

## I. DFT

Consider the ground state,  $\Phi$ , assumed to be non-degenerate (i.e. unique), of a system of  $N$  truly interacting electrons in a local, external potential, whose Hamiltonian is:

$$\hat{\mathcal{H}} = \hat{T} + \hat{U} + \hat{V} \equiv \sum_i (-\Delta_i) + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{2}{r_{ij}} + \sum_i v_{ext}(\mathbf{r}_i). \quad (1)$$

The ground-state energy,  $\langle \Phi | \mathcal{H} | \Phi \rangle \equiv \mathcal{E}$ , is explicitly a functional of the 1st-order density matrix  $n(\mathbf{r}_1, \mathbf{r}_2)$  and the pair function,  $P(\mathbf{r}_1, \mathbf{r}_2)$ , but not obviously of the density,  $n(\mathbf{r})$ .

Hohenberg&Kohn (1964) showed that

- $\Phi(\mathbf{r}_1, s_1; \dots; \mathbf{r}_N, s_N)$  is a *unique* functional of  $n(\mathbf{r})$ .

This is maybe less surprising than it sounds, if one realizes that  $T + U$  is constant for a system of electrons, so that the only variable part of (1) is  $v_{ext}(\mathbf{r})$ .

**Proof.** 1.  $\Phi \implies n(\mathbf{r})$ , because explicitly:  $n(\mathbf{r}) = N \int |\Phi(\mathbf{r}, \sigma_1; 2; 3; \dots; N)|^2 d\sigma_1 d2d3\dots dN$ .

2.  $n(\mathbf{r}) \implies \Phi$ , because assuming  $n(\mathbf{r}) \implies \begin{cases} \Phi \\ \Phi' \end{cases}$ , with  $\Phi \neq \Phi'$  leads to a to an

inconsistency: Since  $\Phi$  was assumed to be non-degenerate,  $\Phi$  and  $\Phi'$  must be generated by two different external potentials,  $V \neq V'$ , and hence:

$$\begin{aligned} \mathcal{E}' &\equiv \langle \Phi' | T + U + V' | \Phi' \rangle \\ &< \langle \Phi | T + U + V' | \Phi \rangle = \langle \Phi | T + U + V - (V - V') | \Phi \rangle = \mathcal{E} - \langle \Phi | V - V' | \Phi \rangle \\ &= \mathcal{E} - \int [v_{ext}(\mathbf{r}) - v'_{ext}(\mathbf{r})] n(\mathbf{r}) d^3r. \end{aligned}$$

Analogously we get:

$$\mathcal{E} < \mathcal{E}' - \langle \Phi' | V' - V | \Phi' \rangle = \mathcal{E}' - \int [v'_{ext}(\mathbf{r}) - v_{ext}(\mathbf{r})] n(\mathbf{r}) d^3r.$$

since  $n \equiv n'$ . Adding these two inequalities gives:  $\mathcal{E}' + \mathcal{E} < \mathcal{E}' + \mathcal{E}$ , which is inconsistent, so we cannot have  $\Phi \neq \Phi'$ ,

Q.E.D. ■

Having proved that  $\Phi$  is a unique functional of the density,  $n$ , where the admissible densities are restricted to have the same number of electrons,  $N = \int n(\mathbf{r}) d^3r$ , it is obvious the the kinetic-plus-potential energy functional,

$$\langle \Phi | T + U | \Phi \rangle \equiv F \{n(\mathbf{r})\}, \quad (2)$$

is universal, and that the *total-energy functional*,

$$F \{n(\mathbf{r})\} + \int v_{ext}(\mathbf{r}) n(\mathbf{r}) d^3r \equiv \mathcal{E}_{v_{ext}} \{n(\mathbf{r})\}, \quad (3)$$

attains its *minimum* for the proper ground-state density, since:

$$\mathcal{E} \{n'(\mathbf{r})\} = \langle \Phi' | \mathcal{H} | \Phi' \rangle > \langle \Phi | \mathcal{H} | \Phi \rangle = \mathcal{E}_{v_{ext}} \{n(\mathbf{r})\}.$$

This minimal property may be generalized to the lowest state of a given symmetry.

Had we know an explicit form of the universal kinetic-plus-potential energy functional (2), we could rather easily use the variational principle to determine the ground-state energy and density for any system by varying the density, keeping the number of electrons constant by means of a Lagrangian multiplier. Formally, this is:

$$E_F = \frac{\delta \mathcal{E} \{n(\mathbf{r})\}}{\delta n(\mathbf{r})} \equiv \frac{\delta T \{n(\mathbf{r})\}}{\delta n(\mathbf{r})} + v_C(\mathbf{r}) + \frac{\delta U_{xc} \{n(\mathbf{r})\}}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r}), \quad (4)$$

where

$$v_C(\mathbf{r}_1) = \int \frac{2n(\mathbf{r}_2)}{r_{12}^{-1}} = \frac{\delta}{\delta n(\mathbf{r}_1)} \frac{1}{2} \int n(\mathbf{r}_1) \int \frac{2n(\mathbf{r}_2)}{r_{12}} d^3r_1 d^3r_2 = \frac{\delta}{\delta n(\mathbf{r})} \langle \Phi | U_C | \Phi \rangle$$

is the classical Coulomb (Hartree) potential, and

$$U_{xc} \{n(\mathbf{r})\} \equiv \langle \Phi | U | \Phi \rangle - \langle \Phi | U_C | \Phi \rangle$$

is the remaining part of the Coulomb functional after large, explicit *Hartree part*,  $\langle \Phi | U_C | \Phi \rangle$ , of the *Coulomb interaction* has been subtracted.

From the past 50 year's success of wave-mechanics (prior to 1965), Kohn&Sham knew that also the proper *kinetic energy* ought to be included as well. That part is, however, *not* an explicit functional of  $n(\mathbf{r})$ , but of  $n(\mathbf{r}, \mathbf{r}')$ , so they had to approximate it. Here, H&K chose the following, ingenious route: Together with the real, interacting system, they

considered a *system of non-interacting electrons* with the *same* density,  $n(\mathbf{r})$ , and number of electrons, i.e. a system with the Hamiltonian,

$$\hat{\mathcal{H}}_0 \equiv \hat{T} + \hat{V}_0,$$

in which the external potential,  $V_0 \equiv \int v_0(\mathbf{r}) n(\mathbf{r}) d^3r$ , is determined in such a way that the *density* of the non-interacting ground state,  $\Phi_0$ , is the same as in the ground state,  $\Phi$ , of the real system; such a choice of  $V_0$  exists and is unique according to the Hohenberg-Kohn theorem. Now,  $\Phi_0$  is a single Slater determinant of one-electron wavefunctions,  $\psi_k(\mathbf{r})$ , determined by the one-electron Schrödinger equation:

$$[-\Delta + v_0(\mathbf{r})] \psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r}), \quad \blacktriangleleft \quad (5)$$

and the total energy, the density, and the kinetic energy of the non-interacting system are respectively

$$\begin{aligned} \mathcal{E}_0 \{n(\mathbf{r})\} &= \sum_k \theta(\varepsilon_F - \varepsilon_k) \varepsilon_k, & n(\mathbf{r}) &= \sum_k \theta(\varepsilon_F - \varepsilon_k) |\psi_k(\mathbf{r})|^2, \text{ and} \\ T_0 \{n(\mathbf{r})\} &= \sum_k \theta(\varepsilon_F - \varepsilon_k) \langle \psi_k | -\Delta | \psi_k \rangle. \end{aligned} \quad (6)$$

The kinetic-energy part, which K&S then separated in the total-energy functional for the proper system, is  $T_0 \{n(\mathbf{r})\}$  :

$$\mathcal{E} \{n(\mathbf{r})\} = T_0 \{n(\mathbf{r})\} + \langle \Phi | U_C | \Phi \rangle + \mathcal{E}_{xc} \{n(\mathbf{r})\} + \int v_{ext}(\mathbf{r}) n(\mathbf{r}) d^3r \quad (7)$$

and the remaining, unknown part of the the total-energy functional for the proper system,

$$\mathcal{E}_{xc} \{n(\mathbf{r})\} \equiv T \{n(\mathbf{r})\} - T_0 \{n(\mathbf{r})\} + U_{xc} \{n(\mathbf{r})\}, \quad (8)$$

is called the *exchange-correlation energy functional*. With this decomposition (7) for the real system, together with

$$\mathcal{E}_0 \{n(\mathbf{r})\} = T_0 \{n(\mathbf{r})\} + \int v_{ext}(\mathbf{r}) n(\mathbf{r}) d^3r$$

for the non-interaction system, the variation with respect to  $n(\mathbf{r})$ , analogous to (4), yields:

$$\begin{aligned} E_F &= \frac{\delta \mathcal{E} \{n(\mathbf{r})\}}{\delta n(\mathbf{r})} = \frac{\delta T_0 \{n(\mathbf{r})\}}{\delta n(\mathbf{r})} + v_C(\mathbf{r}) + \frac{\delta \mathcal{E}_{xc} \{n(\mathbf{r})\}}{\delta n(\mathbf{r})} + v_{ext}(\mathbf{r}), \\ E_{F0} &= \frac{\delta \mathcal{E}_0 \{n(\mathbf{r})\}}{\delta n(\mathbf{r})} = \frac{\delta T_0 \{n(\mathbf{r})\}}{\delta n(\mathbf{r})} + v_0(\mathbf{r}). \end{aligned}$$

This determines

$$v_0(r) = v_C(\mathbf{r}) + v_{xc}(\mathbf{r}) + v_{ext}(\mathbf{r}), \quad \blacktriangleleft \quad (9)$$

apart from an irrelevant constant,  $E_{F0} - E_F$ , which can be set to 0. Here,  $v_{ext}(\mathbf{r}) \equiv \delta\mathcal{E}_{xc}\{n(\mathbf{r})\}/\delta n(\mathbf{r})$  is the unknown so-called *exchange-correlation potential*. With an explicit approximation for this, hopefully small term, the *ground-state problem* has then been reduced to a *one-electron problem* (5) to be solved *self-consistently* (9). Now, the external potential acting on the real system,  $v_{ext}(\mathbf{r})$ , is the one from the protons, plus possibly applied potentials.

One self-consistency has been reached, the total energy is given by

$$\begin{aligned} \mathcal{E} &= \sum_k \theta(\varepsilon_F - \varepsilon_k) \langle \psi_k | -\Delta | \psi_k \rangle + \frac{1}{2} \int n(\mathbf{r}_1) \int \frac{2n(\mathbf{r}_2)}{r_{12}} d^3r_1 d^3r_2 + \mathcal{E}_{xc}\{n(\mathbf{r})\} + \int v_{ext}(\mathbf{r}) n(\mathbf{r}) d^3r \\ &= \sum_k \theta(\varepsilon_F - \varepsilon_k) \varepsilon_k - \int v_0(\mathbf{r}) n(\mathbf{r}) d^3r + \frac{1}{2} \int v_C(\mathbf{r}) n(\mathbf{r}) d^3r + \int v_{xc}(\mathbf{r}) n(\mathbf{r}) d^3r + \int v_{ext}(\mathbf{r}) n(\mathbf{r}) d^3r \\ &\quad + \left( \mathcal{E}_{xc}\{n(\mathbf{r})\} - \int v_{xc}(\mathbf{r}) n(\mathbf{r}) d^3r \right) \\ &= \sum_k \theta(\varepsilon_F - \varepsilon_k) \varepsilon_k - \frac{1}{2} \int v_C(\mathbf{r}) n(\mathbf{r}) d^3r + \left( \mathcal{E}_{xc}\{n(\mathbf{r})\} - \int v_{xc}(\mathbf{r}) n(\mathbf{r}) d^3r \right). \quad \blacktriangleleft \end{aligned} \quad (10)$$

This HKS scheme is designed for calculating ground state properties and the *one-electron energies*,  $\varepsilon_k$ , of the non-interacting system have no direct meaning (although, in practice, they are not bad). They do satisfy a Koopmans-like theorem, which is obtained by substituting in expressions (6) for the single-Slater determinant system  $\sum_k \theta(\varepsilon_F - \varepsilon_k)$  by  $\sum_k n_k$  where the occupation numbers,  $n_k$ , are 1 or 0. Subsequent treatment of the occupation numbers as continuous variables and differentiation with respect to them, then yields:

$$\frac{\delta\mathcal{E}\{n(\mathbf{r})\}}{\delta n_k} = \int \frac{\delta\mathcal{E}\{n(\mathbf{r})\}}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial n_k} d^3r = \left\langle \psi_k \left| \frac{\delta\mathcal{E}\{n(\mathbf{r})\}}{\delta n(\mathbf{r})} \right| \psi_k \right\rangle = \varepsilon_k. \quad \blacktriangleleft \quad (11)$$

In contrast to Koopmans theorem, this one (due to Slater, but named after Janak) contains a differentiation.

The *self-energy*,  $\Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_k)$ , is a ground state property and may herefore in principle be calculated from  $n(\mathbf{r})$ , and if we knew its functional form, we could insert it instead of  $v_{xc}(\mathbf{r})$ , whereby the corresponding one-electron Schrödinger equation would yield excitation energies and quasiparticle lifetimes (Sham&Kohn 1966). During the last decades, accurate

but computationally cumbersome, RPA-like schemes (GW etc) schemes have been developed for this purpose.

Returning again to the ground state, we still need to devise explicit approximations for the exchange-correlation energy functional (8),  $\mathcal{E}_{xc}\{n(\mathbf{r})\}$ . The so-called *local* approximation (LDA) consist of writing

$$\mathcal{E}_{xc}\{n(\mathbf{r})\} \approx \int n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r})) d^3r, \quad (12)$$

where  $\varepsilon_{xc}(n(\mathbf{r}))$  is the best possible estimate of the exchange plus correlation energy per electron in the homogeneous electron gas. Using this, makes the LDA exact in the limit of slowly vaying densities, which is, however far from those in real matter. Since for high snties, the knetic energy dominates, the LDA is also correct in that limit. In practice, it has worked surprisingly well. With the LDA (12), the expression for the exchange-correlation part of the one-electron potential (9) becomes potential we get

$$v_{xc}(\mathbf{r}) \equiv v_{ext}(\mathbf{r}) \equiv \frac{\delta \mathcal{E}_{xc}\{n(\mathbf{r})\}}{\delta n(\mathbf{r})} = \left. \frac{d[n\varepsilon_{xc}(n)]}{dn} \right|_{n(\mathbf{r})} = \mu_{xc}(n(\mathbf{r})),$$

which is a simple local potential. E.g. if correlation is negeted for the hogeneous gas,  $\mu_x(n) = -4\sqrt[3]{(3/8\pi)n}$ .

This density functional scheme can be extended to a spin-density functional scheme (SDFT), a la the unrestricted Hartree-Fock scheme. Over the years also non-local (e.g. gradient-corrected) exchange-correlation functionals have been developed.

## II. DFT COMPUTER PROGRAMS

I just drop a few names, off the top of my head. They can be Google'd:

- WIEN 2k (LAPW+lo)
- VASP (PW-PAW)
- Quantum espresso (PW-Pseudo)
- Abinit (PW-Pseudo)
- Siesta (fireballs)

- Stuttgart code (LMTO and NMTO)

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