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

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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.

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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
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 \textit{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\textsubscript{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 a set of postulates:

Postulate 1:
A system (e.g., an atom, molecule or, really, anything) is described by a wavefunction \( \Psi(r_1, r_2, \ldots, r_N, t) \) over the coordinates \( \{r_N\} \), 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 \( r_1, r_2, \ldots, r_N \) at a time \( t \) is \( |\Psi(r_1, r_2, \ldots, r_N, t)|^2 \).

Postulate 2:
For every observable (measurable) property \( \lambda \) of the system, there corresponds a mathematical operator \( \hat{L} \) that acts on the wavefunction.

Mathematically, this is expressed as follows:

\[
\hat{L}\Psi = \lambda \Psi \tag{1.1}
\]

\( \Psi \) is an eigenfunction of the operator \( \hat{L} \) with eigenvalue \( \lambda \). 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 \( \lambda \). 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

\[
\hat{p} = i\hbar \frac{\partial}{\partial x}
\]

where \( i = \sqrt{-1} \), \( \hbar \) is Planck’s constant divided by \( 2\pi \), 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

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

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
\[ \hat{E} = i\hbar \frac{\partial}{\partial t} \]  

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:

\[ H = E = T + V \]  

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

\[ \hat{H}\Psi = (\hat{T} + \hat{V})\Psi = \hat{E}\Psi \]  

or

\[ \hat{H}\Psi = (\hat{T} + \hat{V})\Psi = i\hbar \frac{\partial\Psi}{\partial t} \]

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:

\[ \Psi(r_1, r_2, \ldots, r_N, t) = \Psi(r_1, r_2, \ldots, r_N)e^{-iEt/\hbar} \]

Substituting this into the Hamiltonian gives:

\[ \hat{H}\Psi = (\hat{T} + \hat{V})\Psi = E\Psi \]

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
The solution to this differential equation is of the form:

$$\Psi(x) = A \sin(kx) + B \cos(kx)$$  \hspace{1cm} (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,

$$\Psi(0) = A \sin(0) + B \cos(0) = 0$$  \hspace{1cm} (1.12)

which implies that $B = 0$. However, since

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

we find that $kL = n\pi$, where $n = 1, 2, 3, \ldots$
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 ($\hbar = 6.6262 \times 10^{-34}$ 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 $\Psi(r)$ where $r$ 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

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(r) - \frac{e^2}{4\pi\varepsilon_0 r} \Psi(r) = E \Psi(r)$$

(1.14)

where $e$ is the charge of the electron and $\varepsilon_0$ 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 = $4.360 \times 10^{-18}$ 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

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

(1.15)

Since the problem has spherical symmetry, it is more convenient to use spherical coordinates $\Psi(r) = \Psi(r, \theta, \phi)$ 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

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

(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
The energy of the electron is quantized with values

\[ E_n = -\frac{1}{2n^2} \]

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 \( r_1 \) and the coordinate of electron 2 is \( r_2. \) We will assume that the nucleus is fixed at the origin. The Schrödinger equation for the system is then
A reasonable approach to solving this might be to assume that

\[ \Psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2) \]  

(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

\[ \frac{1}{|r_1 - r_2|} \]  

(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:

$$\Psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2) \pm \psi_a(r_2)\psi_b(r_1)$$ (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 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 \( \alpha \)-spin; if \( m_s = -1/2 \), we say the spin is “down” or \( \beta \)-spin. Fundamental particles in the universe are either Fermions (with half-integer values of \( s = 1/2, 3/2, \ldots \)) or Bosons (with integer values of \( s = 0, 1, 2, \ldots \)). Fermions must have “antisymmetric” wavefunctions:

$$\Psi(r_1, r_2) = \psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)$$ (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 \( r_1 = r_2 \), then \( \Psi(r_1, r_2) = 0 \) unless \( \psi_a(r_1) \neq \psi_b(r_1) \). 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 \( \alpha \) or \( \beta \). The spin coordinate of an electron will be accounted for by using separate wavefunctions for \( \alpha \)- and \( \beta \)-spin electrons designated as \( \psi_1^\alpha, \psi_1^\beta \). Using separate wavefunctions for \( \alpha \)- and \( \beta \)-spin electrons is referred to as a spin-unrestricted formalism. As we will see later, the two wavefunctions \( \psi_1^\alpha, \psi_1^\beta \) will be numerically different if the number of \( \alpha \)-spin electrons differs from the number of \( \beta \)-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:

$$\Psi(r_1, r_2) = \left| \begin{array}{cc} \psi_1(r_1) & \psi_2(r_1) \\ \psi_1(r_2) & \psi_2(r_2) \end{array} \right| \equiv |\psi_1\psi_2|$$ (1.24)

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

$$\Psi(r_1, r_2, \ldots, r_N) = \left| \begin{array}{ccc} \psi_1(r_1) & \psi_1(r_2) & \cdots & \psi_1(r_N) \\ \psi_2(r_1) & \psi_2(r_2) & \cdots & \psi_2(r_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(r_1) & \psi_N(r_2) & \cdots & \psi_N(r_N) \end{array} \right| \equiv |\psi_1\psi_2\ldots\psi_N|$$ (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

\[ \Psi = |\phi_1^\alpha \phi_1^\beta \phi_2^\alpha \phi_2^\beta \phi_2^\alpha \phi_2^\beta \phi_2^\alpha \phi_2^\beta \phi_3^\alpha \phi_3^\beta \phi_3^\alpha \phi_3^\beta | \]

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 multielectronic 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 \( \Psi \). The expectation value (the mean value of an observable quantity) of the total energy is given by

\[ \langle E \rangle = \frac{\int \Psi^* \hat{H} \Psi \, dr}{\int \Psi^* \Psi \, dr} \]

where the asterisk (*) means the complex conjugate (i.e., replace \( i \) by \( -i \)). Suppose that we did not know \( \Psi \) 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 \( \delta \) 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 \( \Psi \) 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

\[ \langle E \rangle = \sum_j^N \left| \psi_j (r) \left( -\frac{1}{2} \nabla^2 - \frac{Z}{r} \right) \psi_j (r) \right| dr + \sum_{j < k}^N \left| \psi_j (r_1) \psi_k (r_2) \right|^2 \frac{d r_1 d r_2}{|r_1 - r_2|} \]

\[ -\sum_{j < k}^N \delta (\sigma_j, \sigma_k) \left| \psi_j (r_1) \psi_k^* (r_2) \psi_j (r_1) \psi_k (r_2) \right|^2 \frac{d r_1 d r_2}{|r_1 - r_2|} \]

\[ 1.27 \]

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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 \( \psi_j(\mathbf{r}_j) \) and their energies \( \varepsilon_j \):

\[
\begin{align*}
-\frac{1}{2} \nabla^2 \psi_j(\mathbf{r}_1) - \frac{Z}{r_1} \psi_j(\mathbf{r}_1) + \left( \sum_k^N \frac{|\psi_k(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right) \psi_j(\mathbf{r}_1) \\
- \left( \sum_k^N \delta(\sigma_j, \sigma_k) \int \frac{\psi_k^*(\mathbf{r}_2) \psi_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right) \psi_j(\mathbf{r}_1) = \varepsilon_j \psi_j(\mathbf{r}_1)
\end{align*}
\]

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 \( \psi_j(\mathbf{r}_j) \), we need to evaluate the Coulomb and exchange potentials. However, we cannot evaluate the Coulomb and exchange potentials until we know the orbitals \( \psi_j(\mathbf{r}_j) \)! We get around this problem by starting with an initial guess for \( \psi_j(\mathbf{r}_j) \), evaluating the Coulomb and exchange potentials using that guess, and then solving for a better set of \( \psi_j(\mathbf{r}_j) \). 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 is illustrated in the simple molecule \( \text{H}_2 \) (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 \( \text{H}_2 \) as A and B, with atomic orbitals \( \phi_A \) and \( \phi_B \), then the molecular orbitals can be constructed as follows:

\[
\begin{align*}
\psi_+ &= \frac{1}{\sqrt{2}} (\phi_A + \phi_B) \\
\psi_- &= \frac{1}{\sqrt{2}} (\phi_A - \phi_B)
\end{align*}
\]

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:

\[
\Psi(1,2) = \begin{vmatrix}
\psi_+^\alpha(1) & \psi_+^\alpha(2) \\
\psi_+^\beta(1) & \psi_+^\beta(2)
\end{vmatrix}
\]
If we expand the Slater determinant in terms of the atomic orbitals, we find that the wavefunction is

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

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: $\phi_\alpha^A (1) \phi_\beta^A (2)$ corresponds to both electrons being localized to atom A, the term $\phi_\alpha^A (1) \phi_\beta^B (2) + \phi_\alpha^B (1) \phi_\beta^A (2)$ corresponds to the two electrons being delocalized over the two atoms, and the term $\phi_\beta^A (1) \phi_\alpha^B (2) + \phi_\beta^B (1) \phi_\alpha^A (2)$ 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:

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

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.

**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.
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 ground-state total energy $E$ of a system of particles (e.g., electrons) subject to any kind of external potential $V_{\text{ext}}$ can be expressed (exactly) in terms of functionals of the particle density $\rho(r)$:

$$E[\rho(r)] = T[\rho(r)] + U[\rho(r)] + \int V_{\text{ext}}(r)\rho(r)\,dr$$

(1.33)

The $T[\rho(r)]$ functional describes the kinetic energy of the system, while the $U[\rho(r)]$ functional describes the potential energy due to interelectronic repulsion. Here, the external potential $V_{\text{ext}}$ 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 $T[\rho(r)]$ and $U[\rho(r)]$ 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:

\[ U[\rho(r)] = G[\rho(r)] + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} drdr' \]  

(1.34)

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

\[ \rho(r) = \sum_j^{\text{occup}} |\psi_j(r)|^2 \]  

(1.35)

The kinetic energy functional would then be simply

\[ T_0 = -\frac{1}{2} \sum_j^{\text{occup}} \int \psi_j^*(r) \nabla^2 \psi_j(r) dr \]  

(1.36)

We can then write out total energy functional as

\[ E[\rho(r)] = -\frac{1}{2} \sum_j^{\text{occup}} \int \psi_j^*(r) \nabla^2 \psi_j(r) dr + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} drdr' \]  

\[ + \int V_{\text{ext}}(r)\rho(r) dr + E_{\text{xc}}[\rho(r)] \]  

(1.37)

where we have defined a new functional \( E_{\text{xc}}[\rho(r)] \) 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 \( E_{\text{xc}}[\rho(r)] \) 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 \( \psi_j(r) \). The single-particle orbitals are solutions to the Kohn–Sham equations (Kohn and Sham, 1965) that take the form of one-electron Schrödinger equations:

\[ \left( -\frac{1}{2} \nabla^2 + v_{\text{xc}} + V_{\text{ext}}(r) \right) \psi_j(r) = \epsilon_j \psi_j(r) \]  

(1.38)

with

\[ v_{\text{xc}} = \int \frac{\rho(r)\rho(r')}{|r-r'|} dr' + \frac{\delta E_{\text{xc}}[\rho(r)]}{\delta \rho(r)} \]  

(1.39)