Density functional theory

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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 (DFT)

Hohenberg and Kohn proved that the total energy of a system including that of the many-body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy.

In Hartree-Fock theory one works with large basis sets. This poses a problem for large systems. An alternative to the HF methods is DFT. DFT takes into account electron correlations but is less demanding computationally than full scale diagonalization, Coupled Cluster theory or say Monte Carlo methods.

Density Functional Theory, definitions, onebody density

The one-body density in coordinate space is defined as

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i).$$

In second quantization this becomes

$$\hat{\rho}(\mathbf{r}) = \sum_{\alpha\beta}^{\infty} \rho_{\alpha,\beta}(\mathbf{r}) a_\alpha^\dagger a_\beta.$$

where

$$\rho_{\alpha,\beta}(\mathbf{r}) = \psi_\alpha^*(\mathbf{r}) \psi_\beta(\mathbf{r}).$$

Density Functional Theory, definitions, onebody density

The number of particles is N and the integral of the expectation value of the one-body density operator should give you N particles. With an appropriate similarity transformation we can make this operator diagonal in the single-particle basis ψ_α. That is

$$\hat{\rho}(\mathbf{r}) = \sum_{\alpha=1}^{\infty} |\psi_\alpha(\mathbf{r})|^2 a_\alpha^\dagger a_\alpha = \hat{\rho}(\mathbf{r}) = \sum_{\alpha=1}^{\infty} \rho_{\alpha\alpha}(\mathbf{r}) a_\alpha^\dagger a_\alpha.$$

The ground state wave function $|\Psi_0\rangle$ is a linear combination of all D possible Slater determinants $|\Phi_i\rangle$

$$|\Psi_0\rangle = \sum_{i=1}^{D} C_{0i}|\Phi_i\rangle,$$

where the coefficients C_{0i} could arise from an FCI calculation using a given Slater determinant basis

$$|\Phi_i\rangle = a_1^\dagger a_2^\dagger \dots a_N^\dagger|0\rangle.$$

Density Functional Theory, definitions, onebody density

The ground state expectation value of the one-body density operator is

$$\langle\hat{\rho}(\mathbf{r})\rangle = \langle\Psi_0|\sum_{\alpha=1}^{\infty}\rho_{\alpha,\alpha}(\mathbf{r})a_\alpha^\dagger a_\alpha|\Psi_0\rangle,$$

which translates into

$$\langle\hat{\rho}(\mathbf{r})\rangle = \sum_{ij=1}^{D}C_{0i}^*C_{0j}\langle\Phi_i|\sum_{\alpha=1}^{\infty}\rho_{\alpha,\alpha}(\mathbf{r})a_\alpha^\dagger a_\alpha|\Phi_j\rangle.$$

Integrating

$$\int\langle\hat{\rho}(\mathbf{r})\rangle d\mathbf{r},$$

gives us N, the number of particles!

Density Functional Theory, definitions, twobody density

The two-body densities is a simple extension of the one-body density

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_{ij=1}^{N} \delta(\mathbf{r}_1 - \mathbf{r}_i)\delta(\mathbf{r}_2 - \mathbf{r}_j),$$

which in second quantization becomes

$$\hat{\rho}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\alpha\beta\gamma\delta}^{\infty} \rho_{\alpha,\gamma}(\mathbf{r}_1)\rho_{\beta,\delta}(\mathbf{r}_2) a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma,$$

meaning that the ground-state two-body density is

$$\langle \hat{\rho}(\mathbf{r}_1, \mathbf{r}_2) \rangle = \sum_{ij=1}^{D} C_{0i}^* C_{0j} \langle \Phi_i | \sum_{\alpha\beta\gamma\delta}^{\infty} \rho_{\alpha,\gamma}(\mathbf{r}_1)\rho_{\beta,\delta}(\mathbf{r}_2) a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma | \Phi_j \rangle.$$

Hartree-Fock equations and density matrix

The Hartree-Fock algorithm can be broken down as follows. We recall that our Hartree-Fock matrix is

$$\hat{h}_{\alpha\beta}^{HF} = \langle\alpha|\hat{h}_0|\beta\rangle + \sum_{j=1}^{N}\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\langle\alpha\gamma|V|\beta\delta\rangle_{AS}.$$

Normally we assume that the single-particle basis $|\beta\rangle$ forms an eigenbasis for the operator $\hat{h}_0$, meaning that the Hartree-Fock matrix becomes

$$\hat{h}_{\alpha\beta}^{HF} = \epsilon_\alpha\delta_{\alpha,\beta} + \sum_{j=1}^{N}\sum_{\gamma\delta} C^*_{j\gamma}C_{j\delta}\langle\alpha\gamma|V|\beta\delta\rangle_{AS}.$$

Hartree-Fock equations and density matrix

The Hartree-Fock eigenvalue problem

$$\sum_{\beta} \hat{h}^{HF}_{\alpha\beta} C_{i\beta} = \epsilon_i^{\mathrm{HF}} C_{i\alpha},$$

can be written out in a more compact form as

$$\hat{h}^{HF} \hat{C} = \epsilon^{\mathrm{HF}} \hat{C}.$$

Hartree-Fock equations and density matrix

The equations are often rewritten in terms of a so-called density matrix, which is defined as

$$\rho_{\gamma\delta} = \sum_{i=1}^{N} \langle\gamma|i\rangle\langle i|\delta\rangle = \sum_{i=1}^{N} C_{i\gamma}C^*_{i\delta}. \tag{1}$$

It means that we can rewrite the Hartree-Fock Hamiltonian as

$$\hat{h}^{HF}_{\alpha\beta} = \epsilon_\alpha\delta_{\alpha,\beta} + \sum_{\gamma\delta}\rho_{\gamma\delta}\langle\alpha\gamma|V|\beta\delta\rangle_{AS}.$$

It is convenient to use the density matrix since we can precalculate in every iteration the product of two eigenvector components C.
Note that $\langle\alpha|\hat{h}_0|\beta\rangle$ denotes the matrix elements of the one-body part of the starting hamiltonian.

Density Functional Theory

The electronic energy E is said to be a *functional* of the electronic density, $E[\rho]$, in the sense that for a given function $\rho(r)$, 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

$$E[\rho] = -\frac{1}{2}\sum_{i=1}^{N}\int \Psi_i^*(\mathbf{r_1})\nabla_1^2\Psi_i(\mathbf{r_1})d\mathbf{r_1} - \int \frac{Z}{r_1}\rho(\mathbf{r_1})d\mathbf{r_1} + \frac{1}{2}\int \frac{\rho(\mathbf{r_1})\rho(\mathbf{r_2})}{r_{12}}d\mathbf{r_1}d\mathbf{r_2} + E_{XC}[\rho]$$

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

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

where the sum is over the occupied Kohn-Sham orbitals. The last term, $E_{XC}[\rho]$, 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 $E[\rho]$. This approach is similar to the one used for obtaining the HF equation.

Density Functional Theory

The KS equations reads

$$\left\{-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + \int \frac{\rho(\mathbf{r_2})}{r_{12}} d\mathbf{r_2} + V_{XC}(\mathbf{r_1})\right\} \Psi_i(\mathbf{r_1}) = \epsilon_i \Psi_i(\mathbf{r_1})$$

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

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

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

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

where $\epsilon_{XC}[\rho(\mathbf{r})]$ 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 ρ 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

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

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

$$\hat{\Psi}^{\dagger}(\mathbf{r}) \equiv \sum_{\mathbf{k}} \psi^{*}_{\mathbf{k}}(\mathbf{r}) a^{\dagger}_{\mathbf{k}}$$

$\mathbf{k}$ = collection of quantum numbers

$\hat{T}$ = kinetic energy operator

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

$\hat{V}$ = two-particle interaction operator

Theorem I

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

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

gives a non-degenerate N-particle ground state $|\Psi\rangle_0$. For any system of interacting particles in an external potential $\mathcal{V}_{\mathrm{ext}}$, the potential $\mathcal{V}_{\mathrm{ext}}$ is uniquely determined (by a near constant) by the ground state density ρ_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 ρ_0.

Theorem II

The density (assuming normalized state vectors)

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

Theorem II states that a universal functional for the energy $E[\rho]$ (function of ρ) can be defined for every external potential $\mathcal{U}_{\text{ext}}$. 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 ρ_0.

The Hohenberg-Kohn theorem

Assume Hamiltonian of many-fermion system

$$\hat{H} = \hat{T} + \hat{V} + \hat{W},$$

or second quantized form

$$\hat{H} = -\frac{\hbar^2}{2m}\int d^3r\,\hat{\Psi}^\dagger(\mathbf{r})\nabla^2\hat{\Psi}(\mathbf{r}) + \int d^3r\,\hat{\Psi}^\dagger(\mathbf{r})v(\mathbf{r})\hat{\Psi}(\mathbf{r})$$
$$+\frac{1}{2}\int d^3r\int d^3r'\,\hat{\Psi}^\dagger(\mathbf{r})\hat{\Psi}^\dagger(\mathbf{r}')w(\mathbf{r},\mathbf{r}')\hat{\Psi}(\mathbf{r}')\hat{\Psi}(\mathbf{r}),$$

$\hat{\Psi}$, $\hat{\Psi}^\dagger$ = annihilation, creation *field operators*

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

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

$\mathbf{k}$ = collection of quantum numbers

$\hat{T}$ = kinetic energy operator

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

$\hat{W}$ = two-particle interaction operator

The Hohenberg-Kohn theorem

Assume we have a Hamiltonian for a many-fermion system

$$\hat{H} = \hat{T} + \hat{V} + \hat{W},$$

or second quantized form

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

$\hat{\Psi}$, $\hat{\Psi}^\dagger$ = annihilation, creation *field operators*

$\mathcal{V}$ = set of external single-particle potentials $\hat{V}$ so that

$$\hat{H}|\phi\rangle = \left(\hat{T} + \hat{V} + \hat{W}\right) = E|\phi\rangle, \qquad \hat{V} \in \mathcal{V},$$

gives a non-degenerate N-particle ground state $|\Psi\rangle$

$$\Longrightarrow \qquad C : \mathcal{V}(C) \longrightarrow \Psi \qquad \text{surjective},$$

where Ψ = set of ground states (GS) $|\Psi\rangle$

The density

$$\rho(\mathbf{r}) = N \sum_i \int dx_2 \cdots \int dx_N |\Psi(\mathbf{r}i, x_2, \ldots, x_N)|^2$$

gives a second map

$$D : \Psi \longrightarrow \mathcal{N},$$

where $\mathcal{N}$ = set of GS densities. The map trivially surjective.

Lemma

Hohenberg-Kohn states: C and D also injective (one-to-one; $x_1 \neq x_2 \Rightarrow Tx_1 \neq Tx_2$)

$$\Longrightarrow \qquad \textit{C and D bijective (surjective and bijective)}$$
$$\Longrightarrow \qquad CD : \mathcal{V}(CD) \longrightarrow \mathcal{N} \qquad \textit{bijective}$$

Proof I.

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

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

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

Reductio ad absurdum:

Assume $|\Psi\rangle = |\Psi'\rangle$ for some $\hat{V} \neq \hat{V}' + \text{const}$, $\hat{V}, \hat{V}' \in \mathcal{V}$
$\hat{T} \neq \hat{T}[V]$, $\hat{W} \neq \hat{W}[V]$ $\quad \Longrightarrow$[1]

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

$$\Longrightarrow \qquad \hat{V} - \hat{V}' = E_{gs} - E'_{gs}$$

$$\Longrightarrow \qquad \hat{V} = \hat{V}' + \text{constant} \qquad \text{Contradiction!}$$

$\square$

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

Proof II.

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

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

Reductio ad absurdum:

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

Ritz principle $\quad \Longrightarrow$

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

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

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

By symmetry

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

(**??**) & (**??**) $\quad \Longrightarrow$

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

$\square$

Define

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

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

Rayleigh-Ritz principle $\Longrightarrow$ second statement of H-K theorem:

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

Last satement of H-K theorem:

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

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

The Kohn-Sham scheme

The classic Kohn-Sham scheme:

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

where

$$v_{s,0}(\mathbf{r}) = v_0(\mathbf{r}) + \int d^3r' \, w(\mathbf{r},\mathbf{r}')\rho_0(\mathbf{r}') + v_{\mathrm{XC}}([\rho_0];\mathbf{r})$$

The density calculated as

$$\rho_0(\mathbf{r}) = \sum_{i=1}^{N} |\phi_{i,0}(\mathbf{r})|^2,$$

Equation solved selfconsistently
Total energy:

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

Exchange Energy and Correlation Energy

Hartree-Fock equation:

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

Non-local exchange term (Pauli exclusion principle)

Kohn-Sham equation:

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

Local exchange-correlation term

Exchange-correlation energy = Exchange energy + Correlation energy

$$E_{\mathrm{XC}}[\rho] = E_x[\rho] + E_c[\rho]$$

From earlier:

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

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

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

$$F_L[\rho] \equiv \inf_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle$$
$$= \langle \Psi_n^{min} | \hat{T} + \hat{W} | \Psi_n^{min} \rangle,$$

and

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

$\Psi =$ 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*:

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

By definition,

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

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

Since

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

we see that

$$
E_c[\rho] \leq 0
$$

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

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

where $\hat{T}$ is the kinetic energy, $\hat{V}$ is in our case the Coulomb interaction between two electrons an $\hat{v}_{\mathrm{ext}}$ 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

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

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

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

Computing E_{XC} from *ab initio* calculations

Which leads to the Lieb variational principle

$$F_\lambda[\rho] = \sup_{\hat{v}_{\mathrm{ext}}} \left(E_\lambda[\hat{v}^\lambda_{\mathrm{ext}}] - \int d\mathbf{r} \rho(\mathbf{r}) \hat{v}^\lambda_{\mathrm{ext}}(\mathbf{r}) \right).$$

We define

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

which we rewrite as

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

with the standard Hartree term

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

Computing E_{XC} from *ab initio* calculations

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

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

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 caclulation 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

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

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

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