Lecture 1

The Theoretical Description of Matter

This lecture starts from the many-body Schrödinger equation and reworks it into a form suitable for approximate solution. We briefly comment on the Hartree and Hartree-Fock approximations. Finally, we discuss the Thomas-Fermi model to set the stage for the Hohenberg-Kohn formalism in the next lecture.

1.1 The Many-Body Schrödinger Equation

Our starting point is the time independent non-relativistic Schrödinger equation in a description of a system of atoms. It is the eigenvalue equation for the total energy operator, the Hamiltonian $\hat{H}$. The equation defines all many-particle states $\Psi$ of the system and their related energies $E$:

$$\hat{H}\Psi = E\Psi.$$  (1.1)

Adopting the wave-function formulation of quantum mechanics, $\Psi$ is the many-body wave-function. The wave-function has as variables the spatial positions and spin coordinates of all involved particles. A typical matter system is composed by $N_e$ positively charged nuclei and $N$ electrons, and one can then state explicitly the wave-function variables as

$$\Psi(R_1, R_2, ..., R_{N_e}, x_1, x_2, ..., x_N)$$  (1.2)

Here, $R_i$ are the positions of the nuclei (for now we have left out, e.g., nuclear spin, or one can view the $R_i$ as also including such degrees of freedom), and $x_i$ are the combined spatial locations and spin coordinates of the electrons, $x_i = (r_i, \sigma_i)$ where $\sigma_i = \uparrow$ or $\downarrow$. The usual interpretation in quantum mechanics of the wave-function as a probability distribution means that

$$|\Psi(R_1, R_2, ..., R_{N_e}, x_1, x_2, ..., x_N)|^2 dR_1 dR_2 ... dR_3 dx_1 dx_2 dx_3 ...$$  (1.3)

for infinitesimal $\{dR_i\}$ and $\{dx_i\}$ is the probability of finding the complete system in a state where simultaneously the first nuclei is in a position between $R_1$ and $R_1 + dR_1$ and the second nuclei is in a position between $R_2$ and $R_2 + dR_2$, etc., for all the variables in the wave-function.

As we intend to model matter in a reasonably typical state, it is at this point common to assume that the Schrödinger equation can be separated into independent electronic and nucleonic parts. This is the Born-Oppenheimer approximation, which is valid when the electrons reach equilibrium on a time scale that is short compared to the time scale on which...
the nuclei move. The approximation separates the states into independent states for nuclei \( \Psi_n \) and electrons \( \Psi_e \), with energies \( E_n \) and \( E_e \). The result is

\[
\hat{H}_n \Psi_n(R_1, R_2, R_3, \ldots) = E_n \Psi_n(R_1, R_2, R_3, \ldots), \tag{1.4}
\]

\[
\hat{H}_e \Psi_e(x_1, x_2, x_3, \ldots; \{R_i\}) = E_e \Psi_e(x_1, x_2, x_3, \ldots; \{R_i\}), \tag{1.5}
\]

where the dependence on \( \{R_i\} \) in \( \Psi_e \) is a parametric dependence on the classical positions of the nuclei, and not wave-function variables. For the purpose of energy- and electronic structure calculations we will adopt this picture and take the nuclei positions as given. To the extent that we want to compare different nuclei positions we will solve the electronic part of the equation multiple times. Hence, our concern in the following is the electronic part, which now describes interacting electrons which move in a static external potential from the positively charged nuclei. For simplicity we will from now on drop the explicit dependence of the nuclei coordinates.

The energy operator of the electronic part \( \hat{H}_e \) is conventionally split into a sum of three contributions: the \textit{kinetic energy} of the electrons \( \hat{T} \), the \textit{internal potential energy} (the repulsion between individual electrons) \( \hat{U} \), and the \textit{external potential energy} (the attraction between the electrons and nuclei) \( \hat{V} \). It is also common to use \( \hat{F} \) for the total \textit{internal electronic energy}, i.e., \( \hat{T} + \hat{U} \):

\[
\hat{H}_e = \hat{T} + \hat{U} + \hat{V} = \hat{F} + \hat{V}. \tag{1.6}
\]

The solutions to Eq. (1.5) are the energy eigenstates of the system. Every such many-electron wave-function must fulfill two conditions; it must be normalized

\[
\langle \Psi_e | \Psi_e \rangle = \int \ldots \int |\Psi_e|^2 d x_1 d x_2 \ldots d x_N = 1, \tag{1.7}
\]

and \textit{antisymmetric}

\[
\Psi_e(..., x_i, ..., x_j, ...) = - \Psi_e(..., x_j, ..., x_i, ...). \tag{1.8}
\]

The state \( \Psi_e \) with the lowest energy eigenvalue \( E_e \) is the systems \textit{ground state}.

The contributions to the Hamiltonian can be explicitly expressed as

\[
\hat{T} = - \left( \frac{\hbar^2}{2m_e} \right) \sum_{i=1}^{N} \nabla^2_i, \tag{1.9}
\]

\[
\hat{U} = \frac{1}{2} \left( \frac{e^2}{4\pi \epsilon_0} \right) \sum_{i \neq j}^{N} \frac{1}{|r_i - r_j|}, \tag{1.10}
\]

\[
\hat{V} = \sum_{i=1}^{N} v(r_i). \tag{1.11}
\]

where the sum over \( i \neq j \) means to sum over all values of \( i \) and \( j \) up to \( N \), except for the terms where \( i = j \).

Multiplication of both sides of Eq. (1.5) from the left with \( \Psi_e^* \) and integrating over all wave-function variables gives the usual expression for the electronic energy \( E_e \) as the \textit{expectation}
value of the Hamiltonian,
\[ E_e = \langle \Psi_e | \hat{H}_e | \Psi_e \rangle = \langle \Psi_e | \hat{T} + \hat{U} + \hat{V} | \Psi_e \rangle = T + U + V \]  
(1.12)
\[ T = -\left( \frac{\hbar^2}{2m_e} \right) \int \ldots \int \sum_{i=1}^{N} \Psi_e^* \nabla_i^2 \Psi_e dx_1 dx_2 \ldots dx_N \]  
(1.13)
\[ U = \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \int \ldots \int \sum_{i \neq j} \frac{\Psi_e^2}{|r_i - r_j|} dx_1 dx_2 \ldots dx_N \]  
(1.14)
\[ V = \int \ldots \int \sum_{i=1}^{N} \Psi_e^2 v(r_i) dx_1 dx_2 \ldots dx_N \]  
(1.15)

Here \( T, U \) and \( V \) are introduced as the individual scalar expectation values of the corresponding operators.

### 1.2 The Electron Density

The electron density \( n(r) \) is defined as the number of electrons per volume at the point \( r \) in space. We expect the integral of the electron density to give the total number of electrons,
\[ \int n(r) dr = N. \]  
(1.16)

There are several ways to define the electron density. Here we start by defining the spin-independent particle density operator as
\[ \hat{n} = \sum_{i=1}^{N} \delta(r - r_i) \]

From a classical standpoint, this is a reasonable definition. The \( \delta \) function ensures that if the operator is applied to a state where an electron is exactly at \( r' \), the density is infinitely large at this point and zero everywhere else.

The expectation value of this operator is
\[ n(r) = \langle \Psi_e | \hat{n} | \Psi_e \rangle = \int \ldots \int \Psi_e^*(x_1, x_2, \ldots, x_N) \hat{n} \Psi_e(x_1, x_2, \ldots, x_N) dx_1 dx_2 \ldots dx_N. \]  
(1.17)

The antisymmetric requirement of \( \Psi_e \), Eq. (1.8), makes it possible to re-order the coordinates such that the sum in the operator corresponds to \( N \) applications on only one of the coordinates, giving
\[ n(r) = N \int \ldots \int |\Psi_e(r \sigma_1, x_2, \ldots, x_N)|^2 d\sigma_1 dx_2 \ldots dx_N. \]  
(1.18)

The result is an expression very similar to the wave-function normalization integration Eq. (1.7) but leaving out one of the spatial integrals. Which one of the spatial integration that is left out is completely arbitrary due to the antisymmetric property of the wave-function Eq. (1.8). The requirement that the wave-functions are normalized Eq. (1.7) guarantees that the integral of the electron density is \( N \) as required by Eq. (1.16).
If we look closer at the three terms in the expression for the electronic energy Eqs. (1.12)–(1.15) we see that the term for the external potential \( V \) is easily rewritten in terms of the density,

\[
V = \int \cdots \int \sum_{i=1}^{N} |\Psi_{e}|^2 v(r_i) dx_1 dx_2 \cdots dx_N = \\
= \frac{1}{N} \sum_{i=1}^{N} \int n(r_i) v(r_i) dr_i = \int n(r) v(r) dr.
\]

(1.19)

The other two terms of the electronic energy Eq. (1.12) are not as easy to rewrite. In the kinetic energy term \( T \), the derivative operator between the wave-functions prevents rewriting the integrand on the form \( |\Psi_{e}|^2 \) as needed to turn the term into an expression of the electron density. In the term of the internal potential energy \( U \), the particle positions in the denominator preclude a direct term by term integration.

1.3 Wave-function Based Minimization: Hartree and Hartree–Fock

The Rayleigh–Ritz variational principle\(^2,3\) offers a way to solve the electron energy problem to obtain the ground state wave-function \( \Psi_0 \) and energy \( E_0 \). The ground state electronic energy is found through a search for the many-electron wave-function that minimizes the energy expectation value in Eq. (1.12),

\[
E_0 = \min_{\Psi} \langle \Psi | \hat{H}_{e} | \Psi \rangle, \quad \text{has minimum for } \Psi = \Psi_0,
\]

(1.20)

where the search should be constrained by the normalization and anti-symmetric conditions of Eqs. (1.7) and (1.8). A direct application of the Rayleigh–Ritz variational method involves a search for the minimizing wave-function in the space of functions of a dimensionality proportional to the number of electrons in the system. Such a brute-force minimization quickly becomes unfeasible from a practical standpoint. One can even question whether such a ‘solution’ really is a theoretically valid concept for systems with larger number of electrons.\(^4\)

Hence, attempts at finding the electronic ground state through the variational principle typically need to restrict the full freedom of the many-electron wave-function. The original suggestion by Hartree was based a wave-function constructed as a product of single-particle orbitals

\[
\Psi_{e} \approx \psi_1(x_1)\psi_2(x_2)\psi_3(x_3) \cdots
\]

(1.21)

However, this wavefunction approximation does not ensure the antisymmetry requirement of Eq. (1.8). The Hartree-Fock ansatz solves this issue. The wave-function is approximated as an antisymmetric Slater determinant

\[
\Psi_{e} \approx \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(x_1) & \psi_2(x_1) & \cdots & \psi_N(x_1) \\
\psi_1(x_2) & \psi_2(x_2) & \cdots & \psi_N(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(x_N) & \psi_2(x_N) & \cdots & \psi_N(x_N)
\end{vmatrix}
\]

(1.22)

By inserting these wave-function approximations into Eq. (1.20) and simplifying the expressions as far as possible, one arrives at the Hartree and Hartree-Fock methods. However, it is clear...
that neither of Eqs. (1.21) and (1.22) provides a complete basis for representing the anti-symmetric many-electron wavefunction, and hence, one will make a positive error in energy. This can be remedied by further elaborate construction of an approximate wavefunction as a sum of slater-determinants with higher orbital states. This approach is called configuration interaction (CI). By including more and more terms in CI, the basis can be made complete, and in principle an approximation arbitrarily close to the true many-wavefunction can be found; i.e., this is formally a path back to the prohibitly expensive minimization of the full many-electron wavefunction.

A deconstruction of the many-particle wave function into single-particle orbitals is called an orbital theory. The way the full many-electron wave-function is broken down into orbitals in Hartree-Fock theory (and CI) may seem resonable. However, it has grown out of the need to approximate the wave-function, and is not formally unique. Still, it turns out that a lot of physics can be understood from the analysis of the resulting single-particle orbitals. This is good to keep in mind as we later enter into the discussion about the meaning and possible interpretation (or lack thereof) of the orbitals in Kohn-Sham DFT; which, arguably, can be seen as an alternative orbital theory.

1.4 Density-based Minimization: The Thomas–Fermi Model

As an alternative to a direct approximation of the wavefunction, a different approach is to approximate the operators, or rather, the expectation value expressions. In this spirit, Thomas-Fermi approximated the kinetic energy $T$ as that of a uniform non-interacting electron gas,$^5-8$

$$T \approx T_{TF} = \frac{3}{5}(3\pi^2)^{2/3} \left( \frac{\hbar^2}{2m_e} \right) \int n^{5/3}(r)dr.$$  \hspace{2cm} (1.23)

Furthermore, they used the electrostatic energy of a classical repulsive gas $J[n]$ as a simplistic approximation for the internal potential energy $U$,

$$U \approx J = \frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right) \int \int \frac{n(r_1)n(r_2)}{|r_1 - r_2|} dr_1dr_2.$$  \hspace{2cm} (1.24)

The result is the Thomas–Fermi model:

$$E_e \approx T_{TF} + J + \int n(r)v(r)dr.$$  \hspace{2cm} (1.25)

Here, the intention is to seek the electron density that minimizes $E_e$, which can be done with the framework for constrained minimization and Lagrange multipliers that will be discussed the next lecture. However, this minimization in electron density did not rest on firm theoretical ground until the works of Hohenberg-Kohn and Levy-Lieb, which we also will discuss next lecture.

1.5 Bibliography