

Density functional theory

Morten Hjorth-Jensen

Department of Physics and Center for Computing in Science Education
University of Oslo, N-0316 Oslo, Norway

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Litterature I

- ▶ R. van Leeuwen: *Density functional approach to the many-body problem: key concepts and exact functionals*, Adv. Quant. Chem. **43**, 25 (2003).
(Mathematical foundations of DFT)
- ▶ R. M. Dreizler and E. K. U. Gross: *Density functional theory: An approach to the quantum many-body problem*. (Introductory book)
- ▶ W. Koch and M. C. Holthausen: *A chemist's guide to density functional theory*. (Introductory book, less formal than Dreizler/Gross)
- ▶ E. H. Lieb: Density functionals for Coulomb systems, Int. J. Quant. Chem. **24**, 243-277 (1983). (Mathematical analysis of DFT)

Litterature II

- ▶ J. P. Perdew and S. Kurth: In *A Primer in Density Functional Theory: Density Functionals for Non-relativistic Coulomb Systems in the New Century*, ed. C. Fiolhais *et al.* (Introductory course, partly difficult, but interesting points of view)
- ▶ E. Engel: In *A Primer in Density Functional Theory: Orbital-Dependent Functionals for the Exchange-Correlation Energy*, ed. C. Fiolhais *et al.* (Introductory lectures, only about orbital-dependent functionals)

Density Functional Theory

The electronic energy E is said to be a *functional* of the electronic density, $E[n]$, in the sense that for a given function $n(r)$, there is a single corresponding energy. The *Hohenberg-Kohn theorem* confirms that such a functional exists, but does not tell us the form of the functional. As shown by Kohn and Sham, the exact ground-state energy E of an N -electron system can be written as

$$E[n] = -\frac{1}{2} \sum_{i=1}^N \int \psi_i^*(\mathbf{r}_1) \nabla_1^2 \psi_i(\mathbf{r}_1) d\mathbf{r}_1 - \int \frac{Z}{r_1} n(\mathbf{r}_1) d\mathbf{r}_1 + \frac{1}{2} \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + E_{\text{xc}}[n]$$

with ψ_i the *Kohn-Sham (KS) orbitals*. Note that we have limited ourselves to atomic physics here.

How do we arrive at the above equation?

Density Functional Theory

The ground-state charge density is given by

$$n(\mathbf{r}) = \sum_{i=1}^N |\Psi_i(\mathbf{r})|^2,$$

where the sum is over the occupied Kohn-Sham orbitals. The last term, $E_{XC}[n]$, is the *exchange-correlation energy* which in theory takes into account all non-classical electron-electron interaction. However, we do not know how to obtain this term exactly, and are forced to approximate it. The KS orbitals are found by solving the *Kohn-Sham equations*, which can be found by applying a variational principle to the electronic energy $E[n]$. This approach is similar to the one used for obtaining the HF equation.

Density Functional Theory

The KS equations reads

$$\left\{ -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} + \int \frac{n(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{XC}(\mathbf{r}_1) \right\} \psi_i(\mathbf{r}_1) = \epsilon_i \psi_i(\mathbf{r}_1)$$

where ϵ_i are the KS orbital energies, and where the *exchange-correlation potential* is given by

$$V_{XC}[n] = \frac{\delta E_{XC}[n]}{\delta n}.$$

Density Functional Theory

The KS equations are solved in a self-consistent fashion. A variety of basis set functions can be used, and the experience gained in HF calculations are often useful. The computational time needed for a DFT calculation formally scales as the third power of the number of basis functions.

The main source of error in DFT usually arises from the approximate nature of E_{XC} . In the *local density approximation* (LDA) it is approximated as

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

where $\epsilon_{XC}[n(\mathbf{r})]$ is the exchange-correlation energy per electron in a homogeneous electron gas of constant density. The LDA approach is clearly an approximation as the charge is not continuously distributed. To account for the inhomogeneity of the electron density, a nonlocal correction involving the gradient of n is often added to the exchange-correlation energy.

The Hohenberg-Kohn theorems

Assume we have a given Hamiltonian for a many-fermion system

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V},$$

or in second quantized form

$$\begin{aligned}\hat{H} = & -\frac{\hbar^2}{2m} \int d^3r \hat{\Psi}^\dagger(\mathbf{r}) \nabla^2 \hat{\Psi}(\mathbf{r}) + \int d^3r \hat{\Psi}^\dagger(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) \hat{\Psi}(\mathbf{r}) \\ & + \frac{1}{2} \int d^3r \int d^3r' \hat{\Psi}^\dagger(\mathbf{r}) \hat{\Psi}^\dagger(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \hat{\Psi}(\mathbf{r}') \hat{\Psi}(\mathbf{r}),\end{aligned}$$

$$\hat{\Psi}(\mathbf{r}) \equiv \sum_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) a_{\mathbf{k}}$$

$$\hat{\Psi}^{\dagger}(\mathbf{r}) \equiv \sum_{\mathbf{k}} \psi_{\mathbf{k}}^*(\mathbf{r}) a_{\mathbf{k}}^{\dagger}$$

\mathbf{k} = collection of quantum numbers

\hat{T} = kinetic energy operator

\hat{V}_{ext} = external single-particle potential operator

\hat{V} = two-particle interaction operator

Theorem I

We assume that there is a \mathcal{V}_{ext} = set of external single-particle **potentials** v so that

$$\hat{H}|\phi\rangle = \left(\hat{T} + \hat{V}_{\text{ext}} + \hat{V} \right) = E|\phi\rangle, \quad \hat{V}_{\text{ext}} \in \mathcal{V}_{\text{ext}},$$

gives a **non-degenerate** N-particle ground state $|\Psi\rangle_0$. For any system of interacting particles in an external potential \mathcal{V}_{ext} , the potential \mathcal{V}_{ext} is uniquely determined (by a near constant) by the ground state density n_0 . There is a corollary to this statement which states that since \hat{H} is determined, the many-body functions for all states are also determined. All properties of the system are determined via n_0 .

Theorem II

The density (assuming normalized state vectors)

$$n(\mathbf{r}) = \sum_i \int dx_2 \cdots \int dx_N |\Psi(\mathbf{r}, x_2, \dots, x_N)|^2$$

Theorem II states that a universal functional for the energy $E[n]$ (function of n) can be defined for every external potential \mathcal{U}_{ext} . For a given external potential, the exact ground state energy of the system is a global minimum of this functional. The density which minimizes this functional is n_0 .

Proof I.

Let us prove $C : \mathcal{V}(C) \longrightarrow \Psi$ injective:

$$\hat{V} \neq \hat{V}' + \text{constant} \quad \stackrel{?}{\implies} \quad |\Psi\rangle \neq |\Psi'\rangle,$$

where $\hat{V}, \hat{V}' \in \mathcal{V}$

Reductio ad absurdum:

Assume $|\Psi\rangle = |\Psi'\rangle$ for some $\hat{V} \neq \hat{V}' + \text{const}$, $\hat{V}, \hat{V}' \in \mathcal{V}$

$$\hat{T} \neq \hat{T}[V], \hat{W} \neq \hat{W}[V] \implies^1$$

$$(\hat{V} - \hat{V}') |\Psi\rangle = (E_{gs} - E'_{gs}) |\Psi\rangle.$$

$$\implies \quad \hat{V} - \hat{V}' = E_{gs} - E'_{gs}$$

$$\implies \quad \hat{V} = \hat{V}' + \text{constant} \quad \text{Contradiction!}$$



¹Unique continuation theorem: $|\Psi\rangle \neq 0$ on a set of positive measure ▶

Proof II.

Let us prove $D : \Psi \rightarrow \mathcal{N}$ injective:

$$|\Psi\rangle \neq |\Psi'\rangle \stackrel{?}{\implies} n(\mathbf{r}) \neq n'(\mathbf{r})$$

Reductio ad absurdum:

Assume $n(\mathbf{r}) = n'(\mathbf{r})$ for some $|\Psi\rangle \neq |\Psi'\rangle$

Ritz principle \implies

$$E_{gs} = \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle$$

$$\langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' + \hat{V} - \hat{V}' | \Psi' \rangle = E'_{gs} + \int n'(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d^3r$$

$$\implies E'_{gs} < E_{gs} + \int n'(\mathbf{r})[v(\mathbf{r}) - v'(\mathbf{r})]d^3r \quad (1)$$

By symmetry

$$\implies E_{gs} < E'_{gs} + \int n'(\mathbf{r})[v'(\mathbf{r}) - v(\mathbf{r})]d^3r \quad (2)$$

(??) & (??) \implies

$$E_{gs} + E'_{gs} < E_{gs} + E'_{gs} \quad \text{Contradiction!}$$

□

Define

$$E_{v_0}[n] := \langle \Psi[n] | \hat{T} + \hat{W} + \hat{V}_0 | \Psi[n] \rangle$$

\hat{V}_0 = external potential, $n_0(\mathbf{r})$ = corresponding GS density, E_0 = GS energy

Rayleigh-Ritz principle \implies **second statement of H-K theorem:**

$$E_0 = \min_{n \in \mathcal{N}} E_{v_0}[n]$$

Last statement of H-K theorem:

$$F_{HK}[n] \equiv \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle$$

is *universal* ($F_{HK} \neq F_{HK}[\hat{V}_0]$)

The Kohn-Sham scheme

The **classic Kohn-Sham** scheme:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{s,0}(\mathbf{r}) \right) \phi_{i,0}(\mathbf{r}) = \varepsilon_i \phi_{i,0}(\mathbf{r}), \quad \varepsilon_1 \geq \varepsilon_2 \geq \dots ,$$

where

$$v_{s,0}(\mathbf{r}) = v_0(\mathbf{r}) + \int d^3 r' w(\mathbf{r}, \mathbf{r}') n_0(\mathbf{r}') + v_{\text{XC}}([n_0]; \mathbf{r})$$

The density calculated as

$$n_0(\mathbf{r}) = \sum_{i=1}^N |\phi_{i,0}(\mathbf{r})|^2,$$

Equation **solved selfconsistently**

Total energy:

$$E = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \int d^3 r d^3 r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + E_{\text{XC}}[n] - \int d^3 r v_{\text{XC}}([n]; \mathbf{r}) n(\mathbf{r})$$

Exchange Energy and Correlation Energy

Hartree-Fock equation:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_0(\mathbf{r}) + \int d^3 r' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \right) \phi_k(\mathbf{r}) - \underbrace{\sum_{l=1}^N \int d^3 r' \phi_l^*(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \phi_k(\mathbf{r}') \phi_l(\mathbf{r})}_{\text{exchange term}} = \varepsilon_k \phi_k(\mathbf{r}),$$

Non-local exchange term (Pauli exclusion principle)

Kohn-Sham equation:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_0(\mathbf{r}) + \int d^3 r' w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + \underbrace{v_{\text{XC}}([n]; \mathbf{r})}_{\text{exchange + correlation}} \right) \phi_k(\mathbf{r}) = \varepsilon_k \phi_k(\mathbf{r}),$$

Local exchange-correlation term

Exchange-correlation energy = Exchange energy + Correlation energy

$$E_{\text{XC}}[n] = E_x[n] + E_c[n]$$

From earlier:

$$E_{\text{XC}}[n] = F_L[n] - T_s[n] - \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$

We want to show: $E_c[n] \leq 0$

Here we have (assume $F_L[n] = F_{LL}[n]$)

$$\begin{aligned} F_L[n] &\equiv \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \\ &= \langle \Psi_n^{min} | \hat{T} + \hat{W} | \Psi_n^{min} \rangle, \end{aligned}$$

and

$$T_s[n] \equiv \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} | \Psi \rangle = \langle \Phi_n^{min} | \hat{T} | \Phi_n^{min} \rangle,$$

Ψ = normalized, antisymm. N -particle wavefunction,
 Φ_n^{min} lin. komb. of Slater determinants of
single-particle orbitals $\psi_i(r_j)$

Eq. (4.35) in J. M. Thijssen: *Computational Physics*:

$$\langle \Phi_n^{min} | \hat{W} | \Phi_n^{min} \rangle = \frac{1}{2} \sum_{k,l} \left[\iint d^3r d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \right. \\ \left. - \iint d^3r d^3r' \psi_l^*(\mathbf{r}) \psi_l(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \psi_k^*(\mathbf{r}') \psi_k(\mathbf{r}) \right]$$

By definition,

$$E_x[n] \equiv -\frac{1}{2} \sum_{k,l} \iint d^3r d^3r' \psi_l^*(\mathbf{r}) \psi_l(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \psi_k^*(\mathbf{r}') \psi_k(\mathbf{r})$$

$$\begin{aligned}
E_c[n] &= E_{\text{XC}}[n] - E_x[n] \\
&= F_L[n] - T_s[n] - \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \\
&\quad + \frac{1}{2} \sum_{k,l} \iint d^3r d^3r' \psi_l^*(\mathbf{r}) \psi_l(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \psi_k^*(\mathbf{r}') \psi_k(\mathbf{r}) \\
&= \langle \Psi_n^{\text{min}} | \hat{T} + \hat{W} | \Psi_n^{\text{min}} \rangle - \langle \Phi_n^{\text{min}} | \hat{T} + \hat{W} | \Phi_n^{\text{min}} \rangle
\end{aligned}$$

Since

$$\langle \Psi_n^{\text{min}} | \hat{T} + \hat{W} | \Psi_n^{\text{min}} \rangle = \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle,$$

we see that

$$E_c[n] \leq 0$$

Computing E_{XC} from *ab initio* calculations

Question: can we compute the 'exact' E_{XC} that enters DFT calculations? Yes!
Let us define a continuous variable λ and a Hamiltonian which depends on this variable

$$\hat{H}_\lambda = \hat{T} + \lambda \hat{V} + \hat{v}_{\text{ext}},$$

where \hat{T} is the kinetic energy, \hat{V} is in our case the Coulomb interaction between two electrons and \hat{v}_{ext} is our external potential, here the two-dimensional harmonic oscillator potential.

For $\lambda = 0$ we have the non-interacting system, whose solution in our case is a single Slater determinant for the ground state (non-degenerate case). For $\lambda = 1$ we have the full interacting case.

Computing E_{XC} from *ab initio* calculations

The standard variational principle is to find the minimum of

$$E_{\lambda}[\hat{v}_{\text{ext}}] = \inf_{\Psi} \langle \Psi_{\lambda} | \hat{H}_{\lambda} | \Psi_{\lambda} \rangle,$$

with respect to the wave function Ψ_{λ} . If a maximizing potential $\hat{v}_{\text{ext}}^{\lambda}$ exists, then according to the Hohenberg and Kohn, it is the one which has the density n as the ground state density and we have a functional

$$F_{\lambda}[n] = E_{\lambda}[\hat{v}_{\text{ext}}^{\lambda}] - \int d\mathbf{r} n(\mathbf{r}) \hat{v}_{\text{ext}}^{\lambda}(\mathbf{r}).$$

Computing E_{XC} from *ab initio* calculations

Which leads to the Lieb variational principle

$$F_{\lambda}[n] = \sup_{\hat{V}_{\text{ext}}} \left(E_{\lambda}[\hat{V}_{\text{ext}}^{\lambda}] - \int d\mathbf{r} n(\mathbf{r}) \hat{V}_{\text{ext}}^{\lambda}(\mathbf{r}) \right).$$

We define

$$F_{\lambda}[n] = \langle \Psi_{\lambda} | \hat{T} + \lambda \hat{V} | \Psi_{\lambda} \rangle,$$

which we rewrite as

$$F_{\lambda}[n] = \langle \Psi_{\lambda} | \hat{T} | \Psi_{\lambda} \rangle + \lambda J[n] + E_{XC}[n],$$

with the standard Hartree term

$$J = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 n(\mathbf{r}_1) n(\mathbf{r}_2) V(r_{12}).$$

Computing E_{XC} from *ab initio* calculations

We want to find $E_{XC}[n]$ in

$$F_{\lambda}[n] = \langle \Psi_{\lambda} | \hat{T} | \Psi_{\lambda} \rangle + \lambda J[n] + E_{XC}[n].$$

To do this, since we use a variational method, we can employ the Hellmann-Feynman theorem, which states that

$$\Delta E = \int_{\lambda_1}^{\lambda_2} d\lambda \frac{\partial E_{\lambda}}{\partial \lambda} = \int_{\lambda_1}^{\lambda_2} d\lambda \langle \Psi_{\lambda} | \frac{\partial \hat{H}_{\lambda}}{\partial \lambda} | \Psi_{\lambda} \rangle.$$

Setting $\lambda_1 = 0$ and $\lambda_2 = 1$ we arrive at

$$\Delta E = \int_0^1 d\lambda \langle \Psi_{\lambda} | \hat{V} | \Psi_{\lambda} \rangle,$$

where the wave function at $\lambda = 0$ is our single Slater determinant for the reference state. In the case of a VMC calculation there would be no Jastrow factor. For $\lambda = 1$ we can use our best variational Monte Carlo function. Note that \hat{V} is the full interaction at $\lambda = 1$!

Computing E_{XC} from *ab initio* calculations

We wish to relate

$$\Delta E = \int_0^1 d\lambda \langle \Psi_\lambda | \hat{V} | \Psi_\lambda \rangle,$$

to E_{XC} . Recalling that we defined

$$\langle \Psi_\lambda | \lambda \hat{V} | \Psi_\lambda \rangle = \lambda J[n] + E_{XC}[n],$$

we rewrite our equation as

$$E_{XC} = \int_0^1 d\lambda \langle \Psi_\lambda | \hat{W}_\lambda | \Psi_\lambda \rangle,$$

where

$$W_\lambda = \langle \Psi_\lambda | \lambda \hat{V} | \Psi_\lambda \rangle - J.$$

Computing E_{XC} from *ab initio* calculations

Using the fundamental theorem of calculus we have then

$$E_{XC} = \langle \Psi_1 | \hat{V} | \Psi_1 \rangle - \langle \Psi_0 | \hat{V} | \Psi_0 \rangle.$$

We need thus simply to compute the expectation value of \hat{V} for the single Slater determinant $\lambda = 0$ and the fully correlated wave function with, if we do a VMC calculation, the Jastrow factor as well for the $\lambda = 1$ case.

The total correlation energy, including kinetic energy is then (computed at a fixed density) equal to

$$E_C = \langle \Psi_1 | \hat{T} + \hat{V} | \Psi_1 \rangle - \langle \Psi_0 | \hat{T} + \hat{V} | \Psi_0 \rangle.$$

Define

$$E_{v_0}[n] := \langle \Psi[n] | \hat{T} + \hat{W} + \hat{V}_0 | \Psi[n] \rangle$$

\hat{V}_0 = external potential, $n_0(\mathbf{r})$ = corresponding GS density, E_0 = GS energy

Rayleigh-Ritz principle \implies **second statement of H-K theorem:**

$$E_0 = \min_{n \in \mathcal{N}} E_{v_0}[n]$$

Last statement of H-K theorem:

$$F_{HK}[n] \equiv \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle$$

is *universal* ($F_{HK} \neq F_{HK}[\hat{V}_0]$)

The Basic Kohn-Sham Equations

- ▶ So far:
H-K **variational principle** \implies
exact GS density of many-particle system
Practically intractable !!
- ▶ Next step:
Kohn and Sham (1965): **single-particle picture**
 \longrightarrow equations solved **selfconsistently** (iterative scheme)

Hamiltonian of N *non-interacting* particles:

$$\hat{H}_s = \hat{T} + \hat{V}_s$$

Hohenberg and Kohn $\implies \exists$ unique energy functional

$$E_s[n] = T_s[n] + \int v_s(\mathbf{r})n(\mathbf{r})d^3r$$

s. t. $\delta E_s[n] = 0$ gives GS density $n_s(\mathbf{r})$ corresp. to \hat{H}_s

Theorem

Let

$v_s(\mathbf{r})$ = *local single-particle pot.*,

$n(\mathbf{r})$ = *GS density of interacting system*,

$n_s(\mathbf{r})$ = *GS density of non-interacting system*

\Rightarrow for *any interacting system*,

$$\exists \text{ a } v_s(\mathbf{r}) \text{ s. t. } n_s(\mathbf{r}) = n(\mathbf{r})$$

Proof in book by Dreizler/Gross, Sec. 4.2

Assume **nondegenerate GS**. Then

$$n(\mathbf{r}) = n_s(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2,$$

where $\phi_i(\mathbf{r})$ are determined by

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_s(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}), \quad \varepsilon_1 \leq \varepsilon_2 \leq \dots$$

If $\exists v_s(\mathbf{r})$, then H-K theorem gives *uniqueness* of $v_s(\mathbf{r})$
Consequently, we may write

$$\phi_i(\mathbf{r}) = \phi_i([n(\mathbf{r})]) \quad !!$$

Assume

$v_0(\mathbf{r}) = \text{ext. potential}$

$n_0(\mathbf{r}) = \text{GS density}$

of **interacting** system

- ▶ Wanted: **single-particle potential** $v_s(\mathbf{r})$ of **non-interacting** system

Exchange-correlation functional

Many-particle energy functional:

$$\begin{aligned} E_{v_0}[n] &= F_L[n] + \int d^3r v_0(\mathbf{r})n(\mathbf{r}) \\ &= \left(T_s[n] + \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r})w(\mathbf{r}, \mathbf{r}')n(\mathbf{r}') + E_{\text{XC}}[n] \right) + \int d^3r v_0(\mathbf{r})n(\mathbf{r}) \end{aligned}$$

Here **exchange-correlation functional** defined:

$$E_{\text{XC}}[n] = F_L[n] - \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r})w(\mathbf{r}, \mathbf{r}')n(\mathbf{r}') - T_s[n]$$

The exchange-correlation functional defined:

$$E_{\text{XC}}[n] = F_L[n] - \frac{1}{2} \iint d^3r d^3r' n(\mathbf{r}) w(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') - T_s[n]$$

Explicit form of $F_L[n]$ as functional of n unknown

- ▶ $E_{\text{XC}}[n]$ unknown functional, must be approximated
Otherwise, Kohn-Sham scheme exact

Definition

Let $F : B \rightarrow \mathbb{R}$ be a *functional* from normed function space B to real numbers \mathbb{R} .

The **functional derivative** (Gâteaux derivative)

$\delta F[n] \equiv \delta F[n]/\delta n(\mathbf{r})$ is defined as

$$\frac{\delta F}{\delta n}[\varphi] = \lim_{\varepsilon \rightarrow 0} \frac{F[n + \varepsilon\varphi] - F[n]}{\varepsilon}$$

Another useful definition of $\delta F[n]$:

$$\langle \delta F[n], \varphi \rangle = \left. \frac{d}{d\varepsilon} F[n + \varepsilon\phi] \right|_{\varepsilon=0},$$

where

$$\langle \delta F[n], \varphi \rangle \equiv \int d\mathbf{r} (\delta F[n(\mathbf{r})]) \varphi(\mathbf{r}),$$

φ = test function

Gradient expansion

The **gradient expansion approximation (GEA)** – a natural extension of LDA ??

Taylor expansion of $E_{\text{XC}}[n]$

around homogeneous electron gas (HEG)

density n_0 ($(n - n_0)/n_0 \ll 1$):

$$E_{\text{XC}}[n] = E_{\text{XC}}[n_0] + \sum_{m=1}^{\infty} \frac{1}{m!} \int d^3r \left. \frac{\delta^m E_{\text{XC}}}{\delta n(\mathbf{r}_1) \dots \delta n(\mathbf{r}_m)} \right|_{n=n_0} \delta n(\mathbf{r}_1) \dots \delta n(\mathbf{r}_m)$$

Gradient expansion

Shown in article by van Leeuwen:

Expansion can be written

$$E_{\text{XC}}[n] = E_{\text{XC}}^{\text{LDA}}[n] + \int d^3r g_1(n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 \\ + \int d^3r g_2(n(\mathbf{r}))(\nabla^2 n(\mathbf{r}))^2 + \dots,$$

$g_i(n)$ uniquely determined by the density response functions of a HEG

Gradient expansion in principle exact, **provided series converges**

Metallic systems:	good convergence
Insulators:	bad convergence
Finite systems:	bad convergece

Caution!

Numerical tests show:
Inclusion of second-order gradient term
may give a considerably worse $E_{\text{XC}}[n]$ than $E_{\text{XC}}^{\text{LDA}}[n]$

Why?

$E_{XC}^{LDA}[n]$ provides rather realistic results for atoms, molecules, and solids

But: second-order term (next systematic correction
for slowly-varying densities) makes E_{XC} worse

Why does gradient expansion fail?

1. Realistic electron densities not very close to slowly-varying limit
2. LDA: xc hole is the hole of a possible physical system
 \Rightarrow satisfies exact constraints
 GEA: xc hole not physical
 \Rightarrow does not satisfy constraints

Example of constraints:

Physical constraint	LDA	GEA
$E_c < 0$	< 0	> 0
$E_x < 0$	< 0	not restricted
$\int h_{xc}(\mathbf{r}_1; \mathbf{r}_2) d\mathbf{r}_2 = -1$	-1	not restricted

\Rightarrow **Wrong behaviour** of GEA

The Generalized Gradient Approximation

Method: **Enforce** physical **restrictions** for the xc hole
 \implies Generalized gradient approximation (GGA):

$$E_{\text{XC}}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow})$$

- ▶ $f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow})$ not unique,
but formal features of LDA \implies constraints
- ▶ GGA-functionals with/without semiempirical parameters
- ▶ Successful in quantum chemistry
- ▶ No systematic approach to improve GGA-functionals

Typical errors for atoms, molecules, and solids (Perdew/Kurth):

Property	LDA	GGA
E_x	5% (not negative enough)	0.5%
E_c	100% (too negative)	5%
bond length	1% (too short)	1% (too long)
structure	overly favours close packing	more correct
energy barrier	100% (too low)	30% (too low)

- ▶ GGA in most cases better than LDA
- ▶ Typically cancellation of errors between E_x and E_c
- ▶ "Energy barrier" = barrier to a chemical reaction

Situations where GGA fails:

Unaccurate results for **heavy elements**

Does not predict existence of **negative ions**

Fails to reproduce **dispersion forces** (\approx van der Waals forces)

Can not describe properly **strongly correlated systems**

GGA gives unaccurate results for **heavy elements**:

Gold (Au):

$E_{\text{XC}}[n]$	Equilibrium lattice constant	Cohesive energy
LDA	7.68	4.12
relativistic LDA	7.68	4.09
GGA	7.87	2.91
relativistic GGA	7.88	2.89
experiment	7.67	3.78

- ▶ Here: LDA better than GGA
- ▶ Problem not due to relativistic effects
- ▶ GGA: problems with high angular momenta
(higher ion charge \implies higher electron angular momentum)

GGA does not predict existence of **negative ions**:

For neutral atoms exactly:

$$v_s(\mathbf{r}) \xrightarrow{r \rightarrow \infty} -\frac{1}{r}$$

- \Rightarrow additional electron feels a Coulomb-like potential
- \Rightarrow Rydberg series of excited states
- \Rightarrow necessary criterion for negative ion state fulfilled

In LDA:

$$v_s(\mathbf{r}) \xrightarrow{r \rightarrow \infty} \exp(-\alpha r)$$

- \Rightarrow not able to bind additional electron (negative ion)

Same problem with GGA