons i and j. The one-particle Coulomb operator $J^i(1)$ is given by

$$J^i(1) = \int \frac{\phi_i^*(2)\phi_i(2)}{r_{12}} dr_2 \quad (2.29)$$

where r_{12} is the distance between electrons 1 and 2. The matrix element J_{ij} is given by

$$J_{ij} = \int \phi_j^*(1)J^i(1)\phi_j(1)dr_1 = \int \phi_i^*(1)J^j(1)\phi_i(1)dr_1 \qquad (2.30)$$

This element is commonly written $(ii|jj)$, where the first half of the symbol corresponds to electron 1 and the second part of the symbol corresponds to electron 2.

The K_{ij} terms are elements of the exchange operator, which is purely a manifestation of the anti-symmetry of the wave function and has no macroscopic correspondence. The one-particle exchange operator $K^i(1)$ is most easily defined in terms of its action on another orbital ϕ_j:

$$K^i(1)\phi_j(1) = \left(\int \frac{\phi_i^*(2)\phi_j(2)}{r_{12}}dr_2 \right) \phi_i(1). \qquad (2.31)$$

The K_{ij} matrix element is given by

$$K_{ij} = \int \phi_j^*(1)K^i(1)\phi_j(1)dr_1 = \int \phi_i^*(1)K^j(1)\phi_i(1)dr_1 \qquad (2.32)$$

This matrix element is often written as $(ij|ij)$.

2.7 The Fock Equations

The variational principle states that the energy evaluated via 2.28 of any approximate wave function is an upper bound to the exact energy. Therefore, the optimal orbitals ϕ_i are those that give the lowest energy of the total wave function. As orbital ϕ_i changes to $(\phi_i + \delta\phi_i) = (\phi_i + \delta)$, the electronic energy from 2.28 changes to

$$E(i + \delta) = E(i) + 4\sum_i^N \langle \delta | F^i | i \rangle + \mathcal{O}(\delta^2) \qquad (2.33)$$

where F^i is the *Fock operator* given by

$$F^i = h + J^i + \sum_{j \neq i}(2J^i - K^i) \qquad (2.34)$$

The Fock operator corresponds to the first derivative of the electronic energy with respect to variations in the orbitals. Because $J_{ii} = K_{ii}$,

$$J_{ii} = 2J_{ii} - K_{ii} \qquad (2.35)$$

and we can add and subtract self-terms to obtain the closed-shell Fock operator

$$F^c = h + \sum_j(2J^j - K^j) \qquad (2.36)$$

$$F_{ij}^c = \langle i | F^c | j \rangle \qquad (2.37)$$

which is the same for all orbitals in our doubly-occupied core. It is easy to show that variations between occupied orbitals do not change the electronic energy for the closed-shell wave function being considered, and consequently the orbital variations $\delta\phi_i$ must be orthogonal to all occupied orbitals.

2.8 Basis Set Expansions

In practice, the orbital optimization is achieved by expanding the orbitals in a set of Gaussian basis functions χ_μ

$$\phi_i = \sum_\mu^{N_{bf}} c_{\mu i} \chi_\mu \tag{2.38}$$

for a basis set with N_{bf} basis functions. Using Gaussian basis functions both one-electron and two-electron integrals are easily evaluated.

$$h_{ij} = \sum_{\mu\nu}^{N_{bf}} c_{\mu i} c_{\nu j} h_{\mu\nu} \tag{2.39}$$

is the expression for the h_{ij} matrix element, where $h_{\mu\nu}$ is the one electron operator element between basis functions χ_μ and χ_ν, and

$$J_{ij}^k = \langle i|J^k|j\rangle = (kk|ij) = \sum_{\mu\nu}^{N_{bf}} c_{\mu i} c_{\nu j}(kk|\mu\nu) = \sum_{\mu\nu}^{N_{bf}} c_{\mu i} c_{\nu j} \sum_{\sigma\eta}^{N_{bf}} D_{\sigma\eta}^k (\sigma\eta|\mu\nu) \tag{2.40}$$

is the expression for the ij-th element of the J^k Coulomb operator and

$$K_{ij}^k = \langle i|K^k|j\rangle = (ki|kj) = \sum_{\mu\nu}^{N_{bf}} c_{\mu i} c_{\nu j}(k\mu|k\nu) = \sum_{\mu\nu}^{N_{bf}} c_{\mu i} c_{\nu j} \sum_{\sigma\eta}^{N_{bf}} D_{\sigma\eta}^k (\sigma\mu|\eta\nu) \tag{2.41}$$

is the expression for the ij-th element of the K^k exchange operator. The terms

$$(\sigma\eta|\mu\nu) = \int \frac{\chi_\sigma^*(1)\chi_\eta(1)\chi_\mu^*(2)\chi_\nu(2)}{r_{12}} dr_1 dr_2 \tag{2.42}$$

are the two-electron integrals over basis functions, and

$$D_{\sigma\eta}^k = c_{\sigma k} c_{\eta k} \tag{2.43}$$

is the corresponding density matrix element for orbital ϕ_k. The set of orbitals are varied by varying the coefficients $c_\mu i$ of the basis functions.

A wave function of the form of 2.21 that contains only doubly occupied orbitals is called a closed-shell wave function. For closed-shell wave functions, the orbitals are optimized by first forming the closed-shell Fock operator F^c, given by 2.34, and is obtained by first forming the core density matrix D_c

$$D_{\sigma\eta}^c = \sum_i^{occ} c_{\sigma i} c_{\eta i} \tag{2.44}$$

where the summation occurs only over doubly-occupied orbitals. F^c is given by

$$F_{\mu\nu}^c = h_{\mu\nu} + \sum_{\sigma\eta}^{N_{bf}} D_{\sigma\eta}^c \left(2(\mu\nu|\sigma\eta) - (\mu\sigma|\nu\eta)\right) \tag{2.45}$$

in basis-function space, and

$$F_{ij}^c = \sum_{\mu\nu}^{N_{bf}} c_{\mu i} c_{\nu j} F_{\mu\nu}^c \tag{2.46}$$

over molecular orbitals, where i and j now range over both occupied and virtual (un-occupied) orbitals. The Fock matrix in molecular orbital space is diagonalized

$$U^\dagger F U = \epsilon \tag{2.47}$$

and the eigenvectors U_i give the linear combination of occupied and virtual orbitals that give the improved set of orbitals ϕ_i, and the eigenvalues ϵ_i give the orbital energies for these orbitals. This procedure is repeated iteratively until either the orbitals or the energy stops changing; at this point the optimal set of orbitals has been obtained and the wave function is said to be converged.

2.9 Properties from HF Calculations

2.9.1 Energies and Structures

The fundamental quantity we get from quantum chemistry calculations is the *total energy* of the molecular configuration. Suppose we wanted to be able to estimate the energy of different $C_2H_2Cl_2$ configurations: Cl_2CCH_2, *cis*-CHCl-CHCl, and *trans*-CHCl-CHCl. We could guess fairly accurate geometries for each configuration, and then use some quantum chemistry technique (e.g. B3LYP/6-31G**) to compute single-point energies (i.e. with no geometry optimization) for each structure. By comparing the energies, we could get a qualitative understanding of the energy ordering of the different configurations.

But there simply isn't much reason to do guess geometries. As we saw earlier, it is relatively straightforward to compute the forces and use these to optimize our guess geometries. We can then obtain both structural and energetic information about our set of molecules.

When we use a decent quantum chemistry technique, such as B3LYP/6-31G**, we can expect to compute *relative* energies of different compounds to roughly 5 kcal/mol. There are a few systems that might be slightly more reliable (simple alkanes and alkenes), and a few systems that might be slighly less reliable (often systems involving different spin states). Transition states typically involve slightly greater errors in the energies than do ground state calculations. Geometries are typically reliable to > 0.05 Å.

2.9.2 Atomic Charges

We know that molecules consist of localized positively charged nuclei, with a delocalized cloud of electron density glueing them together. For many applications, particularly in describing molecules with a classical *force-field*, it is useful to be able to

simplify this electrostatic distribution into a set of charges that are centered only at the nuclei of the molecules.

The simplest way to obtain atomic charges is through *Mulliken charges*. Mulliken charges assume that the contributions to the atomic charges are determined by the character of the orbitals on the basis functions. Thus, the charge on atom A is given by:

$$q_A = Z_A - \sum_i^{N_{orbs}} \sum_{\mu \in A} \sum_{\nu \in A} c_{\mu i} c_{\nu i} S_{\mu\nu} \tag{2.48}$$

where Z_A is the nuclear charge on atom A, $c_{\mu i}$ is the orbital coefficient on basis function χ_μ, $S_{\mu\nu}$ is the amount that the χ_μ and χ_ν basis function overlap each other, and the $\mu \in A$ notation signifies that the summation occurs over only those basis functions that have their centers on atom A.

Unfortunately, the quality of the Mulliken fit is typically only as good as the quality of the basis set itself. For example, it is possible (though not advisable!) to perform a very good calculation on water by putting all of the basis function on the oxygen atom, and none on either of the two hydrogen atoms. In such a case, the Mulliken charges would predict that all of the electrons would be on the oxygen atom, which would thus have a charge of -2, whereas the hydrogen atoms would each have charges of +1. The point of this argument is not that anyone would ever use such a basis set (they wouldn't, hopefully), but that calculations with similarly *unbalanced* basis sets are one major limitation of Mulliken population analysis. Furthermore, some scientists use *plane wave basis sets*, which are beyond the scope of the current discussion, but where the basis functions do not have origins on *any* atoms.

Because of these limitations, many have begun to use *electrostatic potential* (ESP) fitting to obtain atomic charges. The idea behind this technique is to compute the electrostatic field due to the nuclei and electron on a series of points outside of the molecule; then a *least-squares fit* is performed to find the set of atomic charges that best reproduce this field on the grid of points. There is a certain theoretical elegance to such an approach, in that it is independent of the basis set. However, ESP-based charges can display bizzare irregularities of their own. Since the least-squares fitting procedure is an overdetermined problem, there are typically many different sets of charges that can reproduce a given electrostatic field, and there is no reason to think that the one that the least-squares fitting procedure obtains is necessarily the proper one.

Right now our best recommendation is to use Mulliken charges.

2.10   Suggestions for Further Reading

Roothan's 1951 review article *New Developments in Molecular Orbital Theory* [6] described the Hartree-Fock approximation and the LCAO approach used here. Szabo and Ostlund's *Modern Quantum Chemistry* [7] also provides a detailed description of this material.

Chapter 3

Gaussian Basis Sets

3.1 Introduction

This chapter presents an introduction to the Gaussian basis sets used in electronic structure calculations. Fundamentally, we want to be able to adjust the shape of the orbitals to find the ones that yield the most stable energy. To adjust the shape, we use the *linear combination of atomic orbitals* (LCAO) approach, where we expand an orbital ϕ_i in a set of *basis functions* $\{\chi_\mu\}$

$$\phi_i = \sum_\mu^{nbf} c_{\mu i} \chi_\mu. \tag{3.1}$$

By adjusting the coefficients $c_{\mu i}$ we can change the shape of the orbital ϕ_i, which transforms the problem of finding the best orbital shape to a linear algebra problem.

3.2 Slater Functions

The first basis sets used were of the form

$$\chi(r) = Y_{lm} \exp\{-\zeta r\}. \tag{3.2}$$

These were used because they have the same form as atomic orbitals. However, integrals between these functions proved difficult, and they have largely been abandoned in favor of Gaussian basis functions. Nonetheless, there are still two important advantages that Slater functions have over Gaussians. As $r \to 0$ Slater functions properly form a *cusp* (that is, they have finite slope), whereas Gaussians go to zero with zero slope. Moreover, as $r \to \infty$, Gaussian functions fall off too quickly, as compated to the Slater functions.

3.3 Gaussian Basis Sets

In 1950 Boys suggested that Gaussian functions

$$\chi(r) = x^i y^j z^k \exp\{-\alpha r^2\} \tag{3.3}$$

might be a good type of basis function for quantum chemistry, because of the fact that the product of two Gaussians is also a Gaussian. When the exponents (i, j, k) are zero,

$$\exp\{-\alpha_A r_A^2\}\exp\{-\alpha_B r_B^2\} = \exp\left\{\frac{-\alpha_A \alpha_B r_{AB}^2}{\gamma}\right\}\exp\{-\gamma r_p^2\}, \tag{3.4}$$

where

$$\gamma = \alpha_A + \alpha_B, \tag{3.5}$$

$$r_p = \frac{\alpha_A r_A + \alpha_B r_B}{\gamma}. \tag{3.6}$$

When the exponents (i, j, k) are nonzero, we can expand in a binomial series

$$x_A^{i1} x_B^{i2} = (x_p + x_{pA})^{i1}(x_p + x_{pB})^{i2} = \sum_q f_q(i1, i2, x_{pA}, x_{pB}) x_p^q, \tag{3.7}$$

and we can once again express the product as a sum of Gaussians. The point to remember was that Gaussians were proposed and adopted because they were numerically easier to deal with, rather than being more accurate.

3.3.1 Contracted Basis Sets

Because Gaussian basis functions do not have the proper cusp and tail behavior that Slater functions do, we need to *contract* several of them together to form a single basis function. In the jargon, the functions that are contracted together are each called *primitive basis functions*, and the resulting function is referred to as a *contracted basis function*. When quantum chemists refer to a *basis function* they typically mean a *contracted basis function*.

3.3.2 Naming Gaussian Basis Sets

The naming of commonly used Gaussian basis sets can also be confusing. This section will attempt to briefly categorize some major families of basis sets.

The smallest basis set is (not surprisingly) called a *minimal basis* (MB) description. This basis set has one basis function per occupied atomic orbital on the atom. Thus, H would have one basis function for the $1s$ orbital, and C would have 5 basis functions for the $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals, in a minimal basis description. The most commonly used MB basis set has the name STO-3G, to signify that three contracted Gaussians are used to replace one Slater type orbital.

The problem with the minimal basis description is that it doesn't allow the atoms to change their shape very much. If H only has one function, it doesn't have any degrees of freedom to adjust to adapt to a different bonding situation.

Thus, we can augment our basis sets with an additional basis function per occupied atomic orbital. These basis sets are called *double zeta* (DZ) basis sets. In practice most DZ basis sets are in fact really *valence double zeta* (VDZ) basis sets, because it is only necessary to add additional functions for the valence orbitals, and not the core orbitals, since only the valence orbitals are involved in chemical bonding. A VDZ description of H has 2 basis functions ($1s$ and $2s$), and a VDZ description of C has 9 basis function ($1s$, $2s$, $2p_x$, $2p_y$, $2p_z$, $3s$, $3p_x$, $3p_y$, $3p_z$). Commonly used VDZ basis sets have the names 3-21G and 6-31G; the names signify the number and type of basis functions used in the contraction.

But even a VDZ description doesn't have as much freedom as we would like. Molecules often polarize when near a large charge or in the presence of an external field. VDZ basis sets let the functions get larger or smaller, but don't let them polarize. So we add *polarization functions*, which are functions with one higher angular momentum than the highest occupied basis function. Thus, for H, which has occupied $1s$ functions, we would add $2p$ functions, and for C, which has occupied $2p$ functions, we would add $3d$ functions. This description is now called *double zeta plus polarization* (DZP). H now requires 5 basis functions ($1s$, $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals), and C requires 15 functions ($1s$, $2s$, $2p_x$, $2p_y$, $2p_z$, $3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{xx}$, $3d_{yy}$, $3d_{zz}$, $3d_{xy}$, $3d_{yz}$, $3d_{xz}$). Commonly used DZP basis sets are the 6-31G** basis set and the cc-pvDZ basis set. Sometimes, a 6-31G* basis set is used; here the single * indicates that polarization functions are included on the heavy atoms (everything except H) but not on H itself. The 6-31G** basis is one of the most commonly used basis sets, and is a good default basis set to use when studying a new molecule.

Finally, even DZP basis sets have a difficult time treating negative ions, which typically are in orbitals much more diffuse than the valence orbitals. Diffuse orbitals are also often useful in describing excited states of molecules. For these cases, we augment our basis sets with a set of *diffuse* basis functions. These basis sets are typically denoted using a + suffix, to denote diffuse functions on the heavy atoms, or a ++ suffix to denote diffuse functions on all atoms.

Note that when d-functions are included there are six functions listed (d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{yz}, d_{xz}), rather than the 5 that most students of chemistry are familiar with (d_{xx-yy}, d_{zz}, d_{xy}, d_{yz}, d_{xz}). The six functions are the simple Cartesian forms of the basis functions, and are the easiest way to input the basis functions. However, note that with the six functions listed, it is possible to make a linear combination, $d_{xx}+d_{yy}+d_{zz}$, that actually has s-like angular momentum. Keeping all six functions leads to a basis set that has extra description of s-type angular momentum. Such a description isn't wrong, but might lead to an unbalanced description: the s-type angular momentum has a more accurate description than the d-type. Many people believe that such an unbalanced description is misleading, and thus remove the s-combination of the d-basis functions. Many people do not remove this combination.

Table 3.1 summarizes basis function information.

Table 3.1: Different Levels of Basis Functions. Shown is the level, the number of basis functions used for H and C, and some commonly used examples.

Level	$N_{bf}[H]$	$N_{bf}[C]$	Examples
Minimal Basis (MB)	1	5	STO-3G
Double ζ (DZ)	2	9	3-21G, 4-31G, 6-31G
Double ζ + polarization (DZP)	5	15	6-31G**, cc-pVDZ

3.4   Suggestions for Further Reading

Boys's 1950 article [8] has a very good treatment of Gaussian basis functions and the reasons why they were preferred to Slater functions.

Chapter 4

Open-Shell Hartree-Fock Theory

4.1 Introduction

Chapter 2 described Hartree-Fock theory for closed-shell wave functions, where every electron was spin paired with another in a doubly-occupied orbital. Most molecules that we encounter in the everyday life (water, ethanol, and acetic acid, to mention a few that are probably in your kitchen) are closed-shell molecules. However, some molecules (most notably oxygen), and many important fragments of molecules, contain one or more unpaired electrons residing in singly-occupied orbitals. One way to solve these system is to treat the up-spin and down-spin electrons as if they were in two separate universes; this technique is called *unrestricted Hartree-Fock* (UHF) and is described in section 4.2. UHF techniques have the shortcoming that the orbitals for corresponding up- and down-spins aren't required to be equivalent. This is a phenomenon called *spin contamination* is typically incorrect, although it can lead to more accurate descriptions of wave functions as chemical bonds dissociate. The technique that requires the up- and down-spin electrons to be in equivalent orbitals is called *restricted open-shell Hartree-Fock* (ROHF), and is described in section 4.3.

4.2 Unrestricted Open-Shell Hartree-Fock Theory

A simple way of treating systems with unpaired electrons is *unrestricted Hartree-Fock* (UHF) theory. UHF solves different one-particle equations for the up- and the down-spin electrons.

Consider a section with N_α electrons with α spin, and N_β electrons with β spin. The UHF analogue of the Fock equations are called the *Pople-Nesbet* equations. These are

$$F^\alpha = h + \sum_i^{N_\alpha} (J_i^\alpha - K_i^\alpha) + \sum_i^{N_\beta} J_i^\beta, \tag{4.1}$$

$$F^\beta = h + \sum_i^{N_\beta} \left(J_i^\beta - K_i^\beta\right) + \sum_i^{N_\alpha} J_i^\alpha. \tag{4.2}$$

That is, each α spin electron (equation (4.1)) has a Coulomb and an exchange interaction with each of the other α electrons, and only a Coulomb interaction with the β electrons; each β spin electron (equation (4.2)) has a Coulomb and an exchange interaction with each of the other β electrons, and only a Coulomb interaction with the α electrons. Recall that exchange interaction only occurs between orbitals with the same spin.

UHF calculations do a good job of describing unpaired spins. One shortcoming to the approach is that there is nothing to require that orbital ϕ_i^α has any similarity to orbital ϕ_i^β. This contradicts our normal chemical intuition about these systems, and it also means that the wave function is no longer a pure spin state. This effect is known as *spin contamination*.

4.3   Restricted Open-Shell Hartree-Fock Theory

An alternative approach is to *restrict* the α orbitals to be the same as the β orbitals, a technique known as *restricted open-shell Hartree-Fock* (ROHF). For a molecule that consists of N_c doubly-occupied core orbitals and N_o singly-occupied, high-spin coupled open-shell orbitals, the wave function is given by

$$\Psi = |\phi_1 \bar\phi_1 \cdots \phi_{N_c} \bar\phi_{N_c} \phi_{N_c+1} \cdots \phi_{N_c+N_o}\rangle \tag{4.3}$$

The energy of this wave function is given by

$$E_{el} = \sum_i^{N_c+N_o} 2f_i h_{ii} + \sum_{ij}^{N_c+N_o} (a_{ij} J_{ij} + b_{ij} K_{ij}) \tag{4.4}$$

where f_i is the occupation for orbital i

$$f_i = \begin{cases} 1 & \phi_i \text{ is doubly-occupied} \\ 1/2 & \phi_i \text{ is singly-occupied} \end{cases} \tag{4.5}$$

and

$$a_{ij} = 2f_i f_j \tag{4.6}$$

$$b_{ij} = -f_i f_j \tag{4.7}$$

with the added condition that $b_{ij} = -1/2$ if i and j are both open-shell orbitals. Note that 4.4 reduces to 2.28 when all orbitals are doubly occupied.

Because an open-shell wave function of the form of 4.3 requires two sets of f_i coefficients ($f_i = 1$ and $f_i = 1/2$), the wave function is said to have two shells. Because $(N_o + 1)$ Fock operators are required (see next paragraph), the wave function is said to have $(N_o + 1)$ Hamiltonians.

A special case of restricted open-shell Hartree-Fock is the *open-shell singlet* wave function, where the highest two orbitals are both singly-occupied and singlet paired. Denoting these two orbitals ϕ_i and ϕ_j, if they have a triplet pairing

$$\phi_i\phi_j\alpha\alpha, \tag{4.8}$$

the component of the energy corresponding to these two orbitals would be

$$E_ij = J_{ij} - K_{ij} \tag{4.9}$$

which is consistent with the definitions in equations (4.5) – (4.7). However, if the two orbitals have a singlet pairing

$$(\phi_i\phi_j + \phi_j\phi_i)(\alpha\beta - \beta\alpha) \tag{4.10}$$

the component of the energy corresponding to these two orbitals is now

$$E_ij = J_{ij} + K_{ij}, \tag{4.11}$$

corresponding to $a_{ij} = +1/2$ and $b_{ij} = +1/2$.

Open-shell singlet wave functions correspond to excited states within the restricted Hartree-Fock approximation, and are a good way of describing excited states without having to perform an expensive configuration interaction calculation.

The procedure for optimizing the orbitals is slightly more complicated with the open-shell wave function in 4.3 than it was for the closed shell wave function in 2.21. For optimizing the occupied orbitals with the unoccupied orbitals $(N_o + 1)$ Fock operators are now required. For the core orbitals, F^c, given by

$$F^c_{\mu\nu} = f_c h + \sum_{k}^{N_{ham}} (a_{ck} J^k_{\mu\nu} + b_{ck} K^k_{\mu\nu}) \tag{4.12}$$

is formed, and for each open-shell orbital

$$F^i_{\mu\nu} = f_i h + \sum_{k}^{N_{ham}} (a_{ik} J^k_{\mu\nu} + b_{ik} K^k_{\mu\nu}) \tag{4.13}$$

is formed. Note that the summation here is over N_{ham}, the number of Hamiltonians, equal to $N_o + 1$. One density matrix, D_c, is formed for all the core orbitals, and density matrices D_i are formed for each of the open-shell orbitals. The Coulomb and exchange operators associated with each of these density matrices are given by

$$J^k_{\mu\nu} = \sum_{\sigma\eta}^{N_{bf}} D^k_{\sigma\eta}(\mu\nu|\sigma\eta) \tag{4.14}$$

and

$$K_{\mu\nu}^k = \sum_{\sigma\eta}^{N_{bf}} D_{\sigma\eta}^k (\mu\sigma|\nu\eta) \tag{4.15}$$

Forming the matrices in this fashion saves considerable effort because only one Coulomb and one exchange matrix are needed for all of the N_c core orbitals

Once the N_{ham} Fock operators are formed in the basis function space, they are again transformed into molecular orbital space by multiplying by the appropriate transformation coefficients

$$F_{ij}^k = \sum_{\mu\nu}^{N_{bf}} c_{\mu i} c_{\nu j} F_{\mu\nu}^k \tag{4.16}$$

For the core Fock operator F^c, i and j range over all core orbitals and all unoccupied orbitals; for the open shell Fock operator F^k, i and j range over open-shell orbital k and all unoccupied orbitals. Once each Fock operator is transformed to the molecular orbital basis it is diagonalized; the eigenvectors yield the linear combination of orbitals required for the next more optimized set of orbitals, and the eigenvalues yield the orbital energies.

Unlike the closed-shell example given earlier, mixing occupied orbitals that have different f, a, and b coefficients can change the energy. Starting from the energy expression 4.4 and taking the pairwise mixing of orbitals ϕ_i and ϕ_j

$$\phi_i' = \frac{\phi_i + \delta_{ij}\phi_j}{\sqrt{1 + \delta_{ij}^2}} \tag{4.17}$$

and

$$\phi_j' = \frac{\phi_j + \delta_{ij}\phi_i}{\sqrt{1 + \delta_{ij}^2}} \tag{4.18}$$

to preserve orthonormality, and expanding through second order in δ_{ij} gives the equation for the change in energy

$$\Delta E_{ij}(1 + \delta_{ij}^2) = 2\delta_{ij}A_{ij} + \delta_{ij}^2 B_{ij} \tag{4.19}$$

where

$$A_{ij} = \langle i|F^j - F^i|j \rangle \tag{4.20}$$

$$B_{ij} = \langle i|F^j - F^i|i \rangle - \langle j|F^j - F^i|j \rangle + \gamma_{ij} \tag{4.21}$$

$$\gamma_{ij} = 2(a_{ii} + a_{jj} - 2a_{ij})K_{ij} + (b_{ii} + b_{jj} - 2b_{ij})(J_{ij} + K_{ij}) \tag{4.22}$$

Requiring the energy change be stationary with respect to δ_{ij} gives

$$\delta_{ij} = -\frac{A_{ij}}{B_{ij}} \tag{4.23}$$

To preserve orbital orthonormality, $\delta_{ji} = -\delta_{ij}$. One way of making these variations simultaneously is to form the rotation matrix Δ, the anti-symmetric matrix with zero diagonal defined by

$$\Delta = \begin{bmatrix} 0 & \frac{A_{ij}}{B_{ij}} \\ -\frac{A_{ij}}{B_{ij}} & 0 \end{bmatrix} \tag{4.24}$$

The new set of orbitals $\{\phi^{New}\}$ are obtained from the old set of orbitals $\{\phi^{Old}\}$ via the transformation

$$[\phi^{New}] = \exp(\Delta)[\phi^{Old}] \tag{4.25}$$

This method computes the optimal mixing of the occupied orbitals with respect to each other while preserving orbital orthonormality.

It should be noted that if two orbitals have the same f, a, and b coefficients, as defined by 4.5 and refeq:abdef, $A_{ij} = 0$, and, consequently, no mixing is done between those orbitals. Thus, when the wave function only consists of closed-shell orbitals no occupied-occupied mixing is done, and only occupied-unoccupied mixing is performed via diagonalization of the Fock operator F^c. The occupied-occupied mixing would have no effect because the numerator of the rotation matrix D would be zero, and the orbitals would not change.

In a given iteration, first the optimal occupied-occupied mixing is computed via equation 4.25, and the occupied-virtual mixing is computed by forming and diagonalizing the Fock operators for each Hamiltonian, via equations 4.12–4.16. The iterations continue until the orbitals stop changing, at which point the wave function is said to be *converged*.

4.4   Suggestions for Further Reading

Szabo and Ostlund [7] provide a brief treatment of UHF theory in Chapter 3. Goddard and Bobrowicz's article *The Self-Consistent Field Equations for Generalized Valence Bond and Open-Shell Hartree-Fock Wave Functions*[9], presents a very detailed derivation of ROHF theory.

Chapter 5

Geometry Optimization

5.1 Introduction

This chapter will describe how we can use quantum chemistry techniques to optimize the structures of molecules. Recall that the Born-Oppenheimer approximation reasons that since nuclei are much heavier than electrons, the electronic wave functions can then be solved assuming that the nuclei are fixed. But what if we want the nuclei to move? More to the point, what if we want to use quantum chemistry techniques to determine the most stable structure of a molecule? This chapter will describe techniques for obtaining forces, optimized ground state structures, and optimized transition state structures, using quantum chemistry techniques.

5.2 Forces

We can view the quantum chemistry techniques we have developed as 'black boxes' that take in a geometry—a set of coordinates for the nuclei in the molecule—and produce the corresponding energy. A very inefficient way to optimize a molecule would be to simply vary every nuclear position in every possible way. The most stable structure would be the one with the lowest energy, just as the resting place for a ball between two hills is in the valley between them.

But such an exhaustive search is incredibly time consuming. Recall that molecules with N atoms have $3N - 6$ modes. A simple molecule like acetic acid (CH_3COOH), which has 8 atoms, has 18 internal modes that need to be optimized. Sampling only ten points in each coordinate would require 10^{18} energies to be computed. As there are roughly 3×10^7 seconds in a year, even if we could compute one of these energies in a second, the calculation would require 300 million years.

We can find a better technique by considering the aforementioned analogy of the ball rolling between two hills. The ball doesn't sample each point in the space to determine which is the lowest, it just rolls downhill. Similarly, we can determine the most stable geometry of a molecule by computing the *forces* on the atoms, and then letting the atoms move in the directions dictated by those forces.

Trying yet another naive approach, we can take a finite difference approach to computing forces and use the formula

$$F_\lambda = \frac{\partial E}{\partial \lambda} \approx \frac{E(r + \lambda) - E(r)}{|\lambda|}, \tag{5.1}$$

which says that F_λ, the force in some direction delta, is the energy difference when the molecular coordinates are moved by λ, divided by the length of the move.

Calculating finite difference forces is still an inefficient technique for optimizing a geometry, but it is much faster than the exhaustive search. For our acetic acid molecule with 18 internal coordinates, we would require only 19 energy evaluation per force calculation. Then, requiring 10 force calculations in a geometry optimization only requires 190 calculations, as opposed to the 10^{18} required by the exhaustive search technique.

The best technique for computing forces of molecules arises from the Hellmann-Feynman theorem

$$F_\lambda = \frac{\partial E}{\partial \lambda} = \langle \Psi | \frac{\partial H}{\partial \lambda} | \Psi \rangle. \tag{5.2}$$

A full discussion of the partial derivatives of the Hamiltonian is beyond the scope of the current discussion. But the point to remember is that these derivitaves may be computed by *analytical techniques*, and that the same techniques can be used for higher order derivates, which will be useful in optimizing ground and transition states.

5.3 Ground State Optimization

This technique will be discussed in greater detail in upcoming lectures. For the current purposes, though, we will state a few basic ideas.

Steepest descent techniques simply take steps in the direction of the forces. Some amount of guesswork is required in determining the proper step size, and these techniques typically converge slowly to the optimized geometry.

Conjugate gradient techniques use both the force and the previous direction moved, and move in a direction conjugate to the previous one, which greatly accelerates the convergence.

Fletcher-Powell techniques use the force and approximate the *Hessian*—the matrix formed by the second derivative of the energy with respect to the atomic displacements— to optimize the geometry. Almost all quantum chemistry programs use variations of this approach for their geometry optimizations.

Newton-Raphson techniques are like Fletcher-Powell techniques, except the Hessian is computed analytically. These are the most accurate, and also the most time-consuming, techniques for optimizing geometries.

5.4 Transition State Optimization

A full discussion of transition state optimization is beyond the scope of the current discussion. However, we will again state several important concepts.

Just as in simple calculus one can determine whether an extremum point is a minimum or a maximum by looking at the second derivative, we can use the Hessian matrix to determine whether we are at a ground state, which is a minimum with respect to all atomic displacements, or at a *transition state*, which is at a minimum in every direction but one, for which it is a maximum.

One method of finding a transition state is to start from a ground state structure and to follow the lowest vibrational mode—which can be determined from the Hessian matrix—uphill until a maximum is found. These techniques can be extremely time consuming.

Better techniques involve *linear transit*, where structures for the reactants and the products are used to find the transition state between them. The energy is computed along several points that connect the reactant and product structures, and the maximum along that pathway is determined; this structure, which hopefully is fairly close to the transition state, is used in a traditional transition state search. A similar technique is the *nudged elastic band* technique.

5.5   Quantum Chemistry Molecular Dynamics

Section to be completed later.

Chapter 6

A Case Study of the Singlet-Triplet Gap in Methylene: Part I

6.1   Introduction

Chapter 7

Density Functional Theory

7.1 Introduction

This chapter presents a very basic introduction to Density Functional Theory (DFT). DFT is a remarkable theory that currently has wide use in quantum chemistry, as it has computational requirements comparable to Hartree-Fock (HF) techniques, but accuracy comparable to more exact techniques such as MP2.

DFT starts from very different assumptions than does HF, but winds up with a set of equations (the Kohn-Sham equations) that are extremely similar to the Fock equations. We will therefore introduce the DFT one-particle Hamiltonian as a modification of the HF Hamiltonian. This will allow us to understand most of the salient points about DFT, but we should bear in mind that we are skipping over some very important distinctions.

7.2 Review of the Hartre-Fock One-Particle Hamiltonian

The Fock equations are the one-particle Hamiltonian we solve in HF theory. For a closed-shell system, the same equation,

$$F^c = h + 2J^c - K^c, \tag{7.1}$$

can be solved for every particle in the system. Here h is the part of the Hamiltonian that describes one-electron interactions, such as the kinetic energy of an electron, or the attraction between an electron and a nucleus in the molecule. The term J^c, called the *Coulomb term*, describes the electrostatic repulsion between the electrons in the system. The term K^c, called the *exchange term*, is an artifact of the antisymmetry requirement that the Pauli exclusion principle puts on the wave function, and represents the energy change when two electrons are exchanged.

Recall to get the Fock operator in (7.1) we had to make the *self-consistent field* approximation: electrons no longer see other individual electrons, but rather the average field of all of the other electrons. In reality, however, electrons *do* see each other. The

terms that the self-consistent field approximation leaves out are collectively referred to as *electron correlation*.

As an example of electron correlation, consider the He atom, which has two electrons. The self-consistent field approximation says that there is as much chance of the two electrons being right next to each other as there is for them to be on opposite sides of the molecule. Clearly, since electrons are negatively charged and repel each other, this is not the case.

7.3 The Kohn-Sham Hamiltonian as an extension of the Fock equations

So then what does the true Hamiltonian look like, if we know that the Fock equations are an over-simplification. Perhaps we can take it to look something like

$$F = h + 2J - K + V_{corr}. \tag{7.2}$$

That is, the Hamiltonian is roughly the same as the Fock equation, but has a correction term in it to add in electron correlation effects.

Is it even plausible that such a statement might work? In two landmark papers, Hohenberg and Kohn proved that any property of the ground state wave function can also be derived from the ground state density, and Kohn and Sham derived a set of one-particle self-consistent equations for exchange and correlation effects based on such a *density functional* treatment.

Based on such a treatment, the one-particle equation looks like

$$F = h + v_J[\rho] + v_X[\rho] + v_C[\rho]. \tag{7.3}$$

Here the HF Coulomb and exchange operators are now written as functionals of the ground state electron density ρ, and there is an additional correlation term that is also a function of ρ.

7.4 The Local Density Approximation (LDA)

But what form are the functionals in equation (7.3) to take? The initial guess that people made were that these functionals were actually functionals of the *local density*. That is, the total correlation energy is a sum over lots of points of some function of the density at that point:

$$E_C = \sum_i F(\rho(r_i)). \tag{7.4}$$

There is a compelling elegance to such an approximation. We saw earlier that one of the problems with excluding electron correlation was that there was just as much chance that two electrons in the same orbital were right on top of one another as far apart. Perhaps we could penalize regions in the molecule that had too high density to keep this from happening.

In 1980 Ceperley and Alder performed Quantum Monte Carlo calculations on the homogeneous electron gas at different densities, and allowed very accurate correlation potentials to be derived. The resulting LDA potentials have been found to work well for geometries, particularly in solids, but do not work as well for the energetics of finite molecules.

7.5   The Generalized Gradient Approximation (GGA)

Of course, molecules are not homogeneous electron gases, they contain very inhomogeneous distributions of electrons, peaked near the nucleus. In fact, it is the particular nature of these inhomogeneities that gives rise to chemical bonding, so if we want chemical accuracy (≈ 5 kcal/mol) from our method, we need to make sure we can treat inhomogeneities accurately.

So perhaps, rather than making functionals dependent upon only the local density, we could allow them to be a function of the local density, and the gradient of the local density:

$$E_C = \sum_i F(\rho(r_i), \nabla\rho(r_i)). \tag{7.5}$$

Such an approximation, due mostly to Perdew and Becke allows the functional to more accurately describe inhomogeneities in the electron density. This means that these functionals, which go by names BLYP, PW91, and PBE, among others, can begin to describe molecules with chemical accuracy.

7.6   Exact Exchange

One of the things that this note has been glossing over is that the exchange operator v_X is itself a function of the density, and, like the correlation functional, is a fit to homogeneous and inhomogeneous results. However, we already know that under some boundary conditions, it should look pretty much like the HF exchange operator K. Following these arguments, Becke experimented with *hybrid functionals* that have some of the traditional GGA exchange functional v_X in them, and some amount of the exact (i.e. HF) exchange operator K. By trial and error he found that $\approx 30\%$ was optimal for a variety of molecules. The most commonly used functional is the B3LYP functional, which consists of Becke's three-term hybrid exchange functional, and the LYP correlation functional.

Table 7.1: Summary of data from [**?**] comparing the performance of different density functionals for computing enthalpies of formation of a wide range of molecules. Average absolute deviations from experimental results are reported in kcal/mol.

Method	Non-hydrogen	Hydrocarbons	Substituted Hydrocarbons	Radicals	Inorganic Hydrides	Overall
SVWN	73.58	133.71	124.41	54.56	33.65	90.88
BLYP	10.30	8.09	6.10	5.09	3.13	7.09
BPW91	12.25	4.85	7.99	6.48	4.21	7.85
BP86	16.61	25.82	26.80	15.76	8.16	20.19
B3LYP	5.35	2.76	2.10	2.98	1.84	3.11
B3PW91	5.14	3.96	2.77	3.21	1.99	3.51
B3P96	7.80	30.81	25.49	13.53	7.86	17.97

7.7 The Kohn Sham Equations

7.8 Practical Issues

7.8.1 The Poisson Equation

7.8.2 Atomic Grids

7.9 Performance of a Family of Density Functionals

It is sometimes useful to understand how different density functionals perform over a wide range of molecules. Pople and coworkers have done two excellent studies [10, **?**]. Table 7.1 summarizes information from this study.

One should not take such averages too seriously, but in general terms, these studies by Pople confirm results found by most other workers in the field. With quality (e.g. DZP) basis sets, one can normally anticipate 5-10 kcal/mol accuracy from GGA functionals such as BLYP or PW91, and 3-5 kcal/mol accuracy from Hybrid functionals such as B3LYP. One must be very cautious with the energies from LDA calculations such as SVWN, but the structures are very often reliable.

7.10 Suggestions for Further Reading

Walter Kohn's two landmark papers [11, 12] are both examples of that rare beast: a paper that is both an intellectually signficant breakthrough and that is easy to read. Parr and Yang's book *Density Functional Theory of Atoms and Molecules* presents a very thorough treatment of the entire field, but only covers through the development of LDA. Perdew's [13] and Becke's [14, 15, 16] papers present good descriptions of GGA, and Becke's 1993 paper [17] presents a good description of hybrid functionals.

Chapter 8

Semiempirical Quantum Chemistry Calculations

8.1   Introduction

Semiempirical techniques offer good accuracy at very modest computational cost for a number of different systems. These techniques start with the Fock equations (2.34), but rather than attempt to solve it, first eliminates most of the small elements, and then approximates the rest of the terms with experimental values.

This note covers the theoretical underpinnings of the different semiempirical techniques for computing the electronic structure of molecules [18, 19, 20, 21].

This note is limited to closed-shell molecules. I take some liberties during the derivations. In particular, I mix parts of Pople's original theory with later developments that I believe to be improvements (in particular the Mataga-Nishimoto parameterization of the two-electron integrals). Moreover, my CNDO development follows the spirit of CNDO/2 rather than CNDO/1. I believe that these departures from Pople's original theory make the resulting theory easier to understand and faster to implement.

8.2   The Self Consistent Field Equations

We start by assuming that the wave function of a closed-shell molecule may be written as a product of doubly-occupied orbitals

$$\Psi = \prod_{i}^{N_{occ}} \phi_i^2 (\alpha\beta - \beta\alpha). \tag{8.1}$$

We also assume that these orbitals may be accurately expanded as a linear combination of atomic-like orbitals

$$\phi_i = \sum_{\mu}^{N_{bf}} c_{\mu i} \chi_{\mu}. \tag{8.2}$$

Variational treatment of the orbital coefficients $c_{\mu i}$ leads to the Fock equations

$$\sum_{\nu} F_{\mu\nu} c_{\mu i} = \sum_{\nu} S_{\mu\nu} c_{\nu i} \epsilon_i. \tag{8.3}$$

Here $F_{\mu\nu}$ is the Fock matrix, whose elements are given by

$$F_{\mu\nu} = t_{\mu\nu} + v_{\mu\nu}^N + \sum_{\sigma\eta} P_{\sigma\eta} \left[(\mu\nu|\sigma\eta) - \frac{1}{2}(\mu\sigma|\nu\eta) \right], \tag{8.4}$$

where $t_{\mu\nu}$ is the kinetic energy operator, v^N is the nuclear attraction operator, and

$$(\mu\nu|\sigma\eta) = \int \int \frac{\chi_{\mu}^*(1)\chi_{\nu}(1)\chi_{\sigma}^*(2)\chi_{\eta}(2)}{r_{12}} d^3 r_1 d^3 r_2 \tag{8.5}$$

is a two-electron integral.

We will ignore the finer points of computing the terms in equations (8.4) and (8.5), as the idea behind semiempirical techniques is to approximate the most important of these terms and to exclude the rest.

8.3   CNDO Approximations

CNDO makes several simplifying approximations, which will be discussed in this section.

The fundamental assumption (from which the name of the technique derives) is that the differential overlap of atomic orbitals on the same atom is neglected. The first aspect of this is simplification of the overlap matrix, such that

$$S_{\mu\nu} = \delta_{\mu\nu}. \tag{8.6}$$

For the atomic orbitals for which the theory was developed, the overlap between different atomic orbitals on the same atom is already zero. Consequently, in that basis, the only elements excluded are between atomic orbitals on different atoms.

The next approximation simplifies the two electron integrals:

$$(\mu\nu|\sigma\eta) = (\mu\mu|\sigma\sigma)\delta_{\mu\nu}\delta_{\sigma\eta} = \gamma_{\mu\sigma}. \tag{8.7}$$

The difficulty with this level of approximation is that the integral is no longer rotationally invarient. Consequently, these integrals are normally further simplified to represent s-type integrals on the different atoms, and thus depend only on the two atoms, A and B, on which the functions μ and σ reside.

This integral $\gamma_{\mu\nu} = \gamma_{AB}$ may be further approximated using the Mataga-Nishimoto approximation [22, 23]:

$$\gamma_{AB} = \frac{f_\gamma}{\frac{2f_\gamma}{\gamma_{AA}+\gamma_{BB}} + R_{AB}}. \tag{8.8}$$

The f_γ parameter is widely [23] taken to be 1.2, and the expressions for γ_{AA} are taken from Pariser and Parr [24]:

$$\gamma_{AA} = I_A - A_A \tag{8.9}$$

where I_A and A_A are the ionization potential and the electron affinity of atom A, respectively.

The next approximations deal with the one-electron terms $t_{\mu\nu}$ and $v_{\mu\nu}^N$. The kinetic energy term is treated as a diagonal parameter

$$t_{\mu\nu} = t_{\mu\mu}\delta_{\mu\nu} \tag{8.10}$$

and the diagonal term is parameterized as

$$t_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu), \tag{8.11}$$

the average of the ionization potential I_μ and the electron affinity A_μ for function μ.

The nuclear attraction integral v^N

$$v_{\mu\nu}^N = \sum_B \int \frac{\chi_\mu \chi_\nu}{r_B} d^3 r \tag{8.12}$$

is simplified by ignoring all integrals unless μ and ν are on the same atom A

$$v_{\mu\nu}^N = \begin{cases} \sum_B V_{AB} & \text{if } \mu, \nu \in A \\ 0 & \text{otherwise} \end{cases}. \tag{8.13}$$

This may be further approximated via

$$V_{AB} = Z_B \gamma_{AB}. \tag{8.14}$$

The final approximation concernes $F_{\mu\nu}$, the off-diagonal elements of the Fock matrix. We ignore all of these elements when μ and ν are on the same atom. Of the remaining elements, we approximate the one-electron terms via

$$F_{\mu\nu}^1 = \beta_{AB}^0 S_{\mu\nu} \tag{8.15}$$

and the two-electron terms as

$$F_{\mu\nu}^2 = -\frac{1}{2} P_{\mu\nu} \gamma_{AB}. \tag{8.16}$$

Here the resonance term $\beta_{AB}^0 = \frac{1}{2}(\beta_A + \beta_B)$, and β_A and β_B are parameters. We note that here the $S_{\mu\nu}$ elements represent the true overlap, rather than the diagonal overlap used in equation (8.6).

Combining all of these approximations together, we are left with the following form of the Fock matrix:

Table 8.1: CNDO/2 Parameterization (eV)

Element	$\frac{1}{2}(I_s + A_s)$	$\frac{1}{2}(I_s + A_s)$	β_A
H	7.176		9.0
Li	3.106	1.258	9.0
Be	5.946	2.563	13.0
B	9.594	4.001	17.0
C	14.051	5.572	21.0
N	19.316	7.275	25.0
O	25.390	9.111	31.0
F	32.272	11.080	39.0
Na	2.804	1.302	7.720
Mg	5.125	2.052	9.447
Al	7.771	2.995	11.301
Si	10.033	4.133	13.065
P	14.033	5.464	15.070
S	17.650	6.989	18.150
Cl	21.591	8.708	22.330

$$F_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) + [(P_{AA} - Z_A) - \frac{1}{2}(P_{\mu\mu} - 1)]\gamma_{AA} + \sum_{B \neq A}(P_{BB} - Z_B)\gamma_{AB},$$

(8.17)

$$F_{\mu\nu} = \beta^0_{AB}S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB}.$$

(8.18)

8.4   CNDO Parameters

The most important issue in any NDO technique is that of obtaining accurate parameters. This section will describe some of the more common sets of parameters.

Table 8.1 describes the original CNDO/2 parameters from Pople.

Table 8.2 lists the parameterization of Sichel and Whitehead (reference [25]) for CNDO; these parameters also include γ_{AA} terms for the Mataga-Nishimoto equation (equation (8.8)).

Table 8.2: Sichel and Whitehead (reference [25]) Parameters (eV)

Element	$-\frac{1}{2}(I_s + A_s)$	$-\frac{1}{2}(I_p + A_p)$	γ_{AA}
H	-13.595		12.848
Li	-4.999	-3.673	3.458
Be	-15.543	-12.280	5.953
B	-30.371	-24.702	8.048
C	-50.686	-41.530	10.333
N	-70.093	-57.848	11.308
O	-101.306	-84.284	13.907
F	-129.544	-108.933	15.233

Chapter 9

Electron Correlation: Beyond HF Theory

9.1   Introduction

Hartree-Fock theory is appropriate for many different applications in electronic structure theory, especially for the ground states of molecules near their equilibrium geometries. It does have two major shortcomings: it ignores much of the electron correlation, and excited states are difficult to calculate.

The first shortcoming of HF theory is that electron correlation is ignored [7], except in an averaged sense. Electron correlation is the interactions between the motions of the individual electrons, and HF theory, because it calculates an electron's motion in the average field produced by the other electrons rather than the exact positions of the other electrons, leaves much of the electron correlation out.

One manifestation of the incorrect treatment of electron correlation in HF theory is the well-known fact that HF wave functions of the type of equations 2.21 or 4.3 do not dissociate properly. Consider the H2 molecule described by two basis functions, χ_r and χ_l. The ground state HF wave function will be given by

$$\Psi_{HF} = |(\chi_r + \chi_l)(\chi_r + \chi_l)\alpha\beta\rangle = \frac{1}{\sqrt{2}}[\chi_r\chi_r + \chi_r\chi_l + \chi_l\chi_r + \chi_l\chi_l](\alpha\beta - \beta\alpha) \quad (9.1)$$

which is an accurate description of the bonding when the molecule is near equilibrium bond length. As the molecule dissociates the terms $\chi_l\chi_l$ and $\chi_r\chi_r$ in the wave function become increasingly unstable because they correspond to heterolytic bond cleavage. The wave function should dissociate only to the terms corresponding to homolytic cleavage, $\chi_l\chi_r$ and $\chi_r\chi_l$. The valence bond (VB) wave function starts from the correct dissociation fragments $\chi_l\chi_r$ and $\chi_r\chi_l$. Consequently, the VB wave function is given by

$$\Psi_{VB} = |\chi_l\chi_r\alpha\beta + \chi_r\chi_l\alpha\beta\rangle = \frac{2}{\sqrt{2}}[\chi_l\chi_r + \chi_r\chi_l](\alpha\beta - \beta\alpha) \quad (9.2)$$

Figure 9.1: Dissociation of diatomics using HF and GVB wave functions.

which dissociates to the correct limit because it does not contain the heterolytic cleavage terms $\chi_l\chi_l$ and $\chi_r\chi_r$. A generalization of the VB wave function, the generalized valence bond (GVB) wave function, described at length in the next section, always yields a lower energy than the HF wave functions, but the difference in energies is negligible for small bond distances.

Figure 9.1 shows an example of the incorrect dissociation of HF wave functions. Shown is the dissociation of H_2 using a HF wave function, with respect to the fragment energy of the individual H atoms. On the same plot is the GVB wave function that will be discussed in the next section. As is evident from figure 9.1, the HF wave function dissociates to an incorrect limit, one higher in energy than the individual H fragments. The GVB wave function, on the other hand, dissociates to the correct energy.

Another shortcoming of HF theory is that it is often difficult to converge excited states of wave functions [26]. Unless the excited state has a different overall symmetry than the ground state, it generally collapses to the ground state upon orbital optimization. This prevents HF theory from providing chemically useful information about excitation energies and charge densities of excited states.

The next section presents a simple correction to some of the HF shortcomings, the aforementioned GVB wave function, which generalizes the two electron wave function from equation 9.2 for many electron wave functions.

9.2 Generalized Valence Bond Theory

One simple correction to HF theory that overcomes many of HF's shortcomings is Generalized Valence Bond (GVB) theory [9, 27, 28, 29]. GVB theory replaces the closed-shell HF wave function

$$\Psi_{HF} = \left| \prod_i^{occ} \phi_i^2 \alpha\beta \right\rangle \tag{9.3}$$

with the GVB wave function [9]

$$\Psi_{GVB} = \left| \left[\prod_i^{occ} (\phi_{i1}\phi_{i2} + \phi_{i2}\phi_{i1}) \right] \Theta(1, 2, \ldots, N_{occ}) \right\rangle \tag{9.4}$$

where $\Theta(1, 2, \ldots, Nocc)$ is a general spin wave function for the N_{occ} electrons and the GVB orbitals ϕ_{i1} and ϕ_{i2} are not orthogonal. It is generally convenient to replace the general spin coupling Θ in equation 9.4 with the GVB-Perfect Pairing (GVB-PP) wave function where the two electrons in each GVB pair are paired only with each other. This reduces equation 9.4 to [9]

$$\Psi_{GVB} = \left| \prod_i^{occ} (\phi_{i1}\phi_{i2} + \phi_{i2}\phi_{i1})\alpha\beta \right\rangle, \tag{9.5}$$

or

$$\Psi_{GVB} = \left| \prod_{i}^{occ} \phi_{i1}\phi_{i2}(\alpha\beta - \beta\alpha) \right\rangle. \tag{9.6}$$

Equation 9.6 may be regarded as a generalization of equation 9.3, where each orbital ϕ_i in equation 9.3 is replaced by a GVB pair consisting of two non-orthogonal orbitals $\phi_{i1}\phi_{i2}$

$$\phi_i\phi_i\alpha\beta \to \phi_{i1}\phi_{i2}(\alpha\beta - \beta\alpha) = (\phi_{i1}\phi_{i2} + \phi_{i2}\phi_{i1})\alpha\beta. \tag{9.7}$$

For computational purposes, it is convenient to replace the GVB pair

$$(\phi_{i1}\phi_{i2} + \phi_{i2}\phi_{i1})\,\alpha\beta \tag{9.8}$$

with the natural orbital representation [9]

$$(c_{ig}\phi_{ig}\phi_{ig} + c_{iu}\phi_{iu}\phi_{iu})\,\alpha\beta \tag{9.9}$$

where ϕ_{ig} and ϕ_{iu} are now orthogonal and given by

$$\phi_{i1} = \frac{c_{ig}^{1/2}\phi_{ig} + c_{iu}^{1/2}\phi_{iu}}{\sqrt{c_{ig} + c_{iu}}} \tag{9.10}$$

$$\phi_{i2} = \frac{c_{ig}^{1/2}\phi_{ig} - c_{iu}^{1/2}\phi_{iu}}{\sqrt{c_{ig} + c_{iu}}}. \tag{9.11}$$

With the strong orthogonality constraint, which assumes that GVB orbitals of different pairs are orthogonal, the energy may once again be written in the familiar form

$$E_{el} = \sum_{i}^{N_{occ}} 2f_i h_{ii} + \sum_{ij}^{N_{occ}} (a_{ij}J_{ij} + b_{ij}K_{ij}) \tag{9.12}$$

except now f_i is given by [9]

$$f_i = \begin{cases} 1 & \phi_i \text{ is doubly-occupied} \\ 1/2 & \phi_i \text{ is singly-occupied} \\ c_i^2 & \phi_i \text{ is a pair orbital with} \\ & \text{GVB CI coefficient } c_i. \end{cases} \tag{9.13}$$

Similarly,

$$a_{ij} = 2f_i f_j \tag{9.14}$$

$$b_{ij} = -f_i f_j \tag{9.15}$$

except that $b_{ij} = -1/2$ if ϕ_i and ϕ_j are both singly-occupied.

Furthermore, if ϕ_i is a pair orbital

$$a_{ii} = f_i \tag{9.16}$$

$$b_{ii} = 0 \tag{9.17}$$

and if ϕ_i and ϕ_j are in the same pair,

$$a_{ij} = 0 \tag{9.18}$$

$$b_{ij} = -c_i c_j \tag{9.19}$$

Because equations 4.19–4.22 in chapter 2 are derived based on the general energy expression in equation 4.4, the orbital optimization equations are still appropriate for our modified definitions of f_i, a_{ij}, and b_{ij}. Thus, the same equations that were used to optimize open-shell HF wave functions can be used to optimize GVB-PP wave functions.

For a GVB wave function of the form of equation 9.6 with N_p pairs and $2N_p$ natural orbitals (often referred to as a "GVB $N_p/2N_p$" wave function), $2N_p$ different values of f_i are obtained, and hence the wave function is said to have $2N_p$ shells. $2N_p$ Fock operators must also be formed, and hence the wave function is said to also have $2N_p$ Hamiltonians.

The coefficients c_{ig} and c_{iu} for the GVB orbital are optimized each iteration [9, 28] by solving a two-by-two configuration interaction (*vide infra*) for each GVB pair to minimize the overall energy with respect to the c_{ig} and c_{iu} coefficients. This amounts to solving [9]

$$Y^i c_i = c_i E_i \tag{9.20}$$

where

$$Y^i = \begin{bmatrix} Y^i_{gg} & Y^i_{gu} \\ Y^i_{gu} & Y^i_{uu} \end{bmatrix} \tag{9.21}$$

$$Y^i_{gu} = K_{ig,iu} \tag{9.22}$$

$$Y^i_{gg} = \frac{F^{ig}}{f_{ig}} \tag{9.23}$$

$$Y^i_{uu} = \frac{F^{iu}}{f_{iu}} \tag{9.24}$$

The added functional freedom associated with having a pair of orbitals describe the electron pair allows the GVB-PP wave function to incorporate the appropriate amount of ionic and covalent character for any particular internuclear separation. Such a modification to the wave function for the electron pair is tantamount to including electron correlation between the two electrons in the GVB pair. One important result is that GVB-PP wave functions dissociate to the correct limits, yielding accurate physical

data for chemical systems. Moreover, by selecting a higher root to equation 9.20 excited states can be selected [26].

Generally, molecular wave functions have a combination of orbitals described by (closed- and open-shell) HF and GVB wave functions. The next section summarizes equations for these wave functions.

9.2.1 Summary of Equations for General HF/GVB Wave Functions

The general wave function composed of N_c doubly-occupied core orbitals, N_o singly-occupied open-shell orbitals, and N_p pairs of variably-occupied GVB natural orbitals is given by

$$\Psi = |\Psi_{Core}\Psi_{Open}\Psi_{Pair}\rangle \tag{9.25}$$

where

$$\Psi_{Core} = \prod_{i=1}^{N_c} \phi_i\phi_i\alpha\beta \tag{9.26}$$

$$\Psi_{Open} = \prod_{i=1}^{N_o} \phi_i\alpha \tag{9.27}$$

$$\Psi_{Pair} = \prod_{i=1}^{N_p} (c_{ig}\phi_{ig}^2 + c_{iu}\phi_{iu}^2)(\alpha\beta - \beta\alpha) \tag{9.28}$$

and c_{ig} and c_{iu} are optimized each iteration via equation 9.20.

The electronic energy of this general wave function is given by

$$E = \sum_{i=1}^{N_{occ}} 2f_i h_{ii} + \sum_{i,j=1}^{N_{occ}} (a_{ij}J_{ij} + b_{ij}K_{ij}). \tag{9.29}$$

Here

$$N_{occ} = N_c + N_o + 2N_p, \tag{9.30}$$

h, J, and K, are the standard one- and two-electron operators given by equations 2.39, 2.40, and 2.41.

Once again, f_i is given by [9]

$$f_i = \begin{cases} 1 & \phi_i \text{ is doubly-occupied} \\ 1/2 & \phi_i \text{ is singly-occupied} \\ c_i^2 & \phi_i \text{ is a pair orbital with} \\ & \text{GVB CI coefficient } c_i. \end{cases}, \tag{9.31}$$

$$a_{ij} = 2f_i f_j, \tag{9.32}$$

$$b_{ij} = -f_i f_j, \tag{9.33}$$

except that $b_{ij} = -1/2$ if ϕ_i and ϕ_j are both singly-occupied. Furthermore, if ϕ_i is a pair orbital

$$a_{ii} = f_i \tag{9.34}$$

$$b_{ii} = 0 \tag{9.35}$$

and if ϕ_i and ϕ_j are in the same pair,

$$a_{ij} = 0 \tag{9.36}$$

$$b_{ij} = -c_i c_j \tag{9.37}$$

Because the general wave function in equation 9.25 requires $(2 + 2N_p)$ different values of f_i, this wave function is said to have $(2 + 2N_p)$ shells. Furthermore, because the general wave function requires $(1+N_o+2N_p)$ different Fock operators, the general wave function is said to have $(1 + N_o + 2N_p)$ Hamiltonians. These numbers assume that there are both core and open-shell orbitals. If there are no open-shell orbitals but there are core orbitals, the number of shells and Hamiltonians is $(1 + 2N_p)$; similar changes are made when there are no core orbitals.

To optimize the orbitals of this general wave function, first the optimal mixing of the occupied orbitals with the other occupied orbitals is calculated. The optimal mixing is determined by first calculating the Δ matrix,

$$\Delta = \begin{bmatrix} 0 & \frac{A_{ij}}{B_{ij}} \\ -\frac{A_{ij}}{B_{ij}} & 0 \end{bmatrix} \tag{9.38}$$

where

$$A_{ij} = \langle i | F^j - F^i | j \rangle, \tag{9.39}$$

$$B_{ij} = \langle i | F^j - F^i | i \rangle - \langle j | F^j - F^i | j \rangle + \gamma_{ij}, \tag{9.40}$$

$$\gamma_{ij} = 2(a_{ii} + a_{jj} - 2a_{ij})K_{ij} + (b_{ii} + b_{jj} - 2b_{ij})(J_{ij} + K_{ij}) \tag{9.41}$$

The new set of orbitals $\{\phi^{New}\}$ are obtained from the old set of orbitals $\{\phi^{Old}\}$ via the transformation

$$[\phi^{New}] = \exp(\Delta)[\phi^{Old}] \tag{9.42}$$

The next step in the wave function optimization is the calculation of the optimal mixing of the occupied orbitals with the virtual orbitals. This optimization is done by forming the Fock operator

$$F_{\mu\nu}^i = f_i h_{\mu\nu} + \sum_{k=1}^{N_{ham}} (a_{ik} J_{\mu\nu}^k + b_{ik} K_{\mu\nu}^k) \tag{9.43}$$

One Fock operator is required for all of the core orbitals, and another is required for each open-shell and GVB pair orbital. The Fock operator is transformed into molecular orbitals via equation 4.16, and diagonalized. The eigenvectors yield the optimal linear combination of occupied and virtual orbitals to form the new set of occupied orbitals. The optimization process is repeated until the orbitals stop changing.

9.3 Configuration Interaction

Another method of correcting for the shortcomings of HF theory is Configuration Interaction [7] (CI). CI considers the interaction of excited wave functions with the ground state wave function. As with GVB wave functions, the excited wave functions give additional functional freedom for the total CI wave function to use to adjust to find an optimal energy. For a wave function consisting of N spin orbitals

$$\Psi = |12 \cdots i \cdots j \cdots N\rangle \tag{9.44}$$

with unoccupied spin orbitals $\psi_r, \psi_s, \ldots$ the wave function

$$\Psi_i^r = |12 \cdots i \cdots Nr\rangle \tag{9.45}$$

is a singly excited wave function obtained from taking an electron out of occupied orbital ψ_i and putting it into orbital ψ_r. Similarly, the wave function

$$\Psi_{ij}^{rs} = |12 \cdots Nrs\rangle \tag{9.46}$$

is a doubly excited wave function obtained by taking an electron out of each of the occupied orbitals ψ_i and ψ_j and putting them into unoccupied orbitals ψ_r and ψ_s. In a similar fashion triply, quadruply, and so on, excited wave functions may be formed.

CI wave functions can add electron correlation by including a linear combination of excited wave functions with the ground state wave function [7]

$$\Psi_{CI} = \Psi + \sum_i^{occ} \sum_r^{Virt} C_i^r \Psi_i^r + \sum_{ij}^{occ} \sum_{rs}^{Virt} C_{ij}^{rs} \Psi_{ij}^{rs} + \cdots \tag{9.47}$$

The CI coefficients C are obtained by forming the CI matrix A_{IJ}, whose elements are given by

$$A_{IJ} = \langle \Psi_I | H | \Psi_J \rangle \tag{9.48}$$

where Ψ_I and Ψ_J are any of the ground state or multiply excited wave functions. Diagonalizing A_{IJ} yields the coefficients C as the eigenvectors, and the correlated energy as the lowest eigenvalue. The singly-excited wave functions interact weakly with the ground state, and consequently the doubly-excited determinants are the most important for the correlated energy [7].

The CI wave function can also be used to calculate excited states [26]. When I and J range over the singly-excited determinants the eigenvectors of A_{IJ} yield the linear combination of excited wave functions in the various excited states, and the eigenvalues yield the energies of the excited states.

Although the CI wave function does correct the shortcomings of HF theory, one major drawback is that the elements in A_{IJ} require a full transformation of the two-electron integrals $(\mu\nu|\sigma\eta)$. This transformation scales as $\mathcal{O}(N_{bf}^5)$ where N_{bf} is the number of basis functions. HF and GVB calculations scale only as $\mathcal{O}(N_{bf}^4)$, which means that a CI calculation is significantly more expensive than a HF or GVB calculation for large molecules. For CI calculations diagonalization of the A_{IJ} matrix is often a much more computationally intensive process than the $\mathcal{O}(N_{bf}^5)$ integral transformation, depending on what levels of excitations are included, and so the work required to transform the integrals is negligible. Nonetheless, because the CI calculations scale as at least $\mathcal{O}(N_{bf}^5)$ they are generally too expensive for large molecules, and methods that do not require a full integral transformation, such as the general HF/GVB wave functions described in Section 9.2.1 become more attractive.

9.4 Multi-Configurational Self-Consistent Field Wave Functions

Another method of correcting the shortcomings of HF theory is the Multi-Configurational Self-Consistent Field (MCSCF) method [7, 29]. Whereas a CI wave function merely diagonalizes the Hamiltonian matrix between various excited configurations, the MCSCF solve self-consistently for the optimal orbitals among the excited configurations. Again, the additional functional degrees of freedom afforded by the excited wave functions give the total MCSCF wave function the ability to more accurately adjust to the constraints of the molecule, which allows MCSCF wave functions to describe correlated wave functions and excited states. Each iteration the coefficients of the various component wave functions in the MCSCF wave function are recalculated, and the orbitals are optimized using these coefficients. The GVB wave functions described in Section 9.2 are a special case of MCSCF wave function [9]. The GVB wave function does not require an integral transformation to compute its energy and optimize its wave functions, but in general, the MCSCF energy and orbital optimization equations do require a transformation of the two-electron integrals. Like the CI wave function, the integral transformation makes MCSCF calculations prohibitively expensive for large molecules.

9.5 Moller-Plesset Perturbation Theory

9.6 Coupled Cluster

Chapter 10

Thermochemistry from Quantum Chemistry Calculations

10.1 Introduction

We can obtain a great deal of information from quantum chemistry calculation, and this section will discuss the different types of data and how they are obtained from quantum chemistry.

10.2 Frequencies and Thermal Properties

When we discussed geometry optimization we briefly mentioned the $Hessian matrix$, which is the matrix that contains the second-derivative of the energy with respect to nuclear displacements. From this matrix we may obtain both the *normal modes of vibration* and the *frequencies* associated with these modes. One can use these frequencies, for example, in analyzing infra-red spectra, and they are also often valuable in fitting quantum chemical results to force fields.

We may also use the frequencies to estimate the thermal properties of molecules. Quantum mechanics tells us that a molecule is never at rest, even at absolute zero; the molecule typically has some *zero-point energy* in its vibrational modes. The frequencies may be used to estimate this energy. Moreover, the frequencies may be used to produce heat capacities, entropies, enthalpies, and free energies of the molecule at different temperatures. This information can be particularly useful in comparing to experimental results; the zero-point energy corrected free energy at the experimental temperature is generally the proper quantity to consider rather than the total energy in comparing the results of quantum chemistry caluclations to experiment.

Finally, the frequencies and vibrational modes are often particularly useful in analyzing transition states. A proper transition state should have one imaginary frequency.

The mode corresponding to that frequency should connect the reactant and product geometries. That is, the vibrational mode should correspond to motion along the reaction path that connects the reactants and products. If the vibrational mode does not exhibit this behavior, it is often a sign that something is wrong with the transition state.

10.3 Reaction Energetics

The ability to compute thermal properties as described in the previous section now makes it possible to get accurate approximations of chemical reactions from quantum chemistry. Suppose we are interested in the S_N2 bimolecular nucleophilic reaction Cl- + $CH_3Br \rightarrow CH_3Cl$ + Br-. If we were interested in the gas-phase reaction we would compute ground state structures for Cl-, Br-, CH_3Br, and CH_3Cl, and a C_3v transition state for Cl-CH_3-Br. Each of these structures should have optimized geometries, zero-point energies, and thermochemical data (heat capacity, entropy, enthalpy, and free energy) for the temperatures of interest. We are then able to compute enthalpy and free energy curves for the reactions, and, if desired, use transition state theory to compute rate constants for the reaction kinetics. The process may also be repeated for solution phase reactions.

10.4 Heats of Formation

It is often important to compute *heats of formation*, ΔH_f, the enthalpy required to form the molecule from standard forms of the elements. Suppose we want to compute the heat of formation of methane, CH_4. The standard form of hydrogen is H_2 gas, which is easy to compute using quantum chemistry techniques, but the standard form of carbon is diamond, which is an infinite solid, and which is not easy to compute using the techniques we have discussed so far. A further complication is that very often the 5 kcal/mol accuracy in computing the heat of formation is not accurate enough for the desired application. In this case the best way to obtain quality heats of formation is to compute a range of molecules whose experimental heats of formation are known (the NIST WebBook at http://webbook.nist.gov/chemistry/ is an excellent source for experimental heats of formation), and to then determine by least-squares fitting a set of correction factors to the raw heats of formation. This experimentally corrected approach generally leads to RMS errors of < 3 kcal/mol, which is accurate enough for many applications.

10.4.1 Simple Fits to Ensembles of Data

10.4.2 G2 and G3 Theory

10.5 Summary

Chapter 11

A Case Study of the Singlet-Triplet Gap in Methylene: Part II

Chapter 12

Integrals Between Gaussian Basis Functions

12.1   Overlap Integrals

12.2   Nuclear Attraction

12.3   Coulomb Integrals

12.4   Rys Quadrature

12.5   Horizontal and Vertical Recursion Relations

12.6   Effective Core Potentials

Chapter 13

Solvation

13.1 Introduction

This chapter contains a brief discussion of solvation in quantum chemistry calculations. Chemistry is a science that takes place to a large degree in water and other solvents. Thus far, we have described molecules as if they were in a universe unto themselves, with no other molecules to interact with. This is, of course, a gross oversimplification.

Unfortunately, the description of solvents can be computationally intensive. We first present *explicit solvent models*, which describe the solvent as a collection of individual molecules. This is a potentially rigorous approximation, but one that is generally too expensive for most calculations. We then consider replacing the explicit solvent molecules with a *dielectric continuum* into which the molecule is embedded. The dielectric continuum allows charges in the solute molecule to polarize differently than if the molecule were alone in a vacuum.

13.2 Explicit Solvent Models

The simplest solvation models simply use collections of the actual solvent molecules for the solvent interactions. In many ways this technique is the most accurate way to include a solvent. The full electronic interaction between the solvent and solute molecules in explicitly included. However, there are several practical problems with such an approach. The most serious problem is the computational expense. Many solvent molecules (100–1000) are required to adequately solvate a substrate molecule, and the expense of describing these molecules with quantum chemical techniques generally far outweighs the effort required to describe the substrate itself. A further difficulty is that it is difficult to keep the solvent molecules from drifting off into the vacuum. The solute–solvent complex can be embedded in a periodic cell, but this technique, in addition to being beyond the scope of the current discussion, introduces additional problems when the solute is charged. Finally, adding so many solvent molecules introduces a large number of degrees of freedom that need to be either minimized or averaged over

during the course of the calculation. For these reasons it is typically easier to replace the effect of the solvent molecules with a dielectric continuum.

13.3 Dielectric Continuum Models

The primary effect of the solvent on solute molecules is to act as a dielectric. This dielectric can interact with the electrostatic field produced by the molecule to stabilize charge polarization.

Consider the H-Cl molecule dissociating in the gas phase. With proper treatment, this molecule will dissociate to form neutral H and Cl atoms. However, in water solvent HCl will dissociate to H+ and Cl-, because the dipole moments of the water molecules can stabilize the H+ and Cl- ions separately.

It is possible to embed solute molecules in a slab of dielectric material, that can respond in largely the same way that the solvent molecules would have. The dielectric can be tuned to reproduce the solvent in two ways. The dielectric constant itself is set to that of the solvent. Secondly, an effective solvent radius dictates how close the solvent can approach the solute.

With this information, it is possible to use the *Poisson–Boltzmann* equation to determine the response of the solvent to the solute charges.

Typically, a solvation calculation involves computing the gas phase electronic structure of the solute, fitting that electronic stucture to a set of atomic charges, solving the Poisson–Boltzmann equation to determine the solvent field, fitting the solvent field to a set of charges at the molecular surface, solving the electronic structure of the solute in the present of the solvent field, and repeating until the process converges.

13.4 Acidity and pKa Information

It is often useful to compute the pKa of an acidic bond in a molecule. Quantum chemistry is able to compute these properties, but there are factors that complicate the matter. Many of these reactions involve negative ions, and in these cases diffuse functions must be used to properly describe the anions. Obviously solvation must be used, and describing a solvated proton is often a bad approximation, as this species may in fact be properly described by H_3O+, H_5O_2+, and other similar species. Thus, describing the seemingly simple dissociation reaction HCl $\rightleftharpoons$ H+ + Cl- would probably be better described as HCl + H_2O $\rightleftharpoons$ H_3O+ + Cl-, and all of the species should be described in solution, with diffuse functions on the basis set.

Chapter 14

Electronic Excited States

14.1 Introduction

Most of the discussion of quantum chemical calculations thus far has centered on ground state properties. Quantum chemical techniques can also be used to compute energies and wave functions for electronically excited states.

Excited states are most relevant when considering absorption spectroscopy. Molecules can absorb a photon in the Vis-UV range and convert to an electronically excited state. Koopman's theorem suggests that the orbital energies for the orbitals approximate the energy required to ionize an electron from that orbital. We can also use the orbital energies to approximate the excitation process between two orbitals.

Figure 14.1 shows how the orbital energies may be used approximate excitation energies.

There is one problem with using orbital energies in this fashion. The orbital energies of the virtual (unoccupied) orbitals actually corresponds to the states that contain an additional electron. The orbital energies are computed from interactions where a
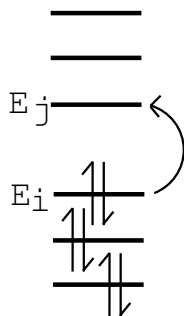
Figure 14.1: Orbital energies approximating the excitation energy between two orbitals. The HOMO–LUMO excitation shown would have an excitation energy $E_j - E_i$.
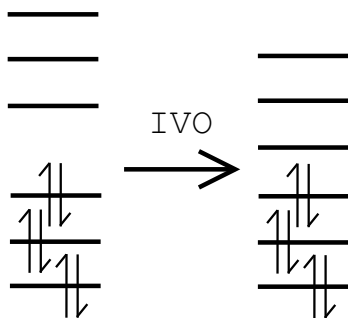
Figure 14.2: IVO treatment leads to more realistic virtual orbitals and orbital energies.

particle in the virtual orbitals sees all of the N_{el} electrons, whereas in reality it should only see $N_{el} - 1$ electrons, since it shouldn't see itself.

We can correct this difficulty by using *improved virtual orbitals* (IVOs). IVOs keep the normal set of occupied orbitals, but use the state with $N_{el} - 1$ electrons for the virtual orbitals. These orbitals and the associated orbital energies much more accurately reproduce the proper excited state energies. Figure 14.2 shows schematically the effect of the ivo treatment.

The following sections detail more rigorous techniques for computing excited states.

14.2 Open Shell Singlet Calculations

An open-shell singlet (OSS) state is very similar to a triplet state, except that the two orbitals are singlet paired rather than triplet paired. A triplet pairing is given by

$$\Psi_T = \phi_{core}\phi_a\phi_b\alpha\alpha \tag{14.1}$$

whereas the open-shell singlet wave function is given by

$$\Psi_{OSS} = \phi_{core}(\phi_a\phi_b + \phi_b\phi_a)(\alpha\beta - \beta\alpha). \tag{14.2}$$

The energy for the triplet wave function is given by $E_{core} + J_{ab} - K_{ab}$, and the energy of the OSS wave function is given by $E_{core} + J_{ab} + K_{ab}$.

OSS wave functions are convenient because they allow standard grand state programs to be used to compute excited state energies and wave functions.

14.3 Configuration Interaction Singles

Open shell singlet descriptions are limited to excited states that can be described as a single excitation process. Most excited states fall into this category, but not all do. For those states we may use a single-excitation configuration interaction approach. Consider a molecule with occupied orbitals ϕ_a, ϕ_b, ϕ_c, ϕ_d, and virtual orbitals ϕ_r, ϕ_s,

Table 14.1: Vertical excitation energies (in kcal/mol) for a few small molecules, computed using the techniques discussed in this chapter, along with experimental results. Computations are performed using the 6-31G** basis set.

Molecule	ΔE Koopman	ΔE IVO	ΔE OSS	ΔE CIS	ΔE Exp.
Ethylene	394.84	171.93	224.88	207.63	163.96
Formaldehyde	363.90	146.65	79.25	109.92	80.71
cis-Butadiene	294.21	149.87	168.15	161.67	126.60
trans-Butadiene	285.12	144.96	173.27	165.55	136.62

ϕ_t, ϕ_u, and ground state wave function Ψ. We write the singly excited state (also known as a singly excited determinant) when we take an electron out of occupied orbital ϕ_a and put it into virtual orbital ϕ_r as Ψ_a^r. We can approximate the excited state wave function as a linear combination of all of these excited configurations

$$\Psi_{CIS} = \Psi_a^r + \Psi_a^s + \Psi_b^r + \Psi_b^s + \dots \tag{14.3}$$

$$= \sum_i^{occ} \sum_m^{virt} a_{im} \Psi_i^m. \tag{14.4}$$

We wish to find the most optimal linear combination, the one with the lowest energy. We determine this by forming the Configuration Interaction (CI) matrix,

$$A_{im,jn} = \left\langle \Psi_i^m \left| H \right| \Psi_j^n \right\rangle. \tag{14.5}$$

The CI matrix is huge: for a molecule with n_o occupied orbitals and n_v virtual orbitals, there are $n_o^2 n_v^2$ elements, which means that forming and diagonalizing the matrix can become computationally expensive very quickly. Typically, only a small range of orbitals close to the HOMO and LUMO are used as the *active space*, since realistically, these are the only orbitals that participate in the excited state to an appreciable degree.

14.4 Comparison of results for test systems

Table 14.1 presents results for the methods discussed in this chapter for a few small molecules whose vertical excitation energies were well studied experimentally.

14.5 Nonlinear optical properties of molecules

Molecules are polarizable: when we put them into an electric field their electrons reorganize. We can use the dipole moment as a way of monitoring this polarization

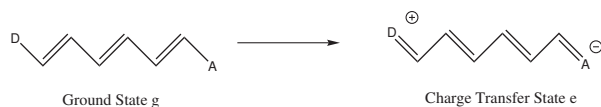$$\mu = \mu_0 \alpha E + \frac{\beta E^2}{2!} + \frac{\gamma E^3}{3!} + \dots \tag{14.6}$$

Figure 14.3: Two valence bond extremes used to model the polarization process in a conjugated polymer.

The term α is the linear polarizability, β is the first hyperpolarizability, and γ is the second hyperpolarizability. Nonlinear optical effects such as frequency doubling and second-harmonic generation are a property primarily of the first hyperpolarizability, so computing this effect efficiently is of great interest to us.

Figure 14.3 shows a two-state model for the polarization process in a conjugated polymer. Here we consider one neutral valence bond structure (g, for the ground state), and one fully charge transferred valence bond structure (e, for the excited state). Using the excited state, we can approximate the hyperpolarizability as

$$\beta \approx \frac{\mu_{ge}^2 (\mu_{ee} - \mu_{gg})}{E_{ge}^2}. \tag{14.7}$$

That is, the further apart the two states are, the harder it is to polarize the molecule. Marder, Perry, and coworkers determined that the bond-length alternation was a good indication of how far apart in energy the two states were for conjugated polymers, and based design of NLO materials on this property.

However, we might wish to determine NLO terms like β directly. The finite field technique computes the dipole moment $\mu(\vec{E})$ at a number of different field strengths and orientations, and use equation (14.6) to fit the values of α, β, etc., that reproduce these data. This is a good technique, but requires many different values of the electric to obtain a good fit.

A better technique, when it is available, is to use *Coupled Perturbed Hartree Fock* (CPHF) techniques. CPHF computes analytical derivatives of the energy $\frac{\partial E}{\partial X}$, $\frac{\partial^2 E}{\partial X \partial Y}$, etc., with respect to the electric field strength $(\vec{E})$ directly. First derivatives are used to compute the dipole moment, second derivatives are used to compute the polarizability, and third and higher derivatives are used to compute the hyperpolarizabilities. Effectively, in the finite field technique we are approximating these derivatives. However, the availablility of this method is dependent upon whether the relevant analytic derivatives have been programmed for the appropriate Hamiltonian.

14.6 Suggestions for Further Reading

Hunt and Goddard [30] discuss IVO calculations. Szabo and Ostlund [7] have a good interaction to CI. CPHF is discussed in more detail in *A New Dimension to Quantum Chemistry* [31].

Chapter 15

Periodic Boundary Conditions

15.1   Introduction

Earlier sections described how quantum chemical techniques can be used to determine the electronic structure of molecules. In addition to molecules, we would also like to be able to describe systems like polymers, surfaces, and crystals, where a simple *unit cell* is replicated periodically in 1, 2, or 3 dimensions. A sample unit cell configuration is shown in Figure 15.1. This section will survey the techniques used to describe systems with periodic boundary conditions.

15.2   Energy Bands

We know from our earlier studies that when we use quantum mechanics to atoms or molecules we obtain a discrete set of states. Solids contain on the order of 10^{23} atoms, and consequently these discrete states are blurred into *bands*.

Figure 15.2 shows a schematic drawing of energy bands in an insulating solid. The gray shading of the core and valence bands indicates that these bands are occupied, and the lack of shading of the conduction band indicates that this band is empty. There is a finite energy gap between the highest occupied electron energy (known as the
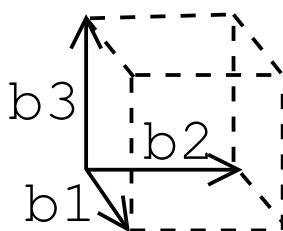
Figure 15.1: Lattice vectors ($\mathbf{b_1}$,$\mathbf{b_2}$,$\mathbf{b_3}$) that define the unit cell in a periodic solid.
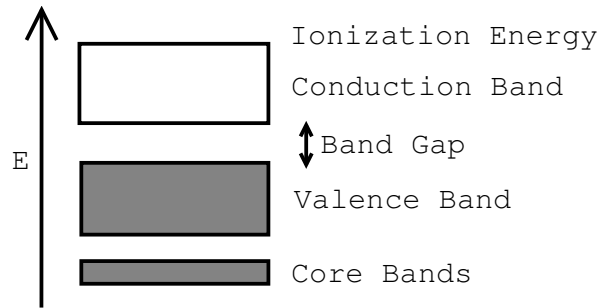
Figure 15.2: Schematic drawing of energy bands in an insulator.

Table 15.1: Band gaps of well-known semiconductors.

Semiconductor	Band Gap (eV)
C (diamond)	5.4
Si	1.17
Ge	0.74
SiC	2.8
GaN	3.5
GaP	2.32
GaAs	1.52
InP	1.42
InAs	0.43

valence band maximum in solids) and the lowest unoccupied electron energy (known as the *conduction band minimum*). Since the valence band is fully occupied, there are no easily accessible states for an electron in the valence band, which means that to move around the crystal, the electron needs to be excited into the conduction band to move around, which requires a finite amount of energy. This energy requirement is why insulators do not conduct electricity; given energy they can conduct, which is why insulators are also known as *semiconductors*. Table 15.1 presents the band gaps of well-known semiconductors.

Figure 15.3 shows analogous filling of the energy bands for a metallic solid. In a metal the highest occupied band is only partially filled, and there are accessible states for electrons in the valence band. The fact that metals do not have a band gap like semiconductors do is why metals can conduct electrons: no additional energy is required to move an electron to an adjacent state. The *Fermi level* or *Fermi energy* E_f is the energy of the highest occupied electron, and is labeled in each figure.

The next section will begin to explore the reasons why states in solid localize into bands.
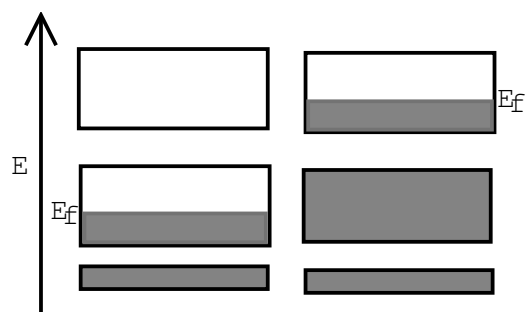
Figure 15.3: Schematic drawing of different fillings of the energy bands in a metal.
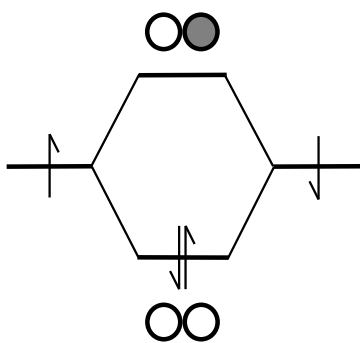

Figure 15.4: The bonding of two H $1s$ orbitals to make bonding σ_g and antibonding σ_u orbitals.
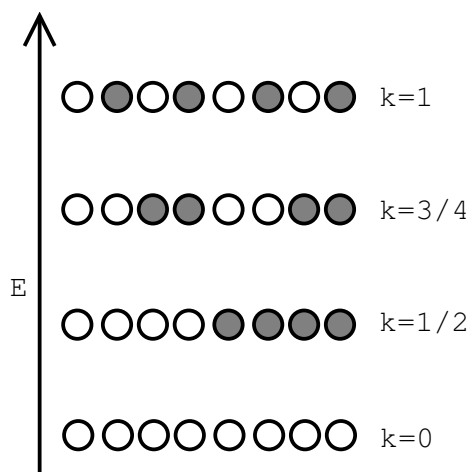
Figure 15.5: Different states that 8 H atoms can have in a one-dimensional chain, indexed by the k-number.

15.3 One-Dimensional Periodic Arrays of Atoms

We already know that the lowest energy state of a hydrogen atom is a $1s$ orbital. When we bond two hydrogen atoms together we form a bonding σ_g state and an antibonding σ_u state; the two electrons from the H atoms will doubly occupy the σ_g state. Figure 15.4 shows this interaction.

What happens when we take chains of hydrogen atoms? We can think of a single hydrogen atom as our unit cell that will be translated in one dimension. Figure 15.5 shows different states that eight H atoms can have. We may approximate the wave function of this system by

$$\phi(x + X) = \phi_{1s}(x) \cos\left(\frac{2\pi}{a} kx\right). \tag{15.1}$$

Here ϕ_{1s} is the $1s$ wave function for an isolated H atom. a is the lattice spacing between the unit cell images. The lowercase coordinate x refers to the coordinate within a unit cell, and the uppercase coordinate X refers to the coordinates between unit cells. The k-number is a measure of how much the phase changes from one unit cell to the next: when $k = 0$ the unit cells are always replicated with the same sign and when $k = 1$ the unit cells alternate signs.

What is remarkable about the k-number is that we can boil bonding configurations, antibonding configurations, and everything in between, down to a single parameter. We will find it useful to consider the energy as a function of the k-number, as shown in Figure 15.6, which shows how the single energy band varies from the bonding to the antibonding limit with the variable k.

Since we have one H atom in each unit cell, we only have one electron in the band, which means that the band will be half-filled: the k-states from 0–1/2 will be occupied,
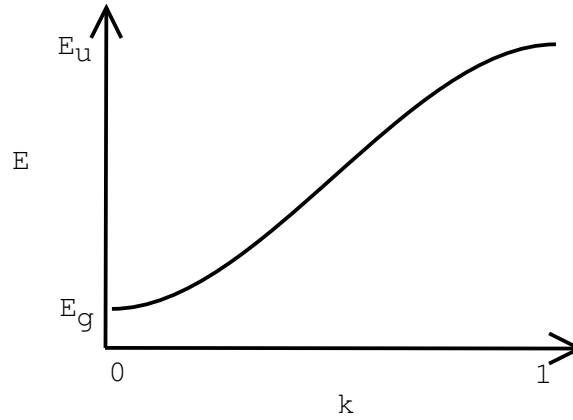
Figure 15.6: The variation of the energy with the k-number for a simple one-dimensional chain of H atoms.

and the k-states from 1/2–1 will be unoccupied. Since there is no gap between occupied and the unoccupied regions, we would predict that this is a metallic system.

How do we make insulating systems? We can look again at our poly-H example, but this time we will *double* the unit cell and put a bonded H_2 in each cell. The wave function for the valence band is

$$\phi_v(x + X) = \sigma_g(x) \cos\left(\frac{2\pi}{a}kx\right), \tag{15.2}$$

and the wave function for the conduction band is

$$\phi_c(x + X) = \sigma_u(x) \cos\left(\frac{2\pi}{a}kx\right). \tag{15.3}$$

The variation of these states is shown in Figure 15.7 and the energy of the resulting bands is shown in Figure 15.8. Since we now have two electrons in each unit cell, we can doubly occupy the lower band, and keep the upper band unoccupied. This configuration leads to an insulating system, since there is a finite band gap between the occupied valence band and the unoccupied conduction band.

In the beginning of the chapter when we were describing how single orbital states were broadened into energy bands we talked about them being *smeared out*. This simple example shows us that the process is really much more precise. We can combine the unit cells with different translational symmetries, and these different symmetries have different energies. The k-number is a useful way to index the translational symmetries.

The concept of k states is also useful when we have systems that are periodic in more than one dimension. Figure 15.9 shows a two dimensional plane of H atoms, with a k-state of (1,0). When we have a three-dimensional system we specify (k_x, k_y, k_z) states. The next section expands on this idea more.
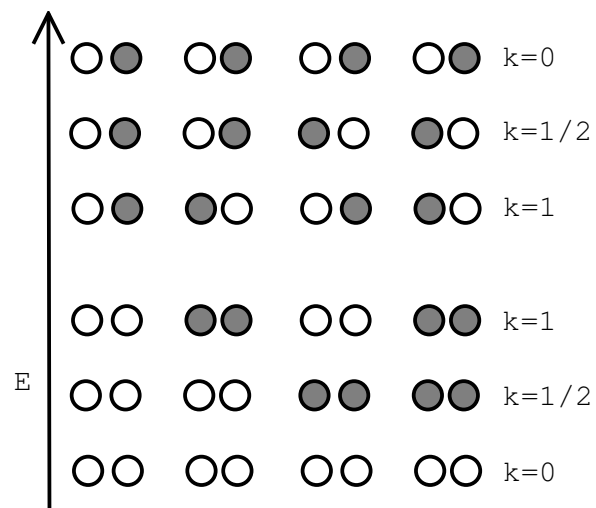
76

Figure 15.7: States of the doubled unit cell with a H_2 molecule in each unit cell.
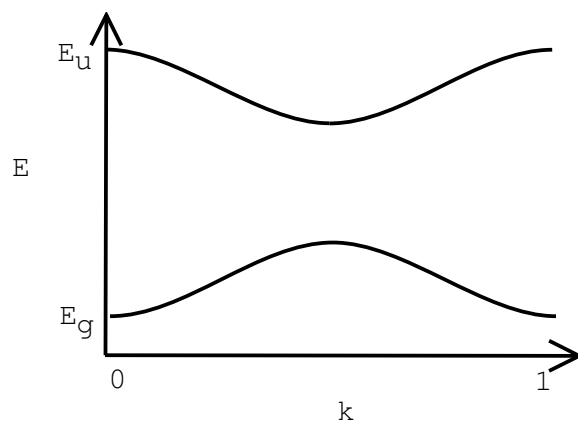

Figure 15.8: Band structure of the doubled unit cell with a H_2 molecule in each unit cell.
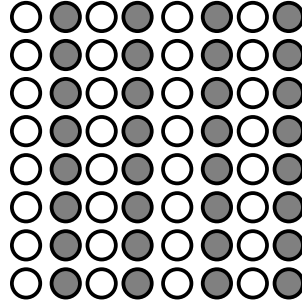
Figure 15.9: A two dimensional plane of H atoms with a k-state (1,0).

15.4   Reciprocal Space and Brillouin Zones

The previous system shows that looking at the behavior of the orbital versus the k-vector can give us information about how the entire energy band works. We can think of the k-space (k_x, k_y, k_z) spanned by all possible k-vectors as the Fourier transform of the real (x, y, z) space. This space is known as *reciprocal space*.

The reciprocal space $\mathbf{d}$ satisfies

$$\mathbf{b} \cdot \mathbf{d} = 2\pi. \tag{15.4}$$

These vectors are given by

$$\mathbf{d_j} = \pm 2\pi \frac{\mathbf{b_k} \times \mathbf{b_l}}{\mathbf{b_1} \cdot (\mathbf{b_2} \times \mathbf{b_3})} \tag{15.5}$$

where the $+$ sign goes with even permutations of jkl, and the $-$ sign goes with odd permutations.

The (first) *Brillouin zone* is the reciprocal space transform of the unit cell. Just as we will have to integrate over all points in the unit cell to perform a real space integration, we will have to integrate over all points in the Brillouin zone to perform a reciprocal space integration. By understanding the behavior of the energy bands across the Brillouin zone we may understand all of the electronic properties of the crystal.

In Figures 15.6 and 15.8 we looked at how the energy varied with the k-state across a band. Unfortunately, for periodicities higher than 1, we can't put together a simple plot like this. What we typically do is define *special points* in the Brillouin zone:

Γ is defined as (0,0,0);

X is defined as (1,0,0);

K is defined as (3/4,3/4,0);

W is defined as (1,1/2,0);

L is defined as (1/2,1/2,1/2).

We can then describe the variation of the electronic structure of the entire Brillouin zone by sampling k-points that connect these special points. That is, by sampling the band structure from Γ to X to W to L back to Γ to K we can understand the behavior of bands over the entire Brillouin zone. Figure 15.10 shows such a band structure.

15.5 Bloch's Theorem

The one-dimensional equations 15.1–15.3 for the periodic wave function may be generalized to higher dimensions. Bloch worked out the solution for the Schrodinger equation in periodic systems. Bloch proved that solutions of the periodic potential have the form

$$\psi(\mathbf{k}, \mathbf{r}) = \mu(\mathbf{k}, \mathbf{r}) \exp\left(i\frac{2\pi}{a}\mathbf{k} \cdot \mathbf{r}\right). \tag{15.6}$$

Here the *modulating function* $\mu(\mathbf{k}, \mathbf{r})$ is the part of the wave function that is the same in every unit cell. The *phase function* $\exp(i\mathbf{k} \cdot \mathbf{r})$ multiplies the modulating function by a wave that has the periodicity of the crystal. In our simple one-dimensional examples we used a cosine function, but for mathematical simplicity for real systems we use the *plane waves* shown here.

15.6 Tight Binding Calculations

To show an example of how kpoints affect the Hamiltonian in a periodic calculation, we now discuss a very simple example of such a calculation. Chadi and Cohen [32] and Harrison [33] define a very useful semiempirical technique for doing band calculations on diamond-like structures such as Si or GaAs. The model Hamiltonian is defined as:

$$\mathbf{H}(\mathbf{k}) = \begin{pmatrix} E_s^c & E_{ss}g_0 & 0 & 0 & 0 & E_{sp}g_1 & E_{sp}g_2 & E_{sp}g_3 \\ E_{ss}g_0 & E_s^a & -E_{sp}g_1^* & -E_{sp}g_2^* & -E_{sp}g_3^* & 0 & 0 & 0 \\ 0 & -E_{sp}g_1 & E_p^c & 0 & 0 & E_{xx}g_0 & E_{xy}g_3 & E_{xy}g_2 \\ 0 & -E_{sp}g_2 & 0 & E_p^c & 0 & E_{xy}g_3 & E_{xx}g_0 & E_{xy}g_1 \\ 0 & -E_{sp}g_3 & 0 & 0 & E_p^c & E_{xy}g_2 & E_{xy}g_1 & E_{xx}g_0 \\ -E_{sp}g_1^* & 0 & E_{xx}g_0^* & E_{xy}g_3^* & E_{xy}g_2^* & E_p^a & 0 & 0 \\ -E_{sp}g_2^* & 0 & E_{xy}g_3^* & E_{xx}g_0^* & E_{xy}g_2^* & 0 & E_p^a & 0 \\ -E_{sp}g_3^* & 0 & E_{xy}g_2^* & E_{xy}g_1^* & E_{xx}g_0^* & 0 & 0 & E_p^a \end{pmatrix}$$
$$\tag{15.7}$$

With the Hamiltonian in this form, one must solve

$$\mathbf{H}(\mathbf{k})\mathbf{c}(\mathbf{k}) = E(\mathbf{k})\mathbf{c}(\mathbf{k}) \tag{15.8}$$

where the values of $\mathbf{k}$ extend over the whole Brillouin zone. The terms E_s^c, E_{ss}, E_{xx}, E_{xy} are parameters fit for each different material. The superscript c refers to the *cation*, that is, the column 3 element in a 3,5 semiconductor, or the column 2 element in a 2,6 semiconductor; the superscript a refers to the *anion*, the other species in each of these. Of course, for a pure semiconductor like Si, Si is both the cation and the anion.
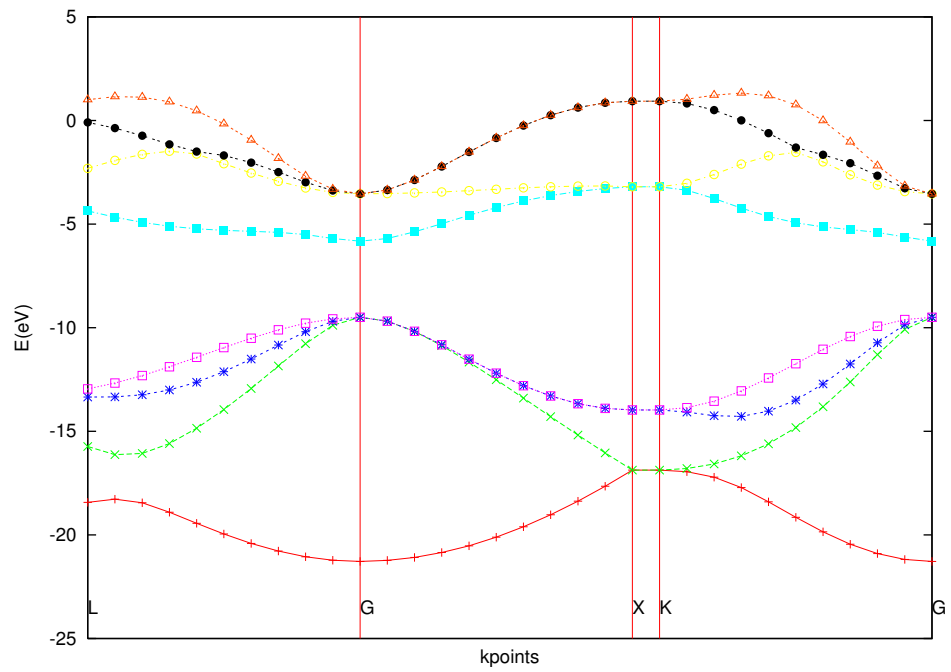
Figure 15.10: Band structure of cubic Si using Harrison's tight binding technique.

The phase factors g_0, g_1, g_2, g_3 determine how the Hamiltonian changes across the Brillouin zone. These are given by

$$g_0(\mathbf{k}) = \exp(i\mathbf{k} \cdot \mathbf{d_1}) + \exp(i\mathbf{k} \cdot \mathbf{d_2}) + \exp(i\mathbf{k} \cdot \mathbf{d_3}) + \exp(i\mathbf{k} \cdot \mathbf{d_4}) \qquad (15.9)$$

$$g_1(\mathbf{k}) = \exp(i\mathbf{k} \cdot \mathbf{d_1}) + \exp(i\mathbf{k} \cdot \mathbf{d_2}) - \exp(i\mathbf{k} \cdot \mathbf{d_3}) - \exp(i\mathbf{k} \cdot \mathbf{d_4}) \qquad (15.10)$$

$$g_2(\mathbf{k}) = \exp(i\mathbf{k} \cdot \mathbf{d_1}) - \exp(i\mathbf{k} \cdot \mathbf{d_2}) + \exp(i\mathbf{k} \cdot \mathbf{d_3}) - \exp(i\mathbf{k} \cdot \mathbf{d_4}) \qquad (15.11)$$

$$g_3(\mathbf{k}) = \exp(i\mathbf{k} \cdot \mathbf{d_1}) - \exp(i\mathbf{k} \cdot \mathbf{d_2}) - \exp(i\mathbf{k} \cdot \mathbf{d_3}) + \exp(i\mathbf{k} \cdot \mathbf{d_4}) \qquad (15.12)$$

where the lattice vectors for a diamond structure are given by

$$\mathbf{d_1} = (1, 1, 1)a/4 \qquad (15.13)$$

$$\mathbf{d_2} = (1, \bar{1}, \bar{1})a/4 \qquad (15.14)$$

$$\mathbf{d_3} = (\bar{1}, 1, \bar{1})a/4 \qquad (15.15)$$

$$\mathbf{d_4} = (\bar{1}, \bar{1}, 1)a/4 \qquad (15.16)$$

and a is the lattice constant.

A sample band structure for Si is shown in Figure 15.10. In a tight binding calculation of this type, one performs the following steps.

1. Form the constants E_s^c, E_{ss}, E_{xx}, E_{xy} based on the cation and anion specified in the problem.

2. For each *kpoint* $\mathbf{k_i}$ in the Brillouin zone:

    (a) Form the Hamiltonian $H(\mathbf{k_i})$ from equation 15.7.
    (b) Diagonalize the $H(\mathbf{k_i})$ and save the energies $\{E(\mathbf{k_i})\}$.

3. Form the band structure by connecting the adjacent points of $\{E(\mathbf{k_i})\}$ for all kpoints in the Brillouin zone.

Simple programs to compute tight-binding band structures using this method are available at http://wag.caltech.edu/home/rpm/project/tight-binding.

15.7 Plane Wave DFT Calculations

The majority of electronic structure calculations that employ periodic boundary conditions use density functional theory calculations with plane waves and pseudopotentials. Several features make plane waves desirable. Plane waves are already periodic functions, and so they are a natural choice for use as basis functions on systems that are also periodic. Furthermore, computing the one- and two-electron integrals is much easier using plane waves, where most of the integrals are zero, than any other type of basis function.

However, several aspects of plane waves make them problematic. The first is that many more plane wave basis functions are required to describe an atom than would be

required using, for example, Gaussian basis functions. One can perform a good calculation on water using a 6-31G** basis set with only 25 basis functions. The same level of accuracy using plane waves requires well over 1000 plane wave functions. Although, as we already noted, Hamiltonian matrix elements are much easier to compute using plane waves than using Gaussians, one still must determine the eigenfunctions of the Hamiltonian, a process which is time consuming for matrices of this size.

The second problem with plane waves is their inability to describe local phenomena. Fourier expansions of smooth, delocalized functions require far fewer plane waves than sharp, localized functions. To keep the basis set size from getting enormous, plane waves higher than a certain angular momentum are typically excluded from the basis set. One of the effects of this exclusion is that plane waves cannot describe core electrons. Typically this is not a terrible problem, because *pseudopotentials* (also known as *effective core potentials*) are typically used to remove the core electrons so that the plane waves need only describe the valence electrons. However, this often requires using core potentials for atoms like carbon that are not always well described with these functions. Nonetheless, in general the replacement of core electrons with pseudopotentials is an accurate and a straightforward process.

However, the inability of plane waves to describe localized phenomena is potentially a difficulty when describing chemical processes that might themselves be localized. The bonding of an adatom to a metal surface will typically be highly localized, and it is not always practical to add enough basis functions to properly describe it. Similarly, when PBC code is used to describe finite systems (the *supercell* method, where the molecule is put in a large enough unit cell to keep it from seeing its periodic neighbors), rarely are enough functions used to describe the molecule adequately.

For most solid systems, however, plane waves do an adequate job of describing the electronic structure. The next section describes attempts to use localized Gaussian functions in calculations using periodic boundary conditions to circumvent the problems plane waves have.

15.8   Gaussian Basis Set DFT Calculations

Techniques using Gaussian basis sets in density functional theory calculations on systems with periodic boundary conditions are currently under development. These calculations work by using a combination of spherically symmetric *reference atoms* to describe the electron density around each atom. The reference atoms are defined by specifying a linear combination of Gaussian basis functions, and must be accurate enough that whatever is omitted is a slowly varying function. This remainder density may then be described using a very sparse set of plane wave functions. The SeqQuest program developed at Sandia National Laboratories with help from the Caltech Materials and Process Simulation Center uses this approach.

15.9   Suggestions for Further Reading

Kittel's *Introduction to Solid State Physics* [34] presents a complete introduction to the field of solid state physics. Harrison's *Electronic Structure and the Properties of Solids* [33] gives a good overview of tight binding calculations for solids. The classic paper on this method is Slater and Koster 1954 Physical Review paper [35]. Martin and Leonard's *Electrons and Crystals* [36] presents a good general discussion on the electronic properties of solids, but is regrettably out of print. Thijssen's excellent book *Computational Physics* [37] has a good chapter on periodic boundary conditions.

Chapter 16

Parameters for Chemical Kinetics Calculations

16.1 Introduction to Chemical Kinetics

Chemical kinetics calculations are a very useful way to take quantum chemical results and compare the predictions to experimental results. With kinetics software one can predict the evolution of large mixtures of reactants over time, can model combustion and detonation processes, and can predict equilibrium mixtures.

In kinetics we're interested in how fast chemical reactions run. Given a reaction, for example,

$$Br + H_2 \rightleftharpoons HBr + H, \tag{16.1}$$

how fast are the products (HBr) produced? Using simple kinetics, we can write the rate of product production as a function of a *rate constant* times the concentrations of the reactants:

$$\frac{\partial[HBr]}{\partial t} = k[Br][H_2]. \tag{16.2}$$

For simple reactions like this it is easy to work out the kinetic equations, and even to integrate them given different starting conditions. However, reaction networks become complex very rapidly. The combustion of hydrogen and oxygen to produce water

$$H_2 + O_2 \rightleftharpoons H_2O \tag{16.3}$$

has 10 elementary reactions in it. People who model hydrocarbon combustion routinely deal with reaction networks that have thousands of reactions. As reaction networks become more complex, we need to use computer programs to integrate all of the variables simultaneously. The first part of this chapter discusses the software used in these simulations and what types of parameters it requires. The second part of this chapter then examines how quantum chemistry calculations may be used to determine these parameters.
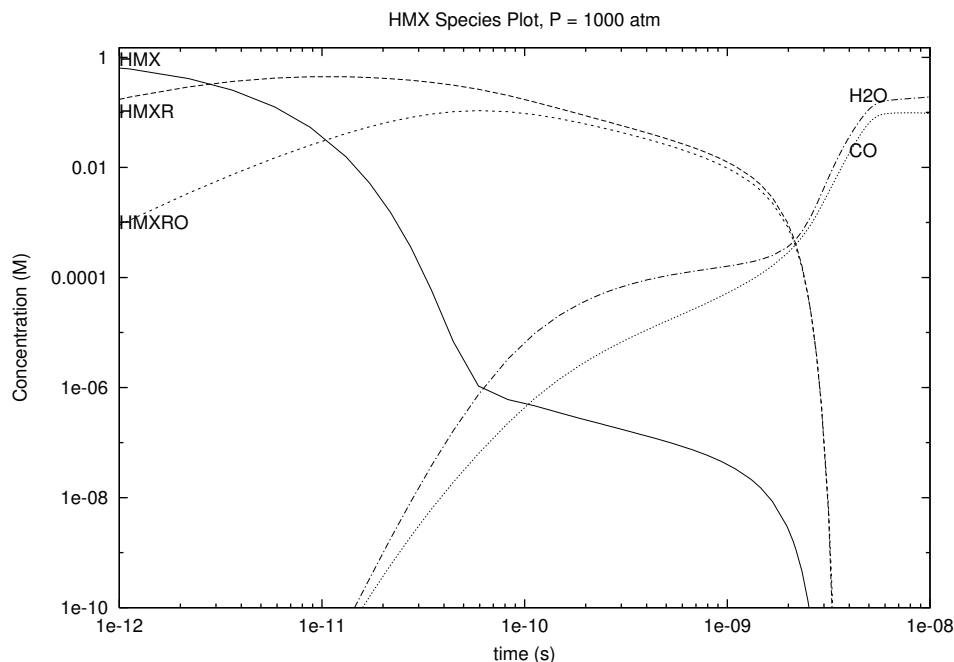
Figure 16.1: Detonation of the explosive material HMX over time, computed using a Chemkin constant volume calculation at P=1000 atm and T=1500 K. The material detonates at $\approx 2 \times 10^{-9}$ sec. The mechanism used to study this process contains over 90 species and 450 reactions, and thus requires a computer program to simulate.

16.2 The Chemkin program and associated parameter files

The most commonly used chemical kinetics program is the Chemkin package, originally developed by Sandia National Laboratories [38], and currently marketed by Reaction Design. Two free alternatives to the Chemkin package are Cantera [39] and Fuego [40], both being developed at Caltech. Of these efforts, Cantera is the most mature, and information on the status of the program may be found at the Cantera web site http://www.cantera.org.

Given a collection of species X_1, X_2, ..., at concentrations $[X_1]$, $[X_2]$, ... and a given temperature T and pressure P, Chemkin determines the rate of change of these variables $\frac{\partial [X_i]}{\partial t}$, $\frac{\partial T}{\partial t}$, $\frac{\partial P}{\partial t}$. Although this may seem very straightforward, it enables one to take a set of initial conditions, and, for example, simulate the detonation of explosive materials over time, as shown in Figure 16.1.

A Chemkin mechanism file has four sections: (i) an elements section that lists the relevant elements in the reaction; (ii) a species section that lists all of the species; (iii)

85

Table 16.1: Examples of reaction parameters in a Chemkin mechanism.

Reaction	A	β	E_a
$O + H_2 \rightleftharpoons H + OH$	5.000E+04	2.670	6290.00
$O + HO_2 \rightleftharpoons OH + O_2$	2.000E+13	.000	.00
$O + H_2O_2 \rightleftharpoons OH + HO2$	9.630E+06	2.000	4000.00

a thermochemistry section that contains composition and thermochemical information for each of the species; and (iv) a reactions section that describes kinetic parameters for each reaction.

An example of a species entry for the thermochemistry section is

```
C2H2                121386C   2H   2      G  0300    5000    1000
 0.04436E+02 0.05376E-01-0.01912E-04 0.03286E-08-0.02156E-12
 0.02566E+06-0.02800E+02 0.02013E+02 0.01519E+00-0.01616E-03
 0.09078E-07-0.01912E-10 0.02612E+06 0.08805E+02
```

This record is for acetylene, C_2H_2. The first record is the name of the species, and the second record (121386) is an (arbitrary) identifying number, generally the date on which the data was generated. The next four records (C   2H   2) indicate that there are 2 carbon and 2 hydrogen atoms in this species. The next record (G) indicates that the species is gaseous, and the next three records say that the thermochemical data is fit from 300–5000 K, and that the turnover point from the low-temperature to the high-temperature regime is 1000 K.

The next 14 records are parameters for the *NASA thermochemical polynomial fit* to the thermochemical data, given by

$$C_p/R = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 \quad (16.4)$$

$$H/RT = a_1 + a_2T/2 + a_3T^2/3 + a_4T^3/4 + a_5T^4/5 + a_6/T \quad (16.5)$$

$$S/R = a_1 \ln T + a_2T + a_3T^2/2 + a_4T^3/3 + a_5T^4/4 + a_7 \quad (16.6)$$

The first 7 records contain a_1–a_7 for the high temperature range, and the next 7 records contain a_1–a_7 for the low temperature range. To determine parameters for these polynomials, the techniques of Chapter 10 are used to compute the heat capacity C_p, the enthalpy H, and the entropy S over a wide range of temperatures. These data are then fit using a standard set of programs to the NASA thermochemical form. Figure 16.2 shows representative data for the energetic material HMX and the NASA fit to these data.

Table 16.1 shows typical reactions from the reactions section of the Chemkin file. The basic information contains the species in the reaction, and A, β, and E_a parameters for the *modified Arrhenius equation*

$$k = AT^\beta \exp\{-E_a/k_bT\} \quad (16.7)$$

where A is the *pre-exponential factor*, T is the temperature of the reaction, β is the temperature exponent, E_a is the *activation energy*, and k_b is Boltzmann's constant.
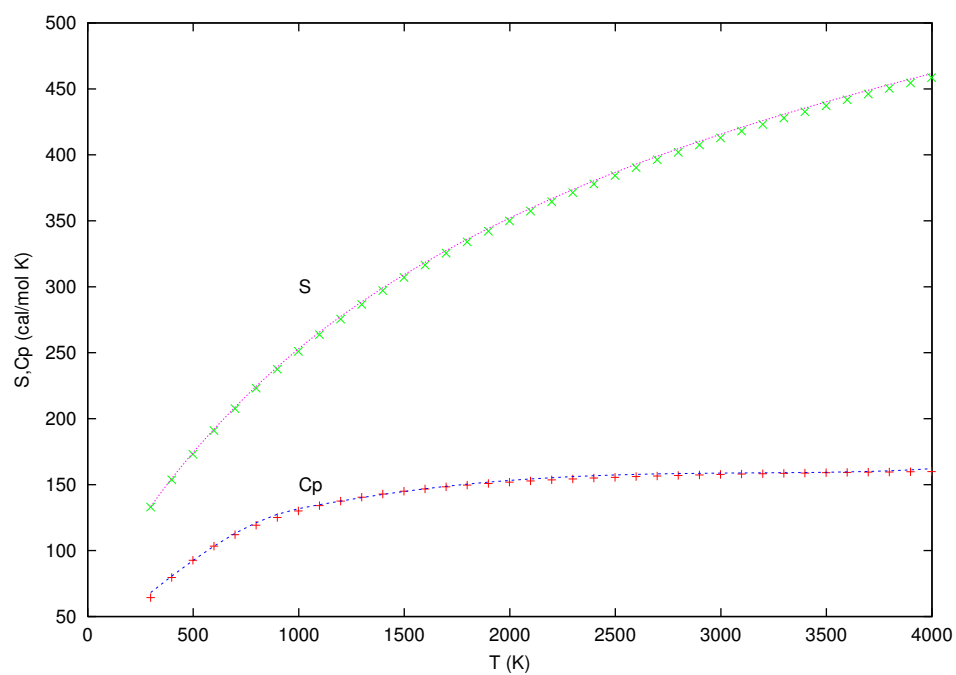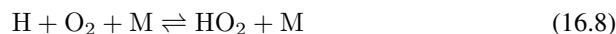
Figure 16.2: HMX molecule thermodynamic data for C_p and S from DFT calculation (points) and fit to NASA polynomial (lines), in cal/mol K.

In many dissociation or recombination reactions a *third body* is required to carry off excess kinetic energy. In Chemkin reactions these processes are normally written as

$$H + O_2 + M \rightleftharpoons HO_2 + M \tag{16.8}$$

where the species M represents a generic third body species. It is often the case that some species act more efficiently than others as a third body, and then the *third body efficiency* is specified as, for example,

```
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/
```

Another type of specification commonly made in Chemkin mechanism files is the *pressure-dependent fall-off reaction* parameters. Consider the recombination reaction of two methyl radicals. In the high-pressure regime, the appropriate reaction is $CH_3 + CH_3 \rightleftharpoons C_2H_6$. In the low-pressure regime, the appropriate reaction is $CH_3 + CH_3 + M \rightleftharpoons C_2H_6 + M$. The regime between these two limits is known as the fall-off regime. Chemkin keywords `LOW` and `TROE` specify parameters for different types of treatments of these regimes.

16.3 Conventional Transition State Theory

We now want to understand how to use the quantum chemistry techniques we have developed in this course to compute parameters to be used in chemical kinetics calculations. How can we go from static properties of the energy at different geometries to obtain intuition about the reaction dynamics of the system? We will use conventional transition state theory (CTST). CTST is built upon four major assumptions

1. Molecular systems that have surmounted the saddle point in the direction of products cannot turn back and form reactants again.

2. The energy distribution among the reactants follows the Maxwell-Boltzmann distribution, and thus the concentration of activated complexes may be computed from equilibrium theory.

3. The motion along the reaction path is separable from the other motions of the activated complex.

4. A chemical reaction may be treated classically, with quantum effects such as tunneling ignored.

There are many different ways to express CTST. The way that we will find the most convenient is known as the *thermodynamic formulation*.

$$k = \frac{k_B T}{h} \exp\{-\Delta G^{\ddagger}/RT\} \tag{16.9}$$

Here k_B is the Boltzmann constant ($1.38066 \times 10^{-23} JK^{-1}$), T is the temperature, h is Planck's constant ($6.62618 \times 10^{-34} Js$), R is the ideal gas constant ($2 cal mol^{-1} K^{-1}$), and $\Delta G^{\ddagger}$ is the free energy change between the ground state and the transition state.
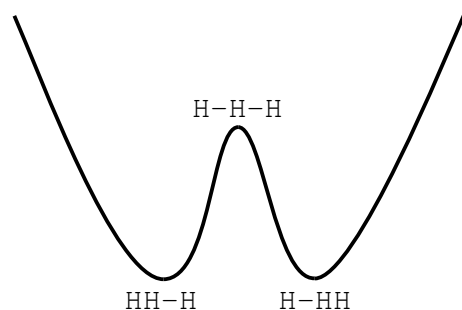
Figure 16.3: Schematic drawing of the H_2+H atom transfer reaction.

Table 16.2: Data for computing kinetics parameters for the H_2+H reaction.

T	E^0	G^0	$E^{\ddagger}$	$G^{\ddagger}$	$\Delta G^{\ddagger}$	$1000/T$	k	$\ln(k)$
0	0	6.74	5.99	11.86	5.12			
298.15	0	-3.36	5.99	3.19	6.56	3.354	9.69×10^7	18.39
398.15	0	-8.01	5.99	-0.54	7.47	2.512	6.59×10^8	20.31
498.15	0	-12.96	5.99	-4.50	8.47	2.007	2.00×10^9	21.42
598.15	0	-18.15	5.99	-8.64	9.52	1.672	4.15×10^9	22.15
698.15	0	-23.54	5.99	-12.94	10.60	1.432	6.97×10^9	22.66

The prefactor $\frac{k_B T}{h}$ has units of s^{-1}, and we can think of it as how rapidly the reactant tries to cross the barrier. The exponential term $\exp\{-\Delta G^{\ddagger}/RT\}$ is dimensionless, and we can think of it as how easy it is to get over the barrier. When we multiply the two terms together we get a good estimate of the ease at which the barrier may be crossed.

As an example of how CTST may be used, we consider the reaction $H_2 + H \rightleftharpoons H+H_2$, shown schematically in Figure 16.3. We first compute the ground and transition state geometries and energies. It turns out that there is an energy difference of 5.99 kcal/mol between the ground and transition state. We also use the techniques described in section 10 to approximate the free energy at a variety of temperatures. Table 16.2 presents the raw data that we will use for our plot.

Our goal is to fit these data to an *Arrhenius equation*

$$k = A \exp\{-E_a/RT\}. \tag{16.10}$$

What we are doing here is effectively removing the temperature dependence of the preexponential factor in the CTST rate expression. Because chemists have been doing these calculations since long before there were computers to analyze them they developed a convenient way to obtain the relevant factors. One makes an *Arrhenius plot* whereby $\ln(k)$ is plotted as a function of $1000/T$. The y-intercept of the plot gives $\ln A$, and the slope of the plot gives $E_a/1000R$, which means that we can determine
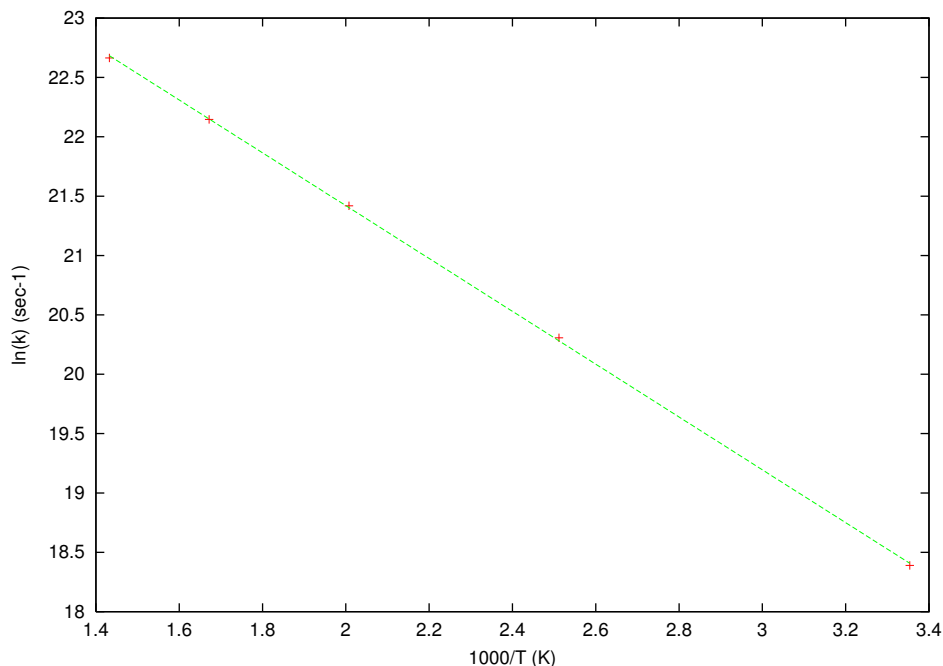
Figure 16.4: H_2+H Arrhenius plot, showing the data from table 16.2 (points) fit to an Arrhenius equation (line). The data in this plot yields $E_a = 4.42$ kcal/mol and $A = 1.7 \times 10^{11}$.

A and E_a with only graph paper and a ruler rather than a computer (but as long as we have one, we may as well use it). Table 16.2 also has columns that convert the H_2+H data to the proper form for plotting, using equation 16.9 to estimate the rate. Figure 16.4 shows the Arrhenius plot of these data, along with the straight line fit that yields $E_a = 4.42 kcal/mol$ and $A = 1.7 \times 10^{11}$.

Before we leave this very simple reaction, let us consider a great simplification of the preexponential factor that is due to (USC professor) Sidney Benson. For bimolecular reactions, Benson estimated that the prefactor was given by

$$A = \frac{k_B T}{h} \exp\{-\Delta S^{\ddagger}/R\} \tag{16.11}$$

where now $\Delta S^{\ddagger}$ is the entropy change between the reactant state and the transtition state. Using this approximation for the H_2+H reaction just studied yields a preexponential factor of $A = 2.3 \times 10^{11}$, in remarkable agreement with the more accurate value.

Lorant and Goddard have also shown that we can use transition state theory techniques to obtain rate constants for barrierless reactions. Consider the reaction hydrogen
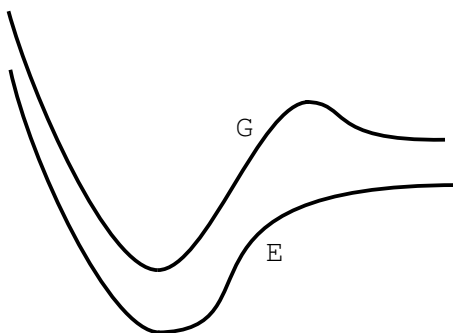
Figure 16.5: The free energy G pathway can have a barrier even for reactions such as radical recombination where the energy E has no barrier.

atom recombination reaction $H + H \rightleftharpoons H_2$. The reaction has no barrier, and traditionally people have assumed that treatment of this reaction with transition state theory was impossible. Lorant and Goddard showed that even when the reaction energy had no barrier, it was still possible to find a barrier along the free energy pathway, and that the same transition state theory could be used to determine the rate constants for these reactions. Figure 16.5 shows a (greatly exaggerated) schematic of exactly how this would work. Lorant and Goddard's technique is a breakthough because it allows rate constants to be determined for reactions that could only otherwise be computed using expensive RRKM techniques.

16.4 Calculation of Rate Constants for Unimolecular Reactions

The calculations we discussed in the previous section are inadequate for describing unimolecular processes. Fortunately, a number of excellent treatments of unimolecular reactions have been developed over the years, culminating in RRKM theory, developed by Rice, Ramsberger, Kassel, and Marcus. A full treatment of RRKM theory is beyond the scope of the current work, but we will present a brief overview here.

RRKM theory assumes that unimolecular reactions proceed according to

$$A + M \quad \overset{k_1}{\rightleftharpoons} \quad A^* + M \tag{16.12}$$

$$A^* \quad \overset{k_2}{\rightarrow} \quad B + C \tag{16.13}$$

where the molecule A is excited by collision with inert species M to some *energized complex* A^* which can then react to form products B and C. Figure 16.6 shows some the energies that enter into such a process.

By standard steady state theory we could assume

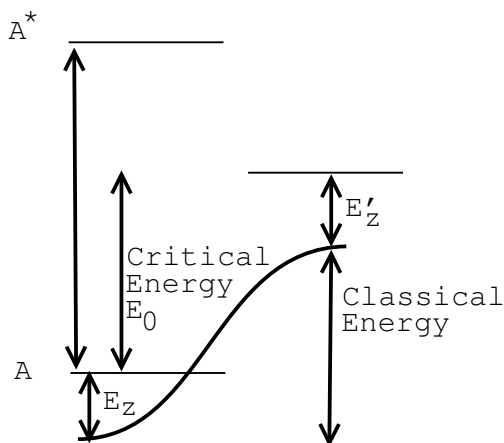$$k = \frac{k_2(k_1/k_{-1})}{1 + k_2/k_{-1}[M]}. \tag{16.14}$$

Figure 16.6: Energies involved in RRKM calculations. The classical energy is corrected by the zero-point energies of the ground and transition states. The molecule A is excited to some energized species A^* that has more energy than the critical energy for reaction, E_0^*.

In RRKM we recognize that both k_2 and $f = k_1/k_{-1}$ are functions of the energy E^*. Thus, in differential form

$$dk = \frac{k_2(E^*)f(E^*)}{1 + k_2(E^*)/k_{-1}[M]}dE^*. \tag{16.15}$$

and in integral form

$$k = \int_{E_0^*}^{\infty} \frac{k_2(E^*)f(E^*)}{1 + k_2(E^*)/k_{-1}[M]}dE^*. \tag{16.16}$$

The distribution function $f(E^*)$ is given by

$$f(E^*)dE^* = \frac{N(E^*)\exp\{-E^*/kT\}dE^*}{\int_0^{\infty} N(E^*)\exp\{-E^*/kT\}dE^*} \tag{16.17}$$

where $N(E^*)$ is the density of states with energies between E^* and $E^* + dE^*$. The expression for $k_2(E^*)$ is given by

$$k_2(E^*) = \frac{l^{\ddagger}\sum E^*_{\text{active}}}{hN(E^*)F_r} \tag{16.18}$$

where $l^{\ddagger}$ is the statistical factor, the ratio of the number of symmetrically identical products to the number of symettrically identical reactants, $P(E)$ is the number of rovibrational states of the activated molecule up to E, and F_r is a scaling factor to account for the fact that the rotations are not the same in the energized and the activated structures.

The UNIMOL program is the most commonly used programs to do RRKM calculations.

Chapter 17

Applications

Appendix A

Sample Programs

A.1 Numeric Solution to the Particle in a Box

Bibliography

[1] E. Anderson, Z. Bai, C. Bischof, S. Blackford, J. Demmel, J. Dongarra, J. Du Croz, A. Greenbaum, S. Hammarling, A. McKenney, and D. Sorensen. *LAPACK Users' Guide*. Society for Industrial and Applied Mathematics, Philadelphia, PA, third edition, 1999.

[2] Richard P. Feynman, Robert B. Leighton, and Matthew Sands. *The Feynman Lectures on Physics*. Addison-Wesley, 1965.

[3] Linus Pauling. *The Nature of the Chemical Bond*. Cornell University Press, 1960.

[4] P. A. M. Dirac. *The Principles of Quantum Mechanics*. Oxford Scientific Publications, 1957.

[5] J. Von Neumann. *Mathematical Foundations of Quantum Mechanics*. Princeton, 1955.

[6] C.C.J. Roothan. New developments in molecular orbital theory. *Reviews of Modern Physics*, 23:69, 1951.

[7] Atilla Szabo and Neil S. Ostlund. *Modern Quantum Chemistry*. McGraw-Hill, New York, 1982.

[8] S. F. Boys. Electronic wave functions. I. A general method of calculation for the stationary states of any molecular system. *Proceedings of the Royal Society*, A200:542, 1950.

[9] Frank W. Bobrowicz and William A. Goddard, III. The self-consistent field equations for generalized valence bond and open-shell Hartree-Fock wave functions. In Henry F. Schaefer, III, editor, *Methods of Electronic Structure Theory*, volume 3 of *Modern Theoretical Chemistry*, page 79. Plenum Press, New York, 1977.

[10] Benny G. Johnson, Peter M. W. Gill, and John A. Pople. The performance of a family of density functional methods. *J. Chem. Phys.*, 98:5612, 1993.

[11] P. Hohenberg and Walter Kohn. Inhomogeneous electron gas. *Phys. Rev.*, 136:B864, 1964.

[12] Walter Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140:A1133, 1965.

[13] J. P. Perdew. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B*, 33:8822, 1986.

[14] Axel D. Becke. Density functional calculations of molecular bond energies. *J. Chem. Phys.*, 84:4524, 1986.

[15] Axel D. Becke. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, 38:3098, 1988.

[16] Axel D. Becke. Correlation energy of an inhomogeneous electron gas: Acoordinate-space approach. *J. Chem. Phys.*, 88:1053, 1988.

[17] Axel D. Becke. Density functional thermochemistry III: The role of exact exchange. *J. Chem. Phys.*, 98:5648, 1993.

[18] John A. Pople, D. P. Santry, and Gerald A. Segal. Approximate self-consistent molecular orbital theory. I. invariant procedures. *J. Chem. Phys.*, 43:S129, 1965.

[19] John A. Pople and Gerald A. Segal. Approximate self-consistent molecular orbital theory. II. calculations with complete neglect of differential overlap. *J. Chem. Phys.*, 43:S136, 1965.

[20] John A. Pople and Gerald A. Segal. Approximate self-consistent molecular orbital theory. III. CNDO results for ab2 and ab3 systems. *J. Chem. Phys.*, 44:3289, 1966.

[21] John A. Pople and David L. Beveridge. *Approximate Molecular Orbital Theory*. McGraw-Hill Book Company, New York, 1 edition, 1970.

[22] N. Mataga and K. Nishimoto. *Z. Phys. Chem.*, 13:140, 1957.

[23] Michael C. Zerner, Gilda H. Loew, Robert F. Kirchner, and Ulrich T. Mueller-Westerhoff. An intermediate neglect of differential overlap technique for spectroscopy of transition-metal complexes. ferrocene. *J. Am. Chem. Soc.*, 102:7863, 1980.

[24] R. Pariser and R. Parr. *J. Chem. Phys.*, 21:767, 1953.

[25] J. M. Sichel and M. A. Whitehead. *Theoretica Chimica Acta*, 7:32, 1967.

[26] J. B. Foresman, Martin Head-Gordon, John A. Pople, and Michael J. Frisch. Toward a systematic molecular orbital theory for excited states. *Journal of Physical Chemistry*, 96:135, 1992.

[27] W. J. Hunt, William A. Goddard, III, and Thomas H. Dunning. The incorporation of quadratic convergence into open-shell self-consistent field equations. *Chem. Phys. Lett.*, 6:147, 1970.

[28] Ray A. Bair, Frank W. Bobrowicz, W. J. Hunt, P. J. Hay, and William A. Goddard, III. *GVB2P5 Program*. California Institute of Technology, 1977.

[29] Larry G. Yaffe and William A. Goddard, III. Orbital optimization in electronic wave functions: Equations for quadratic and cubic convergence in general multi-configuration wave functions. *Phys. Rev. A*, 13:1682, 1976.

[30] W. J. Hunt and William A. Goddard, III. Excited states of H_2O using improved virtual orbitals. *Chem. Phys. Lett.*, 3:414, 1969.

[31] Yukio Yamaguchi, Yoshihiro Osamura, John D. Goddard, and Henry F. Schaefer. *A new dimension to quantum chemistry: analytic derivative methods in ab initio molecular electronic structure theory*. Oxford University Press, New York, 1994.

[32] D. J. Chadi and Marvin L. Cohen. *Phys. Stat. Sol. B*, 68:405, 1975.

[33] Walter A. Harrison. *Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond*. Dover, New York, 1989.

[34] Charles Kittel. *Introduction to Solid State Physics*. John Wiley and Sons, Inc., New York, 7 edition, 1996.

[35] John C. Slater and G. F. Koster. Simplified lcao method for the periodic potential problem. *Phys. Rev.*, 94:1498–1524, 1954.

[36] Thomas L. Martin and William F. Leonard. *Electrons and Crystals*. Brooks/Cole, Belmont, California, 1970.

[37] J. M. Thijssen. *Computational Physics*. Cambridge University Press, Cambridge, UK, 1999.

[38] R. J. Lee, R. M. Rupley, and J. A. Miller. *Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics*. Sandia National Laboratories, Albuquerque, New Mexico, September 1989.

[39] David G. Goodwin and Michael A. Aivazis. A modular, object-oriented software package for chemical kinetics and chemical thermodynamics. *Preprint*, 2002.

[40] Michael A. Aivazis. Fuego. 2002.