

PART I

Basic Topics

2 Fundamental Principles

This chapter is in no way meant to impart a thorough understanding of the theoretical principles on which computational techniques are based. There are many texts available on these subjects, a selection of which are listed in the bibliography. This book assumes that the reader is a chemist and has already taken introductory courses outlining these fundamental principles. This chapter presents the notation and terminology that will be used in the rest of the book. It will also serve as a reminder of a few key points of the theory upon which computation chemistry is based.

2.1 ENERGY

Energy is one of the most useful concepts in science. The analysis of energetics can predict what molecular processes are likely to occur, or able to occur. All computational chemistry techniques define energy such that the system with the lowest energy is the most stable. Thus, finding the shape of a molecule corresponds to finding the shape with the lowest energy.

The amount of energy in a system is often broken down into kinetic energy and potential energy. The kinetic energy may be further separated into vibrational, translational and rotational motion. A distinction is also made between the kinetic energy due to nuclear motion versus that due to electron motion. The potential energy may be expressed purely as Coulomb's law, or it might be broken down into energies of bond stretching, bond bending, conformational energy, hydrogen bonds, and so on.

Chemical processes, such as bond stretching or reactions, can be divided into adiabatic and diabatic processes. Adiabatic processes are those in which the system does not change state throughout the process. Diabatic, or nonadiabatic, processes are those in which a change in the electronic state is part of the process. Diabatic processes usually follow the lowest energy path, changing state as necessary.

In formulating a mathematical representation of molecules, it is necessary to define a reference system that is defined as having zero energy. This zero of energy is different from one approximation to the next. For *ab initio* or density functional theory (DFT) methods, which model all the electrons in a system, zero energy corresponds to having all nuclei and electrons at an infinite distance from one another. Most semiempirical methods use a valence energy that cor-

responds to having the valence electrons removed and the resulting ions at an infinite distance. A few molecular mechanics methods use chemical standard states as zero energy, but most use a strainless molecule as zero energy. For some molecular mechanics methods, the zero of energy is completely arbitrary.

Even within a particular approximation, total energy values relative to the method's zero of energy are often very inaccurate. It is quite common to find that this inaccuracy is almost always the result of systematic error. As such, the most accurate values are often relative energies obtained by subtracting total energies from separate calculations. This is why the difference in energy between conformers and bond dissociation energies can be computed extremely accurately.

2.2 ELECTROSTATICS

Electrostatics is the study of interactions between charged objects. Electrostatics alone will not describe molecular systems, but it is very important to the understanding of interactions of electrons, which is described by a wave function or electron density. The central pillar of electrostatics is Coulomb's law, which is the mathematical description of how like charges repel and unlike charges attract. The Coulomb's law equations for energy and the force of interaction between two particles with charges q_1 and q_2 at a distance r_{12} are

$$E = \frac{q_1 q_2}{r_{12}} \quad (2.1)$$

$$F = \frac{q_1 q_2}{r_{12}^2} \quad (2.2)$$

Note that these equations do not contain the constants that are typically included in introductory texts, such as the vacuum permittivity constant. Theoreticians, and thus software developers, work with a system of units called atomic units. Within this unit system, many of the fundamental constants are defined as having a value of 1. Atomic units will be used throughout this book unless otherwise specified.

Another very useful function from electrostatics is the electrostatic potential ϕ . The electrostatic potential is a function that is defined at every point in three-dimensional real space. If a charged particle is added to a system, without disturbing the system, the energy of placing it at any point in space is the electrostatic potential times the charge on the particle. The requirement that there is no movement of existing charges (polarization of electron density) is sometimes described by stating that the electrostatic potential is the energy of placing an infinitesimal point charge in the system. The application of electrostatic potentials to chemical systems will be discussed further in Chapter 13.

The statement of Coulomb's law above assumes that the charges are sepa-

TABLE 2.1 Conversion Factors for Atomic Units

Property	Atomic Unit	Conversion
Length	Bohr	1 Bohr = 0.529177249 Å
Weight	atomic mass unit (amu)	1 amu = $1.6605402 \times 10^{-27}$ kg
Charge	electron charge	1 electron = 1.602188×10^{-19} Coulombs
Energy	Hartree	1 Hartree = 27.2116 eV
Charge separation	Bohr electron	1 Bohr electron = 2.541765 Debye

rated by a vacuum. If the charges are separated by some continuum medium, this interaction will be modified by the inclusion of a dielectric constant for that medium. For the description of molecules, it is correct to assume that the nuclei and electrons are in a vacuum. However, dielectric effects are often included in the description of solvent effects as described in Chapter 24.

The Poisson equation relates the electrostatic potential ϕ to the charge density ρ . The Poisson equation is

$$\nabla^2\phi = -\rho \quad (2.3)$$

This may be solved numerically or within some analytic approximation. The Poisson equation is used for obtaining the electrostatic properties of molecules.

2.3 ATOMIC UNITS

The system of atomic units was developed to simplify mathematical equations by setting many fundamental constants equal to 1. This is a means for theorists to save on pencil lead and thus possible errors. It also reduces the amount of computer time necessary to perform chemical computations, which can be considerable. The third advantage is that any changes in the measured values of physical constants do not affect the theoretical results. Some theorists work entirely in atomic units, but many researchers convert the theoretical results into more familiar unit systems. Table 2.1 gives some conversion factors for atomic units.

2.4 THERMODYNAMICS

Thermodynamics is one of the most well-developed mathematical descriptions of chemistry. It is the field of thermodynamics that defines many of the concepts of energy, free energy and entropy. This is covered in physical chemistry text books.

Thermodynamics is no longer a subject for an extensive amount of research. The reasons for this are two-fold: the completeness of existing or previous work

and the general inability to provide detailed insight into chemical processes. Very often, any thermodynamic treatment is left for trivial pen-and-paper work since many aspects of chemistry are so accurately described with very simple mathematical expressions.

Computational results can be related to thermodynamics. The result of computations might be internal energies, free energies, and so on, depending on the computation done. Likewise, it is possible to compute various contributions to the entropy. One frustration is that computational software does not always make it obvious which energy is being listed due to the differences in terminology between computational chemistry and thermodynamics. Some of these differences will be noted at the appropriate point in this book.

2.5 QUANTUM MECHANICS

Quantum mechanics (QM) is the correct mathematical description of the behavior of electrons and thus of chemistry. In theory, QM can predict any property of an individual atom or molecule exactly. In practice, the QM equations have only been solved exactly for one electron systems. A myriad collection of methods has been developed for approximating the solution for multiple electron systems. These approximations can be very useful, but this requires an amount of sophistication on the part of the researcher to know when each approximation is valid and how accurate the results are likely to be. A significant portion of this book addresses these questions.

Two equivalent formulations of QM were devised by Schrödinger and Heisenberg. Here, we will present only the Schrödinger form since it is the basis for nearly all computational chemistry methods. The Schrödinger equation is

$$\hat{H}\Psi = E\Psi \quad (2.4)$$

where \hat{H} is the Hamiltonian operator, Ψ a wave function, and E the energy. In the language of mathematics, an equation of this form is called an eigen equation. Ψ is then called the eigenfunction and E an eigenvalue. The operator and eigenfunction can be a matrix and vector, respectively, but this is not always the case.

The wave function Ψ is a function of the electron and nuclear positions. As the name implies, this is the description of an electron as a wave. This is a probabilistic description of electron behavior. As such, it can describe the probability of electrons being in certain locations, but it cannot predict exactly where electrons are located. The wave function is also called a probability amplitude because it is the square of the wave function that yields probabilities. This is the only rigorously correct meaning of a wave function. In order to obtain a physically relevant solution of the Schrödinger equation, the wave function must be continuous, single-valued, normalizable, and antisymmetric with respect to the interchange of electrons.

The Hamiltonian operator \hat{H} is, in general,

$$\hat{H} = - \sum_i^{\text{particles}} \frac{\nabla_i^2}{2m_i} + \sum_{i < j}^{\text{particles}} \sum \frac{q_i q_j}{r_{ij}} \quad (2.5)$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \quad (2.6)$$

where ∇_i^2 is the Laplacian operator acting on particle i . Particles are both electrons and nuclei. The symbols m_i and q_i are the mass and charge of particle i , and r_{ij} is the distance between particles. The first term gives the kinetic energy of the particle within a wave formulation. The second term is the energy due to Coulombic attraction or repulsion of particles. This formulation is the time-independent, nonrelativistic Schrödinger equation. Additional terms can appear in the Hamiltonian when relativity or interactions with electromagnetic radiation or fields are taken into account.

In currently available software, the Hamiltonian above is nearly never used. The problem can be simplified by separating the nuclear and electron motions. This is called the Born–Oppenheimer approximation. The Hamiltonian for a molecule with stationary nuclei is

$$\hat{H} = - \sum_i^{\text{electrons}} \frac{\nabla_i^2}{2} - \sum_i^{\text{nuclei}} \sum_j^{\text{electrons}} \frac{Z_i}{r_{ij}} + \sum_{i < j}^{\text{electrons}} \sum \frac{1}{r_{ij}} \quad (2.7)$$

Here, the first term is the kinetic energy of the electrons only. The second term is the attraction of electrons to nuclei. The third term is the repulsion between electrons. The repulsion between nuclei is added onto the energy at the end of the calculation. The motion of nuclei can be described by considering this entire formulation to be a potential energy surface on which nuclei move.

Once a wave function has been determined, any property of the individual molecule can be determined. This is done by taking the expectation value of the operator for that property, denoted with angled brackets $\langle \rangle$. For example, the energy is the expectation value of the Hamiltonian operator given by

$$\langle E \rangle = \int \Psi^* \hat{H} \Psi \quad (2.8)$$

For an exact solution, this is the same as the energy predicted by the Schrödinger equation. For an approximate wave function, this gives an approximation of the energy, which is the basis for many of the techniques described in subsequent chapters. This is called variational energy because it is always greater than or equal to the exact energy. By substituting different operators, it is possible to obtain different observable properties, such as the dipole moment or electron density. Properties other than the energy are not variational, because

only the Hamiltonian is used to obtain the wave function in the widely used computational chemistry methods.

Another way of obtaining molecular properties is to use the Hellmann–Feynman theorem. This theorem states that the derivative of energy with respect to some property P is given by

$$\frac{dE}{dP} = \left\langle \frac{\partial \hat{H}}{\partial P} \right\rangle \quad (2.9)$$

This relationship is often used for computing electrostatic properties. Not all approximation methods obey the Hellmann–Feynman theorem. Only variational methods obey the Hellmann–Feynman theorem. Some of the variational methods that will be discussed in this book are denoted HF, MCSCF, CI, and CC.

2.6 STATISTICAL MECHANICS

Statistical mechanics is the mathematical means to calculate the thermodynamic properties of bulk materials from a molecular description of the materials. Much of statistical mechanics is still at the paper-and-pencil stage of theory. Since quantum mechanics cannot exactly solve the Schrödinger equation yet, statistical mechanics do not really have even a starting point for a truly rigorous treatment. In spite of this limitation, some very useful results for bulk materials can be obtained.

Statistical mechanics computations are often tacked onto the end of *ab initio* vibrational frequency calculations for gas-phase properties at low pressure. For condensed-phase properties, often molecular dynamics or Monte Carlo calculations are necessary in order to obtain statistical data. The following are the principles that make this possible.

Consider a quantity of some liquid, say, a drop of water, that is composed of N individual molecules. To describe the geometry of this system if we assume the molecules are rigid, each molecule must be described by six numbers: three to give its position and three to describe its rotational orientation. This $6N$ -dimensional space is called phase space. Dynamical calculations must additionally maintain a list of velocities.

An individual point in phase space, denoted by Γ , corresponds to a particular geometry of all the molecules in the system. There are many points in this phase space that will never occur in any real system, such as configurations with two atoms in the same place. In order to describe a real system, it is necessary to determine what configurations could occur and the probability of their occurrence.

The probability of a configuration occurring is a function of the energy of that configuration. This energy is the sum of the potential energy from inter-

molecular attractive or repulsive forces and the kinetic energy due to molecular motion. For an ideal gas, only the kinetic energy needs to be considered. For a molecular gas, the kinetic energy is composed of translational, rotational, and vibrational motion. For a monatomic ideal gas, the energy is due to the translational motion only. For simplicity of discussion, we will refer to the energy of the system or molecule without differentiating the type of energy.

There is a difference between the energy of the system, composed of all molecules, and the energy of the individual molecules. There is an amount of energy in the entire system that is measurable as the temperature of the system. However, not all molecules will have the same energy. Individual molecules will have more or less energy, depending on their motion and interaction with other molecules. There is some probability of finding molecules with any given energy. This probability depends on the temperature T of the system. The function that gives the ratio of the number of molecules, N_i , with various energies, E_i , to the number of molecules in state j is the Boltzmann distribution, which is expressed as

$$\frac{N_i}{N_j} = e^{-(E_i - E_j)/k_B T} \quad (2.10)$$

where k_B is the Boltzmann constant, 1.38066×10^{-23} J/K.

Equation (2.10) is valid if there are an equal number of ways to put the system in both energy states. Very often, there are more states available with higher energies due to there being an increasing number of degenerate states. When this occurs, the percentage of molecules in each state is determined by multiplying the equation above by the number of states available. Thus, there is often a higher probability of finding high-energy molecules at higher temperatures as shown in Figure 2.1. Note that the ground state may be a very poor approximation to the average.

When some property of a system is measured experimentally, the result is an average for all of the molecules with their respective energies. This observed quantity is a statistical average, called a weighted average. It corresponds to the result obtained by determining that property for every possible energy state of the system, $A(\Gamma)$, and multiplying by the probability of finding the system in that energy state, $w(\Gamma)$. This weighted average must be normalized by a partition function Q , where

$$\langle A \rangle = \frac{\sum w(\Gamma) A(\Gamma)}{Q} \quad (2.11)$$

$$Q = \sum w(\Gamma) \quad (2.12)$$

This technique for finding a weighted average is used for ideal gas properties and quantum mechanical systems with quantized energy levels. It is not a convenient way to design computer simulations for real gas or condensed-phase

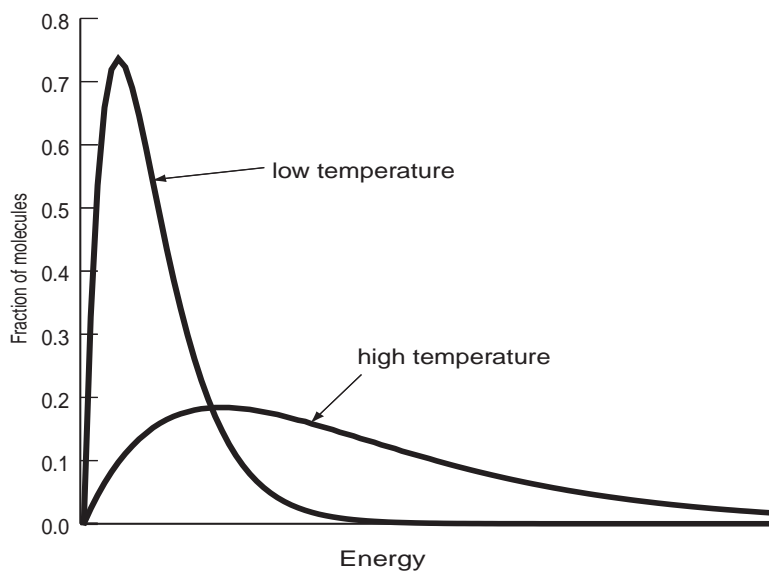


FIGURE 2.1 Fraction of molecules that will be found at various energies above the ground-state energy for two different temperatures.

systems, because determining every possible energy state is by no means a trivial task. However, a result can be obtained from a reasonable sampling of states. This results in values having a statistical uncertainty σ that is related to the number of states sampled M by

$$\sigma \propto \frac{1}{\sqrt{M}} \quad (2.13)$$

There could also be systematic errors that are not indicated by this relationship.

Another way of formulating this problem is to use derivatives of the partition function without a weight function. This is done with the following relationships:

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V \quad (2.14)$$

$$A = -k_B T \ln Q \quad (2.15)$$

$$P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad (2.16)$$

$$C_V = 2k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_V + k_B T^2 \left(\frac{\partial^2 \ln Q}{\partial T^2} \right)_V \quad (2.17)$$

$$H = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V + k_B T V \left(\frac{\partial \ln Q}{\partial V} \right)_T \quad (2.18)$$

$$S = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_V + k_B \ln Q \quad (2.19)$$

$$G = k_B T V \left(\frac{\partial \ln Q}{\partial V} \right)_T - k_B T \ln Q \quad (2.20)$$

Other thermodynamic functions can be computed from these quantities. This is still not an ideal way to compute properties due to the necessity of accounting for all energy states of the system in order to obtain Q .

It is hardest to obtain precise values for the enthalpic values A , S , and G because they depend more heavily on high-energy states, which the system achieves infrequently. These functions depend on the actual value of Q , not just its derivatives.

There are several other, equivalent ways to obtain a statistical average. One of these is to use a time average. In this formulation, a calculation is designed to simulate the motion of molecules. At every step in the simulation, the property is computed for one molecule and averaged over all the time steps equally. This is equivalent to the weighted average because the molecule will be in more probable energy states a larger percentage of the time. The accuracy of this result depends on the number of time steps and the ability of the simulation to correctly describe how the real system will behave.

Another averaging technique is an ensemble average. Simulations often include thousands of molecules. A value can be averaged by including the result for every molecule in the simulation. This corresponds to the concept of an ensemble of molecules and is thus called an ensemble average. It is often most efficient to combine time averages and ensemble averages, thus averaging all molecules over many time steps.

Another type of property to examine is the geometric orientation of molecules. A set of Cartesian coordinates will describe a point in phase space, but it does not convey the statistical tendency of molecules to orient in a certain way. This statistical description of geometry is given by a radial distribution function, also called a pair distribution function. This is the function that gives the probability of finding atoms various distances apart. The radial distribution function gives an indication of phase behavior as shown in Figure 2.2. More detail can be obtained by using atom-specific radial distribution functions, such as the probability of finding a hydrogen atom various distances from an oxygen atom.

The connections between simulation and thermodynamics can be carried further. Simulations can be set up to be constant volume, pressure, temperature, and so on. Some of the most sophisticated simulations are those involving multiple phases or phase changes. These techniques are discussed further in Chapter 7.

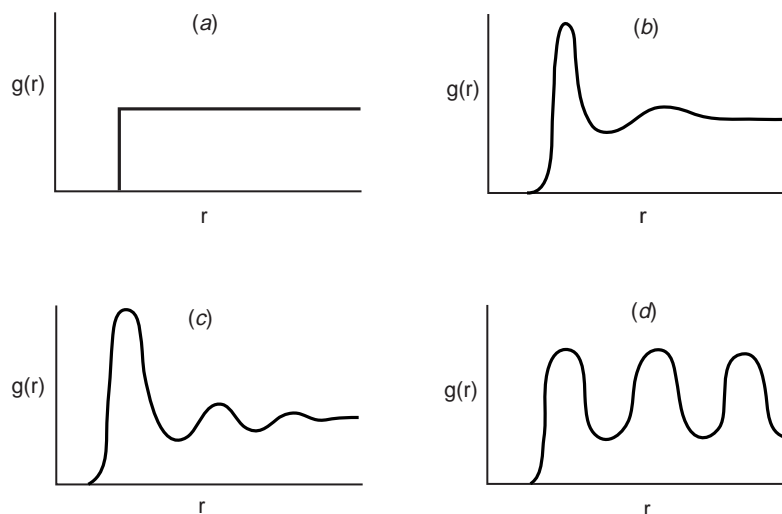


FIGURE 2.2 Radial distribution functions for (a) a hard sphere fluid, (b) a real gas, (c) a liquid, (d) a crystal.

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