

$$H = \sum_{j=1}^N -\frac{\nabla_j^2}{2} + \sum_{j=1}^N v(\vec{r}_j) + \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{1}{|\vec{r}_j - \vec{r}_k|}$$

many-body system
(atomic units: $e = \hbar = m = 1$)

Schrödinger equation: $H\psi(\vec{r}_1, \dots, \vec{r}_N) = E\psi(\vec{r}_1, \dots, \vec{r}_N)$

Example: Nitrogen atom 7 electrons

$$\psi(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_7, y_7, z_7) \rightarrow 21 \text{ coordinates}$$

rough table: 10 entries for each coordinate $\rightarrow 10^{21}$ entries
 1 byte per entry $\rightarrow 10^{21}$ bytes
 $\approx 5 \text{ GB} = 5 \cdot 10^9$ bytes per DVD $\rightarrow 2 \cdot 10^{11}$ DVDs
 10g per DVD $\rightarrow 2 \cdot 10^{12}$ g DVDs
 $= 2 \cdot 10^6 \text{ t}$ DVDs

One would like to calculate the expectation values of relevant operators w.r.t. the many-body wave function directly, i.e. without calculating the wave function itself.

Essence of density functional theory

1. Every observable can be calculated from the ground-state density of a system alone.
2. The ground-state density of the interacting system of interest can be calculated as the ground-state density of an auxiliary system of non-interacting particles which are moving in a local effective external potential

$$H_s = \sum_{j=1}^N \left[-\frac{\nabla_j^2}{2} + v_s(\vec{r}_j) \right]$$

Literature: C. Fiolhais, M.A.L. Marques, F. Noqueira

"A primer in Density Functional Theory"

K. Burke

"Lecture notes in density functional theory"

<http://chem.ps.uci.edu/~kieron/dft>

1. Hohenberg-Kohn Theorem

P. Hohenberg, W. Kohn Phys. Rev. 136, B864 (1964)

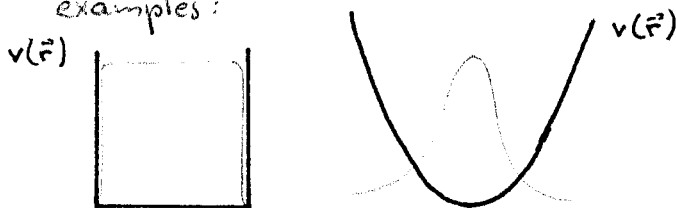
$$H = \sum_{j=1}^N -\frac{\nabla_j^2}{2} + \underbrace{\sum_{j=1}^N v(\vec{r}_j)}_{\text{external potential}} + \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{1}{|\vec{r}_j - \vec{r}_k|}$$

- Solve Schrödinger equation $H\psi = E\psi$ for different external potentials
- Calculate ground-state density

$$s(\vec{r}) = N \int d^3r_2 \dots d^3r_N |\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3 \dots \vec{r}_N)|^2$$

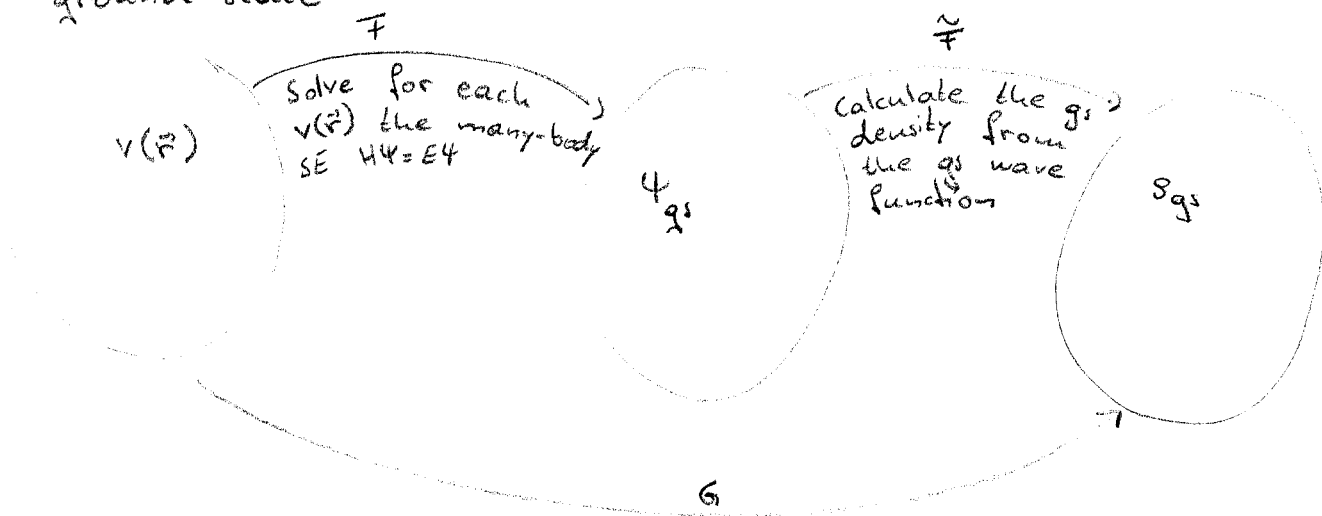
from the ground-state wave function ψ .

examples:



Question: Can two different potentials, $v(\vec{r})$ and $v'(\vec{r})$, lead to the same ground-state density?

- arbitrary function $v(\vec{r})$ that leads to a non-degenerate ground state



F and \tilde{F} are surjective

Question: Is $G: v \rightarrow s_{gs}$ invertible?

3- Hohenberg-Kohn theorem

1. G is invertible (up to an arbitrary additive constant in the potential)

Note: $v'(\vec{r}) = v(\vec{r}) + \text{const.}$

$$H\psi = E\psi \Rightarrow (H + Nc)\psi = (E + Nc)\psi = E'\psi$$

i.e. if ψ is a solution of the SE with $v(\vec{r})$ then ψ is also a solution of the SE with $v'(\vec{r})$

proof: In order to show that G is invertible we prove that \mathcal{F} and $\tilde{\mathcal{F}}$ are invertible.

a) \mathcal{F} is invertible. Solve the SE for $v(\vec{r})$

$$v(\vec{r}_1) + v(\vec{r}_2) + \dots + v(\vec{r}_N) + \text{const.} = - \frac{\left(\sum_{j=1}^N -\frac{\nabla_j^2}{2} \right) \psi}{\psi} - \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{1}{|\vec{r}_j - \vec{r}_k|}$$

This is the inverse mapping of \mathcal{F} .

b) $\tilde{\mathcal{F}}$ is invertible.

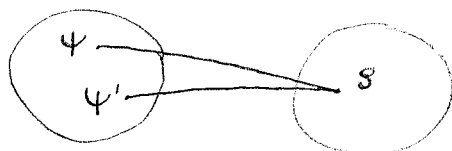
Let ψ and ψ' be two different gs wave functions coming from different potentials $v(\vec{r}), v'(\vec{r})$ with $v'(\vec{r}) \neq v(\vec{r}) + \text{const.}$

$$T = \sum_{j=1}^N -\frac{\nabla_j^2}{2} \quad V = \sum_{j=1}^N v(\vec{r}_j) \quad W = \frac{1}{2} \sum_{\substack{j,k=1 \\ j \neq k}}^N \frac{1}{|\vec{r}_j - \vec{r}_k|}$$

$$(T + V + W)\psi = E\psi$$

$$(T + V' + W)\psi' = E'\psi'$$

We have to show that



cannot happen, i.e. $\psi \neq \psi' \Rightarrow S \neq S'$

Ritz' theorem: $\langle \phi | H | \phi \rangle \geq$ gs energy of H for arbitrary normalized ϕ

"=" if and only if ϕ belongs to the space of degenerate ground states of H , $\phi = \psi_{gs}$ if gs is non degenerate

4- proof by "reductio ad absurdum"

assume: $\Psi \neq \Psi'$ but $s = s'$

$$\begin{aligned} \text{I } E &= \langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle = \langle \Psi' | H' + V - V' | \Psi' \rangle \\ &= \langle \Psi' | H' | \Psi' \rangle + \langle \Psi' | V - V' | \Psi' \rangle \\ &= E' + \int d^3r s'(\vec{r}) (v(\vec{r}) - v'(\vec{r})) \end{aligned}$$

$$\begin{aligned} \text{II } E' &= \langle \Psi' | H' | \Psi' \rangle < \langle \Psi | H' | \Psi \rangle = \langle \Psi | H' | \Psi \rangle + \langle \Psi | V' - V | \Psi \rangle \\ &= E + \int d^3r s(\vec{r}) (v'(\vec{r}) - v(\vec{r})) \end{aligned}$$

$$\text{I+II: } E + E' < E + E' + 0 \quad \downarrow$$

Corollary: Every observable, i.e. the expectation value of an arbitrary operator, can in principle be calculated from the knowledge of the gs density of the system.

proof: given $s(\vec{r}) - G^{-1}$ yields uniquely (up to a constant) the corresponding potential $v(\vec{r})$, $v = v[s]$,
- Solve many-body SE

$$(T + W + V[s]) \Psi_n = E_n \Psi_n$$

all wave functions (not only gs) $\Psi_n = \Psi_n[s]$ are functionals of the gs density

$\Rightarrow A_n[s] = \langle \Psi_n[s] | A | \Psi_n[s] \rangle$ with arbitrary hermitian operator A is a functional of the gs density

2. Variational principle

Consider a given system characterized by a particular external potential $v_0(\vec{r})$, e.g. hydrogen atom $v_0(\vec{r}) = -\frac{1}{r}$

$$N_2 \text{ molecule } v_0(\vec{r}) = -\left(\frac{1}{|\vec{r} - \frac{\vec{R}_0}{2}|} + \frac{1}{|\vec{r} + \frac{\vec{R}_0}{2}|}\right)$$

Question: How can we calculate the gs density $s_0(\vec{r})$ and the gs total energy E_0 of this particular system without solving the SE?

S- HK variational principle

There exists a functional $E_v[s]$ such that

$$E_v[s] > E_0 \quad \text{for } s \neq s_0,$$

$$E_v[s_0] = E_0.$$

Hence, E_0 and s_0 can be determined by minimizing the functional $E_v[s]$.

proof: by construction

$$\text{given } s(\vec{r}): s(\vec{r}) \xrightarrow{G^{-1}} v(\vec{r}) = v[s](\vec{r}) \xrightarrow{\text{solve SE}} \Psi_{g_s}[s]$$

$$E_v[s] := \langle \Psi_{g_s}[s] | T+W+V_0 | \Psi_{g_s}[s] \rangle$$

$$s \neq s_0 \Rightarrow \Psi_{g_s}[s] \neq \Psi_0 \Rightarrow \langle \Psi_{g_s}[s] | T+W+V_0 | \Psi_{g_s}[s] \rangle > E_0$$

because of Ritz principle

$$s = s_0 \Rightarrow \Psi_{g_s}[s] = \Psi_0 \Rightarrow \langle \Psi_0 | T+W+V_0 | \Psi_0 \rangle = E_0$$

3. Universality

$$E_v[s] = \underbrace{\langle \Psi_{g_s}[s] | T+W | \Psi_{g_s}[s] \rangle}_{F[s]} + \underbrace{\langle \Psi_{g_s}[s] | V_0 | \Psi_{g_s}[s] \rangle}_{\int d^3r s(\vec{r}) v_0(\vec{r})}$$

The density dependence of $F[s]$ is universal, i.e. it is the same for all systems where the particles interact with each other by the Coulomb interaction W .

2. Functionals and functional derivatives

Given a space Φ of functions (e.g. $\Phi = \{s(\vec{r}) : \int d^3r s(\vec{r}) = N\}$)

A map $F: \Phi \rightarrow \mathbb{K}$ (\mathbb{K} either \mathbb{R} or \mathbb{C})

is called a functional.

$$\text{examples: } F[\varphi] = \int_a^b dx \varphi(x) \quad N[s] = \int d^3r s(\vec{r})$$

$$L[q] = \int_{t_1}^{t_2} dt \mathcal{L}(q(t), \dot{q}(t)) \quad \text{action functional}$$

$$G[\varphi] = \varphi(x_0)$$

6-
derivative of a function

$$f: \mathbb{R} \rightarrow \mathbb{R} \quad x \mapsto f(x)$$

$$\frac{df}{dx} = \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} [f(x+\epsilon) - f(x)]$$

$$f: \mathbb{R}^m \rightarrow \mathbb{R} \quad (x_1, \dots, x_m) \mapsto f(x_1, \dots, x_m) \in \mathbb{R}$$

$$\begin{aligned} \frac{\partial f}{\partial x_k} &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} [f(x_1, \dots, x_k + \epsilon, \dots, x_m) - f(x_1, \dots, x_m)] \\ &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} [f(x_j + \epsilon \delta_{jk}) - f(x_j)] \end{aligned}$$

Functional derivative

$$\frac{\delta F[\varphi]}{\delta \varphi(z)} := \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} [F[\varphi(x) + \epsilon \delta(x-z)] - F[\varphi(x)]]$$

Examples

$$\begin{aligned} 1. F[\varphi] &= \varphi(x_0) \quad \frac{\delta F[\varphi]}{\delta \varphi(z)} = \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} [\varphi(x_0) + \epsilon \delta(x_0-z) - \varphi(x_0)] \\ &= \delta(x_0-z) \end{aligned}$$

$$\begin{aligned} 2. F[\varphi] &= \varphi(x_0)^2 \quad \frac{\delta F[\varphi]}{\delta \varphi(z)} = \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} [(\varphi(x_0) + \epsilon \delta(x_0-z))^2 - \varphi(x_0)^2] \\ &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} [\varphi(x_0)^2 + 2\epsilon \varphi(x_0) \delta(x_0-z) \\ &\quad + \epsilon^2 \delta(x_0-z)^2 - \varphi(x_0)^2] \\ &= 2\varphi(x_0) \delta(x_0-z) \end{aligned}$$

$$3. F[\varphi] = \int dx A(x) \varphi(x)$$

$$\begin{aligned} \frac{\delta F[\varphi]}{\delta \varphi(z)} &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \left[\int dx A(x) (\varphi(x) + \epsilon \delta(x-z)) \right. \\ &\quad \left. - \int dx A(x) \varphi(x) \right] \\ &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \left[\int dx A(x) \varphi(x) + \epsilon \int dx A(x) \delta(x-z) \right. \\ &\quad \left. - \int dx A(x) \varphi(x) \right] \\ &= A(z) \end{aligned}$$

4.

$$F[\varphi] = \int d\vec{x} (\nabla \varphi(x))^2 \quad \text{with } x \in \mathbb{R}^m$$

$$\begin{aligned} \frac{\delta F[\varphi]}{\delta \varphi(z)} &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \left[\int d\vec{x} (\nabla(\varphi(x) + \epsilon \delta(x-z)))^2 - \int d\vec{x} (\nabla \varphi(x))^2 \right] \\ &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \left[\int d\vec{x} (\nabla \varphi(x) + \epsilon \nabla \delta(x-z))^2 - \int d\vec{x} (\nabla \varphi(x))^2 \right] \\ &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \left[\int d\vec{x} (\nabla \varphi(x))^2 + 2\epsilon (\nabla \varphi(x))(\nabla \delta(x-z)) + \epsilon^2 (\nabla \delta(x-z))^2 \right. \\ &\quad \left. - \int d\vec{x} (\nabla \varphi(x))^2 \right] \\ &= \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \left[2\epsilon \int d\vec{x} (\nabla \varphi(x))(\nabla \delta(x-z)) + \epsilon^2 \int d\vec{x} (\nabla \delta(x-z))^2 \right] \\ &= 2 \int d\vec{x} (\nabla \varphi(x))(\nabla \delta(x-z)) \stackrel{p.i.}{=} -2 \int d\vec{x} (\nabla^2 \varphi(x)) \delta(x-z) \\ &= -2 \nabla^2 \varphi(z) \end{aligned}$$

5. product rule

$$F[\varphi] = G[\varphi] \cdot H[\varphi]$$

$$\frac{\delta F[\varphi]}{\delta \varphi(z)} = G[\varphi] \cdot \frac{\delta H[\varphi]}{\delta \varphi(z)} + \frac{\delta G[\varphi]}{\delta \varphi(z)} \cdot H[\varphi]$$

6. operator

$G: \varphi(x) \rightarrow (G\varphi)(x)$ G is a map from Φ to $\tilde{\Phi}$

define a functional $F_{x_0}: \varphi(x) \rightarrow (G\varphi)(x_0)$

$$\frac{\delta (G\varphi)(x)}{\delta \varphi(z)} = \frac{\delta F_x}{\delta \varphi(z)}$$

example: $G: \varphi(x) \rightarrow v(x) \varphi(x)$

$$F_{x_0}: \varphi(x) \rightarrow v(x_0) \varphi(x_0)$$

$$\frac{\delta F_{x_0}}{\delta \varphi(z)} = v(x_0) \delta(x_0 - z)$$

$$\frac{\delta (G\varphi)(x)}{\delta \varphi(z)} = v(x) \delta(x - z)$$

8-

7. chain rule

$$F[\varphi] = H[G\varphi]$$

↑ functional
↑ operator

$$\frac{\delta F[\varphi]}{\delta \varphi(x)} = \int dx \left. \frac{\delta H[\varphi]}{\delta \varphi(x)} \right|_{\varphi=G\varphi} \cdot \frac{\delta (G\varphi)(x)}{\delta \varphi(x)}$$

3. Kohn-Sham equations

W. Kohn, L.J. Sham Phys. Rev. 140, A1133 (1965)

Consider non-interacting particles moving in the local potential $v_s(\vec{r})$

$$SE : \left(-\frac{\nabla^2}{2} + v_s(\vec{r}) \right) \varphi_j(\vec{r}) = \epsilon_j \varphi_j(\vec{r}) \quad \epsilon_1 \leq \epsilon_2 \leq \dots$$

For N particles the gs density of the system is given

by

$$s_s(\vec{r}) = \sum_{j=1}^N |\varphi_j(\vec{r})|^2$$

Crucial assumption: There exists a potential $v_s(\vec{r})$ such

J.T. Chayes, L. Chayes, M.B. Ruskai, J. Stat. Phys. 38, 497 (1985)

that the density $s_s(\vec{r})$ of non-interacting particles moving in $v_s(\vec{r})$ is identical with the density $s(\vec{r})$ of the interacting system of interest ($s(\vec{r})$ is non-interacting v -representable).

HK theorem for non-interacting particles ($W=0$)

1. $v_s(\vec{r})$ is uniquely determined by $s(\vec{r})$

2. $E_{v_s}[s] = \langle \phi_{gs}[s] | T + V_s | \phi_{gs}[s] \rangle$

ϕ_{gs} is a Slater determinant

$$E_{v_s}[s] = \langle \phi_{gs}[s] | T | \phi_{gs}[s] \rangle + \int d^3r v_s(\vec{r}) s(\vec{r})$$

$$= T_s[s] + \int d^3r v_s(\vec{r}) s(\vec{r})$$

1- $\frac{\delta E_{v_s}}{\delta s(\vec{r})} = 0$ yields the exact q_s density $s_s(\vec{r})$ corresponding to $v_s(\vec{r})$

3. The functional $F[s] = T_s[s]$ is universal

What is $T_s[s]$?

given $s \rightarrow$ HK for non-int. \rightarrow unique $v_s(\vec{r}) \rightarrow$ Solve SE $\rightarrow \varphi_j[s](\vec{r})$
particles

$$T_s[s] = \sum_{j=1}^N \int d^3r \varphi_j^*(\vec{r}) \left(-\frac{\nabla^2}{2}\right) \varphi_j(\vec{r})$$

What is $v_s(\vec{r})$?

total energy of interacting system

$$\begin{aligned} E_{v_s}[s] &= \langle \Psi_{q_s}[s] | T+W | \Psi_{q_s}[s] \rangle + \int d^3r v_o(\vec{r}) s(\vec{r}) \\ &= T[s] + W[s] + \int d^3r v_o(\vec{r}) s(\vec{r}) \\ &= T_s[s] + \underbrace{\frac{1}{2} \iint d^3r d^3r' \frac{s(\vec{r}) s(\vec{r}')}{|\vec{r} - \vec{r}'|}}_{= E_H} + \int d^3r v_o(\vec{r}) s(\vec{r}) \\ &\quad + E_{xc}[s] \end{aligned}$$

where

$$E_{xc}[s] := T[s] - T_s[s] + W[s] - \frac{1}{2} \iint d^3r d^3r' \frac{s(\vec{r}) s(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

exchange-correlation energy

$$\left. \frac{\delta E_{v_s}[s]}{\delta s(\vec{r})} \right|_{s=s_{q_s}} = 0 = \left. \frac{\delta T_s[s]}{\delta s(\vec{r})} \right|_{s=s_{q_s}} + \underbrace{\int d^3r' \frac{s(\vec{r}')}{|\vec{r} - \vec{r}'|}}_{= v_H(\vec{r})} + v_o(\vec{r}) + \left. \frac{\delta E_{xc}[s]}{\delta s(\vec{r})} \right|_{s=s_{q_s}} \quad (*)$$

$$\frac{\delta T_s[s]}{\delta s(\vec{r})} = ?$$

$$\begin{aligned} \delta T_s[s] &= \delta \sum_{j=1}^N \langle \varphi_j | -\frac{\nabla^2}{2} | \varphi_j \rangle = \delta \sum_{j=1}^N \langle \varphi_j | \epsilon_j - v_s | \varphi_j \rangle \\ &= \delta \left[\sum_{j=1}^N \epsilon_j - \sum_{j=1}^N \int d^3r v_s(\vec{r}) |\varphi_j(\vec{r})|^2 \right] \\ &= \delta \left[\sum_{j=1}^N \epsilon_j - \int d^3r v_s(\vec{r}) s(\vec{r}) \right] \\ &= \sum_{j=1}^N \delta \epsilon_j - \int d^3r (\delta v_s(\vec{r})) s(\vec{r}) - \int d^3r v_s(\vec{r}) \delta s(\vec{r}) \end{aligned}$$

0. $\delta \epsilon_j$: change of orbital energy due to an infinitesimal change in the density $s \rightarrow s + \delta s$ which in turn produces an infinitesimal change in the potential $v_s \rightarrow v_s + \delta v_s$

$\delta \epsilon_j = \langle \varphi_j | \delta v_s | \varphi_j \rangle$ 1st order pert. theory, exact for infinitesimal changes

$$\Rightarrow \delta T_s = \underbrace{\sum_{j=1}^N \langle \varphi_j | \delta v_s | \varphi_j \rangle}_{= \int d^3r (\delta v_s(\vec{r})) s(\vec{r})} - \int d^3r v_s(\vec{r}) \delta s(\vec{r})$$

$$\Rightarrow \frac{\delta T_s[s]}{\delta s(\vec{r})} = -v_s(\vec{r})$$

in (*) $\Rightarrow 0 = -v_s(\vec{r}) + v_0(\vec{r}) + v_H(\vec{r}) + v_{xc}(\vec{r})$

$$\Rightarrow v_s(\vec{r}) = v_0(\vec{r}) + v_H(\vec{r}) + v_{xc}(\vec{r})$$

$$\left[-\frac{\nabla^2}{2} + v_0(\vec{r}) + v_H(\vec{r}) + v_{xc}(\vec{r}) \right] \varphi_j(\vec{r}) = \epsilon_j \varphi_j(\vec{r}) \quad \text{KS equations}$$

$$s(\vec{r}) = \sum_{j=1}^N |\varphi_j(\vec{r})|^2$$

Remarks:

1. equations have to be solved self-consistently

2. $v_s(\vec{r})$ is a local potential, i.e. $v_s(\vec{r})$ is a multiplicative operator in r -space (in contrast to HF which involves an integral operator). Hence, it is easier to solve the KS equations numerically than the HF equations.

3. The KS orbitals have, strictly speaking, no physical meaning (except that $s(\vec{r}) = \sum_{j=1}^N |\varphi_j(\vec{r})|^2$ is the exact density of the interacting system). In particular, $\det(\varphi_j(\vec{r}))$ is not to be taken as an approximation of the many-body wave function of the system.