Notes on Density Functional Theory

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1 Introduction

We consider here a system with $N$ electrons subjected to some external potential. The Hamiltonian of this system takes the following general form:

$$H = T + V_{ee} + V_{ext}$$

where

$$T = \sum_{i=1}^{N} \frac{p_i^2}{2m_e}$$

is the kinetic energy operator,

$$V_{ee} = \frac{1}{4\pi \epsilon_0} \sum_{i,j \geq i} e^2 r_{ij}$$

($r_{ij} = \|r_i - r_j\|$) is the potential term arising from the electron-electron (repulsive) interaction and

$$V_{ext} = \sum_{i=1}^{N} v(r_i)$$

is the “external field” acting (in the same way) on each electron of the system.

In the “molecular Hamiltonian” the external potential takes the form

$$v(r) = -\frac{1}{4\pi \epsilon_0} \sum_{\alpha=1}^{M} \frac{Z_{\alpha} e^2}{\|R_{\alpha} - r\|}$$

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where the sum runs over nuclear labels and \( R \) specify the position of the nuclei.

The electronic system Hamiltonian is completely specified once \( N \) and \( v \) are given. We may emphasize this fact by writing

\[
H \equiv H^N_v
\]

Electrons, like any other sets of identical particles, are indistinguishable from each other and this implies that for any state \( \Psi \)

\[
|\Psi(x_1, x_2, ..., x_N)|^2 = |\Psi(x_1, x_2, ..., x_N)|^2 = \ldots
\]

holds. Here, \( x_i = r_i \sigma_i \) is a 4-dimensional vector specifying the position and the spin of the \( i \)-th electron, i.e. the normalization condition

\[
\int |\Psi(x_1, x_2, ..., x_N)|^2 d^N \Gamma = 1
\]

means \( \int d^N \Gamma = \int d^3 r_1 d^3 r_2 \ldots d^3 r_N \sum_{\sigma_1, \sigma_2, \ldots, \sigma_N} (\sigma_i \text{ takes only two values specifying, e.g., the projection of the electron spin along a given axis}) \). Since electrons are fermions

\[
\Psi(x_1, x_2, x_3, x_N) = -\Psi(x_1, x_2, x_3, x_N)
\]

The wave function \( \Psi \) describes a particular state of the \( N \)-electron system. In coordinate representation it is a very complicated, complex-valued function depending on \( 4N \) variables which allows us to determine any system property (for the given state). Indeed, for any observable \( A \) we have:

\[
\langle A \rangle = \langle \Psi | A | \Psi \rangle = \int \Psi^*(x_1 \ldots x_N) A \Psi(x_1 \ldots x_N) d^N \Gamma
\]

where \( A \) is the quantum-mechanical operator corresponding to the observable \( A \). Here, since electrons are equal to each other in any respect, for \( A \) to be experimentally relevant it must be a symmetric “function” of the electron coordinates.

Usually we are interested in one-, two- or few electrons “properties”. One-electron operators are of the form

\[
A = \sum_{i=1}^{N} a_i
\]

where \( a_i \) acts on the \( i \)-th electron only. Two-electron operators are of the form

\[
A = \sum_{i,j \geq 1} a_{ij}
\]

Thus, for example, in our general Hamiltonian \( T \) and \( V_{\text{ex}} \) are one-electron operators and \( V_{\text{ee}} \) is a two electron operator. \( m \)-electron operators are defined in a analogous way.

We now show that in order to compute 1-, 2- or few electron properties \( \Psi \) is much more than we need. Let’s first consider a one-electron operator and its expectation value
\[ \langle A \rangle = \sum_{i=1}^{N} \int \Psi^*(x_1 x_2 \ldots x_i x_{N}) a_i \Psi(x_1 x_2 \ldots x_N) d^N \Gamma \]

\[ = N \int \Psi^* (x_1 x_2 \ldots x_i \ldots x_N) a_1 \Psi(x_1 x_2 \ldots x_{N}) d^N \Gamma \]

where the second line follows from the symmetry properties of the wave function. Now

\[ \int \Psi^* (x_1 x_2 \ldots x_i \ldots x_N) a_1 \Psi(x_1 x_2 \ldots x_{N}) d^N \Gamma = \int a_1 \left[ \Psi(x_1 x_2 \ldots x_{N}) \Psi^*(x'_1 x_2 \ldots x_{N}) \right] \bigg|_{x'_1 = x_1} d^N \Gamma \]

where \( x'_1 = x_1 \) has to be replaced after \( a \) acted on the quantity between brackets. Then

\[ N \int a_1 \left[ \Psi(x_1 x_2 \ldots x_{N}) \Psi^*(x'_1 x_2 \ldots x_{N}) \right] \bigg|_{x'_1 = x_1} dx_1 d^{N-1} \Gamma = \int a_1 \gamma(x_1 | x'_1) \bigg|_{x'_1 = x_1} dx_1 \]

where

\[ \gamma(x_1 | x'_1) = N \int d^{N-1} \Gamma \Psi(x_1 x_2 \ldots x_{N}) \Psi^*(x'_1 x_2 \ldots x_{N}) \]

\( \gamma(x'x) \) defined in this way is known as \textit{first-order reduced density matrix}. Note that

\[ n(r) = \sum_{\sigma} \gamma(r\sigma | r\sigma) = N \int d^{N-1} \Gamma |\Psi(x x_{2} \ldots x_{N})|^2 \]

is the \textit{electron density}, correctly normalized to the number of particles:

\[ \int d^3 r n(r) = N \]

\( \gamma \) is an “extended” density which allows us to compute any one-electron property. With the same token if \( A \) is a two-electron operator we have

\[ \langle A \rangle = \sum_{ij \geq i} \langle \Psi | a_{ij} | \Psi \rangle = \frac{N(N - 1)}{2} \int a_{12} \gamma^{(2)} (x_1 x_2 | x'_1 x'_2) \bigg|_{x'_1 = x_1; x'_2 = x_2} dx_1 dx_2 \]

where

\[ \gamma^{(2)} (x_1 x_2 | x'_1 x'_2) = \frac{N(N - 1)}{2} \int d^{N-2} \Gamma \Psi(x_1, x_2, \ldots, x_{N}) \Psi^*(x'_1, x'_2, \ldots, x_{N}) \]
is the “second-order” reduced density matrix. In general, for an \( m \)-electron operator \( A^{(m)} \),

\[
\left\langle A^{(m)} \right\rangle = \int d_{12}..m \gamma^{(m)}(x_1x_2..x_m|x'_1x'_2..x'_m)|x'_1=x_1,dx_1..dx_m
\]

where

\[
\gamma^{(m)}(x_1,...,x_m|x'_1,...,x'_m) = \binom{N}{m}
\]

\[
\int d^{N-m}x' \Psi(x_1...x_m,x_{m+1}...,x_N)\Psi^{*}(x'_1,...,x'_m,x_{m+1}...,x_N)
\]

is the “\( m \text{th}-\)order” reduced density matrix. Note, that once an \( m \)-th order reduced density matrix is known, any density matrix of order \( n < m \) can easily be obtained by properly integrating the known density matrix,

\[
\gamma^{(m-1)}(x_1..x_{m-1}|x'_1..x'_{m-1}) = \frac{m}{N-m+1}
\]

\[
\int dx_m \gamma^{(m)}(x_1..x_m-1|x'_1..x'_{m-1},x_m)
\]

Since we are only interested in 1-, 2-, or few electron properties, the above arguments suggest that we might replace the complicated function \( \Psi \) with some simpler function. In particular, our general hamiltonian contains only 1- and 2- electron operators: if we were able to compute \( \gamma^{(2)} \) then we could solve any electronic problem, with as many electron as we like! This is the essence of the density matrix theory of the electronic problem. Unfortunately, such a theory has enormous difficulties and cannot be used at present for all but a few model problems. The reason is that is not yet clear how to select a general function \( \rho(x_1x_2|x'_1x'_2) \) in such a way that it represents a second order density matrix of some electron system.

However, a powerful theory based on the simpler electronic density \( n(r) \) turns out to be possible. As we shall see in the following it has the only problem that, in practice, it cannot be considered as truly \textit{ab initio}. This Density Functional Theory (DFT) is possible because of a number of facts.

1. We are usually interested in \textit{stationary states}, that is we replace the Time-Dependent Schrödinger Equation with the equation for stationary states

\[
H\Psi = E\Psi
\]

This is because we are only interested in situations in which \textit{all electrons are bound} to a given “charged (stationary) core”. Note that for such states

\[
\frac{d}{dt} \langle \Psi | A | \Psi \rangle = 0
\]

for any (stationary, i.e. not explicitly time dependent) observable \( A \).

2. We are usually interested in the \textit{ground-state} \( \Psi_0 \), i.e. the state of minimum energy. This is so because in molecules electronic energy levels are well-separated in energy, and at normal temperature only the ground-state is populated. Actually, this condition cannot be satisfied in metallic systems where excited electronic states with vanishing small excitation energy can be accessed even at very low temperatures (“electron-hole excitations”).
Stationarity allows us to use the variational principle

\[ \delta \left( \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right) = 0 \]

or simply

\[ \langle \delta \Psi | H | \Psi \rangle = 0 \]

if the additional norm-conserving condition \( \langle \delta \Psi | \Psi \rangle = 0 \) is enforced. In addition, the ground state has the minimum energy property

\[ E(\Phi) = \langle \Phi | H | \Phi \rangle \geq E_0 = \langle \Psi_0 | H | \Psi_0 \rangle \]

which holds for any “trial”, normalized wavefunction \( \Phi \).

**Note: Functionals and functional derivatives.** The map

\[ \mathcal{H} \to \mathbb{R} \]

\[ \Phi \to E(\Phi) = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} \]

is called energy functional and the results

\[ E(\Phi) \geq E_0 \]

is called wave function variational principle. In general, given a space of functions \( E \) a map

\[ E \to \mathbb{R} \ (\text{or also } \mathbb{C}) \]

\[ \Phi \to F[\Phi] \]

is called a functional. Thus, for example,

\[ E_H [n] = \int d^3 r_1 d^3 r_2 n(r_1)n(r_2) \frac{\|r_1 - r_2\|}{r_1 \cdot r_2} \]

\[ T_{TF} [n] = A \int d^3 r n^3(r) \]

are functionals of the electronic density. The functional derivative \( \frac{\delta F}{\delta n} \) is defined by the equation

\[ \delta F = \int d^3 r \frac{\delta F}{\delta n}(r) \delta n(r) \]

where \( \delta F = F[n + \delta n] - F[n] \). In other words, \( \frac{\delta F}{\delta n} \) is a function of \( r \) (and, in general, also a functional of \( n \) for any \( r \)) which, once multiplied by \( \delta n \) and integrated over \( r \), gives the variation of \( F \). More formally, let us consider the following ordinary function of \( \lambda \)

\[ F[n + \lambda \delta n] \]
where \( n \) and \( \delta n \) are two functions of the domain \( E \). The “variation” of \( F \) is defined with the help of the standard derivative with respect to \( \lambda \), according to

\[
\delta F [n, \delta n] = \frac{d}{d\lambda} F [n + \lambda \delta n] \bigg|_{\lambda=0}
\]

This “variation”, or also “differential” is, in general, a functional of both \( n \) and \( \delta n \). If it is linear in \( \delta n \), that is

\[
\delta F [n, \delta n] = \Delta[n] \delta n
\]

where \( \Delta[n] \) is a linear operator from \( E \) to \( \mathbb{R}(C) \), then we usually write

\[
\Delta[n] \Phi = \int d^3 r \frac{\delta F}{\delta n} (r) \Phi (r)
\]

and \( \frac{\delta F}{\delta n} \), the previously defined functional derivative, is the integral representation of the operator \( \Delta[n] \). Thus, for example,

\[
T_{TF} [n] = A \int d^3 r n \hat{z} (r)
\]

\[
\delta T_{TF} [n, \delta n] = A \int d^3 r \frac{5}{3} n \hat{z} (r) \delta n (r)
\]

i.e.: \( \frac{\delta T_{TF}}{\delta n} (r) = A \frac{5}{3} n \hat{z} (r) \). With the second (formally more correct) definition

\[
\delta T_{TF} [n, \delta n] = \frac{d}{d\lambda} A \int dr (n + \lambda \delta n) \hat{z} \bigg|_{\lambda=0}
\]

\[
= A \int d^3 r \frac{5}{3} (n + \lambda \delta n) \hat{z} (r) \delta n (r) \bigg|_{\lambda=0} = A \int d^3 r \frac{5}{3} n \hat{z} (r) \delta n (r)
\]

For \( E_H \) we have

\[
\delta E_H [n, \delta n] = \int d^3 r_1 d^3 r_2 \frac{\delta n (r_1) n (r_2) + n (r_1) \delta n (r_2)}{\|r_1 - r_2\|} =
\]

\[
= \int d^3 r_1 \left( \int d^3 r_2 \frac{n (r_2)}{\|r_1 - r_2\|} \right) \delta n (r_1)
\]

\[
+ \int d^3 r_2 \left( \int d^3 r_1 \frac{n (r_1)}{\|r_1 - r_2\|} \right) \delta n (r_2) =
\]

\[
= \int d^3 r \frac{\delta E_H}{\delta n} (r) \delta n (r)
\]

with \( \frac{\delta E_H}{\delta n} (r) = 2 \int d^3 r' \frac{n (r')}{\|r - r'\|} \).

\footnote{If \( E \) is not linear one has to consider the curves \( n(\lambda) \) such that \( n(0) = n \) and \( n'(0) = \delta n \).}
Since we are only interested in the ground-state $\Psi$ of our $N$-electron system we may write

$$v, N \rightarrow \Psi^N_v \rightarrow X = X [v, N]$$

where the $\Psi^N_v$ is a functional of $v$ (and a function of $N$) and $X$ is any ground-state property of the system. The above relationship means that once $N$ is fixed any ground-state property is a functional of $v$,

$$v \rightarrow X = X [v]$$

The above relation holds thanks to the chain of relationships

$$v \rightarrow \Psi [v]$$

$$\Psi \rightarrow X [\Psi]$$

The only assumption we need is that the ground-state is non degenerate, in such a way that the potential uniquely determines the ground-state function (apart from an irrelevant phase factor).

## 2 Density Functional Theory

The beauty and power of the so-called Density Functional Theory relies on two very simple theorems, known as Hohenberg-Kohn theorems, whose results can be summarized as follow. In studying ground-state electronic properties one can replace the ground-state electronic wave function $\Psi(x_1, \ldots, x_N)$ with the simple electron density $n(r)$. In other words one can use the electron density as fundamental variable: the ground-state wave function (and therefore any ground-state property) is a functional of the electron density, $\Psi = \Psi [n]$. These properties follow from two very simple theorems:

**Theorem I** The density $n$ uniquely determines $v$, that is $v = v [n]$ or, in other words, for each electron density $n$ there exists one and only one potential $v$ (mathematically, $\forall n \exists ! v$) such that $n$ is its ground-state density.

**Proof.** We use the *reductio ad absurdum* procedure first used by Hohenberg and Kohn. Suppose there exist two potentials $v_1, v_2$ whose ground-state density is $n$, i.e

$$v_1 \rightarrow H_{v_1} \rightarrow \Psi_1 \rightarrow n$$

$$v_2 \rightarrow H_{v_2} \rightarrow \Psi_2 \rightarrow n$$

Let’s consider

$$H_{v_1} = T + V_{ee} + V_{1}^{ext} = U + V_{1}^{ext}$$

$$H_{v_2} = T + V_{ee} + V_{2}^{ext} = U + V_{2}^{ext}$$

where

$$V_{1}^{ext} = \sum_{i=1}^{N} e_1^{(i)}$$

$$V_{2}^{ext} = \sum_{i=1}^{N} e_2^{(i)}$$
Here $U$ is the “internal energy operator”, $U = T + V_{ee}$, a “universal operator” (in the sense that it is the same for any $N$-electron system). We have $(E(\Psi) \geq E_0)$

$$
\langle \Psi_2 | H_{v_1} | \Psi_2 \rangle = \langle \Psi_2 | U | \Psi_2 \rangle + \int dr v_1(r)n(r) >
$$

$$
> \langle \Psi_1 | H_{v_1} | \Psi_1 \rangle \equiv \langle \Psi_1 | U | \Psi_1 \rangle + \int dr v_1(r)n(r)
$$

i.e.

$$
\langle \Psi_2 | U | \Psi_2 \rangle > \langle \Psi_1 | U | \Psi_1 \rangle
$$

With the same token, from

$$
\langle \Psi_1 | H_{v_2} | \Psi_1 \rangle > \langle \Psi_2 | H_{v_2} | \Psi_2 \rangle
$$

it follows

$$
\langle \Psi_1 | U | \Psi_1 \rangle > \langle \Psi_2 | U | \Psi_2 \rangle
$$

Note that we have implicitly assumed that $\Psi$ is uniquely determined by $v$, which is only possible if the ground-state is not degenerate (as it almost always happens). Furthermore, if $v_1$ and $v_2$ give accidentally the same $\Psi$ (e.g. because $v_1 = v_2 + c$) in any case $\Psi$ is still uniquely given by $n$.

Note. To be precise, $n$ is a function with the following properties,

$$
n(r) \geq 0
$$

$$
\int d^3r n(r) = N
$$

$$
n \leftarrow \Psi_v \leftarrow v
$$

Here the last condition means that $n$ must be an electronic density derivable from a ground state wavefunction $\Psi_v$ for some external potential $v$.

This kind of densities are called $v$-representable.

The above theorem makes use of (i) the non-degenerate nature of the ground-state, and (ii) the possibility to identify the class of “$v$-representable” densities. We will relax these two assumptions with a second, more general formulation. Before doing this, however, let us state the second Hohenberg-Kohn theorem, which proves to be extremely useful for the application of the theory.

**Theorem II** For any given external potential $v$ a density variational principle can be formulated, i.e. there exist a functional, called “energy functional” $E_v[n]$ such that

$$
E_v[n] \geq E_0^v
$$

where $E_0$ is the ground-state energy. The equality sign holds if and only if $n$ is the ground-state density.

**Proof.** Let us consider $v$ fixed. Then for any $\Phi$ giving the density $n$ we may write

$$
\langle \Phi | H_v | \Phi \rangle = \langle \Phi | U | \Phi \rangle + \int d^3rv(r)n(r)
$$
Thanks to theorem I we can now focus on
\[ \Phi = \Psi[n] \]
where \( \Psi \) is the ground-state wavefunction for some unspecified potential \( v' \) uniquely determined by \( n \). Then the quantity
\[ E_v[n] = \langle \Psi[n]|H_v|\Psi[n]\rangle \]
is a functional of the electron density and we know that
\[ E_v[n] \geq E_0^v \]
the equality being satisfied by the ground-state density \( n \) of our problem only (since in that case \( v' = v \) is our fixed external potential).

Please note that we have used again the \( v \)-representability property. Note also that
\[ E_v[n] = U[n] + \int d^3r v(r)n(r) \]
and this functional can be minimized subjected to the constraint
\[ N = \int d^3r n(r) \]
This means
\[ \delta \left( E_v[n] - \mu \left( \int d^3r n(r) - N \right) \right) = 0 \]
that is
\[ \delta U[n] + \int d^3r v(r)\delta n(r) - \mu \int d^3r \delta n(r) = 0 \]
(where \( \mu \) is the Langrange multiplier related to the above normalization constraint) or also \( \delta U = \int \frac{\delta U}{\delta n}(r)\delta n(r)d^3r \)
\[ \frac{\delta U}{\delta n}(r) + v(r) = \mu \]
In principle, knowing \( U \) we should solve this equation for \( n(n = n_\mu) \) and \( \mu \) has to be adjusted in order to satisfy the normalization constraint, i.e. \( \int n_\mu d^3r = N \). In practice, \( U \) is an unknown functional and this means that it must be approximated in some way. This explains why the theory is not \textit{ab-initio}, though it comes from \textit{first-principles}.

\textbf{Note: Lagrange multipliers and constrained minimization.} Suppose we have a function \( f = f(x_1, x_2) \) to be minimized. In the absence of constraints we use
\[ df = \frac{\partial f}{\partial x_1}dx_1 + \frac{\partial f}{\partial x_2}dx_2 = 0 \Rightarrow \frac{\partial f}{\partial x_1} = \frac{\partial f}{\partial x_2} = 0 \]
since $dx_1, dx_2$ are arbitrary (i.e. one can take for example $dx_2 = 0$). If the function $f$ has to be minimized with the constraint

$$g(x_1, x_2) = 0$$

we can no longer consider $dx_1$ and $dx_2$ arbitrary. Rather, we have

$$dg = \frac{\partial g}{\partial x_1} dx_1 + \frac{\partial g}{\partial x_2} dx_2 = 0$$

This means that the vector $dx = (dx_1 dx_2)^t$ must be orthogonal to the vector $g = (\frac{\partial g}{\partial x_1}, \frac{\partial g}{\partial x_2})^t$, i.e., $g \cdot dx = 0$. The stationary condition then reads

$$df = f \cdot dx = 0 \quad \forall dx \in g^\perp$$

Here $g^\perp$ is the “orthogonal complement” of $g$, that is the (linear) space of vectors orthogonal to $g$, and $f = (\frac{\partial f}{\partial x_1}, \frac{\partial f}{\partial x_2})^t$ is the gradient vector. It follows

$$f \in dx = g^\perp = V\{g\}$$

where $V\{g\}$ is the space spanned by $g$, $V = \{u$ such that $u = \lambda g$, with $\lambda \in \mathbb{R}$\}$, or also

$$f - \lambda g = 0$$

This equation has to be solved in conjunction with the constraint $g(x) = 0$, which determines the value of the parameter $\lambda$, the so-called Lagrange multiplier. Note that the above equation is equivalent to the constraint-free stationarity condition

$$d(f - \lambda g) = 0$$

of the Lagrange function $L_\lambda = f - \lambda g$. Analogous relations hold for functions of more than two variables, in the presence of a number of constraints.

Before considering the problem of how determining $U$ (at least approximately) let us consider an alternative derivation of Theorems I and II. This is due to Levy and has the merit of removing some restrictions. From the wave function variational principle we have

$$E_n^\omega = \min_{\Psi} \langle \Psi | H_v | \Psi \rangle$$

where minimization is over all possible normalized states. We can separate the minimization in two steps by “grouping” wavefunctions which give the same density

$$\min \equiv \min_n \min_{\Psi \to n}$$

where $\Psi \to n$ means a $\Psi$ which gives the density $n$. Now, let us consider

$$\min_{\Psi \to n} \langle \Psi | H_v | \Psi \rangle = \min_{\Psi \to n} \langle \Psi | U | \Psi \rangle + \int d^3r n(r) v(r)$$

This is a well-defined functional of $n$. 

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\[ E_v [n] = \min_{\Psi \rightarrow n} \langle \Psi | U | \Psi \rangle + \int d^3r n(r)v(r) \]

We also have

\[ E^0_v = \min_n E_v [n] \]

which means that \( E_v [n] \) is minimum when \( n \) is the ground-state density. It follows the following “stationary condition”

\[ \frac{\delta U}{\delta n}(r) + v(r) = \mu \]

where \( \mu \) is the Lagrange multiplier arising from the constraint \( \int dx n(x) = N \).

This equation tells us that \( v \) is uniquely determined by \( n \), or by one of the ground-state densities if the ground-state is degenerate. We therefore have removed the constraint of a non degenerate ground-state. We also note that minimization of \( E_v \) is performed over all \( n \) which come from a wavefunction: it is no longer necessary that \( \Psi \) is a ground-state wavefunction for some potential. Densities satisfying

\[ n(r) \geq 0 \quad \int d^3r n(r) = n \quad n \leftarrow \Psi \]

are called \( N \)-representable, a condition weaker than the \( v \)-representability.

\( N \)-representability is satisfied by any “reasonable” density. Specifically, it can be shown that \( n \) is \( N \)-representable if and only if

\[ n(r) \geq 0 \quad \int n(r)d^3r = n \quad \int \| \nabla n^{\frac{1}{2}} \|^2 d^3r < \infty \]

3 The Kohn-Sham approach

The energy density functional,

\[ E_v [n] = \min_{\Psi \rightarrow n} \langle \Psi | U | \Psi \rangle + \int d^3r n(r)v(r) = \]

\[ = U [n] + \int d^3r n(r)v(r) \]

is quite hard to approximate because of the presence of the term

\[ U [n] = \min_{\Psi \rightarrow n} \langle \Psi | T + V_{ee} | \Psi \rangle \]

which includes both kinetic and electronic repulsion terms. Let us then consider a different form of this term.

\[ ^2 \text{See Parr & Yang, “Density Functional Theory of Atoms and Molecules”, p. 55.} \]
Consider an alternative world, which we call the “Kohn-Sham world”, where electrons do not interact with each other. In this world

\[ U_{KS}[n] \equiv T_{KS}[n] = \min_{\Psi \rightarrow n} \langle \Psi | T | \Psi \rangle \]

where the minimum has to be searched among those independent N-electron wavefunctions that gives the density \( n \), i.e. Slater determinants

\[ \Psi_{KS} = \frac{1}{\sqrt{N}} | \phi_1^{KS} \phi_1^{KS} ... \phi_N^{KS} | \]

\[ n(r) = \sum_{i,\sigma} | \phi_{i,\sigma}^{KS}(r) |^2 \]

For any density \( n \) there exist a potential \( v_{KS}(r) \) in which \( n \) is the ground-state density

\[ \frac{\delta T_{KS}(r)}{\delta n} + v_{KS}(r) = \mu \]

and such potential determines also the orbitals

\[ \left( \frac{p^2}{2m_e} + v_{KS}(r) \right) \phi_{i,\sigma}^{KS} = \epsilon_i \phi_{i,\sigma}^{KS} \]

If the above stationary condition in the Kohn-Sham world has to be equivalent to

\[ \frac{\delta U}{\delta n}(r) + v(r) = \mu \]

(we absorb any possible difference between \( \mu' \) and \( \mu \) in \( v(r) \)) we have to put

\[ v_{KS}(r) = \frac{\delta U}{\delta n}(r) - \frac{\delta T_{KS}}{\delta n}(r) + v(r) \]

In this expression, \( U \) comes as the sum of a kinetic functional, the trivial part of the electron-electron interaction functional (the Hartree functional) and an “exchange-correlation” functional \( E'_{xc} \)

\[ U[n] = T[n] + v_H[n] + E'_{xc}[n] \]

and thus, absorbing the (reasonably small) difference \( T[n] - T_{KS}[n] \) into the working “exchange and correlation” functional

\[ E_{xc}[n] := U[n] - T_{KS}[n] - v_H[n] \]

we arrive at

\[ v_{KS}(r) = v(r) + \frac{\delta v_H}{\delta n}(r) + \frac{\delta E_{xc}}{\delta n}(r) \]

Therefore, one can solve the Kohn-Sham equation for the Kohn-Sham orbitals \( \{ \phi_{i,\sigma}^{KS} \} \)

\[ \left\{ \frac{p^2}{2m_e} + v(r) + \frac{\delta v_H}{\delta n}(r) + \frac{\delta E_{xc}}{\delta n}(r) \right\} \phi_{i,\sigma}^{KS}(r) = \epsilon_i \phi_{i,\sigma}^{KS}(r) \]
and the ground-state density

\[ n(r) = \sum_{i,\sigma} |\phi_i^{KS}(r)|^2 \]

until self-consistency is reached, i.e. until the Kohn-Sham density \( n \) above matches the density \( n' \) used to build up the Kohn-Sham Hamiltonian.

Once done, the total, ground-state energy is given by

\[ E_v = T_{KS}[\bar{n}] + v_H[\bar{n}] + E_{xc}[\bar{n}] + \int d^3r \bar{n}(r)v(r) \equiv \sum_i \Theta(\mu - \epsilon_i) \langle \psi_i | T | \psi_i \rangle + v_H[\bar{n}] + E_{xc}[\bar{n}] + \int d^3r \bar{n}(r)v(r) \]

where \( \bar{n} \) is the self-consistent solution of the Kohn-Sham equation and

\[ \Theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases} \]

This is the popular Kohn-Sham method: the only problem left is now to approximate \( E_{xc}[\bar{n}] \).

Note that from a computational point of view the method is almost equivalent to the Hartree-Fock method. This, however, does not mean that the ground-state wavefunction is a Slater determinant! The latter is the ground-state wave function of a fictitious independent electron problem with potential \( v_{KS} \). Orbitals appear in the theory only as a tool to represent the ground-state density, and to write down an exact expression for the kinetic energy functional.

**Example** We show here how to devise approximate functionals, focusing on the exchange part of the exchange-correlation functional. If we consider a uniform electron gas in the Hartree-Fock approximation the exchange energy (per unit volume) can be easily computed for any value of the density \( n, \epsilon_{ex}^{HF} = \epsilon_{ex}^{HF}(n) \), and thus an approximate exchange functional could be written as

\[ E_{ex} = \int d^3r \epsilon_{ex}^{HF}(n(r)) \]

This is the Local Density Approximation to the exchange functional, also known as Slater exchange (J.C. Slater, Phys. Rev. B, 81 (1951) 385). The calculation is straightforward if we remember that in Hartree-Fock theory the exchange operator takes the form

\[ J(|x| |x'|) = \frac{\gamma(|x| |x'|)}{|r - r'|} \]

where the first-order density matrix reads as

\[ \gamma(|x| |x'|) = \sum_v \phi_v(x)\phi_v^*(x') \]

For a uniform electron gas (writing \( x = (r, \sigma) \))

\[ \phi_v(x) \equiv \phi_{k,\sigma'}(x) = \frac{1}{\sqrt{V}} e^{ikr} \delta_{\sigma \sigma'} \]
where the set of $k$-vectors span the Fermi sphere

$$N = 2 \sum_k 1 = \frac{2}{\Delta k} \int_{k \leq k_F} d^3k = \frac{8}{3\Delta k} \pi k_F^2$$

$\Delta k = (2\pi)^3/V$ being the volume of $k$-space “occupied” by each $k$-vector. That is

$$3\pi^2 n = k_F^2$$

is the relation linking the Fermi momentum to the electron gas density $n$. It follows

$$\gamma_{\alpha\alpha}(r|r') = \sum_k \phi_k^\alpha(r)\phi_k^\alpha(r') = \frac{1}{\Delta kV} \int_{k \leq k_F} d^3k e^{ik(r-r')},$$

i.e., after a straightforward integration,

$$\gamma_{\alpha\alpha}(r|r') \equiv f(\xi_F) = \frac{3n \sin(\xi_F) - \xi_F \cos(\xi_F)}{\xi_F^3},$$

where $\xi_F = k_F\Delta r$ with $\Delta r = ||r-r'||$. Notice that $f \to n/2$ as $\Delta r \to 0$, as it should be since $f$ in such limit represents the density of the $\alpha$ electrons (similarly for the $\beta$ species). Thus,

$$J_{\alpha\alpha}(r|r') = J_{\beta\beta}(r|r') = \frac{f(k_F\Delta r)}{\Delta r}$$

Now, the exchange energy is given by

$$E_{ex} = \frac{1}{2} \sum_\nu \langle \nu | J | \nu \rangle = \sum_k \langle k | J_{\alpha\alpha} | k \rangle$$

where for each $k$

$$\langle k | J_{\alpha\alpha} | k \rangle = \frac{1}{V} \int d^3r_1d^3r_2 J_{\alpha\alpha}(r_1|r_2) e^{ik(r_2-r_1)} \equiv \frac{1}{V} \int d^3r_1d^3r_2 e^{ik(r_2-r_1)} \frac{f(k_F||r_2-r_1||)}{||r_2-r_1||}$$

The integral can be simplified by introducing the relative and the center of mass coordinates (a transformation with unit Jacobian),

$$r = r_2 - r_1$$

$$R = \frac{r_1 + r_2}{2}$$

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$^3$With the same token one can obtain the energy (per unit volume) of the free-electron gas, i.e. the quantity which defines the Thomas-Fermi functional.

$$E = 2 \sum_k \frac{\hbar^2 k^2}{2m_e} = \frac{2}{\Delta k} \frac{\hbar^2}{2m_e} \int_{k \leq k_F} d^3k k^2 \equiv \frac{V\hbar^2}{10\pi^2 m_e} k_F^5$$

Thus

$$\epsilon_{TF}[n] = \frac{E}{V} = 3\sqrt{\frac{1}{3}} \frac{\hbar^2}{10m_e} n^{5/3}$$

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namely
\[ (k|J_{\alpha\alpha}|k) = \int d^3r e^{ikr} \frac{f(k_F)}{r} \]

Summing over \(k\) we obtain
\[ E_{ex} = -\sum_k \langle k|J_{\alpha\alpha}|k \rangle = -\frac{1}{\Delta k} \int d^3r \frac{f(k_F)}{r} \int_{k \leq k_F} d^3k e^{ikr} = -V \int d^3r \frac{f(k_F)^2}{r} \]

and thus, introducing \(\xi = k_F r\),
\[ E_{ex} = \frac{V}{k_F^2} \frac{9n^2}{4} \int d^3\xi \frac{\sin(\xi) - \xi \cos(\xi))^2}{\xi^7} \]

i.e.
\[ \epsilon = \frac{E_{ex}}{V} = -C' \frac{k_F^4}{k_F^4} = -C n^{4/3} \]

where \(C\) is a (positive) numerical coefficient\(^4\).

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\(^4\)Note that the integral above is well defined, since for \(\xi \to 0\) we have \(\sin \xi - \xi \cos \xi \to \xi^3/3\).