

Electron density:

$$\rho(\vec{r}_1) = N \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 ds_1 d\vec{x}_2 \dots d\vec{x}_N$$

Probability of finding one electron of arbitrary spin within a volume element dr_1 (other electrons may be anywhere).

$$\vec{x}_i \equiv \vec{r}_i s_i$$

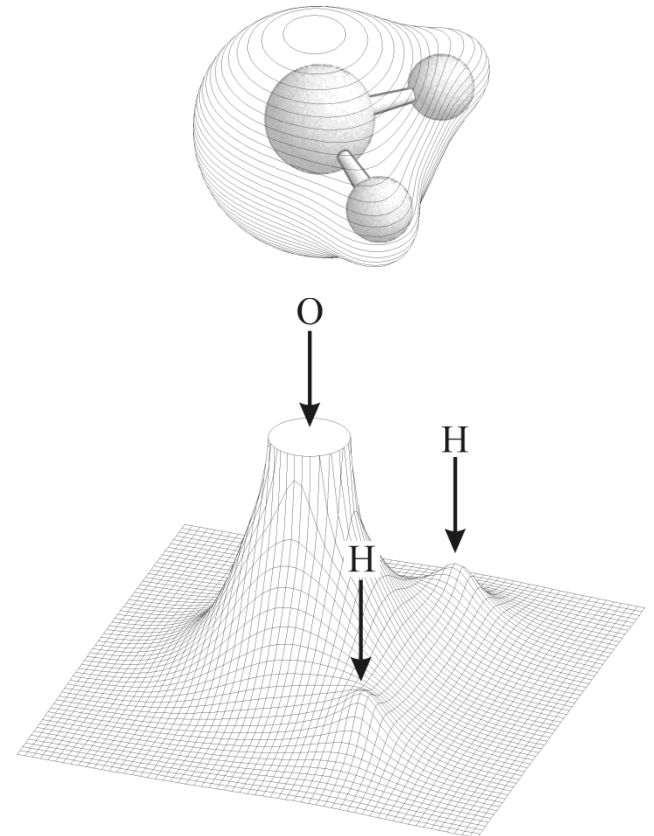
Properties of electron density (non-negative):

1. $\int \rho(\vec{r}_1) d\vec{r}_1 = N$

2. $\rho(\vec{r} \rightarrow \infty) = 0 \quad \rho(\vec{r}) \propto \exp[-2\sqrt{2I} |\vec{r}|]$

3. $\rho(\vec{r} \rightarrow \vec{R}_A) = \max$
 $\nabla \rho(\vec{r} \rightarrow \vec{R}_A) \dots cusp$ } $\lim_{r \rightarrow 0} \left[\frac{\partial}{\partial r} + 2Z \right] \rho(r) = 0$

=> exchange-correlation functionals should respect these conditions



Pair density:

$$\rho_2(\vec{x}_1, \vec{x}_2) = N(N-1) \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\vec{x}_3 \dots d\vec{x}_N$$

Probability of finding a pair of two electrons with particular spins within a volume elements dr_1 and dr_2 (remaining $N-2$ electrons may be anywhere).

Non-correlated motion:

$$\rho_2(\vec{x}_1, \vec{x}_2) = \frac{N-1}{N} \rho(\vec{x}_1) \rho(\vec{x}_2)$$

Non-negative quantity

Normalized to $N(N-1)$, contains all information about electron correlation.

Symmetric

Antisymmetric wavefunction requirement => **reduced density matrix γ_2**

$$\gamma_2(\vec{x}_1, \vec{x}_2; \vec{x}'_1, \vec{x}'_2) = N(N-1) \int \dots \int \Psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) \Psi^*(\vec{x}'_1, \vec{x}'_2, \vec{x}_3, \dots, \vec{x}_N) d\vec{x}_3 \dots d\vec{x}_N$$

Variables in Ψ^* which are not included in integration are primed.

γ_2 changes sign when x_1 and x_2
(or x'_1 and x'_2) are interchanged

$$\gamma_2(\vec{x}_1, \vec{x}_2; \vec{x}'_1, \vec{x}'_2) = -\gamma_2(\vec{x}_2, \vec{x}_1; \vec{x}'_1, \vec{x}'_2)$$

Diagonal elements of reduced density matrix => pair density
(two-electron density matrix)

$$\vec{x}_1 = \vec{x}'_1$$

$$\vec{x}_2 = \vec{x}'_2$$

Probability of finding two electrons with the same spin at the same point is 0 !!!

$$\rho_2(\vec{x}_1, \vec{x}_1) = -\rho_2(\vec{x}_1, \vec{x}_1)$$

Small detour: HF pair density:

$$\rho_2^{\text{HF}}(\vec{x}_1, \vec{x}_2) = 2[\det\{\phi_1(\vec{r}_1)\sigma_1(s_1) \phi_2(\vec{r}_2)\sigma_2(s_2)\}]^2$$

$$\rho_2^{\text{HF}}(\vec{x}_1, \vec{x}_2) = |\phi_1(\vec{r}_1)|^2 |\phi_2(\vec{r}_2)|^2 |\sigma_1(s_1)|^2 |\sigma_2(s_2)|^2 + |\phi_1(\vec{r}_2)|^2 |\phi_2(\vec{r}_1)|^2 |\sigma_2(s_1)|^2 |\sigma_1(s_2)|^2 - 2 \phi_1(\vec{r}_1)\phi_2(\vec{r}_1)\phi_1(\vec{r}_2)\phi_2(\vec{r}_2) \sigma_1(s_1)\sigma_2(s_1)\sigma_1(s_2)\sigma_2(s_2)$$

$$\begin{aligned} & \sigma_1 = \sigma_2 \\ \rho_2^{\text{HF}, \sigma_1 = \sigma_2}(\vec{r}_1, \vec{r}_2) \\ \rho_2^{\text{HF}}(\vec{x}_1, \vec{x}_2) = 0 \end{aligned}$$

$$\begin{aligned} & \sigma_1 \neq \sigma_2 \\ \rho_2^{\text{HF}, \sigma_1 \neq \sigma_2}(\vec{r}_1, \vec{r}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2) \end{aligned}$$

Correlated electron motion

$$\rho_2^{\text{HF}, \sigma_1 = \sigma_2}(\vec{x}_1, \vec{x}_2) \xrightarrow{\vec{x}_1 = \vec{x}_2} 0$$

Completely uncorrelated motion

$$\rho_2^{\text{HF}, \sigma_1 \neq \sigma_2}(\vec{x}_1, \vec{x}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2)$$

=> “Fermi correlation”, “Exchange correlation” - described already at the HF level
 Two electrons with the same spin cannot be at the same point in space.
 This “correlation” does not depend on the electron charge, purely exchange effect.

Fermi correlation has nothing common with (“Coulomb”) correlation defined for post HF methods!

Pair density for completely uncorrelated motion:

$$\rho_2(\vec{x}_1, \vec{x}_2) = \frac{N-1}{N} \rho(\vec{x}_1) \rho(\vec{x}_2)$$

Formulation of pair density in terms of electron density and (whatever) is the correlation:

$$\rho_2(\vec{x}_1, \vec{x}_2) = \rho(\vec{x}_1) \rho(\vec{x}_2) [1 + f(\vec{x}_1; \vec{x}_2)]$$

Correlation factor - defines the difference between uncorrelated and correlated densities:

$f(\vec{x}_1; \vec{x}_2) = 0$ - completely uncorrelated case =>

=> wrong normalization of ρ_2 (N^2)! (due to self-interaction)

Introducing **Conditional probability** - probability of finding electron at position 2 when there is just one electron at position 1.

Integrates to (N-1).

$$\Omega(\vec{x}_2; \vec{x}_1) = \frac{\rho_2(\vec{x}_1, \vec{x}_2)}{\rho(\vec{x}_1)}$$

$$\int \Omega(\vec{x}_2; \vec{x}_1) d\vec{x}_2 = N - 1$$

Exchange-correlation hole:

$$h_{xc}(\vec{x}_1; \vec{x}_2) = \Omega(\vec{x}_1; \vec{x}_2) - \rho(\vec{x}_2)$$

$$\begin{aligned} &= \frac{\rho_2(\vec{x}_1, \vec{x}_2)}{\rho(\vec{x}_1)} - \rho(\vec{x}_2) \\ &= \rho(\vec{x}_2) f(\vec{x}_1; \vec{x}_2) \end{aligned}$$

The difference between conditional probability Ω and uncorrelated (unconditional) probability of finding electron at x_2 .

h_{xc} accounts for: exchange and coulomb correlation and self-interaction

Correlation - typically leads to depletion of electron density

$$\int h_{xc}(\vec{x}_1; \vec{x}_2) d\vec{x}_2 = -1$$

Schrödinger equation in terms of spin-independent *pair density* (two-electron part):

$$E_{ee} = \left\langle \Psi \left| \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}} \right| \Psi \right\rangle = \frac{1}{2} \iint \frac{\rho_2(\vec{x}_1, \vec{x}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 ds_1 ds_2$$

Integration over 8 variables only !

Probability of finding a pair of electrons at x_1, x_2

$$\rho_2(\vec{x}_1, \vec{x}_2) = \rho(\vec{r}_1)\rho(\vec{r}_2) + \rho(\vec{r}_1)h_{xc}(\vec{x}_1; \vec{x}_2)$$

$$E_{ee} = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)h_{xc}(\vec{x}_1; \vec{x}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 ds_1 ds_2$$

J[ρ]

Exchange, correlation, SIC

$$E_{ee} = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)h_{XC}(\vec{r}_1; \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

Classical J[ρ]

QM contribution (correlation) + self-interaction

FORMALLY - exchange-correlation hole can be split into the *Fermi hole* and *Coulomb hole*

$$h_{XC}(\vec{r}_1; \vec{r}_2) = h_X^{\sigma_1=\sigma_2}(\vec{r}_1; \vec{r}_2) + h_C^{\sigma_1, \sigma_2}(\vec{r}_1; \vec{r}_2)$$

Fermi hole - dominates coulomb hole

- contains self-interaction
- integrates to -1
- equals to minus density of electrons (same spin) at the position of this electron (at the same point)
- negative everywhere
- depends also on the density at r_2
- no spherical symmetry

$$h_X(\vec{r}_2 \rightarrow \vec{r}_1; \vec{r}_1) = -\rho(\vec{r}_1)$$

$$h_X(\vec{r}_1; \vec{r}_2) = \rho(\vec{r}_2) f_X(\vec{r}_1; \vec{r}_2)$$

Coulomb hole - integrates to 0

- negative at the position of reference electron
- mirrors the cusp condition

$$\int h_C(\vec{x}_1; \vec{x}_2) d\vec{r}_2 = 0$$

Example – H₂ molecule:

Exchange hole – only SIC

⇒ It is just half of the density!

⇒ It does not depend on the electron position (r_1)

⇒ h_X leads to depletion of electron density

⇒ HF method considers only h_X and it results in too diffuse one-el.

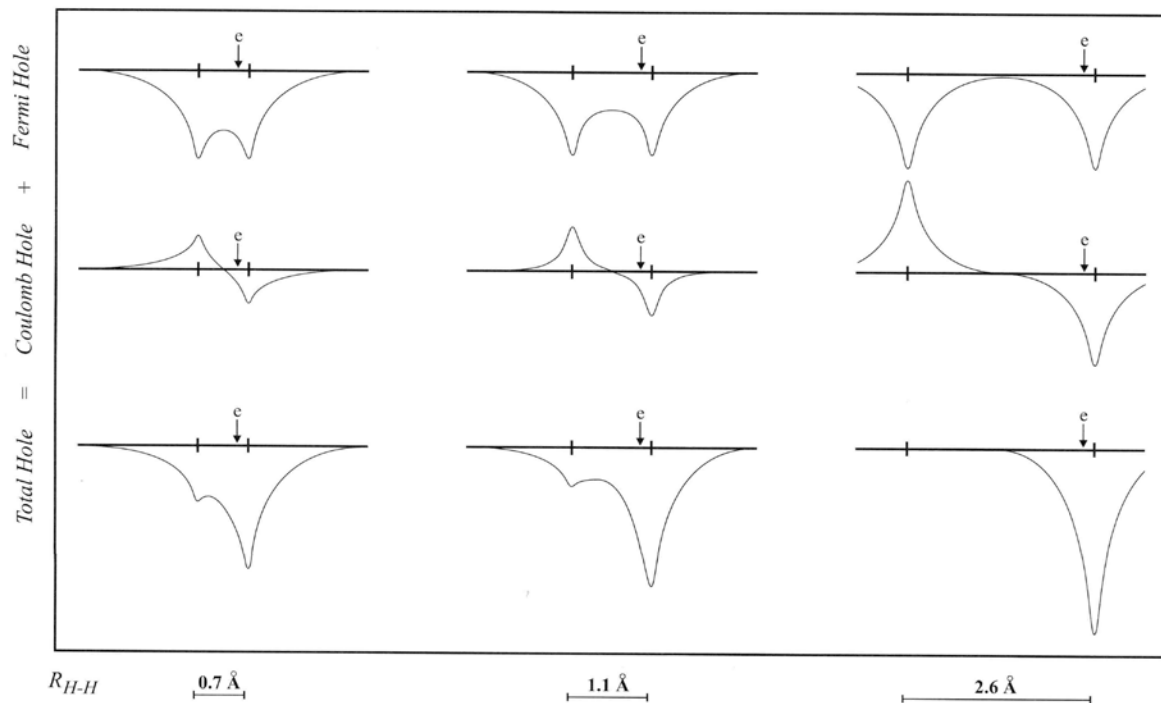
Functions ⇒ underestimating V_{en} , low T_e , and also J_{ee} is underestim.

$$h_X^\alpha(\vec{r}_1; \vec{r}_2) = -\frac{1}{2} \rho(\vec{r}_1) = -\frac{1}{2} |\Psi_{\sigma_g}|^2$$

Coulomb hole

⇒ Changes with the position of reference electron

⇒ For $r_{HH} \rightarrow \infty$ h_C removes halves the electron from one atom and puts it to the other one



Baerends & Gritschenko

J. Phys. Chem. A 101 (1997) 5383

Hamiltonian only contains parts depending on (i) one electron or (ii) on two electrons
 => Schrödinger equation can be rewritten in terms of one- and two-particle density matrices

Knowledge of
 $\rho(\vec{r}_1)$
 $h_{xc}(\vec{r}_1; \vec{r}_2)$



$$E_{ee} = \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)h_{xc}(\vec{r}_1; \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

“Easy” solution of Schrödinger equation in terms of spin-densities (8 variables)

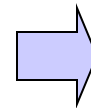
Is it possible?

Does the density contains all the information?

Answer: Hohenberg-Kohn Theorem (1964)

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3. $\rho(\vec{r} \rightarrow \vec{R}_A) = \max$
 $\nabla \rho(\vec{r} \rightarrow \vec{R}_A) \dots cusp$ $\left. \vphantom{\rho(\vec{r} \rightarrow \vec{R}_A)} \right\} \lim_{r \rightarrow \infty} \left[\frac{\partial}{\partial r} + 2Z \right] \rho(r) = 0$



First attempts:
 Thomas-Fermi Model
 (1927)

Small detour: *Uniform Electron Gas*

Hypothetical system, “*Homogeneous Electron Gas*”

Electrons move on the positive background charge

Overall system charge is 0

Volume

$$V \rightarrow \infty$$

Number of electrons

$$N_{el} \rightarrow \infty$$

Electron density (constant)

$$N/V = \rho$$

“So – so” model for simple metals; constant density is far from reality for molecules !

Only system for which we know exchange-correlation functional exactly.

Thomas-Fermi Model

Partially classical

Neglects exchange and correlation contribution

Crude approximation for kinetic energy (far from real molecules)

⇒ Poor performance!

NEVERTHELESS – Energy is given as a functional of electron density !

$$T_{\text{TF}}[\rho(\vec{r})] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d\vec{r}$$

$$E_{\text{TF}}[\rho(\vec{r})] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3}(\vec{r}) d\vec{r} - Z \int \frac{\rho(\vec{r})}{r} d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2$$

Solution – variational principle under the constraint of number of electrons.

Numerous extensions and improvements:

- “chemical” accuracy never reached (by a distance!)
- Even when V_{ee} description improved problems stay – due to kinetic energy description.
- It was rigorously proofed that withing T-F model all molecules will dissociate into their fragments!

Slater's approximation for electron exchange

Used before by Dirac:
Thomas-Fermi-Dirac model

1951 – to find an approximate way to calculate exchange in HF

$$E_x = \frac{1}{2} \iint \frac{\rho(\vec{r}_1) h_x(\vec{r}_1; \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \quad \text{One needs a good approximation to } h_x$$

1. Assuming spherically symmetric hole centered around the reference electron.
2. Assuming that density is constant within the hole and that it integrates to -1.

$$\Rightarrow \text{Sphere radius} \quad r_s = \left(\frac{3}{4\pi} \right)^{1/3} \rho(\vec{r}_1)^{-1/3} \quad (\text{Wigner-Seitz radius})$$

\Rightarrow Simple interpretation – average distance between electrons

$$\Rightarrow \text{Approximate solution:} \quad E_x[\rho] \cong C_x \int \rho(\vec{r}_1)^{4/3} d\vec{r}_1$$

\Rightarrow Density functional for exchange energy!

Original work – Hartree-Fock-Slater (HFS) method known

also as X_α method:

Exchange integrals replaced by

$$E_{X_\alpha}[\rho] = -\frac{9}{8} \left(\frac{3}{\pi} \right)^{1/3} \alpha \int \rho(\vec{r}_1)^{4/3} d\vec{r}_1$$

(α is a parameter between 2/3 and 1)

Density functional theory

Traditional *ab initio*: finding the N-electron wavefunction $\Psi(1,2,\dots,N)$ depending on $4N$ coord.
 DFT: finding the total electron spin-densities depending on 8 coordinates

Hohenberg & Kohn:

Theorem I: Energy of the system is unique functional of electron density

$$\rho(\vec{r}) \Rightarrow N_{el}, \{R_J, Z_J\} \Rightarrow V_{ext} \Rightarrow \hat{H} \Rightarrow E, \Psi$$

Theorem II: Variational principle $E_0[\rho] \leq E[\tilde{\rho}]$

$$E_0[\rho_0] = \underbrace{\int \rho_0(\vec{r}) V_{Ne} d\vec{r}}_{\text{system dependent}} + \underbrace{T[\rho_0] + E_{ee}[\rho_0]}_{\text{universally valid}}$$

Hohenberg-Kohn functional:

$$E_0[\rho_0] = \int \rho_0(\vec{r}) V_{Ne} d\vec{r} + F_{HK}[\rho_0]$$

Kinetic energy of electron
 Coulomb repulsion
 Non-classical interaction
 (self-interaction, exchange, and correlation)

All properties (defined by V_{ext}) are determined by the ground state density

H&K only proofed that F_{HK} exist, however, we do not know it

H&K do not give a direction how can we find density

H&K theorems allow us to construct the rigorous many-body theory using density as a fundamental properties

$$F[\rho(\vec{r})] = T[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{ncl}[\rho(\vec{r})]$$

The Second Hohenberg-Kohn Theorem:

“Density functional $F_{\text{HK}}[\rho]$ will give the lowest energy of the system only if the ρ is a true ground state density.”

~ *VARIATIONAL PRINCIPLE*

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{\text{Ne}}[\tilde{\rho}] + E_{\text{ee}}[\tilde{\rho}]$$

Proof – literally trivial

1. Trial density defines its own Hamiltonian, thus, wave function:
2. Applying variational theorem for this trial wave function:

$$\tilde{\rho}(\vec{r}) \rightarrow \tilde{H} \rightarrow \tilde{\Psi}$$

$$\langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle = T[\tilde{\rho}] + V_{\text{ee}}[\tilde{\rho}] + \int \tilde{\rho}(\vec{r}) V_{\text{ext}} d\vec{r} = E[\tilde{\rho}] \geq E_0[\rho_0] = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

NOTE:

Strictly VP holds only for “exact” functional.

Approximate functionals can easily give energies below a true minimum (different from HF).

Mathematical vs. Physical meaning of VP.

Kohn-Sham Approach – A Basic Idea

$$\text{HK theorems} \quad \left\{ \begin{array}{l} E_0 = \min_{\rho \rightarrow N} \left(F[\rho] + \int \rho(\vec{r}) V_{\text{Ne}} d\vec{r} \right) \\ F[\rho(\vec{r})] = T[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{\text{ncl}}[\rho(\vec{r})] \end{array} \right.$$

Kohn-Sham:

- Most problems of Thomas-Fermi type approaches come from kinetic energy
- Kohn-Sham – establishing a similar strategy as used in Hartree-Fock method

Hartree-Fock method from a different point of view:

- Slater determinant – approximation to the true N-electron wave function
- It can be viewed as the exact wave function of fictitious system of N *non-interacting* electrons moving in the effective potential V_{HF} (“electrons” viewed as uncharged fermions not explicitly interacting via Coulomb repulsion)

- Kinetic energy of such system is then exactly
$$T_{\text{HF}} = -\frac{1}{2} \sum_i^N \langle \chi_i | \nabla^2 | \chi_i \rangle$$

- One electron functions, spin-orbitals, obtained from variational principle

$$E_{\text{HF}} = \min_{\Phi_{\text{SD}} \rightarrow N} \left\langle \Phi_{\text{SD}} \left| \hat{T} + \hat{V}_{\text{Ne}} + \hat{V}_{\text{ee}} \right| \Phi_{\text{SD}} \right\rangle$$

- In analogy with above “non-interacting” electrons K&S introduced a *non-interacting reference system* for particles interacting via effective local potential V_{S} , that in some way includes desired interactions between particles.

⇒ Hamiltonian with effective local potential V_S :

$$\hat{H}_S = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N V_S(\vec{r}_i)$$

⇒ Slater determinant is then exact wave function:

$$\Theta_S = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\vec{x}_1) & \varphi_2(\vec{x}_1) & \cdots & \varphi_N(\vec{x}_1) \\ \varphi_1(\vec{x}_2) & \varphi_2(\vec{x}_2) & & \varphi_N(\vec{x}_2) \\ \vdots & \vdots & & \vdots \\ \varphi_1(\vec{x}_N) & \varphi_2(\vec{x}_N) & \cdots & \varphi_N(\vec{x}_N) \end{vmatrix}$$

⇒ One electron functions obtained (in analogy with Fock equations) by solving Kohn-Sham equations, using a one-electron Kohn-Sham operator \hat{f}^{KS} :

$$\hat{f}^{KS} \varphi_i = \varepsilon_i \varphi_i$$

⇒ Resulting orbitals ~ Kohn-Sham (KS) orbitals

$$\hat{f}^{KS} = -\frac{1}{2} \nabla^2 + V_S(\vec{r})$$

⇒ Effective potential V_S is such that the density constituted from KS orbitals exactly equals the ground state density of “real” system with interacting electrons

$$\rho_S(\vec{r}) = \sum_i^N \sum_s |\varphi_i(\vec{r}, s)|^2 = \rho_0(\vec{r})$$

Kohn-Sham Approach

Adopting a better expression for kinetic energy:

Using exact kinetic energy of the non-interacting reference system that has the same density as a real one.

Such kinetic energy cannot be the same as a true one; it is expected to be close.

Residual part of kinetic energy (T_C) is shifted to the functional.

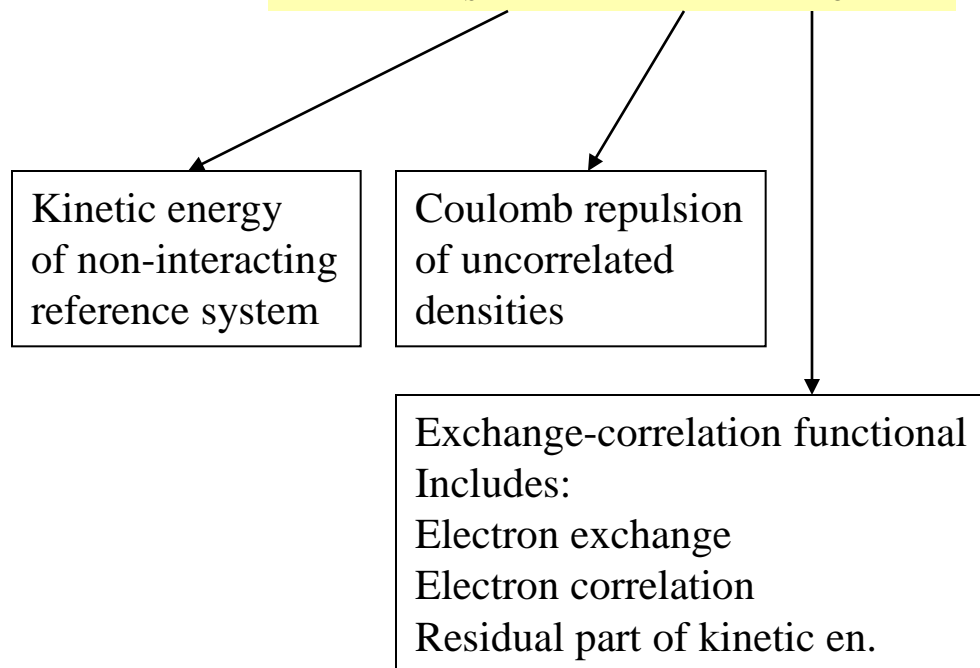
$$T_s = -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle$$

$$T_s \neq T$$

$$E_{xc}[\rho] \equiv (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_C[\rho] + E_{ncl}[\rho]$$

Kohn-Sham functional is then:

$$F[\rho(\vec{r})] = T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})]$$



Putting things together:

$$\begin{aligned}
 E[\rho(\vec{r})] &= T_s[\rho] + J[\rho] + E_{xc}[\rho] + E_{Ne}[\rho] \\
 &= T_s[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho] + \int V_{Ne}\rho(\vec{r})d\vec{r} \\
 &= -\frac{1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \iint |\phi_i(\vec{x}_1)|^2 \frac{1}{r_{12}} |\phi_j(\vec{x}_2)|^2 d\vec{x}_1 d\vec{x}_2 + \underbrace{E_{xc}[\rho(\vec{r})]}_{\text{problematic}} - \sum_i^N \int \sum_A^M \frac{Z_A}{r_{1A}} |\phi_i(\vec{x}_1)|^2 d\vec{x}_1
 \end{aligned}$$

Applying
variational
principle

Contains all problematic terms

$$\begin{aligned}
 \left(-\frac{1}{2} \nabla^2 + \left[\int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{xc}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}} \right] \right) \phi_i &= \epsilon_i \phi_i \\
 = \left(-\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r}_1) \right) \phi_i &= \epsilon_i \phi_i
 \end{aligned}$$

Satisfying the conditions stated
for non-interacting reference system

$$V_S(\vec{r}) \equiv V_{\text{eff}}(\vec{r}) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{xc}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}}$$

Iterative solution.
What is V_{xc} ?

$$V_{xc} \equiv \frac{\delta E_{xc}}{\delta \rho}$$

Kohn-Sham method – in a nut-shell:

Non-interacting reference system with effective local potential V_s introduced:

$$\hat{H}_s = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N V_s(\vec{r}_i)$$

$$\Theta_s = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\vec{x}_1) & \varphi_2(\vec{x}_1) & \cdots & \varphi_N(\vec{x}_1) \\ \varphi_1(\vec{x}_2) & \varphi_2(\vec{x}_2) & & \varphi_N(\vec{x}_2) \\ \vdots & \vdots & & \vdots \\ \varphi_1(\vec{x}_N) & \varphi_2(\vec{x}_N) & \cdots & \varphi_N(\vec{x}_N) \end{vmatrix}$$

$$\hat{f}^{KS} \varphi_i = \varepsilon_i \varphi_i$$

Kohn-Sham equations

$$\hat{f}^{KS} = -\frac{1}{2} \nabla^2 + V_s(\vec{r})$$

Problematic kinetic energy term is divided between non-interacting system and exchange-correlation functional:

$$F[\rho(\vec{r})] = T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})]$$

$$E_{xc}[\rho] \equiv (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]) = T_c[\rho] + E_{ncl}[\rho]$$

$T_c = T - T_s$... the residual part of kinetic energy

How does it work:

$$E[\rho(\vec{r})] = T_s[\rho] + J[\rho] + E_{XC}[\rho] + E_{Ne}[\rho] = T_s[\rho] + \frac{1}{2} \iint \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{XC}[\rho] + \int V_{Ne} \rho(\vec{r}) d\vec{r}$$

$$= -\frac{1}{2} \sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \iint |\varphi_i(\vec{x}_1)|^2 \frac{1}{r_{12}} |\varphi_j(\vec{x}_2)|^2 d\vec{x}_1 d\vec{x}_2 + E_{XC}[\rho(\vec{r})] - \sum_i^N \int \sum_A^M \frac{Z_A}{r_{1A}} |\varphi_i(\vec{x}_1)|^2 d\vec{x}_1$$

Applying variational principle we solve Kohn-Sham equations in iterative way

Everything “unknown” is in E_{XC}

If we know E_{XC} we have an EXACT method

E_{XC} is not known => we have to rely of approximate exchange correlation functionals

Exchange-correlation functionals:

- I. local density approximation - $E_{XC}[\rho]$
- II. Generalized Gradient approx. - $E_{XC}[\rho, \nabla \rho]$
- III. Hybrid density functionals - $E_{XC}[\rho, \nabla \rho]$ + combines with “exact”=HF exchange

Local Density Approximation: (LDA ~ LSD ~ SVWN)

E_{XC} derived for the model of uniform electron gas

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r}) \varepsilon_{XC}(\rho(\vec{r})) d\vec{r}$$

$$\varepsilon_{XC}(\rho(\vec{r})) = \varepsilon_X(\rho(\vec{r})) + \varepsilon_C(\rho(\vec{r}))$$

$$\varepsilon_X = -\frac{3}{4} \sqrt[3]{\frac{3 \rho(\vec{r})}{\pi}} \quad \mathbf{S} \dots \text{used by Slater}$$

ε_C (fit of QMC data) **VWN**