\[ + c_1 |2p_x\rangle \]

eigenfunctions of \( \mathcal{H}_0 \), i.e.,

\[ -r^{1/2} r e^{-r^2} \cos \theta \]

constructing the matrix representation of

\[ \mathcal{H}_0|2p_x\rangle = -\frac{1}{\hbar^2}|2p_x\rangle \]

as an answer in a Taylor series in \( F \), i.e.,

\[ -\frac{1}{2} \alpha F^2 + \cdots \]

the approximate dipole polarizability is.

the result is 4.5.

This chapter introduces the basic concepts, techniques, and notations of quantum chemistry. We consider the structure of many-electron operators (e.g., the Hamiltonian) and discuss the form of many-electron wave functions (Slater determinants and linear combinations of these determinants). We describe the procedure for evaluating matrix elements of operators between Slater determinants. We introduce the basic ideas of the Hartree-Fock approximation. This allows us to develop the material of this chapter in a form most useful for subsequent chapters where the Hartree-Fock approximation and a variety of more sophisticated approaches, which use the Hartree-Fock method as a starting point, are considered in detail.

In Section 2.1, the electronic problem is formulated, i.e., the problem of describing the motion of electrons in the field of fixed nuclear point charges. This is one of the central problems of quantum chemistry and our sole concern in this book. We begin with the full nonrelativistic time-independent Schrödinger equation and introduce the Born-Oppenheimer approximation. We then discuss a general statement of the Pauli exclusion principle called the antisymmetry principle, which requires that many-electron wave functions must be antisymmetric with respect to the interchange of any two electrons.

In Section 2.2, we describe one-electron functions (spatial and spin orbitals) and then construct many-electron functions (Hartree products and
Slater determinants) in terms of these one-electron functions. We then consider the Hartree-Fock approximation in which the exact wave function of the system is approximated by a single Slater determinant and describe its qualitative features. At this point, we introduce a simple system, the minimal basis (1s orbital on each atom) ab initio model of the hydrogen molecule. We shall use this model throughout the book as a pedagogical tool to illustrate and illuminate the essential features of a variety of formalisms that at first glance appear to be rather formidable. Finally, we discuss the multi-determinantal expansion of the exact wave function of an N-electron system.

Section 2.3 is concerned with the form of the one- and two-electron operators of quantum chemistry and the rules for evaluating matrix elements of these operators between Slater determinants. The conversion of expressions for matrix elements involving spin orbitals to expressions involving spatial orbitals is discussed. Finally, we describe a mnemonic device for obtaining the expression for the energy of any single determinant.

Section 2.4 introduces creation and annihilation operators and the formalism of second quantization. Second quantization is an approach to dealing with many-electron systems, which incorporates the Pauli exclusion principle but avoids the explicit use of Slater determinants. This formalism is widely used in the literature of many-body theory. It is, however, not required for a comprehension of most of the rest of this book, and thus this section can be skipped without loss of continuity.

Section 2.5 discusses electron spin and spin operators in many-electron systems and contains a description of restricted and unrestricted spin orbitals and spin-adapted configurations. Spin-adapted configurations, unlike many single determinants derived from restricted spin orbitals, are correct eigenfunctions of the total electron spin operator. Singlet, doublet, and triplet spin-adapted configurations as well as unrestricted wave functions, which are not eigenfunctions of the total electron spin operator, are described.

2.1 THE ELECTRONIC PROBLEM

Our main interest in this book is finding approximate solutions of the non-relativistic time-independent Schrödinger equation

$$\hat{H} |\Phi\rangle = \varepsilon |\Phi\rangle$$  \hspace{1cm} (2.1)

where $\hat{H}$ is the Hamiltonian operator for a system of nuclei and electrons described by position vectors $\mathbf{R}_A$ and $\mathbf{r}_i$, respectively. A molecular coordinate system is shown in Fig. 2.1. The distance between the $i$th electron and $A$th nucleus is $r_{ia} = |\mathbf{r}_i - \mathbf{R}_A|$; the distance between the $i$th and $j$th electron is $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and the distance between the $A$th nucleus and the $B$th nucleus is $R_{AB} = |\mathbf{R}_A - \mathbf{R}_B|$. In atomic units, the Hamiltonian for $N$ electrons and $M$ nuclei is

$$\hat{H} = - \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{1}{r_{ia}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}$$

In the above equation, $M_A$ is the mass of an electron, and $Z_A$ is the atomic number. The operators $\nabla_i^2$ and $\frac{1}{r_{ij}}$ involve differ of the $i$th electron and the $A$th nucleus for the kinetic energy of operator for the kinetic energy of the coulomb attraction between electron terms represent the repulsion be respectively.

2.1.1 Atomic Units

The units we use throughout this book these units arise naturally let us consider hydrogen atom. In SI units, we have $\left[ -\frac{\hbar^2}{2m_e} \nabla^2 - \right]$
one-electron functions. We then consider a simple system, the minimal 
two-electron model of the hydrogen molecule. 
the book as a pedagogical tool to introduce the concept of 
formalisms that are suitable. Finally, we discuss the multi- 
electron wave function of an N-electron system. 
and to evaluate matrix elements of the form of the one- and two-electron 
spin rules for evaluating matrix elements 
expressions involving spin orbitals. We describe a mnemonic device for 
determinants. 
and annihilation operators and the 
quantum formalism is an approach to which incorporates the Pauli exclusion 
Principles. This formalism applies to any-body theory. It is, however, not 
the rest of this book, and thus this is not true. 
and spin operators in many-electron 
restricted and unrestricted spin orbitals 
unrestricted wave functions, which are correct eigen-
operator. Singlet, doublet, and triplet 
(2.1) 
\[ \mathcal{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \] 
(2.2) 
In the above equation, \( M_A \) is the ratio of the mass of nucleus \( A \) to the mass of an electron, and \( Z_A \) is the atomic number of nucleus \( A \). The Laplacian 
operators \( \nabla_i^2 \) and \( \nabla_A^2 \) involve differentiation with respect to the coordinates 
of the \( i \)th electron and the \( A \)th nucleus. The first term in Eq. (2.2) is the 
operator for the kinetic energy of the electrons; the second term is the 
operator for the kinetic energy of the nuclei; the third term represents 
the coulomb attraction between electrons and nuclei; the fourth and fifth 
terms represent the repulsion between electrons and between nuclei, 
respectively. 

2.1.1 Atomic Units 
The units we use throughout this book are called atomic units. To see how 
these units arise naturally let us consider the Schrödinger equation for the 
hydrogen atom. In SI units, we have 
\[ \left( -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \right) \phi = \varepsilon \phi \] 
(2.3)
where \( h \) is Planck's constant divided by \( 2\pi \), \( m_e \) is the mass of the electron, and \( -e \) is the charge on the electron. To cast this equation into dimensionless form we let \( x, y, z \to \lambda x', y', z' \) and obtain
\[
\left[ -\frac{\hbar^2}{2m_\lambda^2} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 \lambda^2} \right] \phi' = \delta \phi'
\] (2.4)

The constants in front of the kinetic and potential energy operators can then be factored, provided we choose \( \lambda \) such that
\[
\frac{\hbar^2}{4\pi\epsilon_0 \lambda^2} = \frac{e^2}{4\pi\epsilon_0 \lambda^2} = \delta_a
\] (2.5)

where \( \delta_a \) is the atomic unit of energy called the Hartree. Solving Eq. (2.5) for \( \lambda \) we find
\[
\lambda = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = a_0
\] (2.6)

Thus \( \lambda \) is just the Bohr radius \( a_0 \), which is the atomic unit of length called a Bohr. Finally, since
\[
\delta_a \left[ -\frac{1}{2} \nabla^2 - \frac{1}{r'} \right] \phi' = \delta \phi'
\] (2.7)

if we let \( \delta' = \delta / \delta_a \), we obtain the dimensionless equation
\[
\left( -\frac{1}{2} \nabla^2 - \frac{1}{r} \right) \phi' = \delta' \phi'
\] (2.8)

which is the Schrödinger equation in atomic units. The solution of this equation for the ground state of the hydrogen atom yields an energy \( \delta' \) equal to \(-0.5\) atomic units \( \equiv -0.5 \) Hartrees. Table 2.1 gives the conversion factors \( X \) between atomic units and SI units, such that the SI value of any quantity \( Q \) is related to its value in a
\[
Q = \delta \delta_a^{-1} \delta_x^{-1} Q_a
\]

Conversion factors for a few other which are necessary to read the e atomic unit of length equals 0.5291 dipole moment (two unit charges sep and one atomic unit of energy 627.51 kcal/mole).

From now on we drop the prime units.

### 2.1.2 The Born-Oppenheimer Ap

The Born-Oppenheimer approximation Our discussion of this approximation, including the clearly discussed by Sutcliffe electrons, they move more slowly. H consider the electrons in a molecule Within this approximation, the sec the nuclei, can be neglected and the nuclei, can be considered to b operator only adds to the operator- operator eigenfunctions. The remain Hamiltonian or Hamiltonian descr field of \( M \) point charges,
\[
\mathcal{H}_{\text{elec}} = - \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}}
\]

The solution to a Schrödinger equati
\[
\mathcal{H}_{\text{elec}} \Phi_{\text{elec}} = \epsilon \Phi_{\text{elec}}
\]

is the electronic wave function,
\[
\Phi_{\text{elec}} = \Phi
\]

which describes the motion of the electronic coordinates but depends \( \rho \) as does the electronic energy,
\[
\epsilon_{\text{elec}} = \epsilon
\]

By a parametric dependence we m; nuclei, \( \Phi_{\text{elec}} \) is a different function of

<table>
<thead>
<tr>
<th>Table 2.1 Conversion of atomic units to SI units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical quantity</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>Length</td>
</tr>
<tr>
<td>Mass</td>
</tr>
<tr>
<td>Charge</td>
</tr>
<tr>
<td>Energy</td>
</tr>
<tr>
<td>Angular momentum</td>
</tr>
<tr>
<td>Electric dipole moment</td>
</tr>
<tr>
<td>Electric polarizability</td>
</tr>
<tr>
<td>Electric field</td>
</tr>
<tr>
<td>Wave function</td>
</tr>
</tbody>
</table>
\[ n_2 \pi, m_e \] is the mass of the electron, if cast this equation into dimensionless form

\[ \frac{e^2}{\pi \varepsilon_0 a^2} \phi' = \phi' \]  

(2.4)

and potential energy operators can be such that

\[ \frac{1}{\varepsilon_0 a^2} = \delta_a \]

(2.5)
called the Hartree. Solving Eq. (2.5)

\[ \hbar^2 \frac{1}{\varepsilon} = a_0 \]

(2.6)

is the atomic unit of length called a

\[ \frac{1}{r} \phi' = \phi' \]

(2.7)

nonsionless equation

\[ \phi' = \phi' \]

(2.8)

atomic units. The solution of this hydrogen atom yields an energy \( \delta' \) in atomic units. Table 2.1 gives the conversion I units, such that the SI value of any

\begin{center}
\begin{tabular}{|l|l|}
\hline
\textbf{SI units} & \textbf{Value of } X \text{ (SI)} \\
\hline
5.2918 \times 10^{-11} \text{ m} & 5.2918 \times 10^{-11} \text{ m} \\
9.1095 \times 10^{-31} \text{ kg} & 9.1095 \times 10^{-31} \text{ kg} \\
1.6022 \times 10^{-19} \text{ C} & 1.6022 \times 10^{-19} \text{ C} \\
4.3598 \times 10^{-18} \text{ J} & 4.3598 \times 10^{-18} \text{ J} \\
1.0546 \times 10^{-34} \text{ J s} & 1.0546 \times 10^{-34} \text{ J s} \\
8.4784 \times 10^{-30} \text{ Cm} & 8.4784 \times 10^{-30} \text{ Cm} \\
1.6488 \times 10^{-41} \text{ C m}^2 \text{ J}^{-1} & 1.6488 \times 10^{-41} \text{ C m}^2 \text{ J}^{-1} \\
5.1423 \times 10^{11} \text{ V m}^{-1} & 5.1423 \times 10^{11} \text{ V m}^{-1} \\
2.5978 \times 10^{14} \text{ m}^{-3/2} & 2.5978 \times 10^{14} \text{ m}^{-3/2} \\
\hline
\end{tabular}
\end{center}

quantity \( Q \) is related to its value in atomic units \( Q' \) by

\[ Q = X Q' \]

(2.9)

Conversion factors for a few other units, which are not related to SI but which are necessary to read the existing literature, are as follows. One atomic unit of length equals 0.52918 Angströms (Å). One atomic unit of dipole moment (two unit charges separated by \( a_0 \)) equals 2.5418 Debyes (D), and one atomic unit of energy equals 27.211 electron volts (eV) or 627.51 kcal/mole.

From now on we drop the primes and all our quantities will be in atomic units.

### 2.1.2 The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is central to quantum chemistry. Our discussion of this approximation is qualitative. The quantitative aspects of this approximation, including the problem of deriving corrections to it, are clearly discussed by Surcliffe.\(^1\) Since nuclei are much heavier than electrons, they move more slowly. Hence, to a good approximation, one can consider the electrons in a molecule to be moving in the field of fixed nuclei. Within this approximation, the second term of (2.2), the kinetic energy of the nuclei, can be neglected and the last term of (2.2), the repulsion between the nuclei, can be considered to be constant. Any constant added to an operator only adds to the operator eigenvalues and has no effect on the operator eigenfunctions. The remaining terms in (2.2) are called the electronic Hamiltonian or Hamiltonian describing the motion of \( N \) electrons in the field of \( M \) point charges,

\[ H_{\text{elec}} = - \sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} Z_A r_{iA} + \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}} \]

(2.10)

The solution to a Schrödinger equation involving the electronic Hamiltonian,

\[ H_{\text{elec}} \Phi_{\text{elec}} = \delta_{\text{elec}} \Phi_{\text{elec}} \]

(2.11)

is the electronic wave function,

\[ \Phi_{\text{elec}} = \Phi_{\text{elec}}(\{r_i\}; \{R_A\}) \]

(2.12)

which describes the motion of the electrons and explicitly depends on the electronic coordinates but depends parametrically on the nuclear coordinates, as does the electronic energy,

\[ \delta_{\text{elec}} = \delta_{\text{elec}}(\{R_A\}) \]

(2.13)

By a parametric dependence we mean that, for different arrangements of the nuclei, \( \Phi_{\text{elec}} \) is a different function of the electronic coordinates. The nuclear
coordinates do not appear explicitly in $\Phi_{\text{elec}}$. The total energy for fixed nuclei must also include the constant nuclear repulsion.

$$\mathcal{E}_{\text{tot}} = \mathcal{E}_{\text{elec}} + \sum_{A=1}^{M} \sum_{B > A}^{M} \frac{Z_A Z_B}{R_{AB}}$$

(2.14)

Equations (2.10) to (2.14) constitute the electronic problem, which is our interest in this book.

If one has solved the electronic problem, it is subsequently possible to solve for the motion of the nuclei under the same assumptions as used to formulate the electronic problem. As the electrons move much faster than the nuclei, it is a reasonable approximation in (2.2) to replace the electronic coordinates by their average values, averaged over the electronic wave function. This then generates a nuclear Hamiltonian for the motion of the nuclei in the average field of the electrons,

$$\mathcal{H}_{\text{nucl}} = -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + \left\langle -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \right\rangle$$

$$+ \sum_{A=1}^{M} \sum_{B > A}^{M} \frac{Z_A Z_B}{R_{AB}}$$

$$= -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + \mathcal{E}_{\text{elec}}(\{R_A\}) + \sum_{A=1}^{M} \sum_{B > A}^{M} \frac{Z_A Z_B}{R_{AB}}$$

$$= -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + \mathcal{E}_{\text{tot}}(\{R_A\})$$

(2.15)

The total energy $\mathcal{E}_{\text{tot}}(\{R_A\})$ provides a potential for nuclear motion. This function constitutes a potential energy surface as shown schematically in Fig. 2.2. Thus the nuclei in the Born-Oppenheimer approximation move on a potential energy surface obtained by solving the electronic problem.

![Figure 2.2 Schematic illustration of a potential surface.](image)

2.1.3 The Antisymmetry or Pauli

The electronic Hamiltonian in Eq. 2.1 constitutes the electronic problem. To complete the theory by introducing two spin functions, we drop the subscript "elec" and only consider the two spin functions. The wave function for an N-electron system $x_1, \ldots, x_N$ is given by $\Phi(x_i)$. The wave function depends on the nuclear coordinates $x_A$ and the electronic coordinates $x_i$. The total wave function is the product of the electronic and nuclear wave functions:

$$\Phi(x_1, \ldots, x_N, x_A) = \Phi_{\text{elec}}(x_i) \Phi_{\text{nucl}}(x_A)$$

The electronic wave function is antisymmetric under the exchange of any two electrons, and the nuclear wave function is symmetric under the exchange of any two nuclei. Therefore, the total wave function is also antisymmetric under the exchange of any two electrons and symmetric under the exchange of any two nuclei. This is known as the Pauli exclusion principle and is a fundamental property of electrons in atoms and molecules.
the total energy for fixed nuclei repulsion.

$$\sum_{i=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}$$  \hspace{1cm} (2.14)$$

We now solve the electronic problem, which is our problem, by replacing the electronic Hamiltonian for the motion of the ns,

$$\nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{N} \frac{1}{r_{ij}}$$  \hspace{1cm} (2.15)$$

potential for nuclear motion. This surface as shown schematically in Born-Oppenheimer approximation move on solving the electronic problem. Solutions to a nuclear Schrödinger equation,

$$\mathcal{H}_{\text{nucl}} \Phi_{\text{nucl}} = \delta \Phi_{\text{nucl}}$$  \hspace{1cm} (2.16)$$
describe the vibration, rotation, and translation of a molecule,

$$\Phi_{\text{nucl}} = \Phi_{\text{nucl}}(\{R_A\})$$  \hspace{1cm} (2.17)$$

and $\delta$, which is the Born-Oppenheimer approximation to the total energy of (2.1), includes electronic, vibrational, rotational, and translational energy. The corresponding approximation to the total wave function of (2.1) is,

$$\Phi(\{r_i\}; \{R_A\}) = \Phi_{\text{elec}}(\{r_i\}; \{R_A\}) \Phi_{\text{nucl}}(\{R_A\})$$  \hspace{1cm} (2.18)$$

From now on, we will not consider the vibrational-rotational problem but concentrate solely on the electronic problem of (2.11) to (2.14). We thus drop the subscript “elec” and only consider electronic Hamiltonians and electronic wave functions. Where it is convenient or necessary, we will distinguish between the electronic energy of (2.13) and the total energy of (2.14), which includes nuclear-nuclear repulsion.

2.1.3 The Antisymmetry or Pauli Exclusion Principle

The electronic Hamiltonian in Eq. (2.10) depends only on the spatial coordinates of the electrons. To completely describe an electron it is necessary, however, to specify its spin. We do this in the context of our nonrelativistic theory by introducing two spin functions $\alpha(\omega)$ and $\beta(\omega)$, corresponding to spin up and down, respectively. These are functions of an unspecified spin variable $\omega$; from the operational point of view we need only specify that the two spin functions are complete and that they are orthonormal.

$$\int d\omega \alpha^*(\omega) \alpha(\omega) = \int d\omega \beta^*(\omega) \beta(\omega) = 1$$  \hspace{1cm} (2.19a)$$

$$\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$  \hspace{1cm} (2.19b)$$

and

$$\int d\omega \alpha^*(\omega) \beta(\omega) = \int d\omega \beta^*(\omega) \alpha(\omega) = 0$$  \hspace{1cm} (2.20a)$$

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0$$  \hspace{1cm} (2.20b)$$

where the integration has been used in a formal way. In this formalism an electron is described not only by the three spatial coordinates $\mathbf{r}$ but also by one spin coordinate $\omega$. We denote these four coordinates collectively by $\mathbf{x}$,

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$  \hspace{1cm} (2.21)$$

The wave function for an $N$-electron system is then a function of $x_1$, $x_2$, $\ldots$, $x_N$. That is, we write $\Phi(x_1, x_2, \ldots, x_N)$.

Because the Hamiltonian operator makes no reference to spin, simply making the wave function depend on spin (in the way just described) does