Molecular Modeling of Geochemical Reactions

An Introduction

EDITOR JAMES D. KUBICKI





Molecular Modeling of Geochemical Reactions

Dedication

To see a World in a grain of sand... —William Blake To my wife, Doris, and son, Cody, who bring much joy to my life.

Molecular Modeling of Geochemical Reactions

An Introduction

Edited by

JAMES D. KUBICKI University of Texas at El Paso, USA

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Preface

Humility is an underrated scientific personality characteristic. When I think of William Blake's famous lithograph of Sir Isaac Newton toiling away at the bottom of a dark ocean, I am always reminded of how much we do not know. Science is a humbling enterprise because even our most notable achievements will likely be replaced by greater understanding at some date in the future. I am allowing myself an exception in the case of publication of this volume, however. I am proud of this book because so many leaders in the field of computational geochemistry have agreed to be a part of it. We all know that the best people are so busy with projects that it is difficult to take time away from writing papers and proposals to dedicate time to a chapter. The authors who have contributed to this volume deserve a great deal of appreciation for taking the time to help explain computational geochemistry to those who are considering using these techniques in their research or trying to gain a better understanding of the field in order to apply its results to a given problem. I am proud to be associated with this group of scientists.

When my scientific career began in 1983, computational geochemistry was just getting a toehold in the effort to explain geochemical reactions at an atomic level. People such as Gerry V. Gibbs and John (Jack) A. Tossell were applying quantum chemistry to model geologic materials, and C. Austen Angell and coworkers were simulating melts with classical molecular dynamics. As an undergraduate, I had become interested in magmatic processes, especially the generation of magmas in subduction zones and the nucleation of crystals from melts. Organic chemistry exposed me to the world of reaction mechanisms which were not being studied extensively at the time in geochemistry. When the opportunity arose in graduate school to use MD simulations to model melt and glass behavior, I jumped at the chance to combine these interests in melts and mechanisms naïve to the challenges that lie ahead. Fortunately, through the guidance of people such as Russell J. Hemley, Ron E. Cohen, Anne M. Hofmeister, Greg E. Muncill, and Bjorn O. Mysen at the Geophysical Laboratory, I was able to complement the computational approach with experimental data on diffusion rates and vibrational spectra. This approach helped benchmark the simulations and provide insights into the problems at hand that were difficult to attain with computation alone. This strategy has worked throughout my career and has led to numerous fascinating collaborations.

A key step in this process occurred while I was working as a postdoc at Caltech under Geoffrey A. Blake and Edward M. Stolper. I met another postdoc, Dan G. Sykes, who also shared a passion for melt and glass structure. As I was learning how to apply quantum mechanics to geochemistry, Dan and I discussed his models for explaining the vibrational spectra of silica and aluminosilicate glasses. Dan's model differed from the prevailing interpretations of IR and Raman spectra, but his hypotheses were testable via construction of the three- and four-membered ring structures he thought gave rise to the observed trends in vibrational frequencies with composition. We argued constantly over the details of his model and came up with several tests to disprove it, but, in the end, the calculations and observed spectra agreed well enough that we were able to publish a series of papers over the objections of reviewers who were skeptical of the views of two young postdocs. Among these papers, a key study was published with the help of George R. Rossman whose patience and insight inspired more confidence in me that the path we were following would be fruitful. This simple paper comparing calculated versus observed H-bond frequencies ended up being more

significant than I had known at the time because this connection is critical in model mineral-water interactions that became a theme later in my career.

When I could not find work any longer doing igneous-related research, I turned to a friend from undergraduate chemistry at Cal State Fullerton, Sabine E. Apitz, to employ me as a postdoc working on environmental chemistry. Fortunately, the techniques I had learned were transferable to studying organic-mineral interactions. This research involving mineral surfaces eventually led to contacts with Susan L. Brantley and Carlo G. Pantano who were instrumental in landing a job for me at Penn State. Numerous collaborations blossomed during my tenure in the Department of Geosciences, and all these interdisciplinary projects kept me constantly excited about learning new disciplines in science. Recently, I made the decision to move to the University of Texas at El Paso to join a team of people who are creating an interdisciplinary research environment while simultaneously providing access to excellent education and social mobility.

The rapid developments in hardware, software, and theory that have occurred since 1983 have propelled research in computational geochemistry. All of us appreciate the efforts of all those developing new architectures and algorithms that make our research possible. We offer this book as a stepping stone for those interested in learning these techniques to get started in their endeavors, and we hope the reviews of literature and future directions offered will help guide many new exciting discoveries to come.

> James D. Kubicki Department of Geological Sciences The University of Texas at El Paso October 3, 2015

1

Introduction to the Theory and Methods of Computational Chemistry

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1.1 Introduction

The goal of geochemistry is to understand how the Earth formed and how it has chemically differentiated among the different reservoirs (e.g., core, mantle, crust, hydrosphere, atmosphere, and biosphere) that make up our planet. In the early years of geochemistry, the primary concern was the chemical analysis of geological materials to assess the overall composition of the Earth and to identify processes that control the Earth's chemical differentiation. The theoretical underpinning of geochemistry was very primitive: elements were classified as chalcophile, lithophile, and siderophile (Goldschmidt, 1937), and the chemistry of the lithophile elements was explained in terms of simple models of ionic bonding (Pauling, 1929). It was not possible to develop a predictive quantitative theory of how elements partition among different phases.

In the 1950s, experimental studies began to measure how elements are partitioned between coexisting phases (e.g., solid, melt, and fluid) as a function of pressure and temperature. This motivated the use of thermodynamics so that experimental results could be extrapolated from one system to another. Equations of state were developed that were based on simple atomistic (hard-sphere) or continuum models (Born model) of liquids (e.g., Helgeson and Kirkham, 1974). This work continued on into the 1980s. By this time, computers had become sufficiently fast that atomistic simulations of geologically interesting materials were possible. However, the computational atomistic simulations were based on classical or ionic models of interatomic interactions. Minerals were modeled as being composed of ions that interact via empirical or *ab initio*-derived interatomic potential functions (e.g., Catlow et al., 1982; Bukowinski, 1985). Aqueous solutions were composed of ions solvated by (usually) rigid water molecules modeled as point charges (Berendsen et al., 1987). Many of these simulations have been very successful and classical models of minerals and aqueous

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solutions are still in use today. However, ultimately, these models will be limited in application insofar as they are not based on the real physics of the problem.

The physics underlying geochemistry is quantum mechanics. As early as the 1970s, approximate quantum mechanical calculations were starting to be used to investigate bonding and electronic structure in minerals (e.g., Tossell et al., 1973; Tossell and Gibbs, 1977). This continued into the 1980s with an emphasis on understanding how chemical bonds dictate mineral structures (e.g., Gibbs, 1982) and how the pressures of the deep earth might change chemical bonding and electronic structure (Sherman, 1991). Early work also applied quantum chemistry to understand geochemical reaction mechanisms by predicting the structures and energetics of reactive intermediates (Lasaga and Gibbs, 1990). By the 1990s, it became possible to predict the equations of state of simple minerals and the structures and vibrational spectra of gas-phase metal complexes (Sherman, 2001). As computers have become faster, it now possible to simulate liquids, such as silicate melts or aqueous solutions, using *ab initio* molecular dynamics.

We are now at the point where computational quantum chemistry can be used to provide a great deal on insight on the mechanisms and thermodynamics of chemical reactions of interest in geochemistry. We can predict the structures and stabilities of metal complexes on mineral surfaces (Sherman and Randall, 2003; Kwon et al., 2009) that control the fate of pollutants and micronutrients in the environment. We can predict the complexation of metals in hydrothermal fluids that determine the solubility and transport of metals leading to hydrothermal ore deposits (Sherman, 2007; Mei et al., 2013, 2015). We can predict the phase transitions of minerals that may occur in the Earth's deep interior (Oganov and Ono, 2004; Oganov and Price, 2005). Computational quantum chemistry is now becoming a mainstream activity among geochemists, and investigations using computational quantum chemistry are now a significant contribution to work presented at major conferences on geochemistry.

Many geochemists want to use these tools, but may have come from a traditional Earth science background. The goal of this chapter is to give the reader an outline of the essential concepts that must be understood before using computational quantum chemistry codes to solve problems in geochemistry. Geochemical systems are usually very complex and many of the high-level methods (e.g., configuration interaction) that might be applied to small molecules are not practical. In this chapter, I will focus on those methods that can be usefully applied to earth materials. I will avoid being too formal and will emphasize what equations are being solved rather than how they are solved. (This has largely been done for us!) It is crucial, however, that those who use this technology be aware of the approximations and limitations. To this end, there are some deep fundamental concepts that must be faced, and it is worth starting at fundamental ideas of quantum mechanics.

1.2 Essentials of Quantum Mechanics

By the late nineteenth and early twentieth centuries, it was established that matter comprised atoms which, in turn, were made up of protons, neutrons, and electrons. The differences among chemical elements and their isotopes were beginning to be understood and systematized. Why different chemical elements combined together to form compounds, however, was still a mystery. Theories of the role of electrons in chemical bonding were put forth (e.g., Lewis, 1923), but these models had no obvious physical basis. At the same time, physicists were discovering that classical physics of Newton and Maxwell failed to explain the interaction of light and electrons with matter. The energy of thermal radiation emitted from black bodies could only be explained in terms of the frequency of light and not its intensity (Planck, 1900). Moreover, light (viewed as a wave since Young's experiment in 1801) was found to have the properties of particles with discrete energies and momenta (Einstein, 1905). This suggests that light was both a particle and a wave. Whereas a classical particle could have any value for its kinetic and potential energies, the electrons bound to atoms were found

to only have discrete (quantized) energies (Bohr, 1913). It was then hypothesized that particles such as electrons could also be viewed as waves (de Broglie, 1925); this was experimentally verified by the discovery of electron diffraction (Davisson and Germer, 1927). Readers can find an accessible account of the early experiments and ideas that led to quantum mechanics in Feynman et al. (2011).

The experimentally observed wave–particle duality and quantization of energy were explained by the quantum mechanics formalism developed by Heisenberg (1925), Dirac (1925), and Schrodinger (1926). The implication of quantum mechanics for understanding chemical bonding was almost immediately demonstrated when Heitler and London (1927) developed a quantum mechanical model of bonding in the H_2 molecule. However, the real beginning of computational quantum chemistry occurred at the University of Bristol in 1929 when Lennard-Jones presented a molecular orbital theory of bonding in diatomic molecules (Lennard-Jones, 1929).

The mathematical structure of quantum mechanics is based on set of postulates:

Postulate 1:

A system (e.g., an atom, molecule or, really, anything) is described by a *wavefunction* $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, t)$ over the coordinates $\{\mathbf{r}_N\}$, the *N*-particles of the system, and time *t*. The physical meaning of this wavefunction is that the probability of finding the system at a set of values for the coordinates $\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N$ at a time *t* is $|\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, t)|^2$.

Postulate 2:

For every observable (measurable) property λ of the system, there corresponds a mathematical operator (\hat{L}) that acts on the wavefunction.

Mathematically, this is expressed as follows:

$$\hat{L}\Psi = \lambda\Psi \tag{1.1}$$

 Ψ is an eigenfunction of the operator \hat{L} with eigenvalue λ . An eigenfunction is a function associated with an operator such that if the function is operated on by the operator, the function is unchanged except for being multiplied by a scalar quantity λ . This is very abstract, but it leads to the idea of the states of a system (the eigenfunctions) that have defined observable properties (the eigenvalues). Observable properties are quantities such as energy, momentum, or position. For example, the operator for the momentum of a particle moving in the x-direction is

$$\hat{p} = i\hbar \frac{\partial}{\partial x} \vec{\mathbf{i}}$$
(1.2)

where *i* is $\sqrt{-1}$, \hbar is Planck's constant divided by 2π , and \vec{i} is the unit vector in the *x*-direction. Since the kinetic energy of a particle with mass *m* and momentum *p* is

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

the operator for the kinetic energy of a particle of mass m that is free to move in three directions (x, y, z) is

$$\hat{T} = \frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = \frac{-\hbar^2}{2m} \nabla^2$$
(1.3)

In general, the operator for the potential energy (\hat{V}) of a system is a scalar operator such that $\hat{V} = V$. That is, we multiply the wavefunction by the function that defines the potential energy. The operator \hat{E} for the total energy E of a system is

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$$\hat{E} = i\hbar \frac{\partial}{\partial t} \tag{1.4}$$

It is important to recognize whether or not a quantity is a "quantum mechanical observable." Chemists (and geochemists) often invoke quantities such as "ionicity," "bond valence," "ionic radius," etc., that are not observables. These quantities are not real; they exist only as theoretical constructs. They cannot be measured.

1.2.1 The Schrödinger Equation

In classical mechanics, we express the concept of conservation of energy in terms of the Hamiltonian H of the system:

$$H = E = T + V \tag{1.5}$$

In quantum mechanics, we express the Hamiltonian in terms of the operators corresponding to E, T, and V:

$$\hat{H}\Psi = (\hat{T} + \hat{V})\Psi = \hat{E}\Psi \tag{1.6}$$

or

$$\hat{H}\Psi = \left(\hat{T} + \hat{V}\right)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$
(1.7)

This is the time-dependent Schrödinger equation. If the kinetic T and potential V energies of the system are not varying with time, then we can write:

$$\Psi(r_1, r_2, \dots, r_N, t) = \Psi(r_1, r_2, \dots, r_N) e^{-iEt/\hbar}$$
(1.8)

Substituting this into the Hamiltonian gives:

$$\hat{H}\Psi = (\hat{T} + \hat{V})\Psi = E\Psi \tag{1.9}$$

This is the time-independent Schrödinger equation, and it is what we usually seek to solve in order to obtain a quantum mechanical description of the system in terms of the wavefunction and energy of each state.

1.2.2 Fundamental Examples

At this point, it is worthwhile to briefly explore several fundamental examples that illustrate the key aspects of quantum mechanics.

1.2.2.1 Particle in a Box

This is, perhaps the simplest problem yet it illustrates some of the fundamental features of quantum reality. Consider a particle of mass m inside a one-dimensional box of length L (Figure 1.1). The potential energy V of the system is 0 inside the box but infinite outside the box. Therefore, inside the box, the Schrödinger equation is



Figure 1.1 Wavefunctions and energy levels for a particle in a one-dimensional box.

$$\frac{-\hbar^2}{2m} \left(\frac{d^2 \Psi(x)}{dx^2} \right) = E \Psi(x) \tag{1.10}$$

The solution to this differential equation is of the form:

$$\Psi(x) = A\sin(kx) + B\cos(kx) \tag{1.11}$$

Since the potential energy is infinite outside the box, the particle cannot be at x = 0 or at x = L. That is, we have $\Psi(0) = \Psi(L) = 0$. Hence,

$$\Psi(0) = A\sin(0) + B\cos(0) = 0 \tag{1.12}$$

which implies that B = 0. However, since

$$\Psi(L) = A\sin(kL) = 0$$

we find that $kL = n\pi$, where n = 1, 2, 3, ...

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If we substitute $\Psi(x)$ back into the Schrödinger equation, we find that

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{n^2 \pi^2}{L^2} \right)$$
(1.13)

That is, the energy is quantized to have only specific allowed values because *n* can only take on integer values. The quantization results from putting the particle in a potential energy well (the box). However, the quantization is only significant if the dimensions of the box and the mass of the particle are on the order of Planck's constant ($h = 6.6262 \times 10^{-34}$ J/s, i.e., if the box is angstroms to nanometers in size). The formalism of quantum mechanics certainly applies to our macroscopic world, but the quantum spacing of a 1 g object in a box of, say, 10 cm in length is too infinitesimal to measure.

1.2.2.2 The Hydrogen Atom

Now, let's consider the hydrogen atom consisting of one electron and one proton as solved by Schrödinger (1926). We will consider only the motion of the electron relative to the position of the proton and not consider the motion of the hydrogen atom as a whole. Hence, our wavefunction for the system is $\Psi(\mathbf{r})$ where \mathbf{r} is the position of the electron (in three dimensions) relative to the proton (located at the origin). The Schrödinger equation for this problem is then

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0 r}\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$
(1.14)

where *e* is the charge of the electron and ε_0 is the permittivity of free space. To avoid having to write all the physical constants, it is convenient to adopt "atomic units," where *m*, \hbar^2 , and $e^2/4\pi\varepsilon_0$ are all set to unity. The unit of energy is now the Hartree (1 H = 27.21 eV = 4.360×10^{-18} J) and the unit of distance is the Bohr (10^{-10} m = 1 Å = 0.529177 Bohr). Computer programs in quantum chemistry often express their results in hartrees and bohrs; it is important that the user be aware of these units and know how to convert to more conventional units such as kJ/mol and angstrom (Å).

In atomic units, the hydrogen Schrödinger equation becomes

$$-\frac{1}{2}\nabla^2 \Psi(\mathbf{r}) - \frac{1}{r}\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$
(1.15)

Since the problem has spherical symmetry, it is more convenient to use spherical coordinates $\Psi(\mathbf{r}) = \Psi(r, \theta, \phi)$ rather than Cartesian coordinates (Figure 1.2). Since the coordinates are independent of each other, we can write

$$\Psi(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi)$$
(1.16)

where $Y_{lm}(\theta, \phi)$ are the spherical harmonic functions; they give the angular shape of the wavefunctions. The radial wavefunction is

$$R_{nl}(r) = \sqrt{\left(\frac{2}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-r\ln\left(\frac{2r}{n}\right)^l} L_{n-l-1}^{2l+1}\left(\frac{2r}{n}\right)$$
(1.17)

where L_{n-l-1}^{2l+1} are special functions called Laguerre polynomials. The important result that emerges from this solution is that the wavefunction can be specified by three quantum numbers *n*, *l*, and *m* with values



Figure 1.2 Spherical coordinates used for solution of the hydrogen atom.

$$n = 1, 2, 3, \dots$$

$$l = 0, 1, 2, \dots, n-1$$

$$m = -l, -l+1, \dots, 0, \dots, l-1, l$$

The energy of the electron is quantized with values

$$E_n = -\left(\frac{1}{2}\right)\frac{1}{n^2}$$
(1.18)

This predicted quantization of the hydrogen electron energies triumphantly explains the empirical model proposed by Bohr for the energies of the lines observed hydrogen atom spectrum. It is standard practice to denote orbitals with l=0 as "s" (not to be confused with the spin-quantum number described later), orbitals with l=1 as "p," orbitals with l=2 as "d," and orbitals with l=3 as "f." The three *m* quantum numbers for the p-orbitals are denoted as p_x , p_y , and p_z . For the d-orbitals, we take linear combinations of the orbitals corresponding to the different m quantum numbers to recast them as d_{xy} , d_{xz} , d_{yz} , $d_{3z^2-r^2}$, and $d_{x^2-y^2}$. The schematic energy-level diagram and the shapes of the hydrogenic orbitals are shown in Figure 1.3.

Unfortunately, we cannot find an exact analytical solution for the Schrödinger equation for an atom with more than one electron. However, the hydrogenic orbitals and their quantum numbers enable us to rationalize the electronic structures of the multielectronic elements and the structure of the periodic table. As will be shown later, we will use the hydrogenic orbitals as building blocks to approximate the wavefunctions for multielectronic atoms.

1.3 Multielectronic Atoms

1.3.1 The Hartree and Hartree–Fock Approximations

Consider the helium atom with two electrons and a nucleus of charge +2. The coordinate of electron 1 is \mathbf{r}_1 and the coordinate of electron 2 is \mathbf{r}_2 . We will assume that the nucleus is fixed at the origin. The Schrödinger equation for the system is then

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Figure 1.3 Schematic energy levels and orbital shapes for the hydrogen atom.

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\right)\Psi(\mathbf{r}_1, \mathbf{r}_2) = E\Psi(\mathbf{r}_1, \mathbf{r}_2)$$
(1.19)

A reasonable approach to solving this might be to assume that

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \tag{1.20}$$

This is known as the Hartree approximation; it provides a very important conceptual reference point because it introduces the idea of expressing our many-body problem in terms of single-particle functions ("one-electron orbitals"). However, because of the interelectronic repulsion, described by the term

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{1.21}$$

the Hartree approximation is too crude to be quantitatively useful; we cannot really separate out the motions of the electrons. We say that the electrons are *correlated*. In spite of this shortcoming, we will still express the wavefunction for a multielectronic system in terms of single-particle wavefunctions. However, we must go beyond the pure Hartree approximation because, in a multielectronic system, the electrons must be indistinguishable from each other. This is more fundamental than stating that the electrons have identical mass, charge, etc. It means that observing one electron in a

system is the same as observing any other electron. Hence, even if we ignore the interelectronic interaction, the wavefunction for a two-electron system must have the following form:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)$$
(1.22)

Here, we must digress: All fundamental particles have a property called "spin"; this is an intrinsic angular momentum with magnitude $S = \hbar \sqrt{s(s+1)}$. For an electron, s = 1/2. The classical analogy is that an electron is a like a little sphere spinning on its axis; however, this is not what is really happening. Spin is a purely quantum mechanical phenomenon. Nevertheless, since spin is a type of angular momentum, it has a z-axis component, s_z . However, s_z can take on only quantized values of $m_s\hbar$ where $m_s = \pm 1/2$. If $m_s = + 1/2$, we say the spin is "up" or α -spin; if $m_s = -1/2$, we say the spin is "down" or β -spin. Fundamental particles in the universe are either Fermions (with halfinteger values of s = 1/2, 3/2, ...) or Bosons (with integer values of s = 0, 1, 2, ...). Fermions must have "antisymmetric" wavefunctions:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)$$
(1.23)

Electrons are Fermions and the electronic wavefunctions must have this antisymmetry. This is a formal and abstract way of stating the *Pauli exclusion principle*. The antisymmetry requirement means that no two electrons can be in the same quantum state or have the same single-particle orbital. An antisymmetric wavefunction obeys the Pauli exclusion principle since, if $\mathbf{r}_1 = \mathbf{r}_2$, then $\Psi(\mathbf{r}_1, \mathbf{r}_2) = 0$ unless $\psi_a(\mathbf{r}_1) \neq \psi_b(\mathbf{r}_1)$. If we build a multielectronic atom in terms of single-particle hydrogenic orbitals, the Pauli exclusion principle means that no two electrons can have the same four quantum numbers (n, l, m_l, m_s) . From now on, instead of using m_s , we will designate the spin of an electron by α or β . The spin coordinate of an electron will be accounted for by using separate wavefunctions for α - and β -spin electrons is referred to as a *spin-unrestricted formalism*. As we will see later, the two wavefunctions ψ_1^{α} , ψ_1^{β} will be numerically different if the number of α -spin electrons differs from the number of β -spin electrons because the interelectronic repulsion and electron experiences will depend on its spin.

The construction of antisymmetric wavefunctions from the single-particle (hydrogenic) orbitals is much easier if we use the algebraic trick of expressing the wavefunction as the determinant of a matrix of the one-electron orbitals:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_2(\mathbf{r}_1) \\ \psi_1(\mathbf{r}_2) & \psi_2(\mathbf{r}_2) \end{vmatrix} \equiv |\psi_1\psi_2|$$
(1.24)

(on the right-hand side is a shorthand notation for the determinant). Or, for an N-electron atom,

$$\Psi(\mathbf{r}_{1},\mathbf{r}_{2},...,\mathbf{r}_{N}) = \begin{vmatrix} \psi_{1}(\mathbf{r}_{1}) & \psi_{1}(\mathbf{r}_{2}) & \cdots & \psi_{1}(\mathbf{r}_{N}) \\ \psi_{2}(\mathbf{r}_{1}) & \psi_{2}(\mathbf{r}_{2}) & \cdots & \psi_{2}(\mathbf{r}_{N}) \\ \vdots & \vdots & \vdots & \vdots \\ \psi_{N}(\mathbf{r}_{1}) & \psi_{N}(\mathbf{r}_{2}) & \cdots & \psi_{N}(\mathbf{r}_{N}) \end{vmatrix} \equiv |\psi_{1}\psi_{2}...\psi_{N}|$$
(1.25)

These are called *Slater determinants*. If any two columns of a matrix are identical, the determinant of the matrix is zero. Hence, if any two electrons occupy the same orbital, we will have two columns to be the same and the determinant (and, hence, the wavefunction) will be zero.

The *Hartree–Fock approximation* is that we can express our multielectronic wavefunction using a single-Slater determinant. This is an important starting point as it gives us a conceptual framework to

understand electronic structure and the powerful concept of electron configuration. We use the Hartree–Fock approximation and construct a wavefunction for the multielectronic atom using the hydrogenic orbitals (1s, 2s, 2p, etc.) and populate those orbitals according to the Pauli exclusion principle. Hence, using the shorthand notation for a determinant, the Hartree–Fock wavefunction for Mg is

$$\Psi = \left| \phi_{1s}^{\alpha} \phi_{1s}^{\beta} \phi_{2s}^{\alpha} \phi_{2s}^{\beta} \phi_{2p_{x}}^{\alpha} \phi_{2p_{y}}^{\beta} \phi_{2p_{y}}^{\alpha} \phi_{2p_{z}}^{\beta} \phi_{2p_{z}}^{\beta} \phi_{3p}^{\beta} \phi_{3s}^{\alpha} \right|$$
(1.26)

which, for simplicity, is written as the electron configuration:

$$(1s)^2(2s)^2(2p)^6(3s)^2$$

Although this is not a quantitative solution, the concept of electronic configuration is an immensely powerful tool in predicting the chemical behavior of the elements. The Hartree–Fock approximation also gives us a starting point in calculating the energies and wavefunctions of a multi-electronic system.

1.3.1.1 The Variational Principle and the Hartree–Fock Equations

Suppose that our system is described by a Hamiltonian \hat{H} and a wavefunction Ψ . The expectation value (the mean value of an observable quantity) of the total energy is given by

$$\langle E \rangle = \frac{\int \Psi^* \hat{H} \Psi^* d\mathbf{r}}{\int \Psi^* \Psi^* d\mathbf{r}}$$

where the asterisk (*) means the complex conjugate (i.e., replace *i* by -i). Suppose that we did not know Ψ for a given \hat{H} but had a trial guess for it (of course, this is true for nearly all of our problems). The variational principle states that the expectation value of the total energy we obtain from our trial wavefunction will always be greater than the true total energy. This is extremely useful because the problem becomes one of minimizing the total energy with respect to the trial wavefunction, and we will obtain the best approximation we can. Formally, we require that

$$\frac{\delta \langle E \rangle}{\delta \Psi} = 0$$

The δ symbol refers to the functional derivative; a functional is a function of a function. The functional derivative comes from the calculus of variations; we will not go into the details here, but a discussion is given in Parr and Yang (1989).

Now, suppose our unknown wavefunction Ψ is that of a multielectronic atom with N electrons and nuclear charge Z. If we use the Hartree–Fock approximation and express the wavefunction as a single-Slater determinant over N single-particle orbitals, then the expectation value of the total energy will be

$$\langle E \rangle = \sum_{j}^{N} \int \Psi_{j}^{*}(\mathbf{r}) \left(-\frac{1}{2} \nabla^{2} - \frac{Z}{r} \right) \psi_{j}(\mathbf{r}) d\mathbf{r}$$

+
$$\sum_{j < k}^{N} \int \frac{|\psi_{j}(\mathbf{r}_{1})|^{2} |\psi_{k}(r_{2})|}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} d\mathbf{r}_{1} d\mathbf{r}_{2}$$

-
$$\sum_{j < k}^{N} \delta(\sigma_{j}, \sigma_{k}) \int \frac{\psi_{j}^{*}(\mathbf{r}_{1}) \psi_{k}^{*}(\mathbf{r}_{2}) \psi_{j}(\mathbf{r}_{1}) \psi_{k}(\mathbf{r}_{2})}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} d\mathbf{r}_{1} d\mathbf{r}_{2}$$
(1.27)

Here, $\delta(\sigma_j, \sigma_k) = 1$ if the spins of electrons *j* and *k* are the same but is 0 if the spins are different. We can now use the variational principle: we minimize the total energy with respect to the single-particle orbitals subject to the constraint that the total number of electrons is held constant. We end up with a set of simultaneous equations for the individual orbitals ψ_i (\mathbf{r}_i) and their energies ε_i :

$$\frac{-1}{2}\nabla^{2}\psi_{j}(\mathbf{r}_{1}) - \frac{Z}{r_{1}}\psi_{j}(\mathbf{r}_{1}) + \left(\sum_{k}^{N}\frac{|\psi_{k}(\mathbf{r}_{2})|^{2}}{|\mathbf{r}_{1} - \mathbf{r}_{2}|}d\mathbf{r}_{2}\right)\psi_{j}(\mathbf{r}_{1}) - \left(\sum_{k}^{N}\delta(\sigma_{j},\sigma_{k})\int\frac{\psi_{k}^{*}(\mathbf{r}_{2})\psi_{j}(\mathbf{r}_{2})}{|\mathbf{r}_{1} - \mathbf{r}_{2}|}d\mathbf{r}_{2}\right)\psi_{j}(\mathbf{r}_{1}) = \varepsilon_{j}\psi_{j}(\mathbf{r}_{1})$$
(1.28)

These are the Hartree–Fock equations. The first summation term (the *Coulomb potential*) describes the repulsive potential experienced by an electron in orbital j at \mathbf{r}_1 due to the presence of all the other electrons in orbitals k at \mathbf{r}_2 . Note, however, that this summation also contains a term where the electron interacts with itself (when j = k). This self-interaction must be compensated for. The second summation (the *exchange potential*) modifies the Coulomb potential to remove the interactions between electrons with the same spin that are in the same orbital. It is important to note that the exchange potential also removes the self-interaction of each electron since it cancels the Coulomb potential when j = k.

Before we can solve the Hartree–Fock equations for the orbitals ψ_j (\mathbf{r}_j), we need to evaluate the Coulomb and exchange potentials. However, we cannot evaluate the Coulomb and exchange potentials until we know the orbitals ψ_j (\mathbf{r}_j)! We get around this problem by starting with an initial guess for ψ_j (\mathbf{r}_j), evaluating the Coulomb and exchange potentials using that guess, and then solving for a better set of ψ_j (\mathbf{r}_j). We then take the new set of wavefunctions and evaluate a new Coulomb and exchange potential. After so many iterations, we should converge to a *self-consistent field* (SCF) solution. All electronic structure methods need to iteratively arrive at a self-consistent solution. To confuse matters, however, the quantum chemistry literature and many textbooks often will equate "SCF" with the Hartree–Fock approximation.

The Hartree–Fock approximation is a major improvement over the Hartree approximation since it accounts for the interelectronic repulsion between electrons with the same spin. However, it completely neglects the correlation between electrons with opposite spin. The consequence of this illustrated in the simple molecule H₂ (Figure 1.4a). As we will discuss later, we can express the one-electron orbitals of a molecule (the molecular orbitals) as linear combination of atomic orbitals centered on the different atoms. If we label the two H atoms in H₂ as A and B, with atomic orbitals ϕ_A and ϕ_B , then the molecular orbitals can be constructed as follows:

$$\psi_{+} = \frac{1}{\sqrt{2}} (\phi_{\rm A} + \phi_{\rm B})$$

$$\psi_{-} = \frac{1}{\sqrt{2}} (\phi_{\rm A} - \phi_{\rm B})$$
(1.29)

These correspond to the bonding and antibonding orbitals (Figure 1.4b). These are not the actual states of the system; those are given by the multielectronic wavefunctions expressed as Slater determinants. The lowest energy state (bonding orbital) is the Slater determinant:

$$\Psi(1,2) = \begin{vmatrix} \psi_{+}^{\alpha}(1) & \psi_{+}^{\alpha}(2) \\ \psi_{+}^{\beta}(1) & \psi_{+}^{\beta}(2) \end{vmatrix}$$
(1.30)



Figure 1.4 (a) The H_2 molecule and (b) schematic energy-level diagram for the first two one-electron molecular orbitals showing the bonding and antibonding combinations of the atomic orbitals.

If we expand the Slater determinant in terms of the atomic orbitals, we find that the wavefunction is

$$\Psi(1,2) = \frac{1}{2} \left(\phi_{A}^{\alpha}(1) + \phi_{B}^{\alpha}(1) \right) \left(\phi_{A}^{\beta}(2) + \phi_{B}^{\beta}(2) \right) - \frac{1}{2} \left(\phi_{A}^{\beta}(1) + \phi_{B}^{\beta}(1) \right) \left(\phi_{A}^{\alpha}(2) + \phi_{B}^{\alpha}(2) \right)$$

$$= \frac{1}{2} \left(\phi_{A}^{\alpha}(1) \phi_{A}^{\beta}(2) + \phi_{A}^{\alpha}(1) \phi_{B}^{\beta}(2) + \phi_{B}^{\alpha}(1) \phi_{A}^{\beta}(2) + \phi_{B}^{\alpha}(1) \phi_{B}^{\beta}(2) \right)$$

$$- \frac{1}{2} \left(\phi_{A}^{\beta}(1) \phi_{A}^{\alpha}(2) + \phi_{A}^{\beta}(1) \phi_{B}^{\alpha}(2) + \phi_{B}^{\beta}(1) \phi_{A}^{\alpha}(2) + \phi_{B}^{\beta}(1) \phi_{B}^{\alpha}(2) \right)$$
(1.31)

The two summations simply differ by flipping the spins of electrons 1 and 2 in order to have an antisymmetric wavefunction. Now, consider the physical meaning of each term in the two summations: $\phi_A^{\alpha}(1)\phi_A^{\beta}(2)$ corresponds to both electrons being localized to atom A, the term $\phi_A^{\alpha}(1)\phi_B^{\beta}(2) + \phi_B^{\alpha}(1)\phi_A^{\beta}(2)$ corresponds to the two electrons being delocalized over the two atoms, and the term $\phi_B^{\alpha}(1)\phi_B^{\beta}(2)$ corresponds to the two electrons localized to atom B.

Suppose that we dissociate the H_2 molecule. It should dissociate into two neutral H atoms, and the wavefunction should be as follows:

$$\Psi_{+} = \frac{1}{2} \Big(\phi_{\rm A}^{\alpha}(1) \phi_{\rm B}^{\beta}(2) + \phi_{\rm B}^{\alpha}(1) \phi_{\rm A}^{\beta}(2) \Big) - \frac{1}{2} \Big(\phi_{\rm A}^{\beta}(1) \phi_{\rm B}^{\alpha}(2) + \phi_{\rm B}^{\beta}(1) \phi_{\rm A}^{\alpha}(2) \Big)$$
(1.32)

However, this is not what is predicted with the single-determinantal wavefunction. Instead, H_2 can only dissociate into a state where the probability of having H + H and $H^+ + H^-$ are the same. This means that the dissociation energy of H_2 will be greatly underestimated since the energy of the ion pair is about 12.85 eV higher than that of the two neutral atoms. The only way to correct this is to mix in other configurations to cancel out the terms where both electrons are localized on the same

atom. This could be done using Valence Bond theory or by expressing the wavefunction in terms of more than one Slater determinant. Neither approach is practical for any system of geochemical interest.

The Hartree–Fock total energy provides a reasonable first approximation from which we can calculate physical properties of a mineral such as compressibility, vibrational frequencies, etc. However it is not usually accurate enough to reliably address the energetics of chemical reactions. The Hartree–Fock approximation fails to completely describe the repulsion of electrons with opposite spin since the single-Slater determinant wavefunction does not go to zero when two electrons with opposite spin occupy the same position in the same orbital. This excess repulsion energy means that the Hartree–Fock energy will always be greater than the true energy.

The difference between the exact energy and the Hartree–Fock energy is known (by convention) as the *correlation energy*. However, the correlation of the motions between electrons with like spin (the "exchange correlation") is accounted for by the Hartree–Fock formalism; the "correlation energy" refers to the correlation motion between electrons with opposite spin (Coulomb correlation). Although the exchange correlation is much larger, the Coulomb correlation is still significant and, because it is neglected, Hartree–Fock energies cannot be used to reliably predict chemical reactions and the energetics of atoms, molecules, and crystals. For example, van der Waals interactions cannot be described at the Hartree–Fock level because the induced dipole is an effect of electron correlation between atoms.

A more accurate approximate wavefunction for a multielectronic system can be obtained by a finite expansion (linear combination) of Slater determinants resulting from the different possible electronic configurations over the one-electron orbitals. This approach is known as *configurational interaction*. It is the gold standard for quantum chemical calculations and can be applied to small molecules to predict properties to high accuracy (Sherrill and Schaefer, 1999). However, configuration–interaction calculations are impractical for the complex systems of interest in geochemistry. Instead, a completely different approach is needed.

1.3.2 Density Functional Theory

Density functional theory or DFT (Parr and Yang, 1989) is an approach to bonding and electronic structure that was developed in the physics community. Until the 1990s, it was not believed to be accurate enough to deal with chemical systems; however, subsequent developments have made DFT the major tool of quantum chemistry. Nearly all quantum mechanical calculations applied to geochemical systems are based on DFT. Note, however, that many traditional quantum chemists will not use the phrase "ab initio" for calculations based on DFT. This is because applied DFT must always use a fundamental approximation in how it describes the interelectronic interactions.

The basis of density functional theory is a theorem (Hohenberg and Kohn, 1964) that the groundstate total energy E of a system of particles (e.g., electrons) subject to any kind of external potential V_{ext} can be expressed (exactly) in terms of functionals of the particle density $\rho(\mathbf{r})$:

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + U[\rho(\mathbf{r})] + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$$
(1.33)

The $T[\rho(\mathbf{r})]$ functional describes the kinetic energy of the system, while the $U[\rho(\mathbf{r})]$ functional describes the potential energy due to interelectronic repulsion. Here, the external potential V_{ext} would include the electron–nuclear interactions in an atom along with the nuclear–nuclear interactions in a molecule. The problem with using the Hohenberg–Kohn theorem, however, is that, for a system of interacting electrons, we do not know what the $T[\rho(\mathbf{r})]$ and $U[\rho(\mathbf{r})]$ functionals are.

Nevertheless, we do know some aspects of these functionals. Our strategy is to first separate out the parts of the functionals that we know. To do this, we first note that part of the interelectronic repulsion is a classical Hartree Coulombic term:

$$U[\rho(\mathbf{r})] = G[\rho(\mathbf{r})] + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$
(1.34)

Here, we have temporarily defined a new functional $G[\rho(\mathbf{r})]$ that includes that part of $U[\rho(\mathbf{r})]$ that we do not know. We also know that if the particles did not interact with each other, than the wave-function of the system would be a single-Slater determinant over single-particle orbitals $\psi_j(\mathbf{r})$ and we could express the charge density in terms of these single-particle orbitals:

$$\rho(\mathbf{r}) = \sum_{j}^{\text{occup}} \left| \psi_{j}(\mathbf{r}) \right|^{2}$$
(1.35)

The kinetic energy functional would then be simply

$$T_0 = -\frac{1}{2} \sum_{j}^{\infty} \int \psi_j^*(\mathbf{r}) \nabla^2 \psi_j(\mathbf{r}) d\mathbf{r}$$
(1.36)

We can then write out total energy functional as

$$E[\rho(\mathbf{r})] = -\frac{1}{2} \sum_{j}^{\infty} \int \psi_{j}^{*}(\mathbf{r}) \nabla^{2} \psi_{j}(\mathbf{r}) d\mathbf{r}$$

+
$$\frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

+
$$\int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + E_{\text{xc}}[\rho(\mathbf{r})] \qquad (1.37)$$

where we have defined a new functional $E_{\rm xc}[\rho(\mathbf{r})]$ that describes the correction to the kinetic energy relative to that used for noninteracting electrons and that part of the interelectronic repulsion that we do not know. The $E_{\rm xc}[\rho(\mathbf{r})]$ term must, therefore, describe the Coulomb correlation (repulsion between electrons with opposite spin) and the exchange energy (repulsion between electrons with like spin). However, even though we are defining the charge density in terms of noninteracting particles, our treatment is still exact since the Hohenberg–Kohn theorem is valid for any potential. This means that we can express our system of electrons in terms of noninteracting quasiparticles. These quasiparticles will have single-particle orbitals $\psi_j(\mathbf{r})$. The single-particle orbitals are solutions to the Kohn–Sham equations (Kohn and Sham, 1965) that take the form of one-electron Schrödinger equations:

$$\left(-\frac{1}{2}\nabla^2 + v_{\rm xc} + V_{\rm ext}(\mathbf{r})\right)\psi_j(\mathbf{r}) = \varepsilon_j\psi_j(\mathbf{r})$$
(1.38)

with

$$v_{\rm xc} = \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{\rm xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}$$
(1.39)

1.3.2.1 Meaning of Kohn–Sham Eigenvalues

Before discussing the exchange–correlation functional and potential, we should think about the meaning of the Kohn-Sham orbitals and their eigenvalues (energies). Strictly speaking, the Kohn-Sham single-particle orbitals have no actual physical meaning; they are wavefunctions for fictitious particles that give a density from which we can determine the total ground-state energy of a system. However, the Kohn–Sham orbitals will have the same symmetry as the one-electron orbitals obtained in a Hartree–Fock (single determinant) picture. It is common practice to relate Kohn–Sham orbitals and their eigenvalues (energies) to the actual electronic states in a system (e.g., Stowasser and Hoffmann, 1999; Cramer and Turhlar, 2009; Sherman, 2009). However, there is nothing in DFT that formally says this is so. The wavefunction for the collection of Kohn-Sham noninteracting quasiparticles for any system is a single-Slater determinant. However, the actual electronic states of many systems (e.g., FeO, the complex $Fe(H_2O)_6^{2+}$) cannot be described by a single-Slater determinant. This has been a subject of much discussion (e.g., Stowasser and Hoffmann, 1999) but goes beyond the scope of this chapter. We would like, however, to be able to relate the electronic structure of a system to its oxidation-reduction potential (see Chapter 7). In this regard, there is a physical meaning for the Kohn–Sham orbital energies, however, since these relate to the total energy as

$$\varepsilon_i = \left(\frac{\partial E}{\partial n_i}\right)_{j \neq i} \tag{1.40}$$

where E is the total energy of the system and n_i is the occupancy of orbital i; that is, the Kohn–Sham eigenvalues correspond to chemical potentials of the electrons. This is to be compared to the Hartree–Fock orbital energies, which obey Koopman's theorem:

$$\varepsilon_i = E(N+1) - E(N) \tag{1.41}$$

where E(N) is the total energy of the system with N electrons. This means that the energy of the highest occupied orbital will be equal to the first ionization energy of the atom or molecule.

1.3.2.2 Local Density and Generalized Gradient Approximations

Although the Kohn–Sham equations are exact, we cannot solve them for a real multielectronic system because we do not know the exchange–correlation functional $E_{\rm xc}[\rho(\mathbf{r})]$.

The first approximation to $E_{xc}[\rho(\mathbf{r})]$ is to consider the case of a system where the electron density is uniform. For such a system, we can separate the exchange and correlation energy:

$$E_{\rm xc}[\rho(\mathbf{r})] = E_{\rm x}[\rho(\mathbf{r})] + E_{\rm c}[\rho(\mathbf{r})]$$
(1.42)

The exchange energy for a uniform electron gas is

$$E_{\rm x}[\rho(\mathbf{r})] = -\frac{3}{4} (3/\pi)^{1/3} \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$$
(1.43)

There is no analytical expression for the correlation energy $E_c[\rho(\mathbf{r})]$ of a uniform electron gas. However, $E_c[\rho(\mathbf{r})]$ can be estimated using stochastic simulations in the limits of high and low electron density; the resulting correlation energy as a function of electron density have been parameterized in several schemes. A recommended version is that provided by Vosko et al. (1980).

| XC functional | Hartree-Fock | LDA | PW91 | PBE96 | B 3LYP | Experimental ^a |
|---|--|--|--|--|--|--|
| $ \begin{array}{c} R(O-H) \text{ Å} \\ \alpha(HOH)^{\circ} \\ \nu_{3} \\ \nu_{2} \\ \nu_{1} \end{array} $ | 0.9393 107.48 1840 4141 4248 | 0.9714 106.11 1622 3672 3800 | 0.9701 105.13 1671 3658 3779 | 0.9710 105.02 1671 3656 3776 | 0.9626 105.87 1705 3766 3881 | 0.9572 104.52 1595 3657 3756 |

Table 1.1 Geometry and vibrational frequencies of gas-phase water calculated using a 6-311G* basis set with different exchange–correlation functionals.

^a Benedict et al. (1956).

The $E_{\rm xc}[\rho(\mathbf{r})]$ for an electron in uniform electron gas only depends on the charge density at the electron's position. For this reason, we call the uniform electron gas the local density approximation (LDA). The uniform electron gas is a drastic approximation to most chemical systems, but it often works reasonably well. In a real system, $E_{\rm xc}[\rho(\mathbf{r})]$ will depend on some complex way on the electron density at distances away from the electron's position. One way to account for nonuniform charge distributions is to come up with an exchange–correlation functional that depends not only on $\rho(\mathbf{r})$ but also on the gradient of the charge density $\nabla \rho(\mathbf{r})$. This would still be a local functional, but at least it contains some influence from the neighboring density. Functionals of the form $E_{\rm xc}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]$ are known as the generalized gradient approximation (GGA). There are a variety of GGA functionals currently in use (Perdew et al., 1996), and they offer a substantial improvement over the LDA at little extra computational cost. In the past 20 years, there have been many attempts to develop improved approximations for $E_{\rm xc}[\rho(\mathbf{r})]$, and now the user has a choice of many possibilities (Cramer and Turhlar, 2009). It is important that the user be aware of the strengths and weaknesses of the different versions of the $E_{\rm xc}[\rho(\mathbf{r})]$ functionals. To this end, it is prudent to explore how the results of a simulation are dependent upon the choice of exchange-correlation functionals. Table 1.1 shows the calculated geometries and vibrational frequencies of gas-phase water molecule obtained using Hartree-Fock and different exchange-correlation functionals. Hartree-Fock exaggerates the bonding interactions making the OH-bond length too short and the vibrational frequencies too high. The LDA (which includes some correlation energy) is a significant improvement, but the generalized gradient schemes are more accurate. The hybrid scheme of B3LYP (discussed later) is closer to experiment.

1.3.2.3 Self-Interaction Error: Hybrid Functionals

Both the LDA and all versions of the GGA suffer from a major error. Recall that in the Hartree– Fock equation (Eq. 1.28), one of the terms in the exchange summation also serves to correct the Coulomb summation for the term that inadvertently describes an electron interacting with itself. Because both the LDA and GGA give the exact Coulombic term but only an approximate exchange term, the self-interaction error is not fully corrected for in these exchange–correlation functionals. The physical consequence of the self-interaction error is that electrons will repel themselves and over-delocalize. This is not a problem for systems that are metallic in the first place, but for systems with localized electrons, it gives rise to erroneous results. For example, the molecule H_2^+ with one electron should dissociate to give $H^+ + H$. However, all LDA and GGA functionals will cause H_2^+ to dissociate to give $H^{+0.5} + H^{+0.5}$ even if the H atoms are infinitely separated. In mixed-valence systems such as magnetite $\{Fe^{+3}\}_A \{Fe^{+2}Fe^{+3}\}_BO_4$, the self-interaction error will cause the system to have a ground-state configuration $\{Fe^{+3}\}_A \{Fe^{+2.5}Fe^{+2.5}\}_BO_4$. More generally, band gaps in solids and the HOMO–LUMO gaps (the gap between the highest occupied and lowest unoccupied molecular orbitals) in molecules are underestimated (Perdew, 1986; Cramer and Truhlar, 2009).

Within DFT, several methods have been developed to approximately correct for the selfinteraction error (e.g., Perdew and Zunger, 1981). Recall, however, that the Hartree–Fock equations correctly accounts for the self-interaction correction. One approach is to use "hybrid functionals" that mix in some degree of Hartree–Fock exchange with a DFT exchange–correlation functional. The most popular in this regard is the B3LYP functional

$$E_{\rm xc}[\rho(r)] = E_{\rm X}^{\rm LDA} + a_0 \left(E_{\rm X}^{\rm HF} - E_{\rm X}^{\rm LDA} \right) + a_{\rm X} \left(E_{\rm X}^{\rm GGA} - E_{\rm X}^{\rm LDA} \right) + E_{\rm C}^{\rm LDA} + a_{\rm C} \left(E_{\rm C}^{\rm GGA} - E_{\rm C}^{\rm LDA} \right)$$
(1.44)

with

$$a_0 = 0.2, a_X = 0.72, a_C = 0.81$$

where E_X^{HF} is the Hartree–Fock exchange, E_X^{LDA} is the LDA exchange, E_X^{GGA} is the GGA exchange (Becke, 1993), E_C^{LDA} is the LDA correlation energy of Vosko et al. (1980), and E_C^{GGA} is the GGA correlation of (Lee et al., 1988). The parameters are variable and one can choose how much Hartree–Fock exchange to mix in. As can be seen in Table 1.1, the B3LYP calculations are an improvement over those done with the GGA functional.

1.4 Bonding in Molecules and Solids

1.4.1 The Born–Oppenheimer Approximation

Consider the hydrogen molecule H_2 (Figure 1.4). This molecule consists of two nuclei A and B located at \mathbf{R}_A and \mathbf{R}_B and two electrons located at \mathbf{r}_1 and \mathbf{r}_2 . The Hamiltonian for this system is

$$\hat{H} = -\frac{1}{2M} \left(\nabla_{A}^{2} + \nabla_{B}^{2} \right) - \frac{1}{2} \left(\nabla_{1}^{2} + \nabla_{2}^{2} \right) + \left(\frac{1}{|\mathbf{R}_{A} - \mathbf{R}_{B}|} - \frac{1}{|\mathbf{r}_{1} - \mathbf{R}_{A}|} - \frac{1}{|\mathbf{r}_{1} - \mathbf{R}_{B}|} - \frac{1}{|\mathbf{r}_{2} - \mathbf{R}_{A}|} - \frac{1}{|\mathbf{r}_{2} - \mathbf{R}_{B}|} + \frac{1}{|\mathbf{r}_{1} - \mathbf{r}_{2}|} \right)$$
(1.45)

The first two terms are the kinetic energies of the nuclei and the electrons. However, the mass of each nucleus is 1848 times greater than the mass of each electron. Accordingly, the electron–nuclear interactions cannot change the kinetic energies of the nuclei. The *Born–Oppenheimer approximation* is to neglect the kinetic energy of the nuclei and write a Hamiltonian that is a function of the nuclear coordinates. The Schrödinger equation for the electrons is then:

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_1^2 + V(\mathbf{R}_A, \mathbf{R}_B)\right)\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_A, \mathbf{R}_B) = E_n(\mathbf{R}_A, \mathbf{R}_B)\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_A, \mathbf{R}_B)$$
(1.46)

What we have done is to remove the nuclear motion and defined electronic states with energies $E_n(\mathbf{R}_A, \mathbf{R}_B)$ that are a function of the nuclear positions.

For practical problems, rather than to deal with the multielectronic Schrödinger equation, we will use DFT and solve the Kohn–Sham equations at a fixed set of nuclear coordinates $\{\mathbf{R}\}$:

$$\left(-\frac{1}{2}\nabla^2 + v_{\mathrm{xc}} + V_{\mathrm{ext}}(\mathbf{r},\{\mathbf{R}\})\right)\psi_j(\mathbf{r}) = \varepsilon_j(\{\mathbf{R}\})\psi_j(\mathbf{r},\{\mathbf{R}\})$$
(1.47)

The total electronic energy $E({\bf R})$ is evaluated in DFT as follows:

$$E(\{\mathbf{R}\}) = \sum_{i}^{N} \varepsilon_{i}(\{\mathbf{R}\}) - V_{\mathbf{C}}(\{\mathbf{R}\}) + E_{\mathbf{x}\mathbf{c}}$$
(1.48)

From such calculations, we can minimize the total energy $E(\{\mathbf{R}\})$ with respect to $\{\mathbf{R}\}$ and predict equilibrium structures of molecules and crystals. When we neglect the energy associated with the nuclear motion, the energy we calculate is referred to as the *static* energy of the system. So, it is common to use codes to predict the static energies of molecules and crystals; however, the static energies give energy differences that neglect the zero-point and thermal energies of the system. We can correct for this once (at least in the harmonic approximation) if we calculate the vibrational modes of the system.

1.4.2 Basis Sets and the Linear Combination of Atomic Orbital Approximation

In principle, we could solve the Kohn–Sham equation for a molecule or crystal numerically. However, this would be unwieldy. In nearly all codes used in computational chemistry and solid-state physics, the electronic wavefunctions $\psi_j(\mathbf{r}, \{\mathbf{R}\})$ are constructed from a *basis set* of simple functions $\phi_i(\mathbf{r}, \{\mathbf{R}\})$:

$$\psi_j(\mathbf{r},\{\mathbf{R}\}) = \sum_k c_k \phi_k(\mathbf{r},\{\mathbf{R}\})$$
(1.49)

An obvious choice of a basis set would be functions that approximate the atomic orbitals of the atoms that make up our molecule. This is the way we think about chemical bonding anyway, so it also offers a very compelling conceptual framework. In this scheme, the one-electron molecular orbitals $\psi_j(\mathbf{r}, \{\mathbf{R}\})$ are expressed as a linear combination of atomic orbitals. By atomic orbitals, we mean functions that are centered on the different atoms and have the same n, l, m_l quantum numbers that a hydrogenic wavefunction would have. If we express our molecular wavefunctions this way, then our solution to the Kohn–Sham equation is obtained by variationally minimizing the energy of the system with respect to the coefficients c_k in the expansion, subject to the constraint that the wavefunction is normalized:

$$\int_{0}^{\infty} \psi_j^*(\mathbf{r}, \{\mathbf{R}\}) \psi_j(\mathbf{r}, \{\mathbf{R}\}) d\mathbf{r} = 1$$
(1.50)

(The normalization requirement simply means that the probability of finding the electron somewhere must be 1.)

The choice of basis functions is crucial, and it is imperative that the user of any quantum chemistry code be aware of the adequacy of the basis set for the problem at hand. According to the variational principle, the more functions we use, the more accurate our total energy will be since we will have more coefficients c_k that we can minimize our total energy with respect to. However, with the more coefficients we have, the more computationally intensive our problem will be. The basis set, therefore, must be something that allows a good approximation with as few parameters as possible. One starting point for a basis set is to use atomic orbitals that are approximately expressed using Slater functions:

$$\phi_{nlm}(\mathbf{r}) = r^{n-1} e^{-\varsigma r} Y_l^m(\mathbf{r}) \tag{1.51}$$

where $Y_l^m(\mathbf{r})$ is the spherical harmonic function that describes the angular shape of the wavefunction and ς is a constant that describes the "effective charge" of the nucleus (i.e., the nuclear charge that the electron sees after it has been screened by the other electrons). Note that the Slater function has a similar form to that of the actual hydrogen orbitals described earlier. However, the adjustable screening parameter ς is needed to approximately correct for the presence of the other electrons.

Slater functions, however, are technically awkward to use when solving for the various multicenter integrals that occur in the Hartree–Fock or Kohn–Sham equations. Few computational quantum chemistry codes actually use Slater Functions as basis sets, therefore. One notable exception is the Amsterdam density functional (ADF) code (te Velde et al., 2001). Most other codes, such as GAUSSIAN (Frisch et al., 2009) and NWCHEM (Valiev et al., 2010), use basis functions that express the atomic orbital wavefunctions in terms of Gaussian functions. The reason for this is that the product of two Gaussian functions is itself a Gaussian function. Hence, the evaluation of the Coulomb and exchange terms in the Hartree–Fock or Kohn–Sham equations becomes much simpler.

Early work approximated the Slater-type orbitals in terms of several Gaussian functions. This lead to basis sets referred to as "STO-NG" where STO means Slater-type orbital and NG means that it was approximated by N Gaussian functions. These basis sets were minimal in that they expressed each atomic orbital in terms of a single function. This is not a bad approximation for the core electrons (e.g., the 1s, 2s, and 2p orbitals in second row elements and transition metals). However, the valence electrons need a much more flexible basis set with more variational degrees of freedom if they are to be used in a range of bonding environments and to describe atoms in different oxidation states. To this end, split-valence basis sets were developed. Such a basis set will express a valence atomic orbital in terms of several independent functions (Gaussians or Slater functions). This provides more variational degrees of freedom.

For most routine calculations on systems of geochemical significance, a split-valence basis set such as 6-31G* is reasonably adequate. For oxygen, with an electron configurations $1s^22s^22p^4$, this basis set would represent the 1s levels with six Gaussian functions, but the 2s and 2p levels would be represented by one function made up of three Gaussians and one function made up of a single Gaussian. Tables 1.2 and 1.3 show the geometries and vibrational modes of gas-phase water molecule calculated using different basis sets and using the B3LYP exchange–correlation functional. A minimal basis set such as STO-3G or SZ gives poor results. The split-valence basis sets give significant improvement albeit with diminishing returns as more functions are added and with significant increases in computational cost.

| Basis set | STO-3G | 6-31G | 6-31G* | 6-311G* | cc-PVTZ | Expt. |
|-----------------------|--------|--------|--------|---------|---------|--------|
| R(O–H) Å | 1.0309 | 0.9759 | 0.9687 | 0.9626 | 0.9611 | 0.9572 |
| $\alpha(HOH)^{\circ}$ | 96.73 | 108.30 | 103.65 | 105.87 | 104.56 | 104.52 |
| ν_3 | 1977 | 1619 | 1713 | 1705 | 1640 | 1595 |
| ν_2 | 3571 | 3616 | 3727 | 3766 | 3803 | 3657 |
| ν_1 | 3793 | 3781 | 3849 | 3881 | 3905 | 3756 |
| Time | 3.9 | 6.9 | 5.9 | 7.2 | 17.3 | |

Table 1.2 Geometry and vibrational frequencies of gas-phase water calculated using a B3LYP functional with different Gaussian basis sets.

| Basis set | SZ | DZ | DZP | TZP | TZ2P | Expt. |
|---|-------|--------|--------|--------|--------|--------|
| $ \begin{array}{c} R(O-H) \ \AA \\ \alpha(HOH)^{\circ} \\ \nu_{3} \\ \nu_{2} \\ \nu_{1} \end{array} $ | 1.025 | 0.983 | 0.968 | 0.965 | 0.963 | 0.9572 |
| | 97.08 | 109.70 | 104.59 | 104.45 | 104.89 | 104.52 |
| | 2006 | 1566 | 1623 | 1623 | 1606 | 1595 |
| | 3551 | 3533 | 3727 | 3780 | 3800 | 3657 |
| | 3776 | 3700 | 3826 | 3874 | 3891 | 3756 |

Table 1.3 Geometry and vibrational frequencies of gas-phase water calculated using a B3LYP functional with different Slater orbital basis sets.

The basis sets we have discussed so far (Slater orbitals or Gaussians) are localized basis sets. That is, each function is centered about some atom. This is an obvious choice for systems where the electrons are more-or-less localized to specific atoms. In metallic systems, however, the electrons are delocalized throughout the crystal. It might be more efficient to start with a basis set that has delocalized functions. A completely delocalized function is a plane wave

$$\phi_{\mathbf{g}} = e^{i\mathbf{g}\mathbf{r}} \tag{1.52}$$

However, we can describe any function in terms of these plane wave (e.g., as in a Fourier series expansion). So, a linear combination of plane waves could also be used to describe fairly localized states:

$$\psi(\mathbf{r}) = \sum_{\mathbf{g}=0}^{g = \text{cutoff}} c_{\mathbf{g}} e^{i\mathbf{g}\mathbf{r}}$$
(1.53)

Moreover, wavefunctions expressed as plane-wave expansions are computationally convenient. The problem with plane waves, however, is that if we need to describe a highly localized orbital (e.g., a 1s, 2s core electrons of an element), then we need a very large number of plane waves. We get around this by ignoring the core-electrons in a system and using a *pseudopotential*. A pseudopotential is something we add to the Kohn–Sham equation to trick the valence electrons into thinking that the core electrons are present! There are a number of different types of pseudopotentials that are available. The Vanderbilt ultrasoft pseudopotentials (Vanderbilt, 1990) are especially useful for oxygen-based systems (i.e., most geochemical systems) as they enable accurate calculations with small values of the plane-wave cutoff for g.

1.4.3 Periodic Boundary Conditions

Most systems of interest in geochemistry and geophysics are crystalline phases or bulk liquids. For a crystalline phase, the potential due to the atomic nuclei has a periodic (translational) symmetry. That is, the potential in one unit cell is repeated in all of the unit cells. If a system is periodic with a translational repeat G, then the potential due to the nuclei must also be periodic

$$V(\mathbf{R}) = V(\mathbf{R} + \mathbf{G}) \tag{1.54}$$

The wavefunction must have the same symmetry as the potential, so

$$\boldsymbol{\psi}(\mathbf{r}) = \boldsymbol{\psi}(\mathbf{r} + \mathbf{G}) \tag{1.55}$$

Bloch's theorem states that any wavefunction that results from a periodic potential must be of the form

$$\psi_k(\mathbf{r}) = u(\mathbf{r})e^{i\mathbf{k}\mathbf{r}} \tag{1.56}$$

where \mathbf{k} is a wave vector that can take on a continuous range of values (it is not quantized if the crystal is infinite). Do not confuse the Bloch wavefunction with the plane-wave expansion described earlier. Usually both are implemented together so we have both the \mathbf{k} -vectors to describe the wavefunction and the \mathbf{g} -vectors to describe the elements of the plane-wave basis set. However, the range of values that \mathbf{k} can have is limited. Suppose, for the sake of simplicity, that we have a one-dimensional system that is periodic; \mathbf{G} is the translation vector. Then

$$e^{i\mathbf{k}(\mathbf{r}+\mathbf{G})} = e^{i\mathbf{k}\mathbf{r}} \tag{1.57}$$

or

$$e^{i\mathbf{kG}} = 1 \tag{1.58}$$

Hence, $\mathbf{kG} = 2\pi$ or $|\mathbf{k}| = 2\pi/|\mathbf{G}|$. We say that **k** is a vector in *reciprocal space*. Now, all the **k** values from 0 to $2\pi/|\mathbf{G}|$ give unique wavefunctions, but for **k**-values greater than $2\pi/|\mathbf{G}|$, the wavefunctions simply repeat. We call the region of reciprocal space where $0 < k < 2\pi/|\mathbf{G}|$ (or equivalently $-\pi/|\mathbf{G}| < k < \pi/|\mathbf{G}|$) the *Brillouin zone*. In a periodic system, all we need to do is to solve for the wavefunctions in the Brillouin zone, and we have all of the information we need to describe the periodic system.

Periodic boundary conditions are not only used for crystalline solids; they can also be used to describe liquids when we do not want to inadvertently have artificial phase boundaries (e.g., if we tried to simulate a bulk liquid with a finite cluster of atoms, we would have an unwanted liquid–vacuum interface at the edge of our cluster). In a liquid simulation, we can define a unit cell (as large as our computer resources allow) and have that cell repeat in three dimensions. If we are doing a dynamical simulation (discussed later), then whenever one atom leaves the unit cell, another atom enters the unit cell on the opposite side.

1.4.4 Nuclear Motions and Vibrational Modes

For most problems in geochemistry and geophysics, we are only interested in the lowest energy electronic state or ground state (E_0) since excited electronic states are several eV (hundreds of kJ/mol) higher in energy and are not thermally accessible.

(Exceptions might include spin pairing in the lower mantle and photochemical processes in the environment.) Even if we restrict ourselves to the ground electronic state, however, the quantum states associated with the nuclear motions are thermally accessible and are responsible for most of the thermal properties of earth materials (see Chapter 3).

Moreover, in many problems in geochemistry and mineralogy, we are interested in knowing the vibrational modes of minerals and metal–ligand complexes in aqueous solutions so that we can interpret infrared and Raman spectra (see Chapter 10).

We can obtain a Schrödinger equation for the nuclear motion of the atoms in a molecule or crystal. Recall that our wavefunction $\Psi({\mathbf{r}}, {\mathbf{R}})$ is both a function of the electronic coordinates ${\mathbf{r}}$ and the nuclear coordinates ${\mathbf{R}}$. We used the Born–Oppenheimer approximation to write

$$\hat{H}_{\text{elec}}\Psi(\{\mathbf{r}\},\{\mathbf{R}\}) = E(\{\mathbf{R}\})\Psi(\{\mathbf{r}\},\{\mathbf{R}\})$$
(1.59)

The assumption here is that the electronic state of the system does not change as the nuclei move.

$$\Psi({\mathbf{r}},{\mathbf{R}}) = \chi({\mathbf{R}})\Psi({\mathbf{r}})$$
(1.60)

This means that the electrons and nuclei do not exchange kinetic energy. From this, we get a Schrödinger equation for the nuclear motion:

$$\left(-\sum_{k}^{N}\frac{1}{2M_{k}}\nabla_{k}^{2}+E(\{\mathbf{R}\})\right)\chi(\{\mathbf{R}\})=W\chi(\{\mathbf{R}\})$$
(1.61)

The potential energy of the nuclei as a function of the nuclear coordinates $\{\mathbf{R}\}$ is given by the total electronic energy $E(\{\mathbf{R}\})$. In a bound system (e.g., a molecule or crystal), this means that for a given electronic state $E(\{\mathbf{R}\})$, the motion of the nuclei will yield a set of quantized vibrational (or rotational) modes with quantized energies W_j . If we know these energies, we could calculate thermodynamic quantities of the system using statistical mechanics (discussed later and also in Chapter 3).

In practice, we do not solve the nuclear Schrödinger equation explicitly as it is too complex. Instead, we assume that, in the vicinity of the equilibrium positions of the atoms $\{\mathbf{R}_0\}$, the nuclear motions are approximately those of a harmonic oscillator with respect to each coordinate \mathbf{R} . So, along one coordinate $\mathbf{R} = |\mathbf{R}|$,

$$E(R-R_0) = \frac{1}{2}k(R-R_0)^2$$
(1.62)

where k is the force constant along that coordinate. The Schrödinger equation for a harmonic oscillator is solvable and yields quantized energies:

$$W_j = \left(j + \frac{1}{2}\right)\hbar\omega \tag{1.63}$$

where $j = \{0, 1, 2, 3, ...\}$ and ω is the angular frequency

$$\omega = \sqrt{\frac{k}{\mu}} \tag{1.64}$$

In a molecule or crystalline solid, many vibrational modes are equivalent to each other because of symmetry. The unique vibrational modes can be obtained by finding the eigenvalues and eigenfunctions of the matrix of force constants (the dynamical matrix). All of the standard quantum chemistry codes do this automatically.

1.5 From Quantum Chemistry to Thermodynamics

Using computational quantum chemistry, we can calculate the total energies of a system as a function of the nuclear coordinates. We can also calculate the energies of the vibrational modes in a molecule or crystal. Ultimately, however, we would like to relate these quantities to macroscopic thermodynamic properties. The macroscopic thermodynamic properties of a system, however, reflect the entropy that a system has. Suppose that a system (e.g., a gas, an aqueous solution, or a mineral) is at a particular thermodynamic state. This state could be defined by any three of the variables N, V, T, P, E and μ , where N is the number of particles, V is the volume, T is the temperature, P is the pressure, E is the total energy, and μ is the chemical potential. We call this a *macrostate*. Associated with that macrostate are a nearly countless number of *microstates*. A microstate of a system is one of the particular arrangements of atomic positions and momenta that are possible within that macrostate of a system. The set of microstates that correspond to a particular macrostate of a system is referred to as a *thermodynamic ensemble*. The probability of a system being in a particular microstate *i* that has an energy E_i is

$$P_i = \frac{1}{Z} e^{-\beta E_i} \tag{1.65}$$

where $\beta = k_{\rm B}T$ and Z is the partition function

$$Z = \sum_{i} e^{-\beta E_i} \tag{1.66}$$

From this, we can calculate the average value (or *expectation value*) $\langle O \rangle$ of any property O of the system

$$\langle O \rangle = \frac{1}{Z} \sum_{i} O_{i} e^{-\beta E_{i}}$$
(1.67)

That is, we simply take a weighted average of the values that O has at each microstate. We can now derive expressions for many thermodynamic quantities. The internal energy U is simply the average energy of all the microstate and works out to be

$$U = \langle E \rangle = \frac{\partial}{\partial \beta} \ln(Z) \tag{1.68}$$

The pressure is

$$P = \beta \left(\frac{\partial \ln(Z)}{\partial V}\right)_{N,T}$$
(1.69)

The Helmholtz free energy is

$$A = \beta \ln(Z) \tag{1.70}$$

Hence, we could use quantum mechanics to evaluate the energy E_i of each microstate and then calculate the partition function for the system. Then we could calculate thermodynamic quantities. The problem we are up against, however, is that the number of microstates in a thermodynamic ensemble is incomprehensibly large. The entropy (S) of a system in a particular macrostate is a measure of the number of microstates Ω consistent with that macrostate:

$$S = k_{\rm B} \ln \Omega \tag{1.71}$$

Consider ice at 273 K; the absolute entropy is 41.3 J/(mol K). Since Boltzmann's constant is 1.4×10^{-23} J/K, we find that the number Ω of microstates (per mole of ice) is $\ln \Omega = 3 \times 10^{22}$. It follows that evaluating the partition function for ice is impossible. However, in crystalline ice, the periodic symmetry means that the way that the vibrational modes are coupled to each other is constrained by the

periodic symmetry of the crystal (every vibrational mode must have the same periodicity of the crystal). Just as for the electronic states, the allowed vibrational modes in a crystal are enumerated using the concept of the *Brillouin zone*. In practice, we can evaluate all of the vibrational modes of a crystalline solid by simply calculating the vibrational modes at selected points in the Brillouin zone and then interpolating between them. The partition function for the crystal would then be evaluated by integrating over the vibrational modes. This methodology is known as *lattice dynamics* and is implemented at the *ab initio* level using codes such as CRYSTAL (Dovesi et al., 2014), VASP (Hafner, 2008), CASTEP (Clark et al., 2005), and SIESTA (Soler et al., 2002).

In the case of an ideal gas, we also have a tractable problem. Each molecule in the ideal gas has only a small number of vibrational/rotational modes, and these are not coupled with the vibrational/ rotational modes of any of the other molecules in the gas. Hence, if we knew the vibrational/rotational modes of a single molecule, we can calculate the partition function for a single molecule and, since the molecules are uncoupled, we can calculate the partition function for one mole of an ideal gas phase by simply multiplying by Avogadro's number.

In the case of a liquid (e.g., a silicate melt or an aqueous solution), however, directly evaluating the partition function is impossible. All of the vibrational/rotational and translational modes are coupled to each other, and there is no symmetry to guide us. However, even though there are an uncountable number of microstates, some of them are far more probable than others. (For example, the microstates where one atom has all of the kinetic energy, but all the other atoms have none, are of no significant probability of occurring.) If we only sampled the most probable microstates, we might be able to estimate thermodynamic properties. This can be done using Monte Carlo simulations or by molecular dynamics (Allen and Tildesley, 1987; Haile, 1992).

1.5.1 Molecular Dynamics

Consider a box in which we have placed N atoms, each with mass \mathbf{m}_j and coordinate \mathbf{R}_j . Each atom has a kinetic energy. Each atom also has a potential energy resulting from the attractive and repulsive interactions with the other atoms in the box. If we ignore the quantized nature of the motions of the atomic nuclei, then the equations of motion for the atoms would be given by Newton's second law:

$$m_j \frac{d^2 \mathbf{R}_j}{dt^2} = \mathbf{F}_j = -\nabla_j E(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) = m_j \mathbf{a}_j$$
(1.72)

where \mathbf{a}_j is the acceleration of atom *j* and $E(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N)$ is the potential energy of the system as a function of the atomic coordinates of the atoms. If we knew the interatomic potential function $E(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_N)$, we could integrate the equation of motion by finite differences. To do this, we discretize the problem with respect to time *t*:

$$t_n = t_0 + n\Delta t$$

$$\left(\mathbf{R}_j\right)_n = \mathbf{R}_j(t_n) \qquad (1.73)$$

$$\left(\mathbf{v}_j\right)_n = \mathbf{v}_j(t_n)$$

where n = 0, 1, 2, 3, ... and Δt is the time interval between steps *n* and n + 1. We need to choose a small time step (e.g., $\Delta t = 0.0025$ fs) to ensure that we accurately integrate the equation of motion. A commonly used method for the integration is the Verlet algorithm (Allen and Tildesley, 1987):

$$(\mathbf{v}_{j})_{n+1} = (\mathbf{v}_{j})_{n} + \frac{1}{2} ((a_{j})_{n} + (a_{j})_{n+1}) \Delta t$$

$$(\mathbf{R}_{j})_{n+1} = (\mathbf{R}_{j})_{n} + (\mathbf{v}_{j})_{n} \Delta t + \frac{1}{2} (a_{j})_{n} \Delta t^{2}$$

$$(1.74)$$

So, we start with a set of atoms with initial positions and velocities. We calculate the forces on those atoms from all the other interactomic interactions; we then move the atoms under those forces (applied for a fraction of a femtosecond) to obtain the new positions and velocities. We repeat this for many time steps (e.g., millions) and watch how the system will evolve. Suppose, for example, our box consisted of 100 water molecules along with 10 Na and Cl atoms. The ground electronic state of this system would yield a system where the Na atoms become Na⁺ ions and the Cl atoms become Cl⁻ ions. As our simulation evolves, we would find that the atoms are rapidly moving in a chaotic motion but, on average, the Na⁺ ions are surrounded by six water molecules as are the Cl⁻ ions. Water molecules may be moving in and out of the solvation shell surrounding the Na⁺ and Cl⁻, but usually there are six waters surrounding each ion. The water molecules themselves form a structure that reflects the hydrogen bonding interactions. However, the hydrogen bonding structure is constantly breaking down and reforming. Sometimes the Na⁺ and Cl⁻ are so attracted to each other that they each discard one of their solvation waters and form an inner-sphere Na-Cl ion pair. This pair may last for a few picoseconds and then dissociate. Simulations like this can provide us a great deal of molecular-scale insight on the nature of geochemically important systems such as hydrothermal fluids and silicate melts (e.g., Sherman, 2007; Mei et al., 2013, 2015). These simulations can also give us thermodynamic information using techniques such as thermodynamic integration or constrained molecular dynamics (Sprik and Ciccotti, 1998).

Molecular dynamics provides a way to estimate thermodynamic properties of liquids without needing to directly calculate the partition function. The trick is that we can estimate the ensemble average $\langle O \rangle$ of a quantity by taking the time average of that quantity during a simulation. This is known as the *ergodic hypothesis*:

$$\langle O \rangle = \frac{1}{Z} \int_{i}^{I} O(r,p) e^{-E(r,p)/kT} dr dp = \frac{1}{\tau} \int_{0}^{t} O(t) dt$$
(1.75)

In the course of our simulation, we are sampling the most probable microstates. As we keep sampling, our time average quantity will get closer and closer to the ensemble average.

There are several types of thermodynamic ensembles: if we constrain N, V and E, we have a *micro-canonical ensemble*; this is the ensemble that would result if we solved the equations of motion as described earlier. However, we could also constrain N, V, and T to yield a *canonical ensemble*. To do this, we need to impose a thermostat on the equations of motion to maintain the temperature (Nose, 1984; Hoover, 1985). We could also constrain N, P, and T to yield an *isobaric-isothermal ensemble*; for this, we need include a barostat (Andersen, 1980). Such simulations are more challenging and it is more common to use the constant-volume NVT ensemble. Because we want to constrain the simulations, it is more convenient to recast the problem using Lagrangian mechanics (this will also enable us to discuss *ab initio* MD using the Car–Parrinello method given later). The Lagrangian of a system is the difference between the kinetic and potential energies:

$$L = T - V \tag{1.76}$$

Or, for a collection of atoms, we can express the Lagrangian as follows:

$$L = \sum_{j} \frac{1}{2} M_{j} \left| \frac{d\mathbf{R}_{j}}{dt} \right|^{2} - E\left[\left\{ \mathbf{R}_{j} \right\} \right] + \text{constraints}$$
(1.77)

26 Molecular Modeling of Geochemical Reactions

In Lagrangian Mechanics, the equation of motion is

$$\frac{d}{dt} \left(\frac{\partial L}{\partial R'_j} \right) - \left(\frac{\partial L}{\partial R_j} \right) = 0 \tag{1.78}$$

which we integrate using finite differences as in the Verlet algorithm.

The fundamental problem with setting up a molecular dynamics simulation is knowing the interatomic potential function $E({\mathbf{R}})$. Until recently, nearly all molecular dynamics simulations were based on using empirically derived classical functions that describe the attractive and repulsive potentials between atoms. Usually, these functions considered only pair-wise interactions so that

$$E(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) = \sum_{ij} E_{ij} \left(\left| \mathbf{R}_j - \mathbf{R}_i \right| \right)$$
(1.79)

This is a very drastic approximation. In our NaCl solution, for example, it means that the interaction between a Na atom and a water molecule is independent of what that water molecule is bonded to. Nevertheless, simulations using these types of pair-wise potentials often give excellent results (Smith and Dang, 1994)! In particular, they seem to work well for highly ionic systems. However, for many systems (e.g., complexation of transition metals in aqueous solutions) this approach usually fails. More elaborate three- and four-body potentials can be developed to cope with conformational changes in covalent molecules. Such potentials play an important role in modeling conformational structures in proteins (Ponder and Case, 2003).

Ultimately, however, the interactions between atoms must be described using quantum mechanics and must be evaluated in a self-consistent manner. This means that for every positional configuration at each time step in our simulation, we must solve the Schrödinger equation (or, more likely, the Kohn–Sham equation). This approach is known as *ab initio molecular dynamics*. If we do this, we can evaluate the force on each atom using the Hellmann–Feynman theorem:

$$F_{R_j} = -\frac{\partial E}{\partial \mathbf{R}_j} = \int \Psi^* \frac{d\hat{H}}{d\mathbf{R}_j} \Psi d\mathbf{r}$$
(1.80)

Here, *d***r** means that we are taking the integral over all the volume. Note that, even if we do this, we can still take those quantum mechanically derived forces and still carry on the simulation using classical (Newtonian) mechanics for the nuclear motion. This is usually a safe approximation because the spacings between the quantum levels of the nuclear motions in a liquid are very small. Intramolecular vibrations, in particular O–H bonds, however, will be in error as the large zero-point energy will be neglected.

Even if we neglect the quantized nature of the nuclear motion, solving the Kohn–Sham equation for the electronic motion to yield the correct interatomic forces at each time step is a formidable task. However, for small systems with modern supercomputer facilities, we are now at a point where geochemically interesting simulations can be done.

There are two approaches to *ab initio* molecular dynamics: the first approach is to simply solve the Kohn–Sham equation at each time step and evaluate the forces using the Hellman–Feynman theorem. At each time step, therefore, we bring the system to the ground electronic state. This method is known as Born–Oppenheimer MD and is used, for example, in the code CASTEP (Clark et al., 2005). The advantage of this approach is that it is very stable; however, it is computationally demanding.

The second approach to *ab initio* molecular dynamics is that developed by Car and Parrinello (1985). Consider what is happening in an *ab initio* MD simulation: as the nuclei move, the wavefunction for the system (as expressed in terms of a set of one-electron orbitals) will change in response to the new atomic positions. To calculate how the wavefunction changes, the Car–Parrinello method incorporates the one-electron orbitals into the dynamics of the system. To do this, we give the one-electron orbitals a fictitious mass (μ) and a fictitious kinetic energy. The Lagrangian therefore becomes

$$L = \frac{1}{2} \left(\sum_{j}^{\text{nuclei}} M_j \left(\frac{d\mathbf{R}_j}{dt} \right)^2 + \mu \sum_{i}^{\text{orbitals}} \int \left| \frac{d\psi_i}{dt} \right| dr \right) - E\left[\{\psi_i\}, \{\mathbf{R}_j\} \right]$$
(1.81)

Note that, if the fictitious mass $\mu \rightarrow 0$, we approach the Born–Oppenheimer molecular dynamics. We impose the constraint that the one-electron orbitals are orthogonal (orthonormal):

$$\int \boldsymbol{\psi}_{i}^{*}(\mathbf{r},t) \int \boldsymbol{\psi}_{k}(\mathbf{r},t) d\mathbf{r} = \delta_{ik}$$
(1.82)

We then have equations of motion for the nuclei and the wavefunctions:

$$M_{j}\frac{d^{2}\mathbf{R}_{j}}{dt^{2}} = -\nabla_{j}E\left[\{\psi_{i}\},\{\mathbf{R}_{j}\}\right] + \sum_{ik}\Lambda_{ik}\frac{d}{d\mathbf{R}_{j}}\int\psi_{i}^{*}\psi_{k}d\mathbf{r}$$

$$\mu\frac{d^{2}\psi_{i}}{dt^{2}} = -\frac{\delta E}{\delta\psi_{i}^{*}} + \sum_{k}^{\text{orbitals}}\Lambda_{ik}\psi_{k}$$
(1.83)

where Λ_{ik} are the Lagrange multipliers for the orthonormalization constraint. The fictitious electron mass is chosen to be between 400 and 800 a.u. In typical simulations, a time step of 5 a.u. (0.12 fs) is reasonable. The Car–Parrinello method is implemented in the CPMD code (Marx and Hutter, 2009).

1.6 Available Quantum Chemistry Codes and Their Applications

Table 1.4 lists some of the more commonly used quantum chemistry codes and describes the level of theory (Hartree–Fock vs. DFT and Hybrid schemes) and the types of basis sets they employ. Many of these codes are freely available and most are well-documented. All of the codes can do static total energy calculations (e.g., energy as a function of geometry), geometry optimizations and the calculations of vibrational modes. Calculations on finite molecules (e.g., using GAUSSIAN or ADF) can be used to predict isotopic fractionation reactions (e.g., Jarzecki et al., 2004; Tossell, 2005; Rustad et al., 2010a, 2010b; Sherman, 2013) in gas-phase clusters. Usually, the calculation of thermodynamic quantities from vibrational modes is done automatically. Calculations on periodic systems can be used, for example, to predict phase transitions between solid minerals. Some of the periodic codes (e.g., VASP and CPMD) are primarily used for *ab initio* molecular dynamics simulations on liquids. Such calculations can be used to predict the properties of silicate melts in the Earth's interior (e.g., Karki and Stixrude, 2010) and metal–ligand complexation reactions in hydrothermal fluids (e.g., Mei et al., 2013).

| Code | Basis set | Systems | Theory | Capabilities | Access and source URL |
|---------------------|-----------------------------|---------------------|----------------------------------|--|--|
| GAUSSIAN | Localized Gaussian | Finite | HF, DFT, and advanced | Molecular structures, energetics, and properties | Commercial www .gaussian. com |
| ADF | Slater orbitals | Finite | HF, DFT, and hybrid | Molecular structures, energetics, and properties | Commercial www.scm |
| GAMMES | Localized Gaussian | Finite | HF, DFT, and advanced | Molecular structures, energetics, and properties | Free upon registration www.msg .ameslab |
| NWCHEM | Gaussian and plane waves | Finite and periodic | HF, DFT, hybrid, and advanced | Structures, energetics, and properties of mole- cules and periodic systems. BO molecular dynamics | Open source www .nwchem-sw .org |
| CRYSTAL | Localized Gaussian | Periodic | HF, DFT, and hybrid | Structures, energetics, and properties of peri- odic systems (crystalline solids and two- dimensional slabs) | Commercial (free to UK) www.crystal .unito.it |
| CPMD | Plane waves | Periodic | DFT | CP and BO molecular dynamics | Free upon registering |
| VASP | Plane waves | Periodic | HF, DFT, hybrids | Energetics and properties of periodic systems. BO molecular dynamics | Commercial www vasp.at |
| Quantum Espresso | Plane waves | Periodic | DFT | | Open source www .quantum- espresso.org |
| Abinit | Plane waves | Periodic | DFT LSD + U | Molecular and periodic systems. BO molecular dynamics | Open source www.abinit |
| CP2K (Quickstep) | Gaussian + plane waves | Periodic | HF, DFT, and hybrid | Molecular and periodic systems. BO molecular dynamics | Open source www.cp2k |
| CASTEP | Plane waves | Periodic | DFT | Energetics and properties of periodic systems. BO molecular dynamics | Commercial (free to UK) www.castep .org |

Table 1.4 Examples of current quantum chemistry software.

References

Allen M. P. and Tildesley D. J. (1987) *Computer Simulation of Liquids*, Oxford University Press, New York. Andersen H. C. (1980) Molecular dynamics simulations at constant pressure and/or temperature. *J. Chem. Phys.* **72**, 2384–2393.