Which electronic structure method? An introduction to Density Functional Theory (part 1)

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Elementary Quantum Mechanics

- The Schrodinger Equation
- Variational Principle
- The Hartree Fock Approximation
- Correlation energy

Density Functional Theory

- Thomas-Fermi model
- The Hohenberg-Kohn theorems
- Orbitals and Kohn-Sham equations

Recommended readings:

- *Density-Functional Theory of Atoms and Molecules* by Robert G. Parr, Yang Weitao - Oxford Science Publications
- *Modern Quantum Chemistry. Introduction to Advanced Electronic Structure Theory* by Attila Szabo and Neil S. Ostlund - Dover Publications
- *Ab initio Molecular dynamics. Basic Theory and Advanced Methods* by Dominik Marx and Jürg Hutter - Cambridge University Press

The Schrodinger Equation

$$\hat{H}\Psi = E\Psi \tag{1}$$

$$\Psi = \Psi(x_1, x_2, \ldots\ldots x_n) \tag{2}$$

$$\hat{H} = \hat{T} + \hat{V}_{ne} + \hat{V}_{ee} \tag{3}$$

$$\hat{H} = \sum_{i=1,}^{N}(-\frac{1}{2}\nabla_i^2) + \sum_{i=1,}^{N} v(r_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{4}$$

where

$$v(r_i) = -\sum_{\alpha} \frac{Z_\alpha}{r_{i\alpha}} \tag{5}$$

- The total energy is $W = E + V_{nn}$ where $V_{nn} = \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}}$

The Schrodinger Equation

$$\hat{H}\Psi = E\Psi$$

must be solved subject to appropriate boundary conditions, namely $\Psi(x_1, ..., x_n)$ decays to zero at infinity, or appropriate periodic boundary condition for a solid.

$$|\Psi(x_1, ..., x_n)|^2 dr_1...dr_N \tag{6}$$

is the probability of finding the system with position coordinates between $x_1, ...x_N$ and $x_1 + dx_1.....x_N + dx_N$.
Ψ must be antisymmetric.

$$\int \Psi_k^* \Psi_l dx^N = \langle \Psi_k | \Psi_l \rangle = \delta_{kl} \tag{7}$$

The Schrodinger Equation

Expectation values of observables are given by:

$$\left\langle \hat{A} \right\rangle = \frac{\int \Psi^* \hat{A} \Psi dx}{\int \Psi^* \Psi dx} = \frac{\left\langle \Psi | \hat{A} | \Psi \right\rangle}{\langle \Psi \Psi \rangle} \tag{8}$$

In particular we also have

$$T\left[\Psi\right] = \left\langle \hat{T} \right\rangle = \int \Psi^* \hat{T} \Psi dx \tag{9}$$

and

$$V\left[\Psi\right] = \left\langle \hat{V} \right\rangle = \int \Psi^* \hat{V} \Psi dx \tag{10}$$

Variational Principle

For a system in a state Ψ

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{11}$$

where $\langle \Psi | \hat{H} | \Psi \rangle = \int \Psi^* \hat{H} \Psi dx$ The variational principles states that

$$E[\Psi] \geq E_0 \tag{12}$$

The total energy computed for a guessed state Ψ is an upper bound to the true ground state energy E_0.

$$E_0 = min_{\Psi} E\,[\Psi]\,. \tag{13}$$

Variational Principle

Formal proof of the variational principle.
Let's expand Ψ in terms of the normalized eigenstates of $\hat{H}$, Ψ_k:

$$\Psi = \sum_k C_k \Psi_k \tag{14}$$

The the energy becomes:

$$E[\Psi] = \frac{\sum_k |C_k|^2 E_k}{\sum_k |C_k|^2} \geq \frac{\sum_k |C_k|^2 E_0}{\sum_k |C_k|^2} \geq E_0 \tag{15}$$

since $E_k \geq E_0$.
(E_k is the energy for the kth eigenstate of $\hat{H}$).

Variational Principle

The variational principle can also be state in the variational form:

$$\delta\left[\left\langle\Psi|\hat{H}|\Psi\right\rangle - E\left\langle\Psi|\Psi\right\rangle\right] = 0 \qquad (16)$$

where E is the Lagrange multiplier.
This eq guarantees extremization of $\left\langle\Psi|\hat{H}|\Psi\right\rangle$ under the constraint $\langle\Psi|\Psi\rangle$=1.
The variational principle can be extended to excited states

$$E\left[\tilde{\Psi_1}\right] \geq E_1 \qquad (17)$$

if $\tilde{\Psi_1}$ is orthogonal to Ψ_0.

The Hartree Fock Approximation

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \dots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \dots & \psi_N(x_2) \\ . & . & & . \\ . & . & & . \\ . & . & & . \\ \psi_1(x_N) & \psi_2(x_N) & \dots & \psi_N(x_N) \end{vmatrix} = \frac{1}{\sqrt{N!}} det[\psi_1\psi_2 \cdots \psi_N] \tag{18}$$

orthogonal orbitals ψ_i are found minimizing $E[\Psi] = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$ where Ψ is in the form of a Slater determinant. $\langle\Psi_{HF}|\Psi_{HF}\rangle = 1$

The Hartree Fock Approximation

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i,j=1}^{N} (J_{ij} - K_{ij}) \tag{19}$$

where

$$H_i = \int \psi_i^*(x) [-\frac{1}{2} \nabla^2 + v(x)] \psi_i(x) dx \tag{20}$$

$$J_{ij} = \iint \psi_i(x_1) \psi_i^*(x_1) \frac{1}{r_{12}} \psi_j^*(x_2) \psi_j(x_2) dx_1 dx_2 \tag{21}$$

$$K_{ij} = \iint \psi_i^*(x_1) \psi_j(x_1) \frac{1}{r_{12}} \psi_i(x_2) \psi_j^*(x_2) dx_1 dx_2 \tag{22}$$

$$J_{ii} = K_{ii} \tag{23}$$

this explain the double sum in (19).

The Hartree Fock Approximation

Minimizing E_{HF}

$$E_{HF} = \langle \Psi_{HF} | \hat{H} | \Psi_{HF} \rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i,j=1}^{N} (J_{ij} - K_{ij}) \qquad (24)$$

subject to the orthonormalization conditions

$$\int \psi_i^*(x) \psi_j(x) dx = \delta_{ij} \qquad (25)$$

gives the Hartree Fock differential equations:

$$\hat{F} \psi_i(x) = \sum_{j=1}^{N} \epsilon_{ij} \psi_j(x) \qquad (26)$$

$\hat{F}\psi_i(x) = \sum_{k=1}^{N} \epsilon_{ij}\psi_j(x)$ where

$$\hat{F} = -\frac{1}{2}\nabla^2 + v(x) + \hat{g} \tag{27}$$

in which the Coulomb-exchange operator $\hat{g}$ is given by

$$\hat{g} = \hat{j} - \hat{k}. \tag{28}$$

Here

$$\hat{j}(x_1)f(x_1) \equiv \sum_{k=1}^{N} \int \psi_k^*(x_2)\psi_k(x_2)\frac{1}{r_{12}}f(x_1)dx_2 \tag{29}$$

and

$$\hat{k}(x_1)f(x_1) \equiv \sum_{k=1}^{N} \int \psi_k^*(x_2)f(x_2)\frac{1}{r_{12}}\psi_k(x_1)dx_2 \tag{30}$$

where $f(x_1)$ is an arbitrary function and the matrix ϵ consists of Lagrange multipliers.

Restricted Hartree Fock (RHF)

For an even number of electrons the alpha and beta electron are chosen so occupy the same orbitals, namely we have N/2 orbitals of form $\phi_k(r)\alpha(s)$ and N/2 orbitals of form $\phi_k(r)\beta(s)$

$$E_{HF} = 2\sum_{k=1}^{N/2} H_k + \sum_{k,l=1}^{N/2}(2J_{kl} - K_{kl}) \tag{31}$$

where

$$H_k = \int \phi_k^*(r)[-\frac{1}{2}\nabla^2 + v(r)]\phi_k(r)dr \tag{32}$$

$$J_{kl} = \iint \phi_k(r_1)\phi_k^*(r_1)\frac{1}{r_{12}}\phi_l^*(r_2)\phi_l(r_2)dr_1dr_2 \tag{33}$$

$$K_{kl} = \iint \psi_k^*(r_1)\psi_l(r_1)\frac{1}{r_{12}}\psi_k(r_2)\psi_l^*(r_2)dr_1dr_2 \tag{34}$$

The Hartree-Fock equations now read:

$$\hat{F}\phi_k(r) = \sum_{l=1}^{N/2} \epsilon_{kl}\phi_l(r) \tag{35}$$

with operator $\hat{F} = -\frac{1}{2}\nabla^2 + v(x) + \hat{g}$ $(\hat{g} = \hat{j} - \hat{k})$ where

$$\hat{j}(r_1)f(r_1) \equiv 2\sum_{m=1}^{N/2} \int \phi_m^*(r_2)\phi_m(r_2)\frac{1}{r_{12}}dr_2 f(r_1) \tag{36}$$

and

$$\hat{k}(r_1)f(r_1) \equiv \sum_{m=1}^{N/2} \int \phi_m^*(r_2)f(r_2)\frac{1}{r_{12}}dr_2\phi_m(r_1)dr_2 \tag{37}$$

the determinant wavefunction for the "closed-shell" case is

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1)\alpha(s_1) & \phi_1(r_1)\beta(s_1) & \dots & \phi_{N/2}(r_1)\beta(s_1) \\ \phi_1(r_2)\alpha(s_2) & \phi_1(r_2)\beta(s_2) & \dots & \phi_{N/2}(r_2)\beta(s_2) \\ . & . & & . \\ . & . & & . \\ . & . & & . \\ \phi_1(r_N)\alpha(s_N) & \phi_1(r_N)\beta(s_N) & \dots & \phi_{N/2}(r_N)\beta(s_N) \end{vmatrix} \tag{38}$$

A unitary transformation of the occupied orbitals ϕ_k to another set of orbitals η_k leaves the wavefunction unchanged except possibly by a phase factor. Also the operators $\hat{F}$, $\hat{k}$ and $\hat{j}$ are invariant to such a transformation.
If we have

$$\eta_m = \sum_k U_{mk}\psi_k \tag{39}$$

where

$$U^+ U = 1 \tag{40}$$

then the Hartree Fock equations become:

$$\hat{F}\eta_m = \sum_{n=1}^{N/2} \epsilon^{\eta}_{mn}\eta_n \tag{41}$$

One can choose U so to diagonalize the Hartree Fock equations:

$$\hat{F}\lambda_m(r) = \epsilon^{\lambda}_m \lambda_m(r) \tag{42}$$

The orbitals solution of

$$\hat{F}\lambda_m(r) = \epsilon_m^{\lambda}\lambda_m(r)$$

are uniquely appropriate for describing removal of electrons from the system.

Koopmans theorem If one assume no reorganization on ionization, then the best (lowest energy) single-determinant description for the ion is the determinant built from the canonical Hartree Fock orbitals $\lambda_m(r)$.

$$\epsilon_m^{\lambda} = -I_m \tag{43}$$

where I_m is the ionization energy associated with the removal of an electron from the orbital λ_m.

When the number of electron is not even, the standard HF approach is called *unrestricted open-shell* HF method.

spatial part of wf for spin α is allowed to be different from the spatial part of the wf for spin β.

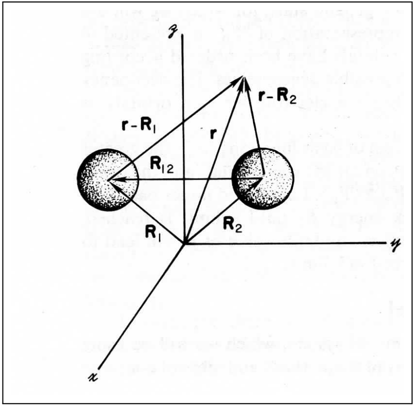
UHF can be used also in the case of even number of electrons. It often doesn't give a lower energy, but there are important examples where the UHF is required. (e.g. H_2).

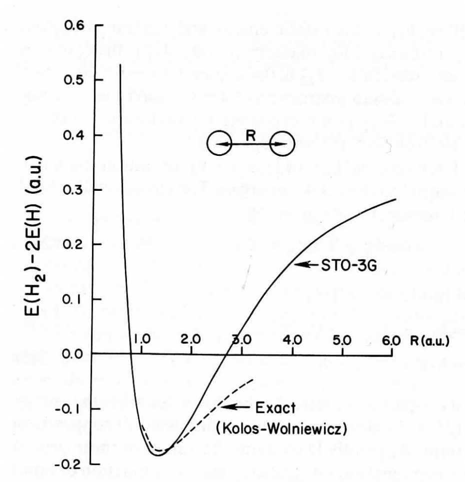
UHF for H_2 molecule

$$\phi_{1s}^{CGF}(\zeta = 1.0, STO-3G) = d_{13}\phi_{1s}^{GF}(\alpha_{13}) + d_{23}\phi_{1s}^{GF}(\alpha_{23}) + d_{33}\phi_{1s}^{GF}(\alpha_{33})$$

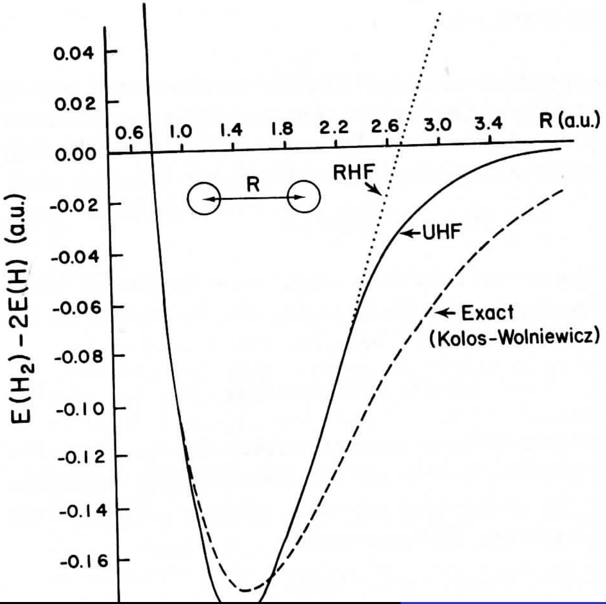
where

$$\phi_{1s}^{GF}(\alpha, r - R_A) = (2\alpha/\pi)^{3/4} e^{-\alpha|r-R_A|^2}$$





Kolos-Wolniewicz, J. Chem. Phys. 41, 3663 (1964); doi:10.1063/1.1725796


0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14
-0.16
E(H$_2$) − 2E(H) (a.u.)
0.6
1.0
1.4
1.8
2.2
2.6
3.0
3.4
R (a.u.)
R
RHF
UHF
Exact
(Kolos-Wolniewicz)

Correlation energy

HF is a single determinant description, but the Exact solution is never a single determinant or a combination of a few determinants. The energy difference between the exact energy and HF energy is the correlation energy.

$$E_{corr} = E - E_{HF} < 0 \tag{44}$$

How to improve?

- CI (linear mixing of several determinants. Conceptually the simplest, but NOT computationally

Correlation energy

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How to improve?

- CI (linear mixing of several determinants. Conceptually the simplest, but NOT computationally
- Many body perturbation theory

Electron Density

$$\rho(r_1) = N \int \dots \int |\Psi(x_1, x_2, \dots, x_N|^2 ds_1 dx_2 \dots dx_N \tag{45}$$

$$\int \rho(r) dr = N \tag{46}$$

- For an atom in its ground state, the density decrease monotonically away from the nucleus
- At any atomic nucleus, the electron density has a finite value. Cusp in the density to avoid $-\frac{1}{2}\nabla^2 - (Z_\alpha/r_\alpha)$ to blow up in $\hat{H}\Psi$.

$$\frac{\partial}{\partial r_\alpha} \bar{\rho}(r_\alpha)|_{\alpha=0} = -2Z_\alpha \bar{\rho}(0) \tag{47}$$

where $\bar{\rho}(r_\alpha)$ is the spherical average of $\rho(r_\alpha)$.

Electron Density

Long-range law for the electron density:

$$\rho \sim exp\left[-2\left(2I_{min}\right)^{1/2} r\right] \tag{48}$$

where I_{min} is the first ionization potential.
The Hartree Fock result following from Koopmans theorem will be:

$$\rho_{HF} \sim exp\left[-2\left(-2\epsilon_{max}\right)^{1/2} r\right] \tag{49}$$

The original idea: the Thomas-Fermi model

The fundamental idea is to replace the N-electron wavefunction with the electron density.

$$\psi(x_1, x_2, ...x_N) \rightarrow \rho(r) \tag{50}$$

How to approximate the the distribution of electrons in an atom? Let's assume electrons are uniformly distributed

$$\epsilon(n_x, n_y, n_z) = \frac{h^2}{8ml^2}(n_x^2 + n_y^2 + n_z^2) \tag{51}$$

$$\epsilon(n_x, n_y, n_z) = \frac{h^2}{8ml^2} R^2 \tag{52}$$

number of distinct energy levels with energy lower than ϵ

$$\Phi(\epsilon) = \frac{1}{8}\frac{4\pi}{3}R^3 \tag{53}$$

$$\Phi(\epsilon) = \frac{\pi}{6}\left(\frac{8ml^2}{h^2}\right)^{3/2}\epsilon^{3/2} \tag{54}$$

The number of energy levels between ϵ and $\epsilon + \delta\epsilon$ is

$$\begin{aligned} g(\epsilon)\Delta\epsilon &= \Phi(\epsilon+\delta\epsilon) - \Phi(\epsilon) && (55)\\ &= \frac{\pi}{4}\left(\frac{8ml^2}{h^2}\right)^{3/2}\epsilon^{1/2}\delta\epsilon && (56)\end{aligned}$$

$$\Delta E = 2\int \epsilon f(\epsilon) g(\epsilon) d\epsilon \tag{57}$$

$$= 2\int_0^{\epsilon_F} \frac{\pi}{4}\left(\frac{8ml^2}{h^2}\right)^{3/2} \epsilon^{3/2}\delta\epsilon \tag{58}$$

$$= \frac{\pi}{5}\left(\frac{8ml^2}{h^2}\right)^{3/2} \epsilon_F^{5/2} \tag{59}$$

$$= \frac{8\pi}{5}\left(\frac{2m}{h^2}\right)^{3/2} l^3 \epsilon_F^{5/2} \tag{60}$$

where we have used the Fermi-Dirac distribution for the electrons:

$$f(\epsilon) = \frac{1}{1 + e^{\beta(\epsilon-\mu)}} \tag{61}$$

which at T=0 becomes

$$f(\epsilon) = \begin{cases} 1 & \text{if } \epsilon < \epsilon_F \\ 0 & \text{if } \epsilon > \epsilon_F \end{cases}$$

$$\begin{aligned}\Delta N &= 2\int f(\epsilon)g(\epsilon)d\epsilon && (62)\\ &= \frac{8\pi}{3}\left(\frac{2m}{h^2}\right)^{3/2} l^3\epsilon_F^{3/2} && (63)\end{aligned}$$

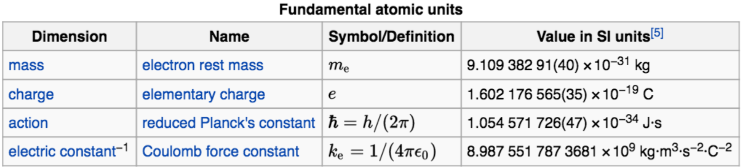
$$\begin{aligned}\Delta E &= \frac{3}{5}\Delta N\epsilon_F && (64)\\ &= \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3}\left(\frac{\Delta N}{l^3}\right)^{5/3} && (65)\\ &= \frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{2/3}\rho^{5/3} && (66)\end{aligned}$$

Adding the contributions from all the cells we get

$$T_{TF}[\rho] = C_F\int\rho^{5/3}(r)\,dr \qquad (67)$$

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(r)\,dr \tag{68}$$

Here we have reverted to atomic units



Fundamental atomic units

Dimension	Name	Symbol/Definition	Value in SI units[5]
mass	electron rest mass	m_e	$9.109\,382\,91(40) \times 10^{-31}$ kg
charge	elementary charge	e	$1.602\,176\,565(35) \times 10^{-19}$ C
action	reduced Planck's constant	$\hbar = h/(2\pi)$	$1.054\,571\,726(47) \times 10^{-34}$ J·s
electric constant^{-1}	Coulomb force constant	$k_e = 1/(4\pi\epsilon_0)$	$8.987\,551\,787\,3681 \times 10^{9}$ kg·m^{3}·s^{-2}·C^{-2}

and introduced the constant:

$$C_F = \frac{3}{10}\left(3\pi^2\right)^{2/3} = 2.871 \tag{69}$$

If we now come back to the Hamiltonian for an atomic system

$$\hat{H} = \sum_{i=1,}^{N}(-\frac{1}{2}\nabla_i^2) + \sum_{i=1,}^{N} v(r_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{70}$$

we can write the Thomas-Fermi functional of atoms

$$E_{TF}[\rho] = C_F \int \rho^{5/3}(r)\, dr - Z \int \frac{\rho(r)}{r} dr + \frac{1}{2} \int\int \frac{\rho(r_1)\,\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 \tag{71}$$

We now assume that for the ground state the electron density minimizes the energy functional under the condition:

$$N = N[\rho(r)] = \int \rho(r)\, dr \tag{72}$$

Or in the Lagrange multiplier formalism:

$$\delta\{E_{TF}[\rho] - \mu_{TF}\left(\int \rho(r)\,dr - N\right)\} = 0 \tag{73}$$

which yields the Euler-Lagrange equation

$$\mu_{TF} = \frac{\delta E_{TF}[\rho]}{\delta\rho(r)} = \frac{5}{3}C_F\rho^{2/3}(r) - \phi(r) \tag{74}$$

where $\phi(r)$ is the electrostatic potential

$$\phi(r) = \frac{Z}{r} - \int \frac{\rho(r_2)}{|r - r_2|}dr_2 \tag{75}$$

At the beginning the model encountered limited success, indeed

- Accuracy for atoms is not high
- No molecular binding is predicted (see Teller, E. (1962). "On the Stability of molecules in the Thomas-Fermi theory". Rev. Mod. Phys. 34 (4): 627-631.

However the situation changed in 1964 with the publication of a landmark paper by Hohenberg and Kohn. They provided the fundamental theorems to show that:

- Thomas-Fermi model can be regarded as an approximation to an exact theory, the *Density Functional Theory*.

The Hohenberg-Kohn theorems

For a given system described by the Hamiltonian:

$$\hat{H} = \sum_{i=1,}^{N} (-\frac{1}{2}\nabla_i^2) + \sum_{i=1,}^{N} v(r_i) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \qquad (76)$$

N and $v(r)$ determines all properties of the ground state.
In place of N and $v(r)$, the first Hohenberg-Kohn theorem legitimizes the use of the electron density $\rho(r)$ as basic variable. It states:
The external potential $v(r)$ is determined, within a trivial additive constant, by the electron density $\rho(r)$.

Let's consider the ground state density $\rho(r)$.
$\rho(r)$ determines N as $N = \int \rho(r) dr$.
$\rho(r)$ also determines $v(r)$. Let's say that is not true and there are two distinct $v(r)$ and $v'(r)$, differing by more than a constant, both giving the same $\rho(r)$. We would have two Hamiltonian H and H'. Using the variational principle we can write

$$\begin{aligned} E_0 < \langle\psi'|H|\psi'\rangle &= \langle\psi'|H - H'|\psi'\rangle + \langle\psi'|H'|\psi'\rangle && (77) \\ &= \int \rho\left(r\right)\left[v(r) - v'(r)\right] dr + E_0' && (78) \end{aligned}$$

In the same way we can write

$$\begin{aligned} E_0' < \langle\psi|H'|\psi\rangle &= \langle\psi|H' - H|\psi\rangle + \langle\psi|H|\psi\rangle && (79) \\ &= -\int \rho\left(r\right)\left[v(r) - v'(r)\right] dr + E_0 && (80) \end{aligned}$$

Summing up the two we arrive to the absurd $E_0 + E_0' < E_0' + E_0$, so it must be $v(r) = v'(r)$.

The second Hohenberg-Kohn theorem states:
For a trial density $\tilde{\rho}(r)$ *such that* $\tilde{\rho}(r) > 0$ *and* $\int \tilde{\rho}(r)\,dr = N$*, there is a variational principle and* $E_0 \leq E_v[\tilde{\rho}]$*.*

$$\begin{aligned} E_v[\rho] &= T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] && (81) \\ &= \int \rho(r)\, v(r)\, dr + F_{HK}[\rho] && (82) \end{aligned}$$

and

$$\begin{aligned} F_{HK}[\rho] &= T[\rho] + V_{ee}[\rho] && (83) \\ &= T[\rho] + J[\rho] + \text{nonclassical term} && (84) \end{aligned}$$

The second HK theorem provides the justification for the variational principle in TF, where $E_{TF}[\rho]$ is an approximation to $E[\rho]$.

From the first HK Theorem we have that
$\tilde{\rho}(r)$ determines $\tilde{v}(r)$ and consequently $\tilde{H}$ and $\tilde{\psi}$.
Let's consider $\tilde{\psi}$ as the trial wf for the problem H

$$\left\langle \tilde{\psi} | H | \tilde{\psi} \right\rangle = \int \tilde{\rho}(r)\, dr + F_{HK}[\tilde{\rho}] = E_v[\tilde{\rho}] \tag{85}$$

$$\left\langle \tilde{\psi} | H | \tilde{\psi} \right\rangle \geq \langle \psi | H | \psi \rangle = E_v[\rho] \tag{86}$$

So it follows that $E_v[\tilde{\rho}] \geq E_v[\rho]$.
In the differential form:

$$\delta \{ E_v[\rho] - \mu \left[\int \rho(r)\, dr - N \right] \} = 0 \tag{87}$$

where

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(r)} = v(r) + \frac{\delta F_{HK}[\rho]}{\delta \rho(r)} \tag{88}$$

Orbitals and Kohn-Sham equations

it is quite appealing that we can get the ground-state energy of a many-electron system as minimum of an energy functional

$$E_v[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$$

we have seen that a drastic approximation to the functional can be obtained by the TF model:

$$V_{ee}[\rho] \rightarrow J[\rho] = \frac{1}{2}\iint \frac{\rho(r_1)\rho(r_2)}{|r_2 - r_2|} dr_1 dr_2$$

$$T[\rho] \rightarrow \text{uniform electron gas}$$

- Can we do better?

Let's consider a *noninteracting reference system* in which there is no electron electron repulsion term and for which the electron density is exactly ρ:

$$\hat{H}_s = \sum_i^N \left(-\frac{1}{2}\nabla_i^2\right) + \sum_i^N v_s\left(r_i\right) \tag{89}$$

For this system we have an exact solution

$$\Psi_s = \frac{1}{\sqrt{N!}} det\left[\psi_1\psi_2 ... \psi_N\right] \tag{90}$$

for such a system the kinetic energy is

$$\begin{aligned} T_s\left[\rho\right] &= <\Psi_s|\sum_i^N\left(-\frac{1}{2}\nabla_i^2\right)|\Psi_s>= && (91)\\ &= \sum_i^N <\Psi_s| -\frac{1}{2}\nabla_i^2|\Psi_s> && (92)\end{aligned}$$

Now the very clever idea by Kohn and Sham was to rewrite

$$E_v[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho]$$

as

$$E_v[\rho] = T_s[\rho] + V_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \tag{93}$$

where

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \tag{94}$$

The quantity $E_{xc}[\rho]$ is the *exchange-correlation energy* , which contains the difference between $T[\rho]$ and $T_s[\rho]$ and the non-classical part of $V_{ee}[\rho]$.