DENSITY FUNCTIONAL THEORY
(VERY PRELIMINARY NOTES)

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1. Introduction

Since the early years of quantum mechanics the variational principle was exploited, as in the Thomas-Fermi and the Hartree-Fock approximations.
In 1964, Pierre Hohenberg and Walter Kohn established the foundations of Density Fuctional Theory (DFT) [3, 12]. Its practicable version has the wonder of reproducing properties of a many-particle system by means of a one-particle equation with a suitable potential; in the words of Kohn, DFT is the "exactification" of the Hartree approximation [6]. Since then, DFT enabled a huge progress in condensed matter physics and chemistry and nuclear physics. Since "exactification" is only in principle, an approximate DFT is often the starting point for many-body perturbation theory, that confronts with present-day experimental precision [10, 11].

Consider the family of Hamiltonians of N interacting electrons $\hat{H} = \hat{H}_0 + \hat{V}$, where $\hat{H}_0$ is fixed and contains the inter-particle interaction, and $\hat{V}$ varies among 1-particle potentials such that the spectrum of $\hat{H}_0 + \hat{V}$ is bounded below. In first and second quantization:

$$\hat{V} = v(\mathbf{x}_1) + \ldots + v(\mathbf{x}_N) = \int d\mathbf{x}\, v(\mathbf{x})\hat{n}(\mathbf{x}) \tag{1}$$

For example, $\hat{H}_0$ may describe the kinetic and Coulomb energies of the electrons, while the potentials $v(\mathbf{x})$ describe diverse assignments of charge distribution.
Once v is specified, Schrödinger's equation for N particles is solved for the ground state (g.s.) Ψ_v, and the total energy E, the chemical potential μ, the g.s. expectation values such as the density $n(\mathbf{x}) = \langle \Psi_v | \hat{n}(\mathbf{x}) | \Psi_v \rangle$, can be evaluated and are functionals of v.

For Coulomb Hamiltonians where $\hat{V}$ is the interaction of the electrons with assigned point ion-charges, Kato proved that the ground state density $n(\mathbf{x})$ has cusps at the positions $\mathbf{R}_i$ of the ions, with ionic charges given by [9]:

$$Z_i = -\lim_{\|\mathbf{x}-\mathbf{R}_i\|\to 0} \frac{a_0}{2} \frac{|\mathrm{grad}\, n(\mathbf{x})|}{n(\mathbf{x})} \tag{2}$$

Therefore, the knowledge of the electronic density $n(\mathbf{x})$ provides the ionic charges $Z_i e$ and their positions $\mathbf{R}_i$, i.e. the potential v.
The question arises: can one trade $v(\mathbf{x})$ *for* $n(\mathbf{x})$*?*. A general answer is provided by the following fundamental theorem:

Date: revised october 2019.

Theorem 1.1 (Hohenberg and Kohn, 1964, [3]). *Given $\hat{H}_0$, if for all 1-particle external potentials v the ground state Ψ_v of $\hat{H}_0 + \hat{V}$ is non-degenerate, then there is a one to one correspondence between potential, ground state and density:*

$$v \Longleftrightarrow \Psi \Longleftrightarrow n \tag{3}$$

provided that potentials differing by a constant, or states differing by a global phase factor, are treated as equivalent.

Proof. The implications $v \Longrightarrow \Psi \Longrightarrow n$ are obvious. Let us prove:
$v \Longleftarrow \Psi$. Suppose that two potentials v_ℓ ($\ell = 1,2$) produce the same ground state Ψ. In the position representation:

$$\left[H_0 + \sum_{k=1..N} v_\ell(\mathbf{x}_k)\right] \Psi(\mathbf{x}_1 \dots \mathbf{x}_N) = E_\ell \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N), \qquad \ell = 1,2$$

Subtraction gives: $\sum_k [v_1(\mathbf{x}_k) - v_2(\mathbf{x}_k)]\Psi(\mathbf{x}_1 \dots \mathbf{x}_N) = (E_1 - E_2)\Psi(\mathbf{x}_1 \dots \mathbf{x}_N)$. Then, for any choice $\mathbf{x}_1, \dots, \mathbf{x}_N$ such that $\Psi(\mathbf{x}_1 \dots \mathbf{x}_N) \neq 0$, it is

$$[v_1(\mathbf{x}_1) - v_2(\mathbf{x}_1)] + \dots + [v_1(\mathbf{x}_N) - v_2(\mathbf{x}_N)] = E_1 - E_2$$

This is only possible if $v_1(\mathbf{x}) - v_2(\mathbf{x})$ is a constant.
$v \Longleftarrow n$. Suppose that two potentials $v_1(\mathbf{x})$ and $v_2(\mathbf{x})$ that do not differ by a constant produce the same density function n. The ground states Ψ_1 and Ψ_2 are different by the previous statement. Since the ground states are non-degenerate, by the Riesz principle we have the *strict* inequality

$$E_1 < \langle \Psi_2 | H_1 \Psi_2 \rangle = E_2 + \int d\mathbf{x}\, [v_1(\mathbf{x}) - v_2(\mathbf{x})]\, n(\mathbf{x}).$$

An analogous relation holds if 1 and 2 are exchanged. Summation term by term gives $E_1 + E_2 < E_2 + E_1$ which is absurd. □

As a consequence, the ground state properties of the system are all determined by the density of particles n in the ground state.

Lieb proved that given a density n with integral N, there exists a Slater determinant of N orthonormal functions in $L^2(\mathbb{R}^3)$ such that $n(\mathbf{x}) = \sum_k |\phi_k(\mathbf{x})|^2$. The functions are reported in [2].

2. Density functionals

To a density n (with integral N) there correspond a potential v and a ground state energy E, computed with v. Since the energy is a minimum and n is given, it is:

$$E = \min_{\Psi \to n} \langle \Psi | H_0 | \Psi \rangle + \int d\mathbf{x}\, v(\mathbf{x}) n(\mathbf{x}) \tag{4}$$

where the minimum is constrained to states that produce the density n. The equation defines the Levy-Lieb functional of the density [8]:

$$F_{LL}[n] =: \min_{\Psi \to n} \langle \Psi | H_0 | \Psi \rangle \tag{5}$$

By means of it, the functional for the ground state energy is:

$$E[n,\mu] = F_{LL}[n] + \int d\mathbf{x}\, v(\mathbf{x})\, n(\mathbf{x}) - \mu \left[\int d\mathbf{x}\, n(\mathbf{x}) \, - \, N\right] \tag{6}$$

The ground state density is obtained by minimizing $E[n,\mu]$ with respect to n and μ (the latter fixes the total number N):

$$0 = \frac{\delta F_{LL}[n]}{\delta n(\mathbf{x})} + v(\mathbf{x}) - \mu \tag{7}$$

The solution n depends on μ, which is fixed by imposing normalization to N. The resulting density n_N is used to evaluate the ground state energy $E(N) = F_{LL}[n_N] + \int d\mathbf{x}\, v(\mathbf{x})\, n_N(\mathbf{x})$.

Proposition 2.1. *μ is the chemical potential.*

Proof.

$$\frac{dE(N)}{dN} = \int d\mathbf{x} \left[\frac{\delta F_{LL}[n_N]}{\delta n_N(\mathbf{x})} + v(\mathbf{x})\right] \frac{dn_N(\mathbf{x})}{dN} = \mu$$

where (7) and the property $\int d\mathbf{x}\; dn_N(\mathbf{x})/dN = 1$ were used. ☐

The unsolved problem remains of the explicit expression of $F_{LL}[n]$. A step forward is provided by the Kohn and Sham theory.

3. THE KOHN-SHAM EQUATION

For a system of N non-interacting particles ($H_0 = T$, kinetic energy), the theorem by Hohenberg and Kohn states that given a density n there exists a potential v_{KS} such that $H = T + \int d\mathbf{x}\, n(\mathbf{x}) v_{KS}(\mathbf{x})$ has ground state density n. This ground state is the Slater determinant of the N lowest energy eigenfunctions of

$$-\frac{\hbar^2}{2m}(\nabla^2\phi_k)(\mathbf{x}) + v_{KS}(\mathbf{x})\phi_k(\mathbf{x}) = \epsilon_k\, \phi_k(\mathbf{x}) \tag{8}$$

and the density is $\sum_{k=1}^N |\phi_k(\mathbf{x})|^2 = n(\mathbf{x})$. v_{KS} is the Kohn-Sham potential, and equation (8) is the Kohn-Sham equation [5].

The same energy and ground-state density can be obtained as the minimum of

$$E[n,\mu] = T[n] + \int d\mathbf{x}\, v_{KS}(\mathbf{x}) n(\mathbf{x}) - \mu\left[\int d\mathbf{x}\, n(\mathbf{x}) - N\right]$$

with Levy-Lieb functional $T[n] = \min_{\Psi\to n}\langle\Psi|T|\Psi\rangle$. The minimum solves

$$0 = \frac{\delta T[n]}{\delta n(\mathbf{x})} + v_{KS}(\mathbf{x}) - \mu. \tag{9}$$

The idea is to use the simple problem (8) *to obtain the density of an interacting many-body problem by an appropriate choice of the Kohn-Sham potential.*

Let us write the unknown Levy-Lieb functional $F_{LL}[n]$ of the interacting problem as a sum of meaningful terms: the kinetic functional of independent particles $T[n]$, the classical two-particle interaction energy with potential $v(x,y)$, and an unknown exchange-correlation functional:

$$F_{LL}[n] = T[n] + \tfrac{1}{2}\int d\mathbf{x}d\mathbf{y}\, n(\mathbf{x})n(\mathbf{y})v(\mathbf{x},\mathbf{y}) + E_{xc}[n] \tag{10}$$

Then, eq.(7) for the density becomes:

$$0 = \frac{\delta T[n]}{\delta n(\mathbf{x})} + \int d\mathbf{y}\, v(\mathbf{x},\mathbf{y})n(\mathbf{y}) + v_{xc}(\mathbf{x}) + v(\mathbf{x}) - \mu, \tag{11}$$

$$v_{xc}(\mathbf{x}) =: \frac{\delta E_{xc}[n]}{\delta n(\mathbf{x})} \tag{12}$$

$\int d\mathbf{y}\, v(\mathbf{x},\mathbf{y})n(\mathbf{y})$ is the Hartree (i.e. mean field) potential and v_{xc} is named exchange-correlation potential. In order that eq.(9) gives the same density of the interacting model, we put

$$\boxed{v_{KS}(\mathbf{x}) = v(\mathbf{x}) + \int d\mathbf{y}\, v(\mathbf{x},\mathbf{y})n(\mathbf{y}) + v_{xc}(\mathbf{x})} \tag{13}$$

The total energy (6) of the many-body system is then evaluated:

$$\begin{aligned} E(N) &= T[n] + \tfrac{1}{2}\int d\mathbf{x}d\mathbf{y}\, n(\mathbf{x})v(\mathbf{x},\mathbf{y})n(\mathbf{y}) + E_{xc}[n] + \int d\mathbf{x}\, v(\mathbf{x})n(\mathbf{x}) \\ &= E_0(N) - \tfrac{1}{2}\int d\mathbf{x}d\mathbf{y}\, n(\mathbf{x})v(\mathbf{x},\mathbf{y})n(\mathbf{y}) + E_{xc}[n] - \int d\mathbf{x}\, v_{xc}(\mathbf{x})\, n(\mathbf{x}) \end{aligned} \tag{14}$$

where E_0 is the energy of the independent particles with Kohn-Sham potential (the sum of the lowest N eigenvalues).

3.1. **LDA.** To overcome the ignorance of $E_{xc}[n]$ the simple Local Density Approximation is often used. Introduce the exchange-correlation energy density:

$$E_{xc}[n] = \int d\mathbf{x}\, \epsilon_{xc}(\mathbf{x}, n)\, n(\mathbf{x})$$

In LDA the density is approximated by the expression valid for the homogeneous electron gas (HEG) where the constant density is replaced by its value at x: $\epsilon_{xc}^{LDA}(\mathbf{x}, n) = \epsilon_{xc}^{HEG}(n(\mathbf{x}))$. Explicit expressions of the latter are available, as functions that interpolate the numerical data of the HEG ground state energy on some range of density [11].

For example, the exchange term for HEG is $E_x(n) = -V\frac{3}{4}e^2(3/\pi)^{1/3}n^{4/3}$. With $V = \int d\mathbf{x}$, and replacing n with $n(\mathbf{x})$ inside the integral, an exchange functional is obtained:

$$E_x^{LDA}[n] = \int d\mathbf{x}\, n(\mathbf{x})\, \epsilon_x^{LDA}(n(\mathbf{x})) = -\frac{3e^2}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \int d\mathbf{x}\, n(\mathbf{x})^{4/3} \tag{15}$$

The functional derivative gives the exchange potential: $v_x^{LDA}(\mathbf{x}) = \frac{4}{3}\epsilon_x^{LDA}(n(\mathbf{x}))$.

A computation starts with an approximate density $n_0(x)$ and some functional expression for ϵ_{xc}. The Kohn-Sham potential is evaluated and the Kohn-Sham equation is solved for the N lowest energy eigenstates. A new density is evaluated, $n'(x) = \sum_k |\phi_k(x)|^2$, and the Kohn-Sham potential is updated. The process continues until the density stabilises.

The density is, in principle, the density of the interacting particles. The total energy of the interacting system is evaluated by (14), the chemical potential μ is the highest Kohn-Sham eigenvalue.

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