

Week 43: Density Functional Theory and start Many-body Perturbation Theory

Morten Hjorth-Jensen^{1,2}

Department of Physics and Center for Computing in Science Education,
University of Oslo, Norway¹

Department of Physics and Astronomy and Facility for Rare Isotope Beams,
Michigan State University, USA²

Week 43, October 21-25

© 1999-2024, Morten Hjorth-Jensen. Released under CC Attribution-NonCommercial 4.0 license

Week 43, October 21-25, 2024

1. Thursday:

- 1.1 Density functional theory, the Hohenberg-Kohn theorems
- 1.2 Kohn-Sham equations

2. Friday:

- 2.1 Kohn-Sham equations and the local density approximation and links with Hartree-Fock theory
- 2.2 Start many-body perturbation theory

3. No exercises this week

Density functional theory

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.

Functional of density

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 theorems (two) confirms that such a functional exists, but does not tell us the form of the functional.

Density functional theory has turned out to be a resounding success. A large majority of crystalline materials, many molecules and molecular structures have been explained using DFT. Walter Kohn, involved in both the Hohenberg-Kohn theory and development of the Kohn-Sham equations, received the Nobel Prize in Chemistry for DFT and computational chemistry in 1998. DFT is used in a broad spectrum of disciplines, including quantum chemistry, materials science, condensed matter physics and low-energy nuclear physics

The many-particle equation

Any material on earth, whether in crystals, amorphous solids, molecules or yourself, consists of nothing else than a bunch of atoms, ions and electrons bound together by electric forces. All these possible forms of matter can be explained by virtue of one simple equation: the many-particle Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} \Phi(\mathbf{r}; t) = \left(- \sum_i^N \frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial \mathbf{r}_i^2} + \sum_{i < j}^N \frac{e^2 Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Phi(\mathbf{r}; t). \quad (1)$$

Here $\Phi(\mathbf{r}; t)$ is the many-body wavefunction for N particles, where each particle has its own mass m_i , charge Z_i and position \mathbf{r}_i . The only interaction is the Coulomb interaction e^2/r .

Born-Oppenheimer approximation

In atomic and molecular physics, materials science and quantum chemistry, the Born-Oppenheimer approximation arises from the physical problem we want to study: the ground state of a collection of interacting ions and electrons. Because even the lightest ion is more than a thousand times heavier than an electron, we approximate our Hamiltonian to not include the dynamics of the ions all-together. This is known as the **Born-Oppenheimer** approximation.

Time-independent equation

We then write the time-independent Schrödinger equation for a collection of N electrons subject to the electric potential created by the fixed ions, labeled $v_{\text{ext}}(\mathbf{r})$,

$$\left(\sum_i^N \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + v_{\text{ext}}(\mathbf{r}_i) \right) + \sum_{i < j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}) = E_0 \Psi(\mathbf{r}),$$

where \mathbf{r}_i are the positions of the electrons.

We can replace the explicit Coulomb repulsion with a generic two-body interaction

$$\sum_i^N \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + v_{\text{ext}}(\mathbf{r}_i) \right) + \sum_{i < j}^N v(r_{ij}) (= E_0 \Psi(\mathbf{r})),$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

Potential term

The potential $v_{\text{ext}}(\mathbf{r}_i)$ is created by the charged ions,

$$v_{\text{ext}}(\mathbf{r}_i) = - \sum_j \frac{e^2 Z_j}{|\mathbf{r}_i - \mathbf{R}_j|}$$

where \mathbf{R} is the (static) positions of the ions and Z_j their charge.

The one-body density

The one-body reduced density matrix of a many-body system at zero temperature gives direct access to many observables, such as the charge density, kinetic energy and occupation numbers. In a coordinate representation it is defined as the expectation value of the number operator

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

resulting in

$$n(\mathbf{r}) = \frac{\langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$

Here Ψ can be any state. In the equations that follow we assume it has been normalized properly.

One-body density

The one-body or just electronic density here, is thus obtained by integrating out all electron degrees of freedom except one, that is (setting $\mathbf{r} = \mathbf{r}_1$)

$$n(\mathbf{r}) = n(\mathbf{r}_1) = \int d^3\mathbf{r}_2 \cdots d^3\mathbf{r}_N |\Psi(\mathbf{r}_1 \cdots \mathbf{r}_N)|^2.$$

If Ψ is a single reference Slater determinant defined in terms of the single-particle functions ψ_i , then we have

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

as derived earlier.

Energy as function of the density

Text to come here.

Hohenberg-Kohn theory

Assume we found a solution for the Hamiltonian from the Born-Oppenheimer approximation, with ground state energy E_0 and a certain electronic density $n(\mathbf{r})$. The strength of the Coulomb interaction and the mass of an electron are constants of nature, so the only input that can possibly influence the electronic density $n(\mathbf{r})$ and the energy E_0 of our ground state is our choice of potential $v_{\text{ext}}(\mathbf{r})$. In other words, the ground state energy is a *functional* of the input potential,

$$E_0[v_{\text{ext}}(\mathbf{r})] = \mathcal{F}_E[v_{\text{ext}}(\mathbf{r})]$$

Energy functional

A functional is nothing else than a function whose input is another function; in this case the functional \mathcal{F} takes as input the electric potential generated by the ions and outputs the ground state energy based on the Born-Oppenheimer approximation.

At first this result seems counterintuitive. After all, the ground state energy clearly contains the kinetic energy T , the interaction energy U and the potential energy. Only the latter term explicitly depends on the potential. We can thus write the ground state energy in terms of a separate functional for the kinetic and interaction energy, and the potential energy

How to find the functional

Knowing this functional, for any given potential $V(\mathbf{r})$ we minimize the right hand side by checking all possible electronic density distributions.

There are only two minor problems. We don't know what this functional looks like. And even if we did, we don't know how to find the right electronic density.

Approximating the functional

The unknown functional $\mathcal{F}[n(\mathbf{r})]$ should describe the kinetic and interaction energy of a system described by for example the Born-Oppenheimer approximation. Even though we cannot find its exact shape, we can look at its shape in some limiting cases that we can solve.

We know that a free homogeneous electron gas (HEG) with density n has a ground state energy of

$$E_0 = \frac{3\hbar^2 (3\pi^2)^{2/3}}{10m} n_0^{5/3}.$$

Using the results from the HEG

For a slowly varying electronic density, we can approximate the kinetic energy contribution to the full functional $\mathcal{F}[n(\mathbf{r})]$ as the energy evaluated at each point separately,

$$\mathcal{T}_0[n(\mathbf{r})] = \frac{3\hbar^2 (3\pi^2)^{2/3}}{10m} \int d^3\mathbf{r} (n(\mathbf{r}))^{5/3}.$$

Hartree term to the energy

We have also earlier derived that the simplest energy contribution from Coulomb interactions is given by the Hartree term

$$\mathcal{U}_{\text{H}}[n(\mathbf{r})] = \frac{e^2}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

Final functional

It is natural to write out the full functional as containing the homogeneous electron gas term and the Hartree term. The remaining terms, though still unknown, should be small. This unknown part is conventionally called the *exchange-correlation potential* $E_{xc}[n(\mathbf{r})]$. The full Hohenberg-Kohn functional, including the potential energy, is thus

$$\mathcal{E}_{\text{HK}}[n(\mathbf{r})] = \mathcal{T}_0[n(\mathbf{r})] + \int d^3\mathbf{r} v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + \mathcal{U}_{\text{H}}[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})].$$

Kohn-Sham equation

We replaced an intractable problem with the task of minimizing an unknown functional $\mathcal{F}[n(\mathbf{r})]$ over infinitely many possible electronic densities $n(\mathbf{r})$. In the previous section we already gave some first suggestions for the functional. But once we found it, how to find the right electronic density $n(\mathbf{r})$?

Because the correct density minimizes the functional, we can find the functional by setting it's derivative to zero,

$$\frac{\delta \mathcal{F}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = 0.$$

Kohn-Sham equations

Using the functional Eq(insert), we write out

$$\frac{\delta \mathcal{T}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' + \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = 0.$$

The equations

The idea of Kohn and Sham was to treat this as if it is a single-particle problem. The first term represents the kinetic energy, and the remaining terms form the Kohn-Sham potential

$$V_{\text{KS}}(\mathbf{r}) = V(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E_{\text{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}.$$

The Kohn-Sham equation is the single-particle Schrödinger equation with the potential given by the last equation,

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V_{\text{KS}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}).$$

Numerical solution

The Kohn-Sham equations have to be solved numerically. As with our discussions of Hartree-Fock theory, this is tractable because the equations are just given by a set of coupled differential equation. The electronic density is obtained by occupying the N solutions $\psi_i(\mathbf{r})$ with the lowest energy,

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

Now the electronic density obtained this way can be used to calculate a new Kohn-Sham potential. We continue this iterative procedure until we reach convergence.

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

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

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

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

can be written out in a more compact form as

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

Hartree-Fock equations and density matrix

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

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

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

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

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

$$E[\rho] = -\frac{1}{2} \sum_{i=1}^N \int \Psi_i^*(r_1) \nabla_1^2 \Psi_i(r_1) dr_1 - \int \frac{Z}{r_1} \rho(r_1) dr_1 + \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1$$

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

$$\left\{ -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} + \int \frac{\rho(r_2)}{r_{12}} dr_2 + V_{XC}(r_1) \right\} \Psi_i(r_1) = \epsilon_i \Psi_i(r_1)$$

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

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

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

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 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)

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

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

Computing E_{XC} from *ab initio* calculations

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

$$\hat{V} \neq \hat{V}' + \text{const}, \quad \hat{V}, \hat{V}' \in \mathcal{V}$$

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

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

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

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

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

Computing E_{XC} from *ab initio* calculations

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

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

Reductio ad absurdum: Assume $\rho(r) = n'(r)$ for some $|\Psi\rangle \neq |\Psi'\rangle$

Ritz principle \implies

$$E_{gs} = \langle \Psi | \hat{H} | \Psi \rangle \langle \Psi' | \hat{H} | \Psi' \rangle. \quad (2)$$

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

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

By symmetry

$$\implies E_{gs} < E'_{gs} + \int n'(r)[v'(r) - v(r)]d^3r \quad (4)$$

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

Computing E_{XC} from *ab initio* calculations

Define

$$E_{v_0}[\rho] := \langle \Psi[\rho] | \hat{T} + \hat{W} + \hat{V}_0 | \Psi[\rho] \rangle \quad (5)$$

\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:**

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

Last statement of H-K theorem:

$$F_{HK}[\rho] \equiv \langle \Psi[\rho] | \hat{T} + \hat{W} | \Psi[\rho] \rangle \quad (6)$$

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

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

The density is calculated as

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

The equation is solved selfconsistently. The total energy

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

Exchange Energy and Correlation Energy

The Hartree-Fock equation

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

Kohn-Sham equation:

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