

# 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,

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

( $r_{ij} = \|\mathbf{r}_i - \mathbf{r}_j\|$ ) is the potential term arising from the electron-electron (repulsive) interaction and

$$V_{ext} = \sum_{i=1}^N v(\mathbf{r}_i)$$

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

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

where the sum runs over nuclear labels and  $\mathbf{R}_\alpha$  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

$$H \equiv H_v^N$$

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

$$|\Psi(x_1, x_2, \dots, x_N)|^2 = |\Psi(x_2, x_1, \dots, x_N)|^2 = \dots$$

holds. Here,  $x_i = \mathbf{r}_i \sigma_i$  is a 4-dimensional vector specifying the position and the spin of the  $i$ -th electron, i.e. the normalization condition

$$\int |\Psi(x_1, x_2, \dots, x_N)|^2 d^N \Gamma = 1$$

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

$$\Psi(x_1, x_2 \dots x_i \dots x_j \dots x_N) = -\Psi(x_1, x_2 \dots x_j \dots x_i \dots x_N)$$

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:

$$\langle A \rangle = \langle \Psi | A | \Psi \rangle = \int \Psi^*(x_1 \dots x_N) A \Psi(x_1 \dots x_N) d^N \Gamma$$

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

$$A = \sum_{i,j \geq 1}^N a_{ij}$$

Thus, for example, in our general Hamiltonian  $T$  and  $V_{ext}$  are one-electron operators and  $V_{ee}$  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

$$\begin{aligned}
\langle A \rangle &= \sum_{i=1}^N \int \Psi^*(x_1 x_2 \dots x_i \dots x_N) a_i \Psi(x_1 x_2 \dots x_i \dots x_N) d^N \Gamma \\
&= N \int \Psi^*(x_1 x_2 \dots x_i \dots x_N) a_1 \Psi(x_1 x_2 \dots x_i \dots x_N) d^N \Gamma
\end{aligned}$$

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

$$\begin{aligned}
&\int \Psi^*(x_1 x_2 \dots x_i \dots x_N) a_1 \Psi(x_1 x_2 \dots x_i \dots x_N) d^N \Gamma = \\
&\int a_1 [\Psi(x_1 x_2 \dots x_N) \Psi^*(x'_1 x_2 \dots x_N)] \Big|_{x'_1=x_1} d^N \Gamma
\end{aligned}$$

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

$$\begin{aligned}
N \int a_1 [\Psi(x_1 x_2 \dots x_N) \Psi^*(x'_1 x_2 \dots x_N)] \Big|_{x'_1=x_1} dx_1 d^{N-1} \Gamma \\
= \int a_1 \gamma(x_1 | x'_1) \Big|_{x'_1=x_1} dx_1
\end{aligned}$$

where

$$\gamma(x_1 | x'_1) = N \int d^{N-1} \Gamma \Psi(x_1 x_2 \dots x_N) \Psi^*(x'_1 x_2 \dots x_N)$$

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

$$n(\mathbf{r}) = \sum_{\sigma} \gamma(\mathbf{r}\sigma | \mathbf{r}\sigma) = N \int d^{N-1} \Gamma |\Psi(x_1 x_2 \dots x_N)|^2$$

is the *electron density*, correctly normalized to the number of particles:

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

$\gamma$  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

$$\begin{aligned}
\langle A \rangle &= \sum_{i,j \geq i} \langle \Psi | a_{ij} | \Psi \rangle = \frac{N(N-1)}{2} \\
&\int a_{12} \gamma^{(2)}(x_1 x_2 | x'_1 x'_2) \Big|_{x'_1=x_1; x'_2=x_2} dx_1 dx_2
\end{aligned}$$

where

$$\begin{aligned}
\gamma^{(2)}(x_1 x_2 | x'_1 x'_2) &= \frac{N(N-1)}{2} \\
&\int d^{N-2} \Gamma \Psi(x_1, x_2, \dots, x_N) \Psi^*(x'_1, x'_2, \dots, x_N)
\end{aligned}$$

is the “second-order” reduced density matrix. In general, for an  $m$ -electron operator  $A^{(m)}$ ,

$$\langle A^{(m)} \rangle = \int a_{12\dots m} \gamma^{(m)}(x_1 x_2 \dots x_m | x'_1 x'_2 \dots x'_m)_{|x'_i=x_i} dx_1 \dots dx_m$$

where

$$\gamma^{(m)}(x_1 \dots, x_m | x'_1 \dots, x'_m) = \binom{N}{m}$$

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

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,

$$\gamma^{(m-1)}(x_1 \dots x_{m-1} | x'_1 \dots x'_{m-1}) = \frac{m}{N-m+1} \int dx_m \gamma^{(m)}(x_1 \dots x_{m-1} x_m | x'_1 \dots x'_{m-1} x_m)$$

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  $\gamma^{(2)}$  than 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  $\rho(x_1 x_2 | x'_1 x'_2)$  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  $n(\mathbf{r})$  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 *ab initio*. This *Density Functional Theory* (DFT) is possible because of a number of facts.

1. We are usually interested in *stationary states*, that is we replace the Time-Dependent Schrodinger Equation with the equation for stationary states

$$H\Psi = E\Psi$$

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

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

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

2. We are usually interested in the *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

$$\begin{aligned} \mathcal{H} &\rightarrow \mathbb{R} \\ \Phi &\rightarrow E(\Phi) = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} \end{aligned}$$

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

$$\begin{aligned} E &\rightarrow \mathbb{R} \text{ (or also } \mathbb{C}) \\ \Phi &\rightarrow F[\Phi] \end{aligned}$$

is called a *functional*. Thus, for example,

$$\begin{aligned} E_H[n] &= \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \\ T_{TF}[n] &= A \int d^3\mathbf{r} n^{\frac{5}{3}}(\mathbf{r}) \end{aligned}$$

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

$$\delta F = \int d^3\mathbf{r} \frac{\delta F}{\delta n}(\mathbf{r}) \delta n(\mathbf{r})$$

where  $\delta F = F[n + \delta n] - F[n]$ . In other words,  $\frac{\delta F}{\delta n}$  is a *function* of  $\mathbf{r}$  (and, in general, also a functional of  $n$  for any  $\mathbf{r}$ ) which, once multiplied by  $\delta n$  and integrated over  $\mathbf{r}$ , 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<sup>1</sup>  $E$ . The “variation” of  $F$  is defined with the help of the standard derivative with respect to  $\lambda$ , according to

$$\delta F [n, \delta n] = \left. \frac{d}{d\lambda} F [n + \lambda \delta n] \right|_{\lambda=0}$$

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  $\mathbb{R}(\mathbb{C})$ , then we usually write

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

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

$$T_{TF} [n] = A \int d^3 \mathbf{r} n^{\frac{5}{3}} (\mathbf{r})$$

$$\delta T_{TF} [n, \delta n] = A \int d^3 \mathbf{r} \frac{5}{3} n^{\frac{2}{3}} (\mathbf{r}) \delta n (\mathbf{r})$$

i.e.:  $\frac{\delta T_{TF}}{\delta n} (\mathbf{r}) = A \frac{5}{3} n^{\frac{2}{3}} (\mathbf{r})$ . With the second (formally more correct) definition

$$\begin{aligned} \delta T_{TF} [n, \delta n] &= \left. \frac{d}{d\lambda} A \int d^3 \mathbf{r} (n + \lambda \delta n)^{\frac{5}{3}} \right|_{\lambda=0} = \\ &= A \int d^3 \mathbf{r} \frac{5}{3} (n + \lambda \delta n)^{\frac{2}{3}} (\mathbf{r}) \delta n \Big|_{\lambda=0} = A \int d^3 \mathbf{r} \frac{5}{3} n^{\frac{2}{3}} (\mathbf{r}) \delta n (\mathbf{r}) \end{aligned}$$

For  $E_H$  we have

$$\begin{aligned} \delta E_H [n, \delta n] &= \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \frac{\delta n (\mathbf{r}_1) n (\mathbf{r}_2) + n (\mathbf{r}_1) \delta n (\mathbf{r}_2)}{\|\mathbf{r}_1 - \mathbf{r}_2\|} = \\ &= \int d^3 \mathbf{r}_1 \left( \int d^3 \mathbf{r}_2 \frac{n (\mathbf{r}_2)}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \right) \delta n (\mathbf{r}_1) \\ &+ \int d^3 \mathbf{r}_2 \left( \int d^3 \mathbf{r}_1 \frac{n (\mathbf{r}_1)}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \right) \delta n (\mathbf{r}_2) = \\ &= \int d^3 \mathbf{r} \frac{\delta E_H}{\delta n} (\mathbf{r}) \delta n (\mathbf{r}) \end{aligned}$$

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

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<sup>1</sup>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

$$v, N \rightarrow \Psi_v^N \rightarrow X = X[v, N]$$

where the  $\Psi_v^N$  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  $\Psi(x_1, \dots, x_N)$  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

$$V_1^{ext} = \sum_{i=1}^N v_1^{(i)} \quad V_2^{ext} = \sum_{i=1}^N v_2^{(i)}$$

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 ( $E(\Phi) \geq E_0$ )

$$\begin{aligned} \langle \Psi_2 | H_{v_1} | \Psi_2 \rangle &= \langle \Psi_2 | U | \Psi_2 \rangle + \int dr v_1(r) n(r) > \\ &> \langle \Psi_1 | H_{v_1} | \Psi_1 \rangle \equiv \langle \Psi_1 | U | \Psi_1 \rangle + \int dr v_1(r) n(r) \end{aligned}$$

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,

$$\begin{aligned} n(\mathbf{r}) &\geq 0 \\ \int d^3\mathbf{r} n(\mathbf{r}) &= N \\ n &\leftarrow \Psi_v \leftarrow v \end{aligned}$$

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

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

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

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



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

$$E_v [n] = U [n] + \int d^3 \mathbf{r} v(\mathbf{r}) n(\mathbf{r})$$

and this functional can be minimized subjected to the constraint

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

This means

$$\delta \left( E_v [n] - \mu \left( \int d^3 \mathbf{r} n(\mathbf{r}) - N \right) \right) = 0$$

that is

$$\delta U [n] + \int d^3 \mathbf{r} v(\mathbf{r}) \delta n(\mathbf{r}) - \mu \int d^3 \mathbf{r} \delta n(\mathbf{r}) = 0$$

(where  $\mu$  is the Lagrange multiplier related to the above normalization constraint) or also  $(\delta U = \int \frac{\delta U}{\delta n}(\mathbf{r}) \delta n(\mathbf{r}) d^3 \mathbf{r})$

$$\frac{\delta U}{\delta n}(\mathbf{r}) + v(\mathbf{r}) = \mu$$

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.  $\int n_\mu d^3 \mathbf{r} = N$ . 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 *ab-initio*, though it comes from *first-principles*.**

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

$$df = \mathbf{f} \cdot d\mathbf{x} = 0 \quad \forall d\mathbf{x} \in \mathbf{g}^\perp$$

Here  $\mathbf{g}^\perp$  is the ‘‘orthogonal complement’’ of  $\mathbf{g}$ , that is the (linear) space of vectors orthogonal to  $\mathbf{g}$ , and  $\mathbf{f} = (\frac{\partial f}{\partial x_1} \frac{\partial f}{\partial x_2})^t$  is the gradient vector. It follows

$$\mathbf{f} \in d\mathbf{x}^\perp = \mathbf{g}^{\perp\perp} = V\{\mathbf{g}\}$$

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

$$\mathbf{f} - \lambda\mathbf{g} = \mathbf{0}$$

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

$$E_0^v = \min_{\Psi} \langle \Psi | H_v | \Psi \rangle$$

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

$$\min_{\Psi} \equiv \min_n \min_{\Psi \rightarrow n}$$

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

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

This is a well-defined *functional* of  $n$ ,

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

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”

$$\frac{\delta U}{\delta n}(\mathbf{r}) + v(\mathbf{r}) = \mu$$

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

$$\begin{aligned} n(\mathbf{r}) &\geq 0 \\ \int d^3\mathbf{r} n(\mathbf{r}) &= n \\ n &\leftarrow \Psi \end{aligned}$$

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<sup>2</sup>

$$n(\mathbf{r}) \geq 0 \quad \int n(\mathbf{r}) d^3\mathbf{r} = n \quad \int \left\| \nabla n^{\frac{1}{2}} \right\|^2 d^3\mathbf{r} < \infty$$

### 3 The Kohn-Sham approach

The energy density functional,

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

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.

<sup>2</sup>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

$$\Psi_{KS} = \frac{1}{\sqrt{N}} |\phi_1^{KS} \phi_1^{KS} \dots \phi_N^{KS}|$$

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

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

$$\frac{\delta T_{KS}}{\delta n}(\mathbf{r}) + v_{KS}(\mathbf{r}) = \mu$$

and such potential determines also the orbitals

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

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

$$\frac{\delta U}{\delta n}(\mathbf{r}) + v(\mathbf{r}) = \mu$$

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

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

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  $E'_{xc}$

$$U[n] = T[n] + v_H[n] + E'_{ex}[n]$$

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

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

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

$$\left\{ \frac{p^2}{2m_e} + v(\mathbf{r}) + \frac{\delta v_H}{\delta n}(\mathbf{r}) + \frac{\delta E_{xc}}{\delta n}(\mathbf{r}) \right\} \phi_{i,\sigma}^{KS}(\mathbf{r}) = \epsilon_i \phi_{i,\sigma}^{KS}(\mathbf{r})$$

and the ground-state density

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

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

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

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  $E_{xc}[n]$ .

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

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

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

$$J(\mathbf{x}|\mathbf{x}') = \frac{\gamma(\mathbf{x}|\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|}$$

where the first-order density matrix reads as

$$\gamma(\mathbf{x}|\mathbf{x}') = \sum_v \phi_v(\mathbf{x}) \phi_v^*(\mathbf{x}')$$

For a uniform electron gas (writing  $\mathbf{x} = (\mathbf{r}, \sigma)$ )

$$\phi_v(\mathbf{x}) \equiv \phi_{\mathbf{k},\sigma'}(\mathbf{x}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\mathbf{r}} \delta_{\sigma\sigma'}$$

where the set of  $k$ -vectors span the Fermi sphere

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

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

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

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

$$\gamma_{\alpha\alpha}(\mathbf{r}|\mathbf{r}') = \sum_{\mathbf{k}} \phi_{\mathbf{k}}^{\alpha}(\mathbf{r}) \phi_{\mathbf{k}}^{\alpha}(\mathbf{r}') = \frac{1}{\Delta k V} \int_{k \leq k_F} d^3 k e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')}$$

i.e., after a straightforward integration,

$$\gamma_{\alpha\alpha}(\mathbf{r}|\mathbf{r}') \equiv f(\xi_F) = \frac{3n \sin(\xi_F) - \xi_F \cos(\xi_F)}{2 \xi_F^3}$$

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

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

Now, the exchange energy is given by

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

where for each  $\mathbf{k}$

$$\begin{aligned} \langle \mathbf{k} | J_{\alpha\alpha} | \mathbf{k} \rangle &= \frac{1}{V} \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 J_{\alpha\alpha}(\mathbf{r}_1 | \mathbf{r}_2) e^{i\mathbf{k}(\mathbf{r}_2 - \mathbf{r}_1)} \\ &\equiv \frac{1}{V} \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 e^{i\mathbf{k}(\mathbf{r}_2 - \mathbf{r}_1)} \frac{f(k_F \|\mathbf{r}_2 - \mathbf{r}_1\|)}{\|\mathbf{r}_2 - \mathbf{r}_1\|} \end{aligned}$$

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

$$\begin{aligned} \mathbf{r} &= \mathbf{r}_2 - \mathbf{r}_1 \\ \mathbf{R} &= \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} \end{aligned}$$

<sup>3</sup>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.

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

Thus

$$\epsilon_{TF}[n] = \frac{E}{V} = \frac{3 \sqrt[3]{9\pi^4/3} \hbar^2}{10m_e} n^{5/3}$$

namely

$$\langle \mathbf{k} | J_{\alpha\alpha} | \mathbf{k} \rangle = \int d^3 \mathbf{r} e^{i\mathbf{k}\mathbf{r}} \frac{f(k_F r)}{r}$$

Summing over  $k$  we obtain

$$E_{ex} = - \sum_{\mathbf{k}} \langle \mathbf{k} | J_{\alpha\alpha} | \mathbf{k} \rangle = - \frac{1}{\Delta k} \int d^3 \mathbf{r} \frac{f(k_F r)}{r} \int_{k \leq k_F} d^3 k e^{i\mathbf{k}\mathbf{r}} = -V \int d^3 \mathbf{r} \frac{f(k_F r)^2}{r}$$

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.

$$\epsilon = \frac{E_{ex}}{V} = -C' k_F^4 = -C n^{4/3}$$

where  $C$  is a (positive) numerical coefficient<sup>4</sup>.

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<sup>4</sup>Note that the integral above is well defined, since for  $\xi \rightarrow 0$  we have  $\sin \xi - \xi \cos \xi \rightarrow \xi^3/3$ .