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

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

where

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

is the kinetic energy operator,

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

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

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

is a *scalar* potential describing an "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 Ψ

$$|\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)|^2 = |\Psi(\mathbf{x}_2, \mathbf{x}_1, ..., \mathbf{x}_N)|^2 = ...$$

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

$$\int |\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)|^2 \, d^N\Gamma = 1$$

means $\int d^N\Gamma\{..\} = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 ... d^3\mathbf{r}_N \sum_{\sigma_1,\sigma_2,...,\sigma_N}\{..\}$ where σ_i takes only two values specifying, *e.g.*, the projection of the electron spin along a given axis[1]. Since electrons are fermions,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2 .. \mathbf{x}_i .. \mathbf{x}_j .. \mathbf{x}_N) = -\Psi(\mathbf{x}_1, \mathbf{x}_2 .. \mathbf{x}_j .. \mathbf{x}_i .. \mathbf{x}_N)$$

The wave function Ψ 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:

$$\langle A \rangle = \langle \Psi | A | \Psi \rangle = \int \Psi^*(\mathbf{x}_1 ... \mathbf{x}_N) A \Psi(\mathbf{x}_1 ... \mathbf{x}_N) d^N\Gamma$$

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 ith electron only. Two-electron operators are of the form

$$A = \frac{1}{2} \sum_{i,j \neq i}^{N} a_{ij}$$

Thus, for example, in our general Hamiltonian T and V_{ext} are one-electron operators while 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 Ψ is much more than we need. Let us first consider a one-electron operator and its expectation value

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[1]More precisely, the Schrödinger-representation wavefunction $\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)$ stands for

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = (\langle \mathbf{r}_1 | \langle \sigma_1 | \otimes \langle \mathbf{r}_2 | \langle \sigma_2 | .. \otimes \langle \mathbf{r}_N | \langle \sigma_N |) | \Psi \rangle$$

where $|\sigma_i\rangle$ is a spin state for the ith electron, e.g. $|-1\rangle = |\beta\rangle$ and $|+1\rangle = |\alpha\rangle$ for the common choice of states with definite spin projection $\mp\hbar/2$ on the z axis.

$$\langle A \rangle = \sum_{i=1}^{N} \int \Psi^*(\mathbf{x}_1\mathbf{x}_2...\mathbf{x}_i...\mathbf{x}_N)a_i\Psi(\mathbf{x}_1\mathbf{x}_2...\mathbf{x}_i...\mathbf{x}_N)d^N\Gamma$$

$$= N \int \Psi^*(\mathbf{x}_1\mathbf{x}_2...\mathbf{x}_i...\mathbf{x}_N)a_1\Psi(\mathbf{x}_1\mathbf{x}_2...\mathbf{x}_i...\mathbf{x}_N)d^N\Gamma$$

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

$$\int \Psi^*(\mathbf{x}_1..\mathbf{x}_N)a_1\Psi(\mathbf{x}_1..\mathbf{x}_N)d^N\Gamma = \int a_1\left[\Psi(\mathbf{x}_1..\mathbf{x}_N)\Psi^*(\mathbf{x}_1'..\mathbf{x}_N)\right]\Big|_{\mathbf{x}_1'=\mathbf{x}_1} d^N\Gamma$$

where $\mathbf{x}_1' = \mathbf{x}_1$ has to be set *after* a acted on the quantity between brackets. Hence,

$$N \int a_1\left[\Psi(\mathbf{x}_1\mathbf{x}_2...\mathbf{x}_N)\Psi^*(\mathbf{x}_1'\mathbf{x}_2...\mathbf{x}_N)\right]\big|_{\mathbf{x}_1'=\mathbf{x}_1} d\mathbf{x}_1 d^{N-1}\Gamma = \int a_1\gamma(\mathbf{x}_1|\mathbf{x}_1')\Big|_{\mathbf{x}_1'=\mathbf{x}_1} d^4\mathbf{x}_1$$

where $\int d^4\mathbf{x}\{..\} = \sum_\sigma \int d^3\mathbf{r}\{..\}$ and

$$\boxed{\gamma(\mathbf{x}|\mathbf{x}') = N \int \Psi(\mathbf{x}\mathbf{x}_2...\mathbf{x}_N)\Psi^*(\mathbf{x}'\mathbf{x}_2...\mathbf{x}_N)\ d^{N-1}\Gamma}$$

is known as **first-order reduced density matrix**[2]. Note that

$$n(\mathbf{r}) = \sum_\sigma \gamma(\mathbf{r}\sigma|\mathbf{r}\sigma) = N \int d^{N-1}\Gamma \left|\Psi(\mathbf{x}\mathbf{x}_2...\mathbf{x}_N)\right|^2$$

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

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

that is, the expectation value of the one-electron operator, the "number-density operator"[3]

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \hat{\mathbf{r}}_i)$$

which is the quantum analogue of the classical number density for a set of particles located at $\mathbf{r}_1, \mathbf{r}_2, ..\mathbf{r}_N$. Indeed, using the above results, a simple calculation shows that

$$\langle\Psi|\hat{n}(\mathbf{r})|\Psi\rangle = \sum_\sigma \int d^3\mathbf{r}_1\delta(\mathbf{r}-\mathbf{r}_1)\gamma(\mathbf{x}_1|\mathbf{x}_1) = \sum_\sigma \gamma(\mathbf{r}\sigma|\mathbf{r}\sigma)$$

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[2]This is of course the coordinate representation of an operator, the first-order reduced density operator, $\hat{\gamma} = N\mathrm{Tr}_{N-1}|\Psi\rangle\langle\Psi|$, where Tr_q denotes the trace over q electron coordinates and $|\Psi\rangle\langle\Psi|$ is the N-th order density operator for a pure state. Note that the term "density operator" takes slightly different meaning depending on the context (see below).

[3]There is some formal advantage in considering such number-density operator and its dynamics. For instance, when particle number is conserved a continuity equation is easily derived and a (number) current-density operator identified, to within a transverse component. For our purposes it may be worth noticing that it allows us to re-write any local monoelectronic operator (e.g. V_{ext} above) in an illuminating form

$$V_{\text{ext}} = \sum_i v(\hat{\mathbf{r}}_i) = \sum_i \int d^3\mathbf{r}\delta(\mathbf{r}-\hat{\mathbf{r}}_i)v(\mathbf{r}) = \int d^3\mathbf{r}v(\mathbf{r})\hat{n}(\mathbf{r})$$

In this perspective, γ is an "extended" density which allows us to compute any one-electron property, no matter whether the target operator is local or not[4]. Similarly, if A is a two-electron operator we have

$$\langle A \rangle = \sum_{i,j \geq i} \langle \Psi | a_{ij} | \Psi \rangle = \frac{N(N-1)}{2} \int a_{12} \gamma^{(2)}(\mathbf{x}_1 \mathbf{x}_2 | \mathbf{x}_1' \mathbf{x}_2') \Big|_{(\mathbf{x}_1',\mathbf{x}_2')=(\mathbf{x}_1,\mathbf{x}_2)} d^4\mathbf{x}_1 d^4\mathbf{x}_2$$

where

$$\boxed{\gamma^{(2)}(\mathbf{x}_1 \mathbf{x}_2 | \mathbf{x}_1' \mathbf{x}_2') = \frac{N(N-1)}{2} \int \Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) \Psi^*(\mathbf{x}_1', \mathbf{x}_2', ..., \mathbf{x}_N) \, d^{N-2}\Gamma}$$

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

$$\langle A^{(m)} \rangle = \int a_{12..m} \gamma^{(m)}(\mathbf{x}_1 \mathbf{x}_2..\mathbf{x}_m | \mathbf{x}_1' \mathbf{x}_2'..\mathbf{x}_m')_{|\mathbf{x}_i'=\mathbf{x}_i} d^4\mathbf{x}_1..d\mathbf{x}_m$$

where[5]

$$\gamma^{(m)}(\mathbf{x}_1..., \mathbf{x}_m | \mathbf{x}_1'..., \mathbf{x}_m') =$$

$$= \binom{N}{m} \int \Psi(\mathbf{x}_1...\mathbf{x}_m, \mathbf{x}_{m+1}..., \mathbf{x}_N) \Psi^*(\mathbf{x}_1'..., \mathbf{x}_m', x_{m+1}..., \mathbf{x}_N) \, d^{N-m}\Gamma$$

is the "m^{th}-order" reduced density matrix. Note, that once an mth order reduced density matrix is known, any density matrix of order $n < m$ can easily be obtained by properly integrating the previously known density matrix,

$$\gamma^{(m-1)}(\mathbf{x}_1..\mathbf{x}_{m-1} | \mathbf{x}_1'..\mathbf{x}_{m-1}') = \frac{m}{N-m+1} \int d^4\mathbf{x}_m \gamma^{(m)}(\mathbf{x}_1..\mathbf{x}_{m-1}\mathbf{x}_m | \mathbf{x}_1'..\mathbf{x}_{m-1}'\mathbf{x}_m)$$

Since we are only interested in 1-, 2-, or few electron properties, the above arguments suggest that we might replace the complicated function Ψ with some simpler function. In particular, our general hamiltonian contains only 1- and 2- electron operators: if we were able to compute $\gamma^{(2)}$ 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 generic function $\rho(\mathbf{x}_1 \mathbf{x}_2 | \mathbf{x}_1' \mathbf{x}_2')$ 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 Schrödinger Equation with the equation for stationary states

$$H\Psi = E\Psi$$

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[4]Note the difference: γ is state-specific and general for mono-electronic properties, $\hat{n}$ is universal and useful for *local* mono-electronic properties only.

[5]The normalization is chosen in such a way that the expectation value of an m-electron operator does not require extra factor. Full integration of the r.h.s. of this definition gives precisely the number of distinct m-tuples in the set of N electrons.

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* Ψ_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 norm-conservation is enforced[6]. 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 Φ.

Functionals and functional derivatives.
The map

$$\mathcal{H} \ni \Phi \to E[\Phi] = \frac{\langle\Phi|H|\Phi\rangle}{\langle\Phi|\Phi\rangle} \in \mathbb{R}$$

is called energy functional and the result

$$E[\Phi] \geq E_0$$

is called wave function variational principle. In general, given a space of functions $\mathcal{E}$, a map

$$\mathcal{E} \ni \Phi \to F[\Phi] \in \mathbb{R} \text{ (or } \mathbb{C})$$

is called a functional. Thus, for example,

$$E_{\mathrm{H}}[n] = \frac{1}{2}\int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{\|\mathbf{r}_1 - \mathbf{r}_2\|}$$

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

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[6]We generally use *complex* variations, meaning that for any variation $|\delta\Psi\rangle$ also $i\,|\delta\Psi\rangle$ is an allowed variation.

are functionals of the electron density. The functional derivative $\delta F/\delta n$ 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, $\delta F/\delta n$ is a function of $\mathbf{r}$ which, once multiplied by δn and integrated over $\mathbf{r}$, gives the variation of F around the given n. Since $\delta F/\delta n$ is also, in general, a functional of n one usually writes

$$\frac{\delta F}{\delta n} = \frac{\delta F}{\delta n}(\mathbf{r}, [n]) \quad \text{or} \quad \frac{\delta F}{\delta n} = \frac{\delta F}{\delta n(\mathbf{r})}[n]$$

More formally, let us consider the following ordinary function $\mathbb{R} \ni \lambda \to F[n + \lambda \delta n]$ where n and δn are two functions of the domain[7] $\mathcal{E}$. The "variation" of F is defined with the help of the standard derivative with respect to λ, according to

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

This "variation" (the "differential" of F) is a functional of both n and δn. If it is linear in δn, that is

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

where $\Delta[n]$ is a linear operator from (the tangent space of) $\mathcal{E}$ to $\mathbb{R}(\mathbb{C})$, then we have linearized the map F and found a linear map Δ that approximates F, in a certain sense, in the neighborhoods of n. One usually write

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

and identifies $\delta F/\delta n$ with the integral representation of the operator $\Delta[n]$. Thus, for example,

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

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

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

$$\delta T_{\text{TF}}[n, \delta n] = \frac{d}{d\lambda} A \int d\mathbf{r}(n(\mathbf{r}) + \lambda \delta n(\mathbf{r}))^{\frac{5}{3}} \Big|_{\lambda=0} =$$

$$= A \int d^3\mathbf{r} \frac{5}{3}(n(\mathbf{r}) + \lambda \delta n(\mathbf{r}))^{\frac{2}{3}} \delta n(\mathbf{r}) \Big|_{\lambda=0} = A \int d^3\mathbf{r} \frac{5}{3} n^{\frac{2}{3}}(\mathbf{r}) \delta n(\mathbf{r})$$

For E_{H} we have

$$\delta E_{\text{H}}[n, \delta n] = \frac{1}{2} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\delta n(\mathbf{r}_1) n(\mathbf{r}_2) + n(\mathbf{r}_1) \delta n(\mathbf{r}_2)}{\|\boldsymbol{r}_1 - \boldsymbol{r}_2\|} =$$

$$= \frac{1}{2} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{n(\mathbf{r}_2)}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \delta n(\mathbf{r}_1) + \frac{1}{2} \int d^3\mathbf{r}_2 d^3\mathbf{r}_1 \int \frac{n(\mathbf{r}_1)}{\|\mathbf{r}_1 - \mathbf{r}_2\|} \delta n(\mathbf{r}_2)$$

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

with $\delta E_{\text{H}}/\delta n(\mathbf{r}) = \int d^3\mathbf{r}\, n(\mathbf{r}')/\|\mathbf{r} - \mathbf{r}'\|$.

Since we are only interested in the ground-state Ψ of our N-electron system we may write

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

where the Ψ_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 follows

> *In studying ground-state electronic properties one can replace the ground-state electronic wave function $\Psi(\mathbf{x}_1, ..., \mathbf{x}_N)$ with the simpler electron density $n(\mathbf{r})$. 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

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

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

and consider

$$H_{v_1} = T + V_{ee} + V_1^{\text{ext}} = U + V_1^{\text{ext}}$$

$$H_{v_2} = T + V_{ee} + V_2^{\text{ext}} = U + V_2^{\text{ext}}$$

where

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

Here U is the "internal energy operator", $U = T + V_{ee}$. It is a "universal operator", meaning that it is the same for any N-electron system. We have ($E[\Phi] \geq E_0$)

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

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

i.e.

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

By the same token, from

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

it follows

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

which is clearly absurd.

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

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

$$n(\boldsymbol{r}) \geq 0 \quad \int d^3 \mathbf{r} n(\mathbf{r}) = N \quad n \leftarrow \Psi_v \leftarrow v$$

Here the last condition means that n must be an electronic density derivable from a ground state wavefunction Ψ_v for some external potential v. Densities of this kind 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 lift 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 Φ giving the density n we may write

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

Thanks to theorem I we can now focus on

$$\Phi = \Psi[n]$$

where Ψ 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

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

When employing Langrange's mulitpliers[8] the stationary condition reads as

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

where μ is the Lagrange multiplier related to the above normalization constraint, hence

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

and we obtain Euler's equation

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

In principle, knowing U we should solve this equation for $n(n = n_\mu)$ and μ has to be adjusted in order to satisfy the normalization constraint, i.e. $\int n_\mu(\mathbf{r})d^3\mathbf{r} = N$. 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*.**

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

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

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[8]It may be worth noticing that application of the technique requires $E_v[n]$ to be *extended* to non-integer electronic systems (densities that integrate to non-integer number of electrons).

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

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

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

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

where $\mathcal{V}\{\mathbf{g}\}$ is the space spanned by $\mathbf{g}$, $\mathcal{V} = \{\mathbf{u}$ such that $\mathbf{u} = \lambda\mathbf{g},$ 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 λ, 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

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

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

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

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

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

in which the first term,

$$\boxed{U[n] = \min_{\Psi \to n} \langle\Psi|U|\Psi\rangle}$$

extends the previous HK internal energy functional to non-v-representable densities, provided they are derived from a wavefunction[9]. We also have

$$E_0^v = \min_n E_v[n]$$

---

[9]This is known as "Levy-Lieb" extension, denoted $U_{\text{LL}}[n]$. A further extension due to Lieb, $U_L[n]$ adds some desirable mathematical properties (e.g. convexity) and is usually preferred.

which means that $E_v[n]$ is *minimum* when n is the ground-state density. It follows that the ground-state density satisfies the following "stationary condition" (Euler's equation)[10]

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

where μ is the Lagrange multiplier associated with the constraint $\int d\mathbf{r}n(\mathbf{r}) = N$. 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 Ψ is a ground-state wavefunction for some potential. Densities satisfying

$$n(\mathbf{r}) \geq 0 \quad \int d^3\mathbf{r}n(\mathbf{r}) = n \quad n \leftarrow \Psi$$

are called $N-$**representable**, a condition which is clearly *weaker* than the $v-$representability. N-representability is satisfied by any "reasonable" density: it can be shown that n is N-representable if and only if[11]

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

Note however that the fact that v is uniquely determined by n does *not* imply, in general, that any ground-state property is a functional of n. For this it is yet necessary that the ground-state is non-degenerate, since degenerate ground-state wavefunctions gives different expectation values and may yet correspond to the *same* electron density[12] (*e.g.*, in a non-interacting world Li has a four-fold degenerate ground-state, with configurations $(1s^2, 2s)$, $(1s^2, 2p_0)$ and $(1s^2, 2p_\pm)$; the latter two gives rise to the same electron density).

3 The Kohn-Sham approach

The energy density functional,

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

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

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

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

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

Consider an alternative world, which we call the "Kohn-Sham world", where electrons do *not* interact with each other. In this world

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

---

[10]As above, application of the Lagrange's method requires $E_v[n]$ to be *extended* to non-integer electronic systems (denisities that integrate to non-integer number of electrons).

[11]See Parr&Yang, "Density Functional Theory of Atoms and Molecules", p. 55

[12]See Dreizler & Gross, "Density Functional Theory - An approach to the quantum many-body problem".

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

$$\Psi_{\text{KS}} = \frac{1}{\sqrt{N}} \left| \phi_1^{\text{KS}} \phi_2^{\text{KS}} ... \phi_N^{\text{KS}} \right|$$

built with simple spin-orbitals[13] $\phi_i^{\text{KS}}(\mathbf{x}) = \psi_i(\mathbf{r})\chi_i(\sigma)$

$$n(\mathbf{r}) = \sum_i^{\text{occ}} \left| \psi_i^{\text{KS}}(\mathbf{r}) \right|^2$$

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

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

and such potential also determines the orbitals

$$\left(\frac{p^2}{2m_e} + v_{\text{KS}}(\mathbf{r}) \right) \psi_i^{\text{KS}}(\mathbf{r}) = \epsilon_i \psi_i^{\text{KS}}(\mathbf{r})$$

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

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

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

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

In this expression, U comes as the sum of a kinetic functional, the trivial part of the electron-electron interaction functional (the Hartree energy functional) and an "exchange-correlation" functional ΔV_{ee}

$$U[n] = T[n] + E_{\text{H}}[n] + \Delta V_{\text{ee}}[n]$$

and thus, absorbing the (reasonably small) difference $T[n] - T_{\text{KS}}[n]$ into the working "exchange and correlation" energy functional[14]

$$\boxed{E_{\text{xc}}[n] := U[n] - T_{\text{KS}}[n] - E_{\text{H}}[n] = T[n] - T_{\text{KS}}[n] + \Delta V_{\text{ee}}[n]}$$

we arrive at

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

where $v(\mathbf{r})$ is the external potential, the second term on the r.h.s. is the Hartree *potential* $v_{\text{H}}(\mathbf{r})$ and the third one is the **exchange-correlation potential** $v_{xc}(\mathbf{r})$. Therefore, one can solve the **Kohn-Sham equation** for the orbitals $\{\psi_{i,}^{\text{KS}}\}$

$$\boxed{\left\{ \frac{p^2}{2m_e} + v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right\} \psi_i^{\text{KS}}(\mathbf{r}) = \epsilon_i \psi_i^{\text{KS}}(\mathbf{r})}$$

---

[13]We use i to label the spin-orbitals, meaning (see below), that the same spatial orbital can be doubly occupied.

[14]Note that it has both a *kinetic* and a *potential* contribution.

and the ground-state density

$$n^{\text{out}}(\mathbf{r}) = \sum_i^{\text{occ}} \left| \psi_i^{\text{KS}}(\mathbf{r}) \right|^2$$

until self-consistency is reached, i.e. until the Kohn-Sham density n^{out} above matches the density n used to build up the Kohn-Sham Hamiltonian. Once done, the total, ground-state energy is given by

$$
\begin{aligned}
E_v &= T_{\text{KS}}[n_0] + v_{\text{H}}[n_0] + E_{\text{xc}}[n_0] + \int d^3\mathbf{r}\, n_0(\mathbf{r})v(\mathbf{r}) \\
&= \sum_i^{\text{occ}} \langle \psi_i | T | \psi_i \rangle + v_{\text{H}}[n_0] + E_{\text{xc}}[n_0] + \int d^3\mathbf{r}\, n_0(\mathbf{r})v(\mathbf{r}) \\
&= \sum_i^{\text{occ}} \epsilon_i - E_{\text{H}}[n_0] + E_{\text{xc}}[n_0] - \int d^3\mathbf{r}\, n_0(\mathbf{r})v_{\text{xc}}(\mathbf{r})
\end{aligned}
$$

where n_0 is the self-consistent solution of the Kohn-Sham equation. This is the popular Kohn-Sham method: the only problem left is now to approximate $E_{\text{xc}}[n]$.

Note that from a computational point of view the method is almost equivalent to the Hartree-Fock method. This, however, does not means 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 (or, better, to its most important part).

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, $\epsilon_{\text{ex}}^{\text{HF}} = \epsilon_{\text{ex}}^{\text{HF}}(n)$, and thus an approximate exchange functional could be written as

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

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

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

For a uniform electron gas, upon using $\nu = (\mathbf{k}, \sigma)$,

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

where the set of $\mathbf{k}-$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 $\mathbf{k}$-vector. That is

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

is the relation linking the Fermi momentum to the electron gas density n. Notice that one obtains similarly the energy (per unit volume) of the free-electron gas, *i.e.*, the quantity defining the Thomas-Fermi functional,

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

which then follows as

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

For our exchange functional we have

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

i.e., after a simple integration,

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

where $\xi_F = k_F\Delta r$ with $\Delta r = ||\mathbf{r} - \mathbf{r}'||$. 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 α electrons (similarly for the β species). Hence,

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

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 $\mathbf{k}$

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

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

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$$

$$\mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}$$

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

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

and thus, introducing $\xi = k_F r$,

$$E_{\text{ex}} = -\frac{V}{k_F^2}\frac{9n^2}{4}\int d^3\boldsymbol{\xi}\frac{[\sin(\xi) - \xi\cos(\xi)]^2}{\xi^7}$$

i.e.,

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

where C is a (positive) numerical coefficient [the integral is well defined, since for $\xi \to 0$ we have $\sin\xi - \xi\cos\xi \to \xi^3/3$].