GS - Basic Theorems of Density Functional Theory (DFT)

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The problem of a system of many particles in the quantum regime is made fairly hard by the need of working with the many-body wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$, that even for spinless particles has 3N variables (for N particles in 3 dimension)! This is a formidable task, even for systems of a few particles, and thus the search of schemes where one can work with objects simpler than the many-body wavefunction has had a special appeal since the birth of quantum mechanics. One such a scheme is provided by the so called Density Functional Formalism (DFF) , whereby one focusses on the one-body density $\rho(\mathbf{r})$ rather than on Ψ, as it is done in the Schrodinger equation. The prototype of the modern Density Functional Theory (DFT) is the scheme devised by Thomas and Fermi in the early days of quantum mechanics.

In a DFF one writes the ground-state energy E of the system of interest as a functional of $\rho(\mathbf{r})$, $E[\rho]$, with the limited objective of calculating just E and $\rho(\mathbf{r})$ in the ground state. People often try to get additional information, but it should be kept in mind that such an information is usually beyond the reach of DFF, at the exact level. Below we shall outline some basic aspects of the Hohenberg-Kohn-Sham (HKS) DFT starting, historically, from a set of two theorems due to Hohenberg and Kohn.

HKS DFT is the base of modern DFF, and is used in the majority of electronic structure calculations of materials of technological, chemical, biological interest, by a community that keeps growing day after day.

1 Hohenberg-Kohn Theorems

1.1 The first theorem

Let us consider a system of N identical particles with mass m, interparticle interaction $U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$, in an external potential $v(\mathbf{r})$. The Hamiltonian describing the system will then be:

$$H = T + U + V, \tag{1}$$

with

$$T = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} \tag{2}$$

and

$$V = \sum_i v(\mathbf{r}_i). \tag{3}$$

As an example we may consider the familiar point particles with charge e, in which case $U = (1/2) \sum_{i \neq j} e^2/|\mathbf{r}_i - \mathbf{r}_j|$; however, *we stress that in most of the following we do not need to specify*

the form of U, which may contain contribution of all order (two-body, three-body, ...). Similarly we note that for the time being we do not need specify whether the identical particles are Fermions or Bosons.

Here, we shall assume that N and $U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ are fixed, while the external potential can be chosen within a suitable class of functions. Two external potentials v and v' will be considered different if

$$v(\mathbf{r}) - v'(\mathbf{r}) \neq cost \tag{4}$$

It is evident that the external potential v fixes the Hamiltonian and in turn its ground state $|G\rangle$, which in all of the following will be assumed *non degenerate,*

$$v(\mathbf{r}) \to H \to |G\rangle, \tag{5}$$

as well as the ground state energy
$$E_G = \langle G|H|G\rangle \tag{6}$$

and the ground state one-body density

$$\rho(\mathbf{r}) = \langle G|\hat{\rho}(\mathbf{r})|G\rangle. \tag{7}$$

We note that different potentials v and v' (4) yield different ground states $|G\rangle \neq |G'\rangle$. Indeed, assuming *per absurdum* that different potential yield the same ground state, one is immediately lead to the conclusion that (apart on a set of negligible measure, the nodal surface of the wavefunction) v and v' are the same (i.e., they differ at most by a constant), which contradicts the hypothesis.

It is clear that Eqs. 4-7 establish a functional application from the space of external potentials to that of ground state densities! In other words a choice for $v(\mathbf{r})$ fixes the ground state density function $\rho(\mathbf{r})$:

$$v \to \rho. \tag{8}$$

Note the absence of the spatial argument in the equation above: it is to emphasize *the functional correspondence, which means that the value of $\rho(\mathbf{r})$ at a given point $\mathbf{r}$ depends on the value taken by the function $v(\mathbf{r})$ at all points in its domain.*

We recall that the one-body density operator is defined as

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1,N} \delta(\mathbf{r} - \mathbf{r}_i), \tag{9}$$

so that

$$\begin{aligned} \rho(\mathbf{r}) &= \langle G| \sum_{i,=1,N} \delta(\mathbf{r} - \mathbf{r_i})|G\rangle \\ &= N \int d\mathbf{r}_2 \int d\mathbf{r}_3 \cdots \int d\mathbf{r}_N |\Phi_G(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \cdots, \mathbf{r}_N), \end{aligned} \tag{10}$$

where we have used the symmetry of the wavefunction under interchange of the coordinates of two particles and the fact that integration variables are dummy ones and can be freely relabelled. Note that

$$V = \sum_i v(\mathbf{r}_i) \;=\; \int d\mathbf{r}\, \mathbf{v}(\mathbf{r})\hat{\rho}(\mathbf{r}), \tag{11}$$

$$\langle G|V|G\rangle \;=\; \int d\mathbf{r}\, \mathbf{v}(\mathbf{r})\rho(\mathbf{r}). \tag{12}$$

Having established the correspondence $v \to \rho$ we now want to demonstrate that this correspondence can be in fact inverted, so that $v \longleftrightarrow \rho$. In other words, we want to show that given a one-body density $\rho(\mathbf{r})$ there exists one and only one potential $v(\mathbf{r})$ that produces $\rho(\mathbf{r})$ as ground state density of the Hamiltonian 1. We shall proceed by *reductio to absurdum*. Let us assume that indeed two different (see Eq.4) potentials exist, v and v', which yield the same ground state density:

$$\begin{cases} v \to \rho \\ v' \to \rho \end{cases}. \tag{13}$$

They will, however (see above) yield different ground states $|G\rangle \neq |G'\rangle$, with energies E an E', respectively. The minimum principle then implies

$$E' = \langle |G'|H'|G'\rangle < \langle |G|H'|G\rangle = \langle |G|H + V' - V|G\rangle = E + \int d\mathbf{r}\rho(\mathbf{r})[v'(\mathbf{r}) - v(\mathbf{r})] \tag{14}$$

and

$$E = \langle |G|H|G\rangle < \langle |G'|H|G'\rangle = \langle |G'|H' + V - V'|G'\rangle = E' + \int d\mathbf{r}\rho(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]. \tag{15}$$

Summing Eqs. 14 and 15 one gets

$$E + E' < E + E',$$

which is manifestly *absurdum*. Therefore there cannot exist two different external potential v and v' yielding the same one-body density ρ and $v \longleftrightarrow \rho$. This completes the proof of the first Hohenberg-Kohn theorem.

It is evident that from the invertibility $v \longleftrightarrow \rho$ it follows in particular

$$\rho \longmapsto v, \tag{16}$$

which establishes a functional application from the one-body density $\rho(\mathbf{r})$ into the external potential, and therefore into the Hamiltonian, the ground state and ground state averages such as the internal energy–to mention a few notable quantities!

1.2 The second theorem

It is clear that fixing a density $\rho'(\mathbf{r})$ fixes a unique external potential $v'(\mathbf{r})$, which in turn fixes the ground-state$|G'\rangle$ and the internal energy

$$\rho'(\mathbf{r}) \longmapsto E_I[\rho'] = \langle G'|T + U|G'\rangle. \tag{17}$$

Evidently, $\rho'(\mathbf{r})$ also fixes another quantity $E_G[\rho']$

$$\rho'(\mathbf{r}) \longmapsto E_G[\rho'] = E_I[\rho'] + \int d\mathbf{r}\rho'(\mathbf{r})v(\mathbf{r}), \tag{18}$$

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a functional of the one-body density that, for fixed $v(\mathbf{r})$, may be shown to be minimum at the (ground-state) one-body density $\rho(\mathbf{r}) \equiv \rho_G(\mathbf{r})$, providing at such one-body density the ground-state energy. Indeed, let $\rho'(\mathbf{r}) \neq \rho_G(\mathbf{r})$; then $\rho' \longmapsto v' \longmapsto |G'\rangle$ and, since necessarily $v' \neq v$, it follows $|G'\rangle \neq |G\rangle$; then

$$E_G[\rho'] = E_I[\rho'] + \int d\mathbf{r}\rho'(\mathbf{r})v(\mathbf{r}) \;=\; \langle G'|T + U + V|G'\rangle = \langle G'|H|G'\rangle \tag{19}$$

$$>\; \langle G|H|G\rangle = \langle G|T + U + V|G\rangle = E_I[\rho] + \int d\mathbf{r}\rho(\mathbf{r})v(\mathbf{r}) = E_G[\rho]$$

or in brief

$$E_G[\rho'] > E_G[\rho], \quad \rho'(\mathbf{r}) \neq \rho(\mathbf{r}). \tag{20}$$

Clearly, if one knows the density functional $E_G[\rho]$, solving the associated minimum problem delivers the ground state one-body density (i.e. that non negative function that minimizes the functional) and the ground-state energy (i.e. the value of the functional at the minimum). It will be clear to the reader that a necessary condition for $E_G[\rho]$ (in brief $E[\rho]$) to be minimum is

$$\frac{\delta E}{\delta\rho(\mathbf{r})} = \mu, \tag{21}$$

2 The density functional for non-interacting particles

The first surprise, once one has accepted the fact that the ground-state energy can be regarded as a functional of the one-body density (from now on simple the *density*), is that such a functional is non explicitly known even in the simple case of independent (or non-interacting) particles. In such a case in fact one is lead to consider the one-particle problem

$$\left[-\frac{\hbar^2\nabla^2}{2m} + v(\mathbf{r})\right]\phi_\alpha(\mathbf{r}) = \epsilon_\alpha\phi_\alpha(\mathbf{r}), \tag{22}$$

whose solutions provide the density

$$\rho(\mathbf{r}) = \sum_{\alpha,occ.} |\phi_\alpha(\mathbf{r})|^2, \tag{23}$$

where the sum runs over the occupied states, namely for N particles the N orbitals with the lowest energy eigenvalues. According to the results above the energy functional is readily calculated. In fact the kinetic energy functional is

$$T[\rho] = \sum_{\alpha,occ.} \langle\phi_\alpha| - \frac{\hbar^2\nabla^2}{2m}|\phi_\alpha\rangle^2 \equiv T_0[\rho], \tag{24}$$

which yields the energy functional as

$$E[\rho] = T_0[\rho] + \int d\mathbf{r}\rho(\mathbf{r})v(\mathbf{r}). \tag{25}$$

The minimum condition will then read

$$\frac{\delta E}{\delta\rho(\mathbf{r})} = \frac{\delta T_0}{\delta\rho(\mathbf{r})} + v(\mathbf{r}) = \mu \tag{26}$$

In other words, we know how to calculate the energy functional from the one-particle orbitals of the independent-particle problem in an external field, but we do not know the functional in closed form! Given this, we may hope at most to have a similar situation in the interacting-particle case.

2.1 The Konh-Sham scheme (formalism)

Our aim here is to demonstrate that the density functional problem of interacting particles can be cast into a selfconsistent problem of independent (i.e., non-interacting particles). Let's indicate with $\{\rho(\mathbf{r})\}_U$ the set of ground state densities for the interacting system when the external potential $v(\mathbf{r})$ is varied, i.e. is chosen within a specified set of functions. We shall call the functions in the set $\{\rho(\mathbf{r})\}_U$ the v-representable interacting density. In principle one may think that the set of densities corresponding to different interparticle interactions, i.e. different choices for U, would be different. However we shall assume, with Kohn and Sham that

$$\{\rho(\mathbf{r})\}_U \subset \{\rho(\mathbf{r})\}_{U=0} \equiv \{\rho(\mathbf{r})\}_0. \tag{27}$$

This amounts to say that any interacting one-body density is also solution of the non-interacting problem. In general we expect the external potential for the non-interacting case to be different from the one in the interacting situation. If Eq. (27) holds, then for any interacting density $\rho(\mathbf{r})$ there will be a suitable external potential $\tilde{v}(\mathbf{r})$ that delivers $\rho(\mathbf{r})$ as solution of the on-interacting problem, so that one may construct $T_0[\rho]$, from which an excess functional can be obtained by subtraction as

$$E_{ex}[\rho] = E_I[\rho] - T_0[\rho]. \tag{28}$$

In fact for system of Coulomb particles (i.e. e^2/r interaction) it is customarily to define an exchange-correlation (xc) functional by subtracting from the internal energy also the Hartree energy:

$$E_{xc}[\rho] = E_I[\rho] - T_0[\rho] - U_H[\rho]. \tag{29}$$

Whence it follows that the ground state functional can be written as

$$E_G[\rho] = T_0[\rho] + U_H[\rho] + E_{xc}[\rho] + \int d\mathbf{r}\rho(\mathbf{r})v(\mathbf{r}). \tag{30}$$

It follows that the minimum condition for the interacting system may be written as:

$$\frac{\delta E}{\delta\rho(\mathbf{r})} = \frac{\delta T_0}{\delta\rho(\mathbf{r})} + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) + v(\mathbf{r}) = \frac{\delta T_0}{\delta\rho(\mathbf{r})} + \tilde{v}(\mathbf{r}) = \mu, \tag{31}$$

where clearly the effective (density-dependent non-interacting potential) $\tilde{v}([\rho];\mathbf{r})$ is the sum of the external potential $v(\mathbf{r})$ for the interacting system, the Hartree potential $v_H([\rho];\mathbf{r})$ and the so-called exchange potential $v_{xc}([\rho];\mathbf{r})$: the last two terms are functionals of the density, in addition to being functions of $\mathbf{r}$,

$$v_{xc}([\rho];\mathbf{r}) = \frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}, \tag{32}$$

$$v_H([\rho];\mathbf{r}) = \frac{\delta U_H}{\delta\rho(\mathbf{r})} = e^2 \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{33}$$

Eqs. (31,26) show that indeed the interacting problem can be solved as a non-interacting one in an effective density-dependet external potential. This suggests to solve the so-called Kohn-Sham equations

$$\left[-\frac{\hbar^2\nabla^2}{2m} + \tilde{v}(\mathbf{r})\right]\phi_\alpha(\mathbf{r}) = \epsilon_\alpha\phi_\alpha(\mathbf{r}). \tag{34}$$

From these one selfconsistently obtains the density as

$$\rho(\mathbf{r}) = \sum_{\alpha,occ.} |\phi_\alpha(\mathbf{r})|^2 \,, \tag{35}$$

as it is done in Hartree or Hartree-Fock (HF) equations. In other words one starts from a guess density $\rho(\mathbf{r})$ and iterates Eqs. (34-35) up to selfconsistency (i.e. when $\rho(\mathbf{r})$ obtained from Eq. (35) is not appreciably different from the one used to construct the effective potential in Eq. (34). As is the case with HF, at selfconsistency the eigenvalue sum differs form the ground state energy and in the present case it is straightforward to show that

$$E[\rho] = \sum_{\alpha,occ.} \epsilon_\alpha - U_H[\rho] - \int d\mathbf{r}\rho(\mathbf{r})v_{xc}([\rho];\mathbf{r}) + U_{xc}[\rho]. \tag{36}$$

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