

School on DFT and QIT
São Paulo, Oct. 23-26, 2017

Giovanni Vignale

University of Missouri-Columbia

Static density functional theory

Reference - G. F. Giuliani and G. Vignale, *Quantum Theory of the Electron Liquid*
(Cambridge University Press, 2005), Chapter 7

I. LECTURES 1-2

1. Problem: study the ground-state properties of a system of N electrons in a static external potential $V(\mathbf{r})$. Hamiltonian:

$$\begin{aligned}\hat{H} &= \sum_{i=1}^N \frac{|\hat{\mathbf{p}}_i|^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} + \sum_{i=1}^N V(\hat{\mathbf{r}}_i) \\ &= \hat{T} + \hat{U} + \hat{V}\end{aligned}\tag{1}$$

2. Introduce the density operator

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \hat{\mathbf{r}}_i),\tag{2}$$

and its ground state expectation value

$$n(\mathbf{r}) = \langle \psi_0 | \hat{n}(\mathbf{r}) | \psi_0 \rangle\tag{3}$$

where $|\psi_0\rangle$ is the ground state. Then define the universal functional

$$F[n] \equiv \min_{\psi \rightarrow n} \langle \psi | \hat{T} + \hat{U} | \psi \rangle,\tag{4}$$

where the minimum is searched among the antisymmetric N -electron wave functions ψ that yield density $n(\mathbf{r})$. For any reasonable density there are such wave functions and the search returns at least one $\psi[n]$ and a single value of $F[n]$. A slight generalization of this functional (extending the search to ensembles that yield the same density) can be shown to be continuous and convex. Noting that

$$\hat{V} = \int d\mathbf{r} V(\mathbf{r}) \hat{n}(\mathbf{r}),\tag{5}$$

we see that the ground-state energy and density of \hat{H} are obtained by minimizing the functional

$$E_V[n] = F[n] + \int d\mathbf{r} V(\mathbf{r})n(\mathbf{r}) \quad (6)$$

with respect to $n(\mathbf{r})$ for a given $V(\mathbf{r})$.

3. *Hohenberg-Kohn theorem: If a density $n(\mathbf{r})$ is the ground-state density of the hamiltonian \hat{H} with some local potential $V(\mathbf{r})$ then $V(\mathbf{r})$ is uniquely defined, up to an additive constant.* Notes: (1) The theorem *does not* say that every density can be realized in the ground-state of a local potential, although it is believed that the set of V-representable densities is dense enough to approximate every reasonable density. (2) The ground-state associated with a given density can be one of a degenerate set. (3) Some densities are representable only in ensembles of degenerate ground-states.
4. Kohn-Sham equation: Define the non-interacting F functional, denoted by $T_s[n]$ as follows:

$$T_s[n] \equiv \min_{\psi \rightarrow n} \langle \psi | \hat{T} | \psi \rangle, \quad (7)$$

where \hat{T} is the kinetic energy operator. Then define the exchange-correlation (xc) energy functional $E_{xc}[n]$ from the relation

$$F[n] = T_s[n] + E_H[n] + E_{xc}[n], \quad (8)$$

where

$$E_H[n] = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (9)$$

is the *Hartree energy functional*. Then, minimization of the energy $E_V[n]$ leads to the variational condition

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} = -V(\mathbf{r}) - U_H(\mathbf{r}) - V_{xc}(\mathbf{r}) \equiv -V_s(\mathbf{r}), \quad (10)$$

where

$$V_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad (11)$$

is the exchange-correlation potential and

$$U_H(\mathbf{r}) \equiv \frac{\delta E_H[n]}{\delta n(\mathbf{r})} = e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (12)$$

is the Hartree potential. The potential $V_s(\mathbf{r}) = V(\mathbf{r}) + U_H(\mathbf{r}) + V_{xc}(\mathbf{r})$ is known as Kohn-Sham potential and is a unique functional of the density, up to an additive constant. Observe that the variational condition

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} = -V_s(\mathbf{r}), \quad (13)$$

is equivalent to the solution of the non-interacting Schrödinger equation

$$-\frac{\nabla^2}{2m}\psi_\alpha(\mathbf{r}) + V_s(\mathbf{r})\psi_\alpha(\mathbf{r}) = \epsilon_\alpha\psi_\alpha(\mathbf{r}) \quad (14)$$

with density self-consistently determined by occupying the N lowest-lying orbitals $\psi_\alpha(\mathbf{r})$ (*aufbau principle*):

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_\alpha(\mathbf{r})|^2. \quad (15)$$

The solution of these equations determines the ground-state density $n(\mathbf{r})$ and the ground-state energy E via the relation

$$E = \sum_{i=1}^N \epsilon_\alpha - E_H[n] - \int d\mathbf{r} n(\mathbf{r}) V_{xc}(\mathbf{r}) + E_{xc}[n], \quad (16)$$

provided $E_{xc}[n]$ and $V_{xc}[n]$ are known exactly. In practice the xc potential and energy functionals must be approximated, but for a given ground state density they can be obtained from the exact ground-state wave function.

5. Physical significance of Kohn-Sham eigenvalues and eigenfunctions: none in general, but the highest occupied eigenvalue is the negative of the ionization energy when the Kohn-Sham potential vanishes at infinity.
6. Spin density functional theory. Replace

$$\int d\mathbf{r} V(\mathbf{r}) \hat{n}(\mathbf{r}) \rightarrow \int d\mathbf{r} V_\uparrow(\mathbf{r}) \hat{n}_\uparrow(\mathbf{r}) + \int d\mathbf{r} V_\downarrow(\mathbf{r}) \hat{n}_\downarrow(\mathbf{r}), \quad (17)$$

where $\hat{n}_\uparrow(\mathbf{r})$ and $\hat{n}_\downarrow(\mathbf{r})$ are the density operators of spin up and spin down respectively, and $V_\uparrow(\mathbf{r})$ and $V_\downarrow(\mathbf{r})$ are their conjugate fields. The formalism goes through as before, e.g. one has

$$F[n_\uparrow, n_\downarrow] = \min_{\psi \rightarrow n_\uparrow, n_\downarrow} \langle \psi | \hat{T} + \hat{U} | \psi \rangle, \quad (18)$$

etc...However, there are some subtle differences, related to the possibility of changing $V_\uparrow(\mathbf{r})$ and $V_\downarrow(\mathbf{r})$ by *two different* additive constants (the so-called non-uniqueness

problem). In practice, spin density functional theory is needed to treat situations in which a spin density exists in the absence of a magnetic field, and more generally it allows for a more accurate description of many-body effects when approximations are made (without approximations, it would in principle be equivalent to basic DFT).

7. Adiabatic continuation formula for $E_{xc}[n]$. Introduce the hamiltonian

$$\hat{H}(\lambda) = \hat{T} + \lambda\hat{U} + \hat{V}_\lambda, \quad 0 \leq \lambda \leq 1 \quad (19)$$

where the local potentials $V_{\lambda,\sigma}(\mathbf{r})$ ($\sigma = \uparrow$ or \downarrow) are chosen so that the ground-state densities $n_\sigma(\mathbf{r})$ are independent of λ . This hamiltonian interpolates between the ‘‘Kohn-Sham hamiltonian’’ $\hat{H}(0)$ and the physical hamiltonian of the system $\hat{H}(1)$. Making use of the Hellman-Feynman theorem we arrive at

$$E_{xc}[n_\uparrow, n_\downarrow] = \int_0^1 d\lambda U(\lambda) - E_H[n], \quad (20)$$

where $U(\lambda)$ is the expectation value of the interaction energy in the ground state $|\psi_\lambda\rangle$ of the Hamiltonian $\hat{H}(\lambda)$. Define the pair-correlation function

$$g_{\lambda,\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \equiv \frac{\langle \psi_\lambda | \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_\sigma(\mathbf{r}) | \psi_\lambda \rangle}{n_\sigma(\mathbf{r}) n_{\sigma'}(\mathbf{r}')}, \quad (21)$$

which is a functional of the densities $n_\sigma(\mathbf{r})$. Then we have

$$\begin{aligned} E_{xc}[n_\uparrow, n_\downarrow] &= \frac{e^2}{2} \int_0^1 d\lambda \int d\mathbf{r} \int d\mathbf{r}' \frac{n_\sigma(\mathbf{r}) n_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} [g_{\lambda,\sigma\sigma'}(\mathbf{r}, \mathbf{r}') - 1] \\ &= \int_0^1 d\lambda E_{xc,\lambda}[n_\uparrow, n_\downarrow]. \end{aligned} \quad (22)$$

The central problem is to approximate $E_{xc,\lambda}[n_\uparrow, n_\downarrow]$.

8. Exchange-correlation hole and sum rule. We define the exchange-correlation hole of spin σ as

$$n_{xc\sigma,\lambda}(\mathbf{r}, \mathbf{r}') = \sum_{\sigma'} n_{\sigma'}(\mathbf{r}') [g_{\lambda,\sigma\sigma'}(\mathbf{r}, \mathbf{r}') - 1]. \quad (23)$$

The $E_{xc,\lambda}$ functional is then given by

$$E_{xc,\lambda}[n_\uparrow, n_\downarrow] = \sum_\sigma \int d\mathbf{r} \int d\mathbf{r}' \frac{n_\sigma(\mathbf{r}) n_{xc\sigma,\lambda}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (24)$$

It is straightforward to verify that

$$\int d\mathbf{r}' n_{xc\sigma}(\mathbf{r}, \mathbf{r}') = -1. \quad (25)$$

In the non-interacting Kohn-Sham system ($\lambda = 0$) one has

$$n_{xc\sigma,0}(\mathbf{r}, \mathbf{r}') = - \sum_{\sigma'} \frac{|\sum_{\alpha=1}^N \psi_{\alpha}^*(\mathbf{r}, \sigma) \psi_{\alpha}(\mathbf{r}', \sigma')|^2}{n_{\sigma}(\mathbf{r})} \leq 0. \quad (26)$$

9. Exchange-only approximation. In this approximation one replaces $n_{xc\sigma,\lambda}(\mathbf{r}, \mathbf{r}')$ by $n_{xc\sigma,0}(\mathbf{r}, \mathbf{r}') \equiv n_{x\sigma,0}(\mathbf{r}, \mathbf{r}')$. The resulting functional is called $E_x[n_{\uparrow}, n_{\downarrow}]$ and it is equal to $E_{xc,0}[n_{\uparrow}, n_{\downarrow}]$. It can be shown that the exact $E_{xc}[n_{\uparrow}, n_{\downarrow}] \leq E_x[n_{\uparrow}, n_{\downarrow}]$. The difference

$$\begin{aligned} E_c[n_{\uparrow}, n_{\downarrow}] &= E_{xc}[n_{\uparrow}, n_{\downarrow}] - E_x[n_{\uparrow}, n_{\downarrow}] \\ &= \langle \psi_1 | \hat{T} + \hat{U} | \psi_1 \rangle - \langle \psi_0 | \hat{T} + \hat{U} | \psi_0 \rangle \leq 0, \end{aligned} \quad (27)$$

is called *correlation energy*. Notice that the correlation energy is always negative.

10. Local density approximation. In this approximation one replaces $n_{xc\sigma,\lambda}(\mathbf{r}, \mathbf{r}')$ by $n_{xc\sigma,\lambda}^h(\mathbf{r} - \mathbf{r}')$ of the homogeneous electron gas of densities $n_{\sigma}(\mathbf{r})$. This approximation automatically preserves the sum rule and is nearly exact for the “on-top hole” $n_{xc\sigma,\lambda}(\mathbf{r}, \mathbf{r})$. The expression for E_{xc} takes the form

$$E_{xc}^{LDA}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{xc}^h(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})), \quad (28)$$

where $\epsilon_{xc}^h(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r}))$ is the xc energy per electron in the homogeneous electron gas of densities $n_{\sigma}(\mathbf{r})$. This is the most widely used approximation for E_{xc} .

II. LECTURES 3-4

1. Behavior of $E_{xc,\lambda}$ as a function of λ .

(i) Small λ . At $\lambda = 0$ we have $E_{xc,0} = E_x$, the exact exchange functional. The initial slope of $E_{xc,\lambda}$ vs λ at $\lambda = 0$ is negative (why?) and has a finite value, which can be calculated by doing second order perturbation theory on the hamiltonian $H(\lambda)$ (This type of perturbation theory at constant density is known as *Görling-Levy perturbation theory*). So we have

$$E_{xc,\lambda}[n] \xrightarrow{\lambda \rightarrow 0} E_x[n] + 2\lambda E_c^{(2)}[n], \quad (29)$$

where

$$E_c^{(2)}[n] = \sum_k \frac{|\langle \Phi_{k,s} | \hat{H}_1 | \Phi_{0,s} \rangle|^2}{E_{0,s} - E_{k,s}}, \quad (30)$$

where the sum runs over the excited states (\mathbf{k} , with eigenvalue $E_{k,s}$) of the Kohn-Sham system and the first-order correction to the Kohn-Sham Hamiltonian is $\hat{H}_1 = \hat{U} - \hat{V}_H - \hat{V}_x$.

(ii) Large λ . Potential energy dominates and electrons get locked in strictly correlated positions determined by the “co-motion function” $\{\mathbf{f}_1(\mathbf{r}), \mathbf{f}_2(\mathbf{r}), \dots, \mathbf{f}_N(\mathbf{r})\}$ ($\mathbf{f}_1(\mathbf{r}) = \mathbf{r}$). The i -th function determines the position of the i -th electron in terms of \mathbf{r} , which is conventionally taken to be the position of the first electron. The comotion functions are determined by the density via the invariance relation $n(\mathbf{r})d\mathbf{r} = n(\mathbf{f}_i(\mathbf{r}))d\mathbf{f}_i(\mathbf{r})$ (See Seidl, Gori-Giorgi and Savin, PRA **75**, 042511 (2007) and PRA **59**, 51 (1999)). This in turn implies that the potential energy grows as λ for large λ and $E_{xc,\lambda}$ tends to a constant. The leading correction to the strictly correlated energy arises from zero-point oscillations about the rigid relative arrangements. This contribution scales as $1/\lambda^{1/2}$. Further corrections can be shown to vanish faster than $1/\lambda$. Thus we have

$$E_{xc,\lambda}[n] \xrightarrow{\lambda \rightarrow \infty} U_{SCE}[n] + 2 \frac{T_{ZP}[n]}{\lambda^{1/2}}, \quad (31)$$

where

$$U_{SCE}[n] = \frac{e^2}{2} \int d\mathbf{r} \sum_{i \neq j} \frac{n(\mathbf{r})}{N|\mathbf{f}_i(\mathbf{r}) - \mathbf{f}_j(\mathbf{r})|} \quad (32)$$

and

$$T_{ZP}[n] = \int d\mathbf{r} \frac{n(\mathbf{r})}{N} \sum_{n=1}^{Nd-d} \frac{\omega_n(\mathbf{r})}{2}, \quad (33)$$

where $\omega_n(\mathbf{r})$ are the $Nd-d$ zero-point frequencies around the degenerate SCE minimum (see our JCTC **5**, 743 (2009).)

An interpolation formula between these two limits can be found in our JCTC paper (reference above), in Eqs. 85–89.

2. Critique of the LDA. Major problem of the LDA: the exchange energy is approximated in such a way that the self-interaction contained in the Hartree functional is not cancelled. This is known as *the self-interaction (SI) error*. For example, if you consider a single electron, it is evident that there is no correlation, and the exchange potential must cancel the Hartree potential to leave us with the bare external potential. A similar problem arises in the external region of every atom. Here the electron must feel the potential $-e^2/r$. Since the Hartree potential exactly screens the nuclear potential

The self-interaction error in the H atom (in Hartrees)

	LSD	PBE	exact
E_x	-0.264	-0.302	-0.307
E_c	-0.22	-0.06	0
E_{xc}	-0.286	-0.308	-0.307

it follows that the exact $V_{xc}(r) \rightarrow -e^2/r$ for $r \rightarrow \infty$. By contrast, $V_{xc}^{LDA}(\mathbf{r})$ tends to zero exponentially.

3. Exchange and correlation in LDA. Because of the SI error, the $dE_{xc,\lambda}[n]/d\lambda$ vs λ curve in *LDA* starts at higher values at $\lambda = 0$ than the exact curve. Its behavior generally improves with increasing λ . This explains why it is not such a good idea to use the LDA for the correlation energy alone, reserving the exact treatment for the exchange. This approach is equivalent to a rigid down-shift of the $dE_{xc,\lambda}[n]/d\lambda$ vs λ curve. This fixes the $\lambda = 0$ limit, but introduces even larger errors at large λ . Several ad-hoc methods have been introduced to reduce the self-interaction error. Hybrid functionals, in which only a fraction of the exchange is treated exactly have also been introduced. The form of these approximations is

$$E_{xc}^{hybrid} = w(E_x - E_x^{DFA}) + E_{xc}^{FDA}, \quad (34)$$

where E_{xc}^{FDA} stands for one of the standard density functional approximations, i.e. LDA or GGA, and w , with $0 \leq w \leq 1$ is a weight factor. The most recent generation of meta-GGA functionals are free of SI error, in the sense that they become exact for one and two-electron densities.

4. Proof of concavity of $E_{xc,\lambda}$: $d^2E_{xc,\lambda}/d\lambda^2 < 0$.

It is sufficient to show that

$$Q(\lambda) \equiv \min_{\psi \rightarrow n} \langle \psi | T + \lambda U | \psi \rangle \quad (35)$$

is concave:

$$d^2Q(\lambda)/d\lambda^2 < 0 \quad (36)$$

[here U is the interaction energy] This is obvious because, given λ_1 and λ_2 , with $\lambda_1 < \lambda_2$, and a value of λ intermediate between λ_1 and λ_2 , $\lambda = (1 - x)\lambda_1 + x\lambda_2$, with $0 < x < 1$, we have

$$Q(\lambda) = \min_{\psi \rightarrow n} \langle \psi | (1 - x)(T + \lambda_1 U) + x(T + \lambda_2 U) | \psi \rangle. \quad (37)$$

Evidently, the minimum of the sum is larger than or equal to the sum of the minima, therefore we have

$$Q(\lambda) > (1 - x)Q(\lambda_1) + xQ(\lambda_2). \quad (38)$$

Since λ_1 and λ_2 are arbitrary, this shows that the function is concave.

5. Beyond the LDA: GGA and meta-GGA. Naive attempts to improve the LDA by including “gradient corrections” to the xc hole run into difficulties, because the approximate xc hole develops a spurious long-range tail and therefore ends up violating the sum rule on the integrated strength. This problem is avoided in the GGA. By ensuring that the xc hole satisfies the known physical constraints

$$\begin{aligned} n_{x,\sigma}(\mathbf{r}, \mathbf{r}') &\leq 0 \\ \int n_{x,\sigma}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' &= -1 \\ \int n_{c,\sigma}(\mathbf{r}, \mathbf{r}') d\mathbf{r}' &= 0, \end{aligned} \quad (39)$$

this approximation achieves considerable improvements, particularly in the calculation of dissociation energies. The general form of this approximation is

$$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}). \quad (40)$$

and simple parametrizations for the function f have been introduced. Finally, the meta-GGA removes the self-interaction error for one- and two-particle densities by including the new variable $\tau_{\sigma} - |\nabla n_{\sigma}|^2/8n_{\sigma}$ (curvature of the exchange hole), which is known to vanish for such densities. The form of this approximation is

$$E_{xc}^{meta-GGA}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} g(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}). \quad (41)$$

6. Addition and removal energies: the band gap problem. We now consider systems with variable particle number. A quantity of great interest in physics and chemistry is the *addition energy*

$$\mu_+(N) \equiv E(N+1) - E(N) \quad (42)$$

defined as the difference between the ground-state energies of the same hamiltonian with $N+1$ and N electrons. Notice that chemists prefer to talk instead of *affinity energy*

$$A(N) = E(N) - E(N+1) = -\mu_+(N) \quad (43)$$

and *ionization energy*

$$I(N) = E(N-1) - E(N) = -\mu_+(N-1) = A(N-1). \quad (44)$$

A particularly important quantity is the so-called “gap”:

$$E_g = I(N) - A(N) = \mu_+(N) - \mu_+(N-1) \quad (45)$$

To see why it is called “gap” consider the Hamiltonian for open systems

$$\hat{K} = \hat{H} - \mu\hat{N}, \quad (46)$$

where \hat{N} is the number operator. Denote by $K(N)$ the minimum eigenvalue of \hat{K} for given N . Then $\mu_+(N)$ is the value of μ for which $K(N+1) = K(N)$, and $\mu_-(N)$ is the value of μ for which $K(N-1) = K(N)$. Then we see that $\mu_-(N) \leq \mu \leq \mu_+(N)$ is the range of values of the chemical potential for which the system has N electrons as the stable state. *As long as μ is “in the gap” the number of particle does not change.* This is why we call $E_g \equiv \mu_+ - \mu_-$ the gap.

Because it is a difference of ground-state energies, the gap appears to be within the realm of applicability of ground-state DFT. However, the fact that the particle number changes, opens a new class of problems. We have already seen that the ionization energy $I(N)$ can be obtained exactly from the negative of the highest occupied Kohn-Sham eigenvalue for a system of N electrons (when the Kohn-Sham potential vanishes at infinity). From this we can say that the gap should be exactly given by the difference of Kohn-Sham eigenvalues calculated for different numbers of particles

$$E_g = \epsilon_{N+1}(N+1) - \epsilon_N(N) \quad (47)$$

Band gaps (in eV) of selected semiconductors and insulators

	Diamond	Si	Ge	LiCl	GaAs
LDA	3.9	0.52	0.07	6.0	0.12
Expt.	5.48	1.17	0.744	9.4	1.52

This is different from the naive Kohn-Sham gap

$$E_{g,s} = \epsilon_{N+1}(N) - \epsilon_N(N) \quad (48)$$

However, in the limit of large N , for periodic systems, the difference between $N + 1$ and N disappears in the density and one would expect $E_g = E_{g,s}$. Indeed, this is what happens, but the problem is that the calculated E_g does not agree with experiment, it is systematically too small in semiconductors and insulators. Detailed calculations show that this is not a problem that can be easily solved by going beyond the LDA: using the exact xc potential from the exact ground-state density of Si improves things somewhat, but not enough (see papers by Sham and Schluter, 1980s). On the other hand, Hartree-Fock calculations systematically overestimate the gap in semiconductors and insulators.

7. Derivative discontinuity.

The resolution of the paradox lies in the fact that, although the density changes infinitesimally when the electron number changes from N to $N + 1$, the xc potential changes by a finite and constant amount. The reason for this is the discontinuous jump in the chemical potential, which in turn results in a (constant) discontinuity of the functional derivative of F and T_s at integer particle numbers. Since these discontinuities are different for an interacting and non-interacting systems we conclude that the exchange-correlation functional must also have a derivative discontinuity Δ_{xc} . The true gap is then given by

$$E_g = E_{g,s} + \Delta_{xc}. \quad (49)$$

What happens in LDA is that the cusps in the xc energy functional as a function of N are smoothed into convex curves. Thus, one misses the Δ_{xc} contribution and

the gap comes out underestimated. In Hartree-Fock, on the other hand, the straight-line segments of the exact functional are replaced by concave curves. The derivative discontinuities are accentuated and the gap comes out too large.

8. DFT for strongly correlated systems.

For systems close to the strong correlation limit (e.g. weakly confined quantum dots) an approach complementary to the Kohn-Sham approach has been recently proposed by us. [PRL **103** 166402 (2009)]. In this approach we write

$$F[n] = U_{SCE}[n] + E_{kd}[n] \quad (50)$$

where $U_{SCE}[n]$ is the Coulomb potential energy of strictly correlated electrons [PRA **75**, 042511 (2007) and PRA **59**, 51 (1999)], and E_{kd} is a remainder, which, in this formulation, plays a role analogous to the xc energy of the Kohn-Sham approach. We call it *kinetic-decorrelation* functional. In the presence of an external potential $V(\mathbf{r})$ minimization of the energy entails

$$\frac{\delta U_{SCE}[n]}{\delta n(\mathbf{r})} = -\frac{\delta E_{kd}[n]}{\delta n(\mathbf{r})} - V(\mathbf{r}) \quad (51)$$

Compare this with the solution of a strictly correlated electron system (no kinetic energy) in an effective potential $V_{SCE}(\mathbf{r})$:

$$\frac{\delta U_{SCE}[n]}{\delta n(\mathbf{r})} = -V_{SCE}(\mathbf{r}). \quad (52)$$

In order for these two problems - the true one and the strictly correlated one - to yield the same ground-state density we must choose

$$V_{SCE}(\mathbf{r}) = V(\mathbf{r}) + \frac{\delta E_{kd}[n]}{\delta n(\mathbf{r})}. \quad (53)$$

V_{SCE} is the analogue of the Kohn-Sham potential. The functional derivative of $E_{kd}[n]$ with respect to density defines the kinetic-decorrelation potential. Thus, the solution of the many-body problem with kinetic energy has been mapped to the solution of a strictly correlated electron system in the presence of an effective potential that yields the same density. A formal expression for $E_{kd}[n]$ can be constructed from the Hamiltonian

$$\hat{H}(\alpha) = \alpha \hat{T} + \hat{U} + \hat{V}_\alpha, \quad 0 \leq \alpha \leq 1 \quad (54)$$

where the potential \hat{V}_α ensures the constancy of the density as α is varied. This hamiltonian interpolates between the strictly correlated hamiltonian of our effective problem ($\alpha = 0$) and the physical Hamiltonian ($\alpha = 1$). Making use of the Hellman-Feynman theorem it is easy to see that

$$E_{kd}[n] = \int_0^1 d\alpha \langle \psi_\alpha | \hat{T} | \psi_\alpha \rangle \equiv \int_0^1 d\alpha E_{kd,\alpha}, \quad (55)$$

where ψ_α is the ground-state of $\hat{H}(\alpha)$. In the limit $\alpha \rightarrow 0$ we have

$$E_{kd,\alpha}[n] \xrightarrow{\alpha \rightarrow 0} \frac{T_{ZP}[n]}{\alpha^{1/2}}, \quad (56)$$

where $T_{ZP}[n]$ is the zero-point kinetic energy discussed above (reference). From which we deduce

$$E_{kd}[n] \xrightarrow{\alpha \rightarrow 0} 2T_{ZP}[n]\alpha^{1/2}. \quad (57)$$

We can also introduce the ‘‘LDA’’:

$$E_{kd}^{LDA}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{kd}^h(n(\mathbf{r})), \quad (58)$$

where

$$\epsilon_{kd}^h(n) = \epsilon^h(n) - \frac{a_M}{r_s(n)}, \quad (59)$$

$\epsilon^h(n)$ is the total energy (kinetic plus potential) per electron of the homogeneous interacting electron gas and a_M/r_s ($a_M = 1.8$ is the Madelung constant) is the classical energy of the Wigner crystal at that density. These and other approximations have recently been used to study the ground-state energy of a two-electron quantum dot in the strongly correlated regime, with encouraging results (see table).

ω	KS-LDA	SCE	SCE-ZP	SCE-LDA	SCE-ZP-LDA
1.000×10^0	2.0	40.4	17.7	3.4	14.3
1.667×10^{-1}	2.4	32.7	11.2	4.8	14.9
5.393×10^{-2}	1.6	27.1	8.0	5.5	14.1
2.368×10^{-2}	0.1	23.0	6.1	5.8	13.1
7.285×10^{-3}	4.2	17.6	4.2	5.6	10.9
2.211×10^{-3}	11.6	13.0	2.8	4.8	8.1
1.221×10^{-3}	16.5	11.0	2.3	4.3	6.8
5.973×10^{-4}	23.4	9.0	1.8	3.6	5.3
3.353×10^{-4}	29.7	7.6	1.5	3.1	4.2
2.408×10^{-4}	33.6	6.9	1.4	2.8	3.6

TABLE I: Fractional % errors on the total energy of a model 2D quantum dot consisting of two electrons confined in an harmonic potential $v_{\text{ext}}(\mathbf{r}) = \frac{1}{2}\omega^2 r^2$. Columns as follows: KS-LDA are the results for standard Kohn-Sham LDA, SCE are the results obtained by setting $E_{kd}[\rho] = 0$, SCE-LDA, SCE-ZP and SCE-ZP-LDA are the results of different approximations for E_{kd} .

A. Review questionnaire

1. Which of the following quantities can be calculated exactly from the Kohn-Sham equation (assuming the exact exchange-correlation potential and exchange-correlation functional are known)?
 - (i) Ground-state density
 - (ii) Ground-state wave function
 - (iii) Ground-state energy
 - (iv) Pair correlation function
 - (v) Ionization energy

2. Define the exchange-correlation functional, the exact exchange functional, and the correlation functional in terms of an energy minimization over wave functions that give density n .

3. Why is the correlation functional always negative?

4. What is the exact exchange-correlation potential for a hydrogen atom?
5. What is the exact exchange-correlation potential for an atom, in the limit of large distance from the nucleus ($r \rightarrow \infty$)?
6. What is the origin of self-interaction error? Which of the following approximations suffers from self-interaction error?
 - (i) Local density approximation
 - (ii) Exact exchange
 - (iii) Hartree-Fock
 - (iv) Generalized gradient approximation.
7. What is the origin of the “band gap problem”?
8. In a strictly correlated electron system the Kohn-Sham orbitals are replaced by the so-called “co-motion functions”. What are the co-motion functions?