Electronic Structure According to the Orbital Approximation and the Hartree-Fock Theory with Electron Correlation Methods

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October 20, 2016
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Chapter 1

Introduction

Structures and properties of microscopic systems can be understood in the framework of physics [1], especially quantum mechanics [2]. Quantum chemistry [3, 4] is a branch of quantum physics specialized in atoms, molecules and solids. The properties of such systems are described by their electronic structure, in which phenomena of relatively small energies (< keV) [5, 6, 7] compared to the typical energies of nuclear or particle physics (> MeV) [8, 9] occur. Quantum chemistry provides powerful analysis tools for how the different phenomena affect the behaviour of matter [3, 10].

The main problem is that the electronic structure is in general impossible to solve exactly [1, 2] It is necessary to rely on different approximations and numerical methods. Calculations are performed within the Born-Oppenheimer realm [11] where the electronic and the nuclear parts of the wavefunction are separated [2]. The electronic part is from now on called briefly the wavefunction. It describes the electronic structure. Nuclear positions are treated as fixed, since the electrons can adjust instantaneously to the dynamic changes in the nuclear positions due to the mass differences between nuclei and electrons [12]. When the nuclei are in their equilibrium positions, the electronic ground-state energy is minimized [13, 14].

In chemistry, electron configuration is an established way to describe the electronic structure of atoms and molecules [15]. It is based on the orbital approximation in which electrons are thought to be moving independently from each other in orbitals, volumes that are occupied by an electron with a certain probability. The orbital approximation is surprisingly effective in giving good qualitative explanation to the behaviour of molecules [3]. Its main concepts are introduced in the second chapter of this thesis where the emphasis is in the most simple “molecules”, closed-shell atoms. Orbitals of many-electron atoms resemble hydrogen-like orbitals to a large extent, which is utilized in classifying them [2]. Otherwise, molecular symmetry properties are determined particularly by the nuclear positions, giving their own flavour to the electronic structure calculations and orbital classification [2, 16, 17, 18].
but this is omitted in the context of this thesis.

The orbital approximation forms the basis of the numerical scheme that is widely used in exploring the electronic structure of the molecular ground state. This scheme is called the Hartree-Fock method [2, 3, 19] and it is the topic of the third chapter. The method is iterative and adjusts the one-electron orbitals closer to the ground-state orbitals with each step [20] till there is no longer a measurable change between the orbitals of the adjacent steps. Electrons are thought to be moving in the nuclear Coulomb potential and the spherically averaged Coulomb potential [21, 22] induced by the other electrons of the system. The iteration process is known as the self-consistent-field procedure. Due to the variation principle, Hartree-Fock solutions give an upper bound to the true ground-state energy [2].

Even at its best, the Hartree-Fock method is only able to treat the electron-electron interactions in a spherically averaged manner. To recover the rest of the electron-electron interaction, many electron correlation methods have been developed and implemented. In the fourth chapter, three post-Hartree-Fock correlation methods are introduced: the configuration interaction method [23, 24], the Møller-Plesset method [25] and the coupled-cluster method [26, 27]. All these methods use the Hartree-Fock solution as the starting point for calibrating the wavefunction closer to the true wavefunction of the system [2, 3]. Hence, the name post-Hartree-Fock methods.

The fifth chapter concludes the thesis with the summary of different electronic-structure methods and descriptions. The similarities and differences, as well as the strengths and weaknesses of the methods are highlighted, and their application scopes are presented.
Chapter 2

Orbital approximation

In the orbital approximation [2, 3], electrons are assumed to be moving independently from each other within their orbitals. According to the Pauli principle [28, 29], any one-electron state is maximally occupied by one electron. They are visualized, e.g., as the volume within which it is possible to find electrons occupying them with 95% probability [30]. In Figure 2.1, a visualization of the hydrogen-like 2s, 3s, and some of 2p, 3p and 4d atomic orbitals is presented. As it can be seen, the 2s and the 3s orbitals are spherically symmetric, while the probability densities of the 2p, 3p and 3d orbitals have a nodal plane perpendicular to the axis of the orbital.

The orbital approximation can be justified by the magnitude differences between the interaction terms of the molecular Hamiltonian

\[
\hat{H} = \sum_k \left[ -\frac{\hbar^2}{2m} \nabla_k^2 - \frac{e^2}{4\pi\varepsilon_0} \sum_M Z_M \frac{1}{r_{Mk}} + \frac{e^2}{8\pi\varepsilon_0} \sum_{l \neq k} \frac{1}{r_{lk}} \right]
\]

(2.1)

where \(\hbar\) is the reduced Planck constant, \(m\) is the mass of an electron, \(\nabla_k\) is the gradient applied to the electron \(k\), \(e\) is the elementary charge, \(Z_M\) is the atomic number of the atom \(M\), and \(r_{Mk}\) (or \(r_{lk}\)) is the distance between the nucleus \(M\) (or the electron \(l\)) and the electron \(k\). The first, second and third terms in the Hamiltonian (2.1) correspond to the kinetic energy of electrons, the electron-nucleus interaction and the electron-electron interaction, respectively. The electron-electron repulsion is small compared to the sum of the electron-nucleus Coulomb attraction and the kinetic energy of the electrons [31], indicating that the degree of mixture between the electronic states determined solely from two first sum terms of the Hamiltonian (2.1) is low. The orbital approximation is thus able to describe the electronic structure at least in a qualitative manner. The non-interacting electronic picture can still be improved by spherically averaging [22] the electron-electron repulsion effect.

The following sections provide tools for building up the total electronic structure description of atoms within the framework of the orbital approxi-
CHAPTER 2. ORBITAL APPROXIMATION

Figure 2.1: Visualization of the atomic orbitals (a) 2s, (b) 3s, (c) 2p with $m_l = 0$, (d) 2p with $m_l = 1$ (e) 3p with $m_l = 0$, and (f) 4d with $m_l = 0$. Modified picture of "Hydrogen Density Plots.png". Source: Wikimedia Commons (4.3.2016).

Atomic one-electron states are classified, basics for defining electron configurations of atomic ground states are introduced and a mathematical formalism to present configurations - Slater determinants [2, 3] - is displayed. Symmetries of molecules [2, 18], needed in the general classification of molecular orbitals, are omitted in this thesis. The concepts of the orbital approximation provide the foundation, for example, to the Hartree-Fock theory which is the motivation of this chapter.
2.1 Classification of atomic orbitals

Atomic orbitals are classified according to so-called “good” quantum numbers of stationary observables, measurable properties of the system that are mathematically expressed as Hermitian operators. Probability densities corresponding to the states of good quantum numbers are independent of time [2]. The eigenvalues of the operators describe the possible outcomes of a single measurement. Good quantum numbers are identified by commutation of the Hamiltonian with other operators. The Schrödinger picture is chosen here as the framework, in which operators are time-independent and the states evolve with time. If the Hamiltonian commutes with an operator \( \hat{B} \) of some observable, i.e., \([\hat{B}, \hat{H}] = 0\), \( \hat{B} \) and \( \hat{H} \) have simultaneous eigenstates, and the expectation value of \( \hat{B} \) is constant in time [32, 33].

Symmetry properties of the system can be used for exploring good quantum numbers. For example, many-electron atoms are a lot like hydrogen-like atoms\(^1\) in the sense that the many-electron Coulomb field can be described to a large extent spherically symmetrically, deduced from a comparison of the correlation energy with the HF energy [34]. The spin-orbit coupling\(^2\) is usually weak and neglected at this point, and treated only as a small perturbation [2, 35]. Thus, many-electron atomic orbitals resemble hydrogen-like orbitals and are classified with the same set of quantum numbers in the orbital approximation picture. To give some insight to the orbital classification, solutions of hydrogen-like atomic Schrödinger equation are treated in more detail.

The first point to note is that the Hamiltonian of hydrogen-like atoms can be expressed in terms of radial and angular parts so that the solution of the Schrödinger equation

\[
\hat{H} \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi) \tag{2.2}
\]

is possible to separate into the radial and angular factors, \( \Psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \), respectively. The polar angle is \( \theta \), the azimuthal angle is \( \phi \), the distance between the electron and the nucleus is \( r \) and the energy corresponding to the solution \( \Psi \) is \( E \). The time-independent formulation (2.2) is obtained by separating the time-dependent and space-dependent parts from the time-dependent Schrödinger equation,\(^3\) which is possible since the potential energy terms of the Hamiltonian (2.1) are time-independent. The terms \( R(r) \) and \( Y(\theta, \phi) \) are then solved from the equations following the separation. In Appendix A, the wave function of

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\(^1\)A hydrogen-like atom constitutes a nucleus with one electron.

\(^2\)The spin-orbit coupling is the interaction between the orbital and the spin angular momenta of a single particle or a system.

\(^3\)The time-dependent Schrödinger equation is \( \hat{H} \Psi = i\hbar \frac{\partial}{\partial t} \Psi \).
hydrogen-like atoms is solved thoroughly starting from the time-dependent Schrödinger equation.

Without spin-orbit coupling, the Hamiltonian $\hat{H}$ commutes with angular momentum operators $\hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{L}_z, \hat{S}_z, \hat{J}_z$ which are related to the orbital motion, the spin, the total angular momentum and their projections to the chosen $z$-axis, respectively. In this situation, the spin dependence of the wavefunction can be incorporated by multiplying the spin factor $\sigma(s)$ with the spatial factor of the wavefunction, $\Psi(r, \theta, \phi, s) = \Psi(r, \theta, \phi)\sigma(s)$. Thus, each solution of the Schrödinger equation (2.2) is at least doubly degenerate\(^4\) with the same spatial term but the opposite spin terms. Table 2.1 lists the names of the operators and the quantum numbers associated with them.

### Table 2.1: Angular momentum operators and their quantum numbers.

<table>
<thead>
<tr>
<th>Operator</th>
<th>Quantum number</th>
<th>Observable</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hat{L}^2$</td>
<td>$l$</td>
<td>The square of orbital angular momentum</td>
</tr>
<tr>
<td>$\hat{S}^2$</td>
<td>$s$</td>
<td>The square of spin angular momentum</td>
</tr>
<tr>
<td>$\hat{J}^2 = (\hat{L} + \hat{S})^2$</td>
<td>$</td>
<td>l - s</td>
</tr>
<tr>
<td>$\hat{L}_z$</td>
<td>$m_l$</td>
<td>The $z$ component of $\hat{L}$</td>
</tr>
<tr>
<td>$\hat{S}_z$</td>
<td>$m_s$</td>
<td>The $z$ component of $\hat{S}$</td>
</tr>
<tr>
<td>$\hat{J}_z$</td>
<td>$m_j$</td>
<td>The $z$ component of $\hat{J}$</td>
</tr>
</tbody>
</table>

The set of quantum numbers $(n, l, m_l)$ characterizes orbitals in the limit of small spin-orbit coupling compared to the kinetic energy and Coulomb interaction terms. It can be deduced from the general solutions of the hydrogen-like atomic Schrödinger equation [2]

$$\Psi_{n,l,m_l}(r, \theta, \phi) \sim e^{-\frac{2Zr}{na_\mu}} \left( \frac{2Zr}{na_\mu} \right)^l L_{n-l-1}^{2l+1} \left( \frac{2Zr}{na_\mu} \right) P_{l}^{m_l}(\cos \theta) e^{im_l\phi}, \quad (2.3)$$

that the principal quantum number $n$ gives the total number of nodes, the angular momentum quantum number $l$ determines the number of angular nodes and the magnetic quantum number $m_l$ affects the orientation of the orbital. Here, $\mu$ is the reduced mass of the nucleus-electron system, $a_\mu = \frac{4\pi\varepsilon_0\hbar^2}{\mu c^2}$, $L_{n-l-1}^{2l+1}(\frac{2Zr}{na_\mu})$ is a generalized Laguerre polynomial [36] and $P_{l}^{m_l}(\cos \theta)$ is

---

\(^4\)Degenerate states correspond to the same energy with different sets of quantum numbers.
an associated Legendre polynomial [36]. In the absence of external fields, the energy is determined by the principal quantum number $n$, and each energy state is $2n^2$ times degenerate with $n - 1$ number of nodes. The azimuthal quantum number can have values of $l = 0, 1, \ldots, n - 1$ for a given $n$, and the magnetic quantum number can have values of $m_l = -l, -l + 1, \ldots, l - 1, l$ for a given $l$.

Classification of orbitals according to the set of $(n, l, m_l)$ is valid within the nonrelativistic\(^5\) orbital approximation picture when external fields, the spin-orbit coupling and instantaneous electron-electron interactions are not taken into consideration. Relativistic solutions have different symmetry due to the Lorentz invariance [37]. Quantum numbers $l$ and $m_l$ are no longer good once the spin-orbit coupling is included to the Hamiltonian. Instead, the system can still be characterized by $j$ and $m_j$. The instantaneous electron-electron interactions of real many-electron atoms make cracks to the spherical symmetry of the Coulomb potential. It is good to note that classification of many-electron atomic orbitals in terms of $(n, l, m_l)$ is in the end an artificial concept, since the existence of orbitals is based on an approximation of the real, interacting electron system [2]. It is still capable of giving good description of the electronic structure and forms a basis of defining the electron configurations of atomic systems.

2.2 Electron configuration

Electron configurations describe the electronic structure of atoms and molecules as sets of filled orbitals [15]. To develop the intuition for determining electron configurations, some simple techniques to define the filling order of atomic ground-state orbitals are introduced here. At this point, orbitals with the same set of $(n, l)$ are held degenerate\(^6\) regardless of the magnetic quantum number $m_l$. All techniques have to follow the Pauli principle [28, 29] so that a maximum of two electrons with different spin can occupy an orbital.

The most rudimentary technique, the original rules of the Aufbau principle [1, 2], state that the increasing orbital-energy order is determined mainly by the principal quantum number $n$. Within the same $n$, orbitals with increasing azimuthal quantum number $l$ are energetically at higher level. The filling order of orbitals according to the original Aufbau principle is demonstrated in the left side of Figure 2.2 where arrows display the direction of the increasing-energy order of the orbitals. The original rules neglect electron-electron interactions to such a degree that they are applicable only to the

\(^5\)At the nonrelativistic limit, the kinetic energy of a particle $E_{\text{kin}}$ is considerably less than its rest energy $mc^2$, that is, $E_{\text{kin}}/mc^2 \ll 1/10$.

\(^6\)The degeneracy of the same-$n$ states with different $l$, valid in hydrogen-like atoms, is broken due to the electron-electron interactions in many-electron atoms.
lightest atoms (up to the 3p orbital), requiring for more advanced ways to determine the ground-state electron configurations in more general cases.

![Figure 2.2: The Aufbau principle. The left side of the figure shows the filling order of the ground-state orbitals according to the original rules of the Aufbau principle, and the right side of the figure shows the filling order according to the Madelung rules.](image)

An improvement to the previous is obtained by the Madelung rules [38, 39], which fill the orbitals with increasing $n+l$ order starting from the smallest value of $n$. For example, the 4s orbital is at lower energy than the 3d orbitals. The right side of Figure 2.2 illustrates the filling order of the Madelung rules up to the 6s orbital. Comparing this with the left side of Figure 2.2 it can be seen that the filling order of the original Aufbau principle and the Madelung rules is the same up to the 3p orbitals. After this, the Madelung rules give corrections to the erroneous predictions of the original Aufbau principle.

There are situations in which the Madelung rules give erroneous electron configurations. The well-known examples are chromium and copper, which are transition-metal atoms and whose 4s orbital is only once occupied, while the 3d orbitals of chromium and copper are filled by 5 and 10 electrons, respectively. These anomalies can be explained by the low $LS$-terms of the configurations [40, 41]. Also, relativistic effects\(^7\) become substantial to heavy atoms, implying that $l$ and $m_l$ are no longer good quantum numbers. Despite

\(^7\)In here, relativistic effects are rather a vague concept that includes all corrections arising from the comparison of the results of accurate relativistic theory with the corresponding results of nonrelativistic theory. For example, spin-orbit coupling is also a relativistic effect.
2.3. SLATER DETERMINANTS

This, electron configurations of heavy atoms are also built up in terms of $nl$ orbitals. Some electron configurations are listed in Table 2.2 as an example, from which the utility and anomalies of the Madelung rules can be seen.

Table 2.2: The ground-state electron configurations of hydrogen, beryllium, sulfur, argon, copper, chromium, krypton and xenon atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Electron configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1s$^1$</td>
</tr>
<tr>
<td>Be</td>
<td>1s$^2$2s$^2$</td>
</tr>
<tr>
<td>Ne</td>
<td>1s$^2$2s$^2$2p$^6$</td>
</tr>
<tr>
<td>S</td>
<td>[Ne]3s$^2$3p$^4$</td>
</tr>
<tr>
<td>Ar</td>
<td>[Ne]3s$^2$3p$^6$</td>
</tr>
<tr>
<td>Cr</td>
<td>[Ar]3d$^5$4s$^1$</td>
</tr>
<tr>
<td>Cu</td>
<td>[Ar]3d$^{10}$4s$^1$</td>
</tr>
<tr>
<td>Kr</td>
<td>[Ar]3d$^{10}$4s$^2$2p$^6$</td>
</tr>
<tr>
<td>Xe</td>
<td>[Kr]4d$^{10}$5s$^2$5p$^6$</td>
</tr>
</tbody>
</table>

Electron configurations give more understanding to the structure of the periodic table of elements and chemical bonds [15]. A mathematical construction of the electron configuration introduced in the following section, the Slater determinant, is used as the trial function of the Hartree-Fock method.

2.3 Slater determinants

Electron configurations are realized into the mathematical formalism by Slater determinants [1, 2]

$$\Phi(1, 2, \ldots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \ldots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \ldots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \ldots & \phi_N(N) \end{vmatrix},$$

(2.4)

where $N$ is the number of electrons and $\{\phi_k\}$ are orthonormal, occupied one-electron states. Slater determinants are always antisymmetric with respect to the exchange of electrons, and satisfy the Pauli principle. Each Slater determinant can be associated to the electron configuration including exactly the same orbitals. This is not necessary valid vice versa, since the same electron configuration with partially occupied $np$ orbitals can be associated to several Slater determinants. In such cases it is not apparent, which Slater
determinant corresponds to the ground state. Usually it does not even make sense to describe the ground state with just one Slater determinant, and in such cases the ground state can be described by a linear combination of the nearly degenerate lowest-energy Slater determinants [42, 43].

The spin-orbit interaction is treated as perturbation [35] throughout this thesis, and the theoretical treatment is limited to the spin-restricted formalism [2]. One-electron orbitals are thought to be doubly degenerate with antiparallel spins. One-electron states can be expressed as

$$
\phi_{k,\alpha}(l) = \psi_k(l)\alpha \quad \text{or} \quad \phi_{k,\beta}(l) = \psi_k(l)\beta
$$

(2.5)

where \(\{\phi_{k,\alpha}(l), \phi_{k,\beta}(l)\}\) form a degenerate spin-restricted pair whose spatial parts \(\psi_k(l)\) are the same but the spins are antiparallel with each other. Here, \(\alpha\) and \(\beta\) correspond to the spin projection states with quantum numbers \(m_s = 1/2\) and \(m_s = -1/2\), respectively.
Chapter 3

Hartree-Fock theory

The Hartree-Fock (HF) theory is an iterative variational method that solves one-electron states of many-particle systems [2, 44]. It treats electrons as they are moving independently of each other in the Coulomb field of nuclei and the spherically averaged Coulomb field of the other electrons. In other words, effects of electron-electron interactions are spherically averaged and their instantaneous influences are ignored [2]. Figure 3.1 shows interactions affecting one atomic electron when the other electrons are treated as (a) point charges and (b) their effect is spherically averaged. It can be seen that the center of the averaged electronic Coulomb field is at the site of the nucleus and the electron is uncoupled from the motion of other electrons.

In the beginning, the initial set of one-electron states is guessed, for example, to be hydrogen-like orbitals [45]. This set determines spherically averaged Coulomb potential experienced by each electron, whose orbitals are then solved. The solutions are used as the reference set in the following iteration step, where the procedure is repeated once again. This is continued till the one-electron states and the Coulomb potential do not change significantly between the adjacent steps. At this point, the iteration process is converged and has followed the self-consistent field (SCF) procedure, which is treated in the following section, where the HF equations used for solving the HF orbitals are also derived.

The HF theory is a single-determinant method meaning that the trial wave function of the method constitutes of a single Slater determinant. This is applicable for describing the ground states of molecular systems fairly well. For the excited and the ionic states, near-degenerate correlation effects can be substantial and cannot be convincingly taken into consideration with only one Slater determinant [46, 47]. For this reason, only the ground-state wavefunctions are sought for in this and the next chapters.
### 3.1 Hartree-Fock equations

The total electronic energy of a molecular system is

$$E = \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \left( \sum_k \hat{h}_k + \frac{1}{2} \sum_{k \neq l} \hat{h}_{kl} \right) | \Psi \rangle \quad (3.1)$$

where the sums are over all electrons and electron-electron pairs, respectively. The Hamiltonian $\hat{H}$ is divided into the one-electron part $\sum_k \hat{h}_k$ and the two-electron part $\frac{1}{2} \sum_{kl} \hat{h}_{kl}$, where

$$\hat{h}_k = -\frac{\hbar^2}{2m} \nabla_k^2 - \frac{e^2}{4\pi \varepsilon_0} \sum_M \frac{Z_M}{r_{Mk}} \quad \text{and} \quad \hat{h}_{kl} = \frac{e^2}{4\pi \varepsilon_0} \frac{1}{r_{kl}} \quad (3.2)$$

The last term in the one-particle operator is abbreviated as $V_{Mk} = -e^2Z_M/(4\pi \varepsilon_0 r_{Mk})$.

The variational principle [36] provides the manifest for the HF theory, while looking for the minimum energy subject to the constraints of orthonormal one-electron states. This is mathematically stated as

$$\delta E = 0 \quad \text{subject to} \quad \delta \langle \phi_k | \phi_l \rangle = 0. \quad (3.3)$$
3.1. HARTREE-FOCK EQUATIONS

Energies corresponding to any other than the true ground-state wavefunction are always greater than the true ground-state energy [45, 48],

\[ E = \frac{\langle \Psi_{\text{trial}} | \hat{H} | \Psi_{\text{trial}} \rangle}{\langle \Psi_{\text{trial}} | \Psi_{\text{trial}} \rangle} \geq E_0, \quad (3.4) \]

where \( \Psi_{\text{trial}} \) is the trial wavefunction, \( E \) is the energy corresponding to \( \Psi_{\text{trial}} \), and \( E_0 \) is the true ground-state energy.

A single Slater determinant composed of the least energetic one-electron states is chosen as the trial ground-state wavefunction. One-electron states are guessed in the initial step of calculations. Each constraint in the variation expression is multiplied by a constant, a Lagrange multiplier, and added to the variation of energy:

\[ \delta (E - \sum_{kl} \epsilon_{kl} \langle \phi_k | \phi_l \rangle) = 0. \quad (3.5) \]

Now, the right side of Equation (3.1) is substituted to the energy \( E \). With the HF trial ground-state wavefunction, the above equation can be manipulated in order to gain conditions for each one-electron states, so that

\[ \hat{f}_1 \phi_k (1) = \sum_{kl} \epsilon_{kl} \phi_l (1) \quad (3.6) \]

where the Fock operator

\[ \hat{f}_1 = \hat{h} + \sum_l \{ \hat{J}_l (1) - \hat{K}_l (1) \} \quad (3.7) \]

is a practical way to write out the interaction terms of the energy equation in short. The operators \( \hat{J} \) and \( \hat{K} \) in the above describe the direct term and the exchange term of the Coulomb repulsion between electrons

\[ \hat{J}_k (1) \phi_l (1) = \frac{e^2}{4 \pi \varepsilon_0} \left[ \int \phi_k^* (2) \frac{1}{r_{12}} \phi_l (2) \delta_{s_k,s_l} d \tau_2 \right] \phi_l (1) \]
\[ \hat{K}_k (1) \phi_l (1) = \frac{e^2}{4 \pi \varepsilon_0} \left[ \int \phi_k^* (2) \frac{1}{r_{12}} \phi_l (2) \delta_{s_k,s_l} d \tau_2 \right] \phi_k (1) \quad (3.8) \]

respectively, where both integrals are computed over the spatial coordinates and \( s \) is the spin state.

Equation (3.6) is one form of Hartree-Fock equations. It can be simplified by changing into the basis in which \( \epsilon_{kl} \) becomes diagonal, that is, \( \epsilon_{kl} \rightarrow \delta_{kl} \varepsilon_l \). In this new basis, the Hartree-Fock equations (3.6) can be written in their canonical form:

\[ \hat{f}_1 \phi_k (1) = \epsilon_k \phi_k (1) \quad (3.9) \]
CHAPTER 3. HARTREE-FOCK THEORY

3.2 Roothaan-Hall equations

An alternative way to solve HF equations is introduced in this section, where the one-electron orbitals are built up as linear combinations of a set of fixed basis functions \( \{\chi_i\} \),

\[
\Phi_k = \sum_i c_{ik} \chi_i, \tag{3.10}
\]

where \( \{c_{ik}\} \) are coefficients that remain to be optimized. This linear combination is known as the basis set expansion and it makes the HF calculations generally affordable in molecular studies [2]. Basis sets can be grouped into different \( l \) types, since different orbitals with the same \( l \) have the similar angular dependence as the hydrogenic orbitals. Substituting the basis set expansion to the HF wavefunction enables to write the HF equations as the set of Roothaan-Hall equations [49], which can be expressed as a single matrix equation

\[
\mathbf{F} \mathbf{c} = \mathbf{S} \mathbf{c}, \tag{3.11}
\]

The elements of the overlap matrix and the Fock matrix are

\[
S_{ij} = \int \chi_i^*(1) \chi_j(1) d\tau_1 \quad \text{and} \quad F_{ij} = \int \chi_i^*(1) \hat{f}_1 \chi_j(1) d\tau_1, \tag{3.12}
\]

respectively. The coefficient matrix \( \mathbf{c} \) and the diagonal orbital energy matrix \( \mathbf{\varepsilon} \) are \( N_B \times N_B \)-dimensional, where \( N_B \) is the number of the basis functions. The number of one-electron states obtained from the Roothaan-Hall equations is determined by the number of the basis functions, and is also \( N_B \) [2].

In the Roothaan-Hall equations, the coefficients \( \{c_{ik}\} \) are optimized to give the minimum of energy, and can be solved by the matrix-equation techniques. The ability to gain reliable results is bound by one more factor, the quality of the basis set. Discussion of basis sets is omitted here, and it is enough only to be aware of different techniques to solve the HF equations. Molecular orbitals are usually solved from the Roothaan-Hall equations (3.11) rather than the HF equations (3.9), since the latter are usually impractical from the viewpoint of computational demands [2].
Electron correlation methods revive such effects of electron-electron interactions that are not included in the spherically averaged Coulomb potential: near-degeneracy correlation \[46, 47\], dynamic correlation \[50\], and polarization of spin and charge density \[51, 52, 53\]. They can be numerically included approximately to the full extent in the calculations. In practice, computational demands of current methods and computer capacity enable this only for the smallest systems \[54, 55\]. In general, only the terms describing most of the correlation are included to the calculations \[2\]. Three post-Hartree-Fock correlation methods are introduced in this chapter. They all use the HF wavefunction as the reference state and are applicable to determine the ground-state wavefunction. These methods are the Møller-Plesset perturbation theory, the configuration interaction method and the coupled-cluster method.

The amount of the post-HF correlation is expressed as the difference between the HF limit of the molecular energy \(E_{\text{HF}}\) and the exact energy \(E_{\text{true}}\), i.e.

\[
\Delta E = E_{\text{true}} - E_{\text{HF}},
\]

which is called the correlation energy. In practice, the difference is made within the accuracy of the basis set and the chosen correlation method used for the calculations \[2\].

In this chapter, the basis-set expansion is assumed to be applied to the introduced electron-correlation methods, and only the ground-state wavefunction is sought for.
CHAPTER 4. POST-HARTREE-FOCK ELECTRON CORRELATION METHODS

4.1 Configuration interaction

The configuration interaction theory uses a linear expansion of Slater determinants

\[ \Psi^{(\text{CI})} = \sum_J C_J^{(\text{CI})} \Phi_J^{(\text{HF})}. \]  

(4.2)

as a trial wavefunction. The number of one-electron states is the same as the number of the basis functions \( N_B \) solved from the Roothaan-Hall equations. For closed-shell atoms, \( N_B!/[ (N_B - N/2)! (N/2)! ] \) different Slater determinants can be constructed [2]. Each Slater determinant is classified according to its excitation number, expressing the number of the excited one-electron states in the Slater determinant when the reference state is the HF ground state. Figure 4.1 demonstrates the orbital occupation of a 4-electron system with different excitation numbers. The electrons are in the ground state corresponding to the reference Slater determinant in Figure 4.1 (a), one electron is excited corresponding to singly excited Slater determinants in (b,c), and two electrons are excited corresponding to doubly excited Slater determinants in (d,e). Triply and higher excited Slater determinants can be built up similarly. In the CI theory, configuration state functions (CSFs) [2] can be formed from the Slater determinants, which is an alternative and more compact way to build up a many-electron basis.

In the full-CI method, all Slater determinants that can be obtained from the Roothaan-Hall method within the chosen basis set are included in the CI expansion. It provides a numerical limit to the correlation energy. The method involves a high computation cost, which can be reduced by omitting Slater determinants of negligible importance for the electron correlation [56]. Symmetry properties of the system and the excitation numbers of Slater determinants are used to estimate the significance of each Slater determinant to the calculations [57].

For example, the predominant matrix elements

\[ H_{0J} = \langle \Phi_0^{\text{HF}} | \hat{H} | \Phi_J^{\text{HF}} \rangle \]  

(4.3)

are nonzero only when \( | \Phi_J^{\text{HF}} \rangle \) correspond to the reference and doubly excited Slater determinants. Thus, most of the electron correlation is revived by doubly excited Slater determinants. On the other hand, singly excited Slater determinants couple with doubly excited Slater determinants and take significantly part in determining the electronic charge distribution. Higher-order (triply, quadratically, etc.) excited Slater determinants do refine the solution, but their contribution is much smaller than doubly excited or singly excited Slater determinants [2].

The CI technique with only doubly excited Slater determinants in addition to the HF wavefunction is denoted DCI. When singly excited Slater determinants are also included, the technique is called SDCI. Both are examples
4.1. CONFIGURATION INTERACTION

Figure 4.1: Orbital occupation of electrons in a four-electron atomic system corresponding to (a) the ground-state configuration, (b,c) singly excited configurations, (d,e) doubly excited configurations, based on the orbital approximation picture. Solid spheres represent electrons and transparent spheres vacancies that would be filled when the system is in the ground state.

of the limited CI techniques not including all possible Slater determinants and lacking size-consistency\(^1\) [58].

CI calculations provide a systematic way to study electron correlation effects in terms of the excitation numbers. Practical applications of the method usually include only singly and doubly excited Slater determinants. Sometimes, triply and quadratically excitation Slater determinants are also added in order to analyse the dependence of the correlation energy on the excitation number. Unfortunately, such analysis cannot be done using large basis sets due to the computational requirements.

\(^1\)Size-consistency means the consistent behaviour of energy when interaction between the involved particles is nullified. For example, the total energy of two helium atoms far away from each other is two times the total energy of one helium atom when the energy is solved with size-consistent methods.
4.2 Møller-Plesset perturbation theory

The Møller-Plesset perturbation theory (MPPT) is a special case of the Rayleigh-Schrödinger perturbation theory on the many-particle molecular systems [2]. It uses Fock operators as the unperturbed Hamiltonian

\[ \hat{H}^{(0)} = \hat{H}_{\text{HF}} = \sum_{k=1}^{N} \hat{f}_k \]  

(4.4)

and the remaining term of the exact Hamiltonian as the perturbation

\[ \hat{H}^{(1)} = \hat{H} - \hat{H}_{\text{HF}} = \sum_{k} \left[ \epsilon^2 \pi \varepsilon_0 \sum_{l \neq k}^{N} \frac{1}{r_{lk}} - \sum_{m}^{N/2} \{2\hat{J}_m(k) - \hat{K}_m(k)\} \right] \],  

(4.5)

which is also called either the correlation or the fluctuation potential.

The zeroth-order wavefunction is an eigenfunction of the zeroth-order Hamiltonian, the HF wavefunction:

\[ |\Psi^{(0)}\rangle = |\Phi^{(\text{HF})}\rangle. \]  

(4.6)

The first-order correction to the wavefunction is the sum over all doubly excited Slater determinants

\[ |\Psi^{(1)}\rangle = -\sum_{j(2)} \frac{\langle \Phi^{(\text{HF})}_{j(2)} | \hat{H} | \Psi^{(0)} \rangle}{E^{(0)}_{j(2)} - E_{\text{MP}}^{(0)}} |\Phi^{(\text{HF})}_{j(2)}\rangle \]  

(4.7)

where \( E_{j}^{(0)} = \langle \Phi^{(\text{HF})}_{j} | \hat{H}^{(0)} | \Phi^{(\text{HF})}_{j} \rangle \). Specifically, the zeroth-order MP energy correction term is the sum of the occupied orbital energies

\[ E_{\text{MP}}^{(0)} = \langle \Psi^{(0)} | \hat{H}^{(0)} | \Psi^{(0)} \rangle = \sum_{k=1}^{N} \varepsilon_k. \]  

(4.8)

With the zeroth-order wavefunction and its first-order correction, it would be possible to construct the energy up to the third-order correction term [2].

Systematic studies of MPPT have revealed that the method does not necessarily converge at high orders due to oscillating terms. The order-wise convergence rate, as well as the goodness and existence of convergence, depend on the precise chemical system or basis set. The convergence of the MPPT is thoroughly studied in Leininger, Allen and Schaefer’s article [59].

The second-order Møller-Plesset (MP2) calculations [25] provide the best accuracy with respect to the computational cost. It is nowadays the most
used level of MP calculations. The first-order and the second-order correction terms,

\[ E_{\text{MP}}^{(1)} = \langle \Psi^{(0)} | \hat{H}_{\text{PB}} | \Psi^{(0)} \rangle \quad \text{and} \]

\[ E_{\text{MP}}^{(2)} = \langle \Psi^{(0)} | \hat{H}_{\text{PB}} | \Psi^{(1)} \rangle = \sum_{j \neq 0} \frac{\langle \Phi_j | \hat{H}_{\text{PB}} | \Phi_0 \rangle \langle \Phi_0 | \hat{H}_{\text{PB}} | \Phi_j \rangle}{E_0^{(0)} - E_j^{(0)}}, \quad (4.9) \]

respectively, are needed in MP2 in addition to the terms already mentioned.

Hartree-Fock energy is expressed in terms of MP2 theory as

\[ E_{\text{HF}} = \langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle = E_{\text{MP}}^{(0)} + E_{\text{MP}}^{(1)} + h_{\text{nuc}} \quad (4.10) \]

where \( h_{\text{nuc}} \) is the electronic-nuclear HF interaction energy. Electron correlation is estimated in MP2 by the second-order energy correction term \( E_{\text{MP}}^{(2)} \).

The MP2 approximation of the true total energy is then

\[ E_{\text{true, MP2}} = E_{\text{HF}} + E_{\text{MP}}^{(2)}. \quad (4.11) \]

MP2 is a coarse non-variational way to determine electron correlation from the viewpoint of the accuracy, and is mostly applied nowadays only to give estimation to the effects of electron-electron interactions ignored in the HF method.

### 4.3 Coupled-cluster method

The coupled-cluster (CC) theory is the most successful approach to solve the accurate many-electron molecular wavefunction, as long as the many-electron system is reasonably precisely described by a single-determinant wavefunction. Electron correlation is revived according to the exponent ansatz [26] and the approximate many-electron wavefunction is expressed as

\[ |\Psi^{(CC)}\rangle = e^{\hat{T}} |\Phi^{(\text{HF})}\rangle. \quad (4.12) \]

The cluster operator \( \hat{T} \) is partitioned into classes of excitation operators

\[ \hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_N, \quad (4.13) \]

where subscripts refer to the number of excitations in the simultaneous process. The excitation operators are most conventionally represented in the second-quantization formalism [60], which uses creation \( \{ \hat{a}_k^\dagger \} \) and annihilation operators \( \{ \hat{a}_k \} \) as the basis. The most important excitation processes, single excitations and double excitations, are described as

\[ \hat{T}_1 = \sum_{k,u} t_{k,u} u_k^\dagger \hat{a}_u^\dagger \hat{a}_k \quad \text{and} \quad \hat{T}_2 = \frac{1}{4} \sum_{k,l,u,v} t_{k,l,u,v}^{u,v} u_k^\dagger \hat{a}_u^\dagger \hat{a}_k \hat{a}_l \hat{a}_l \quad (4.14) \]
where $t_{k}^{u}$ is the amplitude related to the probability that an electron is excited from state $k$ to state $u$, and $t_{k,l}^{u,v}$ is the amplitude related to the probability that two electrons are simultaneously excited from the states $k$ and $l$ to the states $u$ and $v$.

Since maximum two electrons can locate in the same spatial orbital, double excitations dominate the excitation processes [55]. Single excitations couple with double excitations and are needed for the accuracy of the calculations. The contribution of triple and higher excitations is considerably less important.

The same excited configuration states can be acquired through different types of excitation processes [2]. As an example, Figure 4.2 demonstrates two different excitation processes leading to the doubly excited configuration of a four-electron atom, which has two electrons excited from the $2s$ orbital to the $2p$ orbital. In Figure 4.2(b), two single excitations occur with the probability amplitude $(t_{2s}^{2p})^2$, and in Figure 4.2(c) a double excitation lifts up both electrons with the probability amplitude $t_{2s,2s}^{2p,2p}$. The first case is an example of a disconnected excitation process, in which the excited state is a result of different excitation processes. The second case is an example of a connected excitation process, in which the excited state is a result of a simultaneous excitation process. CC method is size-consistent and includes higher-order disconnected excitation processes due to the exponential ansatz (4.12) even when the cluster operator is truncated (4.13), which are the main reasons behind the success of the method.

![Figure 4.2](image-url)

Figure 4.2: (a) A double-excitation state of a four-electron atomic system with two electrons in the $1s$ orbital and another two electrons in the $2p$ orbitals. The excited state can be achieved either by (b) two single one-electron excitations or (c) a double two-electron excitation.

The most conventional way to determine the excitation amplitudes is to form a solvable set of nonlinear equations from the conditions

$$
\begin{align*}
\langle \Psi_{HF} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_{HF} \rangle &= E \\
\langle \Psi_{HF}^{(\mu)} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_{HF} \rangle &= 0,
\end{align*}
$$
where $|\Psi_{\text{HF}}^{(\mu)}\rangle$ is an excited HF determinant. Different variational ways to solve the excitation amplitudes are also implemented [61], but they have not gained a remarkable popularity.

The cluster operator is truncated for practical implementations. Coupled-cluster singles and doubles (CCSD) calculations are the most popular way to apply the CC theory, leaving only the single and double excitation operators in $\hat{T}$ [62]. The operators give contributions of single, double and their disconnected excitation processes to all excited Slater determinants obtained by the Roothaan-Hall method, covering the majority of correlation effects. It is applicable to large systems especially when there are no degenerate or near-degenerate configurations for the reference state. In general, CC method is size-consistent. For high-accuracy calculations, triple excitation operators are also included. The method with triples is abbreviated CCSDT, but it is computationally expensive and not applied to any other but the smallest systems.
CHAPTER 4. POST-HARTREE-FOCK ELECTRON CORRELATION METHODS
Chapter 5

Conclusions

Strategies for solving the electronic structure of atoms and molecules starting from the fundamental physical laws were introduced in this thesis. The review was limited to the Hartree-Fock method and a few of the post-Hartree-Fock electron correlation methods. The relations between the various concepts of relevance are schematically shown in Figure 5.1.

Figure 5.1: Schematic picture of the relations between the concepts introduced in this thesis.

The orbital approximation provides a framework for working on the electronic structure when the interaction between electrons are spherically averaged. Similarities between hydrogenic atoms and many-electron atoms are exploited to classify the many-electron atomic orbitals with the same set of good quantum numbers as the hydrogenic atoms. The Pauli principle restricts the occupation number of an orbital at most to two and, together with the chosen classification, the electronic structure of many-electron atoms can
be expressed either by an electron configuration or a Slater determinant, which is a mathematical construction. One Slater determinant corresponds always to one electron configuration. The same correspondence is not valid vice versa, since one electronic configuration might be described by several Slater determinants especially in the case of open-shell atoms and molecules. Hence, only the one-way arrow is drawn from the Slater determinant to the electron configuration in Figure 5.1.

Orbital approximation provides the framework for the Hartree-Fock method, which uses a Slater determinant as the trial function for a many-electron wave function. The orbitals are optimized in the iterative self-consistent-field procedure. The orbitals can be expressed either numerically or in terms of the basis set expansion. This choice affects the formalism and the computational cost of the calculations, but the idea behind the Hartree-Fock scheme remains the same in both cases. The Hartree-Fock wavefunction is the starting point for various post-Hartree-Fock electron correlation methods: the coupled-cluster method, Møller-Plesset perturbation method and the configuration interaction method. The features and applications of different methods are listed in Table 5.1.

The Hartree-Fock method with various post-Hartree-Fock electron correlation methods provide a robust mechanism to study the electronic structure of materials purely theoretically. They have established themselves as reliable research tools for quantum-chemical purposes. This thesis has omitted several concepts also useful for studying chemical systems. Only the electronic structure is obtained from the methods introduced here, excluding many molecular properties such as different spectral parameters, bond lengths, etc. from the review. All of these can be studied once the electronic structure is known. Another important approach for solving the electronic structure, the density functional theory, is omitted from the thesis. The HF theory and the electron correlation methods were treated only in the non-relativistic framework, which is an insufficient level for heavy atoms. All of these excluded topics are important for a comprehensive picture of quantum chemistry. The purpose of this thesis was only to provide a review on an idea how to obtain a reliable electronic structure description relying purely on theoretical reasoning. Numerical solutions at least for the orbitals of light atoms and molecules can be obtained using the strategies introduced here.
Table 5.1: Features of the electronic structure methods introduced in this thesis.

<table>
<thead>
<tr>
<th>Theory</th>
<th>Hartree-Fock</th>
<th>Configuration interaction</th>
<th>Møller-Plesset perturbation</th>
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<tr>
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<td>Iterative, Variational, Self-consistent-field</td>
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<tr>
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<td>Slater determinant</td>
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<td>No trial function. Unperturbed wavefunction is the HF wavefunction</td>
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<tr>
<td>Popular levels of theory</td>
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<tr>
<td>Electron correlation taken into account</td>
<td>Spherically averaged electron-electron interactions</td>
<td>In terms of excitation numbers</td>
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<td>In terms of excitation processes</td>
</tr>
<tr>
<td>Size consistency</td>
<td>YES</td>
<td>Limited CI: NO, Full CI: YES</td>
<td>-</td>
<td>YES</td>
</tr>
<tr>
<td>Application</td>
<td>Qualitative description of the ground-state electronic structure of atoms and molecules</td>
<td>Systematic study of electron correlation in terms of excitation numbers. Expensive, so only for small systems.</td>
<td>Cost-efficient estimation of the magnitude of the electron correlation.</td>
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Bibliography


BIBLIOGRAPHY
Appendix A

Hydrogenic orbitals

The time-dependent Schrödinger equation for the electrons of hydrogenic atoms is

\[ \hat{H} \psi = \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \right) \psi = i\hbar \frac{\partial}{\partial t} \psi \] (A.1)

where \( \hbar \) is the reduced Planck constant, \( m \) is the electron mass, \( Z \) is the atomic mass number, \( e \) is the elementary charge, \( \varepsilon_0 \) is the dielectric constant of vacuum and \( r \) is the distance between the electron and the nucleus. The Laplace operator \( \nabla^2 \) is in the spherical coordinates

\[ \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \] (A.2)

where \( \Lambda^2 = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \) contains only the angular terms of the Laplace operator.

The wavefunction is separated into terms depending either on the spatial or the time coordinates, \( \Psi(r, \theta, \varphi, t) = \psi(r, \theta, \varphi)X(t) \). This is substituted to the Schrödinger equation (A.1), which becomes after dividing by \( \psi(r, \theta, \varphi)X(t) \):

\[ \left( -\frac{\hbar^2}{\psi(r, \theta, \varphi) 2m} \nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 \psi(r, \theta, \varphi)} \right) \psi(r, \theta, \varphi) = i\hbar \frac{1}{X(t)} \frac{\partial X(t)}{\partial t} = E, \] (A.3)

which has to be constant since the left side of the equation depends only on the spatial components and the right side only on the time component. From
this, it is easy to solve the time-dependent term of the wavefunction:

\[
\frac{i\hbar}{X(t)} \frac{dX(t)}{dt} = E
\]

\[
\Leftrightarrow \frac{dX(t)}{dt} = -iE X(t)
\]

\[
\Rightarrow X(t) = Ke^{-iEt},
\]

where \(K\) is a constant that can be chosen to be 1, for example.

The remaining part left to be solved

\[
\hat{H}\psi(r, \theta, \varphi) = \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0} \right) \psi(r, \theta, \varphi) = E\psi(r, \theta, \varphi)
\]

depends only on the spatial coordinates. It is known as the time-independent Schrödinger equation for hydrogenic atoms and was disclosed in Eq. (2.2).

The separation into the radial and the angular terms is applied, \(\psi(r, \theta, \varphi) = R(r)Y(\theta, \varphi)\), and the time-independent Schrödinger equation (A.4) is divided by \(R(r)Y(\theta, \varphi)\):

\[
-\frac{\hbar^2}{2m} \left\{ \frac{1}{rR(r)} \frac{\partial^2}{\partial r^2} [rR(r)] + \frac{1}{r^2 Y(\theta, \varphi)} \Lambda^2 Y(\theta, \varphi) \right\} - \frac{Ze^2}{4\pi\varepsilon_0 r} = E
\]

\[
\Rightarrow \frac{r}{R(r)} \frac{\partial^2}{\partial r^2} (rR(r)) + \frac{Ze^2 m}{4\pi\varepsilon_0 \hbar^2} r + \frac{2mE}{\hbar^2} - \frac{1}{Y(\theta, \varphi)} \Lambda^2 Y(\theta, \varphi) = k,
\]

where \(k\) is constant.

**Solving the angular part of the Eq. (A.5)**

The angular part of the Eq. (A.5) is written out in terms of the polar angle \(\theta\) and the azimuth angle \(\varphi\), and the angular part of the wavefunction is separated into the terms depending on the corresponding angles, \(Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)\):

\[
\Lambda^2 Y(\theta, \varphi) = \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \Theta(\theta)\Phi(\varphi) = k\Theta(\theta)\Phi(\varphi).
\]

(A.6)

The similar manipulation of the equation as earlier in the appendix is applied, which leads to the equation

\[
\frac{1}{\Phi(\varphi)} \frac{d^2\Phi(\varphi)}{d\varphi^2} = -\frac{1}{\Theta(\theta)} \sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + k\sin^2 \theta = -m_l^2,
\]

(A.7)

where \(m_l\) is constant.
The general solution of the azimuthal part

\[ \frac{1}{\Phi(\varphi)} \frac{d^2}{d\varphi^2} \Phi(\varphi) = -m_l^2 \]  

is

\[ \Phi(\varphi) = Ae^{im_l \varphi} + Be^{-im_l \varphi}, \]  

where \( A \) and \( B \) are constants. Physically meaningful solutions are continuous and thus periodic in full lap of \( 2\pi \), that is

\[ \Phi(\varphi) = \Phi(\varphi + 2\pi n), \quad \text{where} \quad n = 0, \pm 1, \pm 2, \ldots. \]  

This restricts the solutions of Eq. (A.9) to the integer numbers,

\[ m_l = 0, \pm 1, \pm 2, \ldots. \]  

The different terms of the solution (A.9) correspond to the different states, and it is common to choose only the first term as the solution of azimuthal angular term,

\[ \Phi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im_l \varphi}, \]  

where \( A = \frac{1}{\sqrt{2\pi}} \) has been determined from the normalization condition

\[ 1 = \int_0^{2\pi} \Phi(\varphi)^* \Phi(\varphi) d\varphi. \]

Solving the polar angular term is a bit more complicated, since the equation to be solved is of the form:

\[ -\sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta(\theta)}{d\theta} \right) - k \sin^2 \theta \Theta(\theta) = -m_l^2 \Theta(\theta). \]  

The solution of such equation, taking the normalization of the wavefunction into consideration and including only the physically meaningful solutions, is

\[ \Theta(\theta) = \left( \frac{2l + 1}{2} \right)^{1/2} P_l^{m_l} \cos \theta, \]  

where \( \cos \theta = z \Rightarrow \sin^2 \theta = 1 - z^2; \)

\[ \Theta(\theta) = Q(z) \Rightarrow \frac{d\Theta(\theta)}{d\theta} = \frac{dQ(z)}{dz} \frac{dz}{d\theta} = -\frac{dQ(z)}{dz} \sin \theta, \]  

which simplifies the equation (A.13) to the

\[ \frac{d}{dz} \left( (1 - z^2) \frac{dQ(z)}{dz} \right) + \left( k - \frac{m_l^2}{1 - z^2} \right) = 0. \]  

The solution of such equation, taking the normalization of the wavefunction into consideration and including only the physically meaningful solutions, is

\[ \Theta(\theta) = \left( \frac{2l + 1}{2} \right)^{1/2} P_l^{m_l} \cos \theta, \]  

where \( A = \frac{1}{\sqrt{2\pi}} \) has been determined from the normalization condition

\[ 1 = \int_0^{2\pi} \Phi(\varphi)^* \Phi(\varphi) d\varphi. \]
where \( l(l+1) = k \) and \( l = |m_l|, |m_l|+1, \ldots \), and \( P_l^{|m_l|}(\cos \theta) \) is the associated Legendre function.

Operating on the obtained angular solutions with the angular operator \( \Lambda^2 \) results in

\[
\Lambda^2 \Theta(\theta) \Phi(\varphi) = -l(l+1) \Theta(\theta) \Phi(\varphi). \tag{A.17}
\]

**Solving the radial part of the Eq. (A.5)**

Substituting the Eq. (A.17) to the Eq. (A.5) gives the differential equation for the radial function

\[
\frac{1}{r R(r)} \frac{d}{dr} \left( r R(r) \right) + \frac{Z e^2 m}{4 \pi \varepsilon_0 \hbar^2 r} + \frac{2mE}{\hbar^2} = \frac{l(l+1)}{r^2}. \tag{A.18}
\]

The solution for this equation is

\[
R(r) = e^{-\frac{Ze^2}{2\pi\varepsilon_0\hbar^2}r} R_{nl}(r) = -e^{-\frac{Ze^2}{2\pi\varepsilon_0\hbar^2}r} \left\{ \left( \frac{2Z}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^2} \right\} \rho L_{n+l}^{2l+1}(\rho) e^{-\rho/2}; \tag{A.19}
\]

where \( \rho = \frac{Ze^2}{2\pi\varepsilon_0\hbar^2}r \) and \( L_{n+l}^{2l+1}(\rho) \) is the associated Laguerre function. The limitations of the quantum numbers \( n, l, m_l \) are:

\[
\begin{align*}
n & = 1, 2, 3, \ldots \\
l & = n - 1, n - 2, \ldots, 0 \quad \text{for a given } n, \\
m_l & = l, l - 1, \ldots, -l + 1, -l \quad \text{for a given } l. \tag{A.20}
\end{align*}
\]