

## Hartree-Fock equations for jellium model

System — electrons moving over a spatially uniform (positive charge) background somehow produced by the ions. [charge neutrality is ensured]

box with periodic boundary conditions  
volume  $V$

$N$ -electrons

plane-waves will satisfy the HF equations

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \varphi_j(\vec{r}) + \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}} \int \frac{|\varphi_{\mathbf{k}}(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' \varphi_j(\vec{r})$$

$$- \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}} \underbrace{\delta_{x_k, x_j}}_{\text{ensures parallel spins}} \int d\vec{r}' \frac{\varphi_{\mathbf{k}}^*(\vec{r}') \varphi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} \varphi_{\mathbf{k}}(\vec{r})$$

$$= E_j \varphi_j(\vec{r})$$

$$\rightarrow V(\vec{r}) = -\frac{e^2}{4\pi\epsilon_0} \frac{N}{V} \int d\vec{r}' \frac{1}{|\vec{r} - \vec{r}'|}$$

$$\rightarrow \text{Plane waves will have form } \varphi_j(\vec{r}) = \frac{e^{i\vec{k}_j \cdot \vec{r}}}{\sqrt{V}}$$

(spin part is already taken care of in the equation separately)

$\rightarrow$  We will use these solutions (plane waves) in the HF eqn, while remembering that the density of  $\vec{k}$  states per volume and per spin  $\frac{1}{(2\pi)^3}$ .

$$\rightarrow E_j \psi_j(\vec{r}) = \underbrace{-\frac{\hbar^2}{2m} \nabla^2 \psi_j(\vec{r})}_{\text{kinetic energy part}} - \underbrace{\frac{e^2}{4\pi\epsilon_0} \frac{N}{V} \int d\vec{r}' \frac{1}{|\vec{r}-\vec{r}'|}}_{\text{interaction with ions}}$$

$$+ \frac{e^2}{4\pi\epsilon_0} \sum_k \int \frac{|\psi_k(\vec{r}')|^2}{|\vec{r}-\vec{r}'|} d\vec{r}' \psi_j(\vec{r}) \quad \text{coulomb interaction}$$

$$- \underbrace{\frac{e^2}{4\pi\epsilon_0} \sum_{k \parallel \text{spin}} \int \frac{\psi_k^*(\vec{r}') \psi_j(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' \psi_k(\vec{r})}_{\text{exchange interaction}}$$

$\rightarrow$  The kinetic energy term will yield  $\frac{\hbar^2}{2m} k_j^2 \psi_j(\vec{r})$ .

$\rightarrow$  The contribution from the interaction with ions and the coulomb interaction will be equal and they cancel each other. Note  $|\psi_j(\vec{r}')|^2 = 1/V$ .

$\rightarrow$  The exchange term can be evaluated as follows.

$$- \frac{e^2}{4\pi\epsilon_0} \sum_{k \parallel \text{spin}} \int \frac{d\vec{r}'}{V} \frac{e^{i\vec{k}_e \cdot \vec{r}'} e^{i\vec{k}_j \cdot \vec{r}'}}{|\vec{r}-\vec{r}'|} \frac{e^{i\vec{k}_e \cdot \vec{r}}}{\sqrt{V}}$$

$$= - \frac{e^2}{4\pi\epsilon_0} \sum_{k \parallel \text{spin}} \int \frac{d\vec{r}'}{V} \frac{e^{-i\vec{k}_e \cdot \vec{r}'} e^{i\vec{k}_j \cdot \vec{r}'}}{|\vec{r}-\vec{r}'|} \frac{e^{i\vec{k}_e \cdot \vec{r}}}{\sqrt{V}} \frac{e^{-i\vec{k}_j \cdot \vec{r}'}}{\sqrt{V}} \frac{e^{i\vec{k}_e \cdot \vec{r}''}}{\sqrt{V}}$$

introduce  $\vec{r}_2 = \vec{r}' - \vec{r}''$ .

$$= - \frac{e^2}{4\pi\epsilon_0} \psi_j(\vec{r}) \sum_k \int \frac{d\vec{r}''}{V} \frac{e^{i(\vec{k}_j - \vec{k}_e) \cdot \vec{r}_2}}{|\vec{r}_2|} \delta_{x_j, x_e}$$

$$= -\frac{e^2}{4\pi\epsilon_0} \varphi_j \sum_l \frac{1}{\nu} \frac{4\pi}{|\vec{k}_j - \vec{k}_l|^2} \delta_{x_j, x_l}$$

$$= -\frac{e^2}{4\pi\epsilon_0} \varphi_j \int_0^{k_F} \frac{d\vec{k}}{(2\pi)^3} \frac{4\pi}{k_j^2 + k^2 - 2\vec{k} \cdot \vec{k}_j}$$

we have assumed that the states are occupied up to a Fermi wave vector. Also, remember the restriction that  $x_e = x_j$ , which halves the density of states.

$$= -\frac{e^2}{4\pi\epsilon_0} \varphi_j \int_0^{k_F} \int_{-1}^1 \frac{(4\pi) k^2 dk d(\cos\theta)}{k_j^2 + k^2 - 2kk_j \cos\theta}$$

$$= -\frac{e^2}{4\pi\epsilon_0} \varphi_j \int_0^{k_F} \frac{(4\pi) k^2 dk}{(-2kk_j)} \left\{ \ln[k_j^2 + k^2 - 2kk_j] - \ln[k_j^2 + k^2 + 2kk_j] \right\}$$

$$= -\frac{e^2}{4\pi\epsilon_0} \varphi_j \frac{4\pi}{k_j} \int_0^{k_F} k \left[ \ln|k+k_j| - \ln|k-k_j| \right]$$

Note:  $\int x \ln(x+a) dx = \frac{x^2 - a^2}{2} \ln(x+a) - \frac{1}{4}(x-a)^2$ .

$$\Rightarrow = -\frac{e^2}{4\pi\epsilon_0} \varphi_j \frac{4\pi}{k_j} \left[ \begin{aligned} & \frac{k_F^2 - k_j^2}{2} \ln|k_F + k_j| - \frac{1}{4} (k_F - k_j)^2 - \frac{(-k_j^2)}{2} \ln k_j + \frac{(-k_j^2)}{4} \\ & - \left\{ \frac{(k_F^2 - k_j^2)}{2} \ln|k_F - k_j| - \frac{1}{4} (k_F + k_j)^2 \right. \\ & \left. - \frac{k_j^2}{2} \ln k_j + \frac{1}{4} k_j^2 \right\} \end{aligned} \right]$$

$$\begin{aligned}
 &= -\frac{e^2}{4\pi\epsilon_0} g_j \frac{4\pi}{k_j} \left[ \frac{k_F^2 - k_j^2}{2} \ln \left| \frac{k_F + k_j}{k_F - k_j} \right| - \frac{1}{4} (k_F - k_j)^2 \right. \\
 &\quad \left. + \frac{1}{4} (k_F + k_j)^2 \right] \\
 &= -\frac{e^2}{\epsilon_0} g_j \frac{1}{k_j} \left[ \frac{k_F^2 - k_j^2}{2} \ln \left| \frac{k_F + k_j}{k_F - k_j} \right| + k_F k_j \right] \\
 &= -\frac{e^2}{\epsilon_0} g_j(\vec{r}) k_F \left[ 1 + \frac{k_F^2 - k_j^2}{2k_j k_F} \ln \left| \frac{k_F + k_j}{k_F - k_j} \right| \right]
 \end{aligned}$$

Therefore, plane waves satisfying the Hartree-Fock eqn, yield the following expression for the energy of state  $j$

$$\epsilon_j = \frac{\hbar^2}{2m} k_j^2 - 2\frac{e^2}{\epsilon_0} k_F F(k_j/k_F),$$

where the Lindhard dielectric function  $F(x)$  is

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|.$$

If we have a collection of independent electrons, then the total energy is given by the sum of the one-particle energies. This observation doesn't hold for the Hartree-Fock theory described energies  $\epsilon_j$ . The sum of all  $\epsilon_j$  counts terms resulting from the Coulomb and exchange interactions twice.

The expression for the total energy is

$$E = \sum_j \left[ \frac{t^2}{2m} k_j^2 - \frac{e^2}{\epsilon_0} k_F F(k_j/k_F) \right]$$

Exercise

$$= N \left[ \frac{3}{5} \epsilon_F - \frac{3}{4} \frac{e^2 k_F}{\epsilon_0} \right].$$

# Density Functional Theory (DFT)

- A method for the calculation of the properties of complex electronic systems: molecules, solids, polymers.
- Introduced by Hohenberg, Kohn and Sham in 1960s.  
(Basic idea)
  - P. Hohenberg and W. Kohn. Inhomogeneous electron gas, Physical Review 136, B864–871, 1964
  - W. Kohn and L.J. Sham. Self-consistent Equations Including Exchange and Correlation effects, Physical Review 140, A1133–A1138, 1965.
- The basic idea is to describe the system in terms of the electron density (and possibly other additional densities such as the spin density, the current density) without explicit reference to the many-body wave function.

↓

A bold proposal  $\Rightarrow$  The electron density contains in principle all the information contained in a many-electron wave function.

How can the subtle correlations encoded in an  $N$ -electron wave function be adequately represented by a simple collective variable, such as the density?

- The ground state energy of a quantum system can be determined by minimizing the energy as a functional of density. [Hohenberg & Kohn 1964].  
(This is similar to what is done in QM, wherein we can determine the energy by minimizing the expectation value of the hamiltonian w.r.t. to the wave function.)
- Also, the nontrivial part of this functional is universal, that is, it has the same form for all physical systems.
- The implementation of the Hohenberg-Kohn minimum principle leads to mean-field like equations, known as the Kohn-Sham equations.  
(Those are simpler than the HF eqns.)
- The main advantage of this approach is that the KS eqns. can be solved on a computer in a time that grows as a power of the number of electrons, whereas the exact soln. of the N-electron Schrödinger eqn. requires a time that grows exponentially with N.
- In a nutshell, by abandoning the traditional program of approximating the ground-state wave function of a specific system, DFT affords a simpler and broadly applicable formalism for the ground-state energy and density of many systems.

## Ground-state formalism

We shall be mostly concerned with the ground state description in our discussion of DFT.

The variational principle for the density

Consider an  $N$ -electron system described by the hamiltonian

$$H = T + H_{\text{el-el}} + V, \quad (\text{operators}) \longrightarrow ①$$

where  $T$  and  $H_{\text{el-el}}$  are kinetic energy and the electron-electron interaction part respectively, and  $V$  is the potential energy associated with an external local potential  $V(\vec{r})$  (for example the nuclear potential, if the system is an atom).

The operator  $V$  can be written as

$$V = \int V(\vec{r}) n(\vec{r}) d\vec{r} \quad \longrightarrow ②$$

Where

$$n(\vec{r}) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \quad \longrightarrow ③$$

is the density operator.

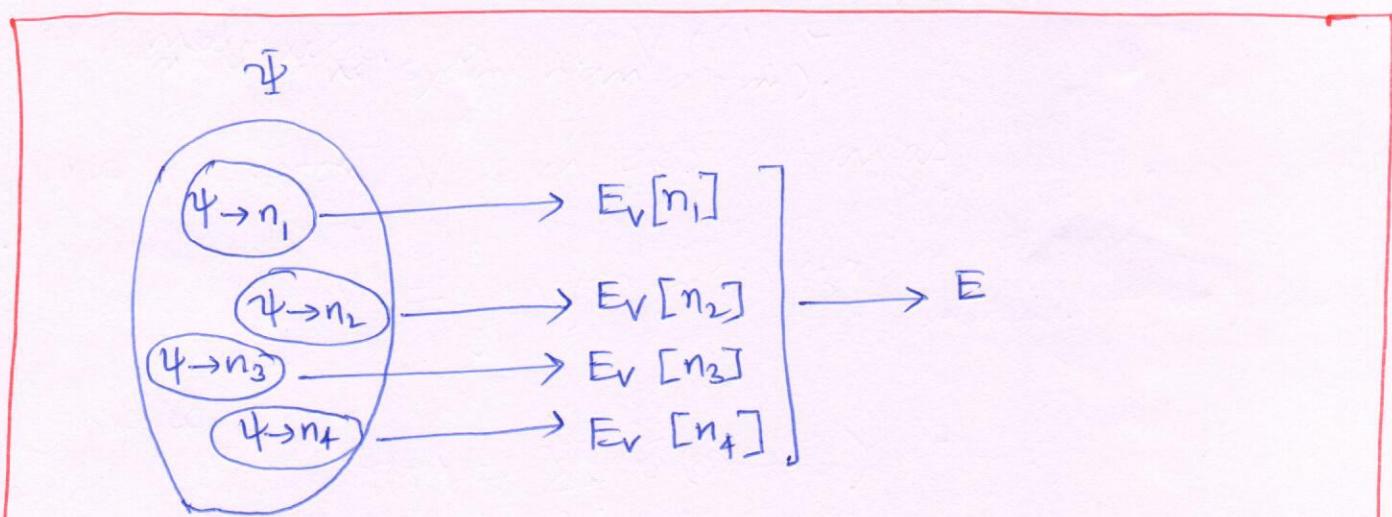
The crucial step in the formulation of DFT is the construction of a variational principle for the density.

This is achieved by converting the Rayleigh-Ritz variational principle for the quantum mechanical wave function into the desired variational principle for the density by means of a constrained search algorithm (M Levy 1979).

According to the Rayleigh-Ritz principle the ground-state energy  $E$  is found by minimizing the expectation value of the Hamiltonian with respect to the wave function  $\Psi$ , i.e.,

$$E = \min_{\Psi} \langle \Psi | H | \Psi \rangle, \quad \text{--- (4)}$$

where  $\Psi$  must be antisymmetric under interchange of two <sup>electron</sup> orbital and spin coordinates and satisfy the boundary conditions appropriate to the system under study.



Schematic: constrained search algorithm.

The minimization of the energy within the full set of admissible wave functions is carried out in two steps. In the first step the energy is minimized within subsets at fixed density, yielding a functional  $E_v[n]$ . In the second step  $E_v[n]$  is minimized with respect to the density.

## First step

Pick a density  $n(\vec{r})$  and minimize eqn. (4) within the subset of wave functions that yield this density.

Note that any reasonable density must, of course, be positive and continuous, and add up to the total number of electrons in the system, i.e.  $\int n(\vec{r}) d\vec{r} = N$ .

This gives the constrained minimum

$$\begin{aligned} E_V[n] &= \min_{\psi \rightarrow n(\vec{r})} \langle \psi | H | \psi \rangle \\ &= \min_{\psi \rightarrow n(\vec{r})} \langle \psi | T + H_{\text{el-el}} | \psi \rangle \\ &\quad + \int V(\vec{r}) n(\vec{r}) d\vec{r}. \end{aligned} \quad (5)$$

Define

$$F[n] = \min_{\psi \rightarrow n(\vec{r})} \langle \psi | T + H_{\text{el-el}} | \psi \rangle. \quad (6)$$

The notation  $\min_{\psi \rightarrow n(\vec{r})}$  indicates that the search for

the minimum is restricted to antisymmetric wave functions  $\psi$  which yield the density  $n(\vec{r})$ , i.e.,

$$\begin{aligned} N \sum_{\sigma_1, \dots, \sigma_N} \int d\vec{r}_2 \dots d\vec{r}_N &| \psi(\vec{r}, \sigma_1; \vec{r}_2, \sigma_2; \dots; \vec{r}_N, \sigma_N) |^2 \\ &= n(\vec{r}). \end{aligned} \quad (7)$$

Exercise: Show that one can always find a complete set of antisymmetric wave functions that yield any given reasonable density.

The minimization problem posed by eqn. (6) is therefore guaranteed to have a solution, and this solution defines the functional  $F[n]$  and  $E_v[n]$ .

Second step.

Minimize  $E_v[n]$  with respect to the density.

This gives the desired variational principle for the density

$$E = \min_{n(\vec{r})} \left\{ F[n] + \int V(\vec{r}) n(\vec{r}) d\vec{r} \right\}. \quad (8)$$

The functional  $F[n]$  is universal in the sense that it is an intrinsic property of the inhomogeneous electron liquid, and thus is the same for all systems, regardless of what the external potential  $V(\vec{r})$  is.

Existence of the functional derivative of  $F[n]$  with respect to the density.

$D(\vec{r})$  is the functional derivative of  $F[n]$  with respect to  $n(\vec{r})$  if, for any density variation  $\delta n(\vec{r})$ , and positive number  $\eta$ ,

$$\lim_{\eta \rightarrow 0} \frac{F[n + \eta \delta n] - F[n]}{\eta} = \int D(\vec{r}) \delta n(\vec{r}) d\vec{r}. \quad (9)$$

Important point is that  $D(\vec{r})$  does not depend on the choice of  $\delta n(\vec{r})$ . If this is the case, then

$$D(\vec{r}) = \frac{\delta F[n]}{\delta n(\vec{r})}, \text{ which itself a functional of } n(\vec{r}). \quad (10)$$

consider the variation of the energy functional  $E_v[n]$  due to an infinite variation of the density.

Assume that the functional derivative of  $F[n]$  exists.

$$E_v[n + \eta \delta n] - E_v[n] = \eta \int \left[ \frac{\delta F[n]}{\delta n(\vec{r})} + V(\vec{r}) \right] \delta n(\vec{r}) d\vec{r} + O(\eta^2)$$

→ (11)

It follows from the minimum condition (2) that the quantity in the square brackets must vanish at the ground-state density, because, if it did not, we could lower the energy by appropriately choosing the sign of  $\eta$ .

Therefore, the ground-state density must satisfy the equation

$$\frac{\delta F[n]}{\delta n(\vec{r})} = -V(\vec{r}),$$

→ (12)

subject to the condition  $\int n(\vec{r}) d\vec{r} = N$ .

If eqn. (12) has multiple solutions, then the one with the minimum energy must be selected.

## The Hohenberg-Kohn theorem

The external potential is a unique functional of the electron density.

One cannot find two truly different local potentials (i.e., two potentials that differ by more than a trivial constant) that yield the same ground-state density.

A given potential can yield degenerate ground-states and multiple densities associated with them, but two different potentials will never give the same density.

A knowledge of the ground-state density could, at least in principle, determine the hamiltonian, the ground-state wavefunction, and therefore all the ground-state properties of a many body system.

The proof of the theorem is by reductio ad absurdum.

Assume that there are two <sup>different</sup> potentials  $V(\vec{r})$  and  $V'(\vec{r}')$  differing by more than a constant, such that the two hamiltonians  $H = T + H_{\text{el-el}} + V$  and  $H' = T + H_{\text{el-el}} + V'$  have the same ground-state density  $n(\vec{r})$ .

Let  $|4\rangle$  and  $|4'\rangle$  be the (possibly degenerate) ground-states of  $H$  and  $H'$ , respectively. Also, let  $E$  and  $E'$  be the energies associated with  $|4\rangle$  and  $|4'\rangle$ , respectively.

→ Observe that  $|4'\rangle$  cannot be an eigenstate of  $H$  and, conversely,  $|4\rangle$  cannot be an eigenstate of  $H'$ .

This is because if  $|4\rangle$  were to be an eigenstate of  $H$  with eigenvalue  $E$  and, at the same time, an eigenstate of  $H'$  with eigenvalue  $\tilde{E}$ , then

$$[V(\vec{r}) - V'(\vec{r})] |4\rangle = (E - \tilde{E}) |4\rangle, \quad (13)$$

which would make  $V$  and  $V'$  differ by a mere constant, against the hypothesis.

It then follows from the Rayleigh-Ritz Variational Principle that the following inequality is strictly satisfied:

$$\begin{aligned} E &= \langle 4 | H | 4 \rangle < \langle 4' | H | 4' \rangle = \langle 4' | H' + V - V' | 4' \rangle \\ &= E' + \int [V(\vec{r}) - V'(\vec{r})] n(\vec{r}) d\vec{r} \end{aligned} \quad (14)$$

If we interchange the primed and unprimed variables we also obtain

$$E' < E + \int [V'(\vec{r}) - V(\vec{r})] n(\vec{r}) d\vec{r}, \quad (15)$$

Summing the inequalities (14) and (15) we arrive at the contradiction

$$E + E' < E' + E.$$

— (16)

This proves that the initial assumption was false.

**Conclusion:** The ground-state density uniquely determines (upto a constant) the local external potential  $V(\vec{r})$  that gives rise to it.

Note that the ground-state wavefunction is not uniquely determined by the density because the ground-state of  $\hat{H}$  can be degenerate.

⇒ This ambiguity is of no consequence in the evaluation of  $F[n]$ .

If  $\Psi_1$  and  $\Psi_2$  are two degenerate ground-states with energy  $E$  and density  $n(\vec{r})$ , then

$$\begin{aligned} E &= \langle \Psi_1 | T + H_{\text{el-el}} | \Psi_1 \rangle + \int V(\vec{r}) n(\vec{r}) d\vec{r} \\ &= \langle \Psi_2 | T + H_{\text{el-el}} | \Psi_2 \rangle + \int V(\vec{r}) n(\vec{r}) d\vec{r}, \end{aligned}$$

showing that  $F[n] = \langle \Psi | T + H_{\text{el-el}} | \Psi \rangle$  has the same value in the two states.

## The Kohn-Sham equation

In their 1965 work Kohn & Sham argued that the ground-state density of the interacting system can be represented as the ground-state density of a non-interacting system in some local external potential  $V_{KS}(\vec{r})$ .

Then, following the general DFT formalism, the ground-state density can be obtained by minimizing the non-interacting energy functional

$$E_{KS}^{(0)}[n] = T_S[n] + \int V_{KS}(\vec{r}) n(\vec{r}) d\vec{r}, \quad (17)$$

where  $T_S[n] = \min_{\Psi \rightarrow n(\vec{r})} \langle \Psi | T | \Psi \rangle \quad (18)$

is the non-interacting kinetic energy functional, i.e., the kinetic energy of a non-interacting system whose ground state energy density is  $n(\vec{r})$ .

The stationarity condition for the non-interacting energy functional has the form

$$\frac{\delta T_S[n]}{\delta n(\vec{r})} = -V_{KS}(\vec{r}), \quad (19)$$

which is analogous to eqn. (12) and formally defines  $V_{KS}(\vec{r})$  as a functional of the density.

Decompose  $F[n]$  as follows (Kohn & Sham 1965) :

$$F[n] = T_S[n] + E_H[n] + E_{xc}[n], \quad \text{--- (20)}$$

where  $T_S[n]$  is defined by eqn. (18),  $E_H[n]$  is the Hartree energy functional

$$E_H[n] = \frac{e^2}{8\pi\epsilon_0} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}, \quad \text{--- (21)}$$

and  $E_{xc}[n]$  is a remainder, known as exchange-correlation (xc) energy functional, which is effectively defined by eqn. (20).

Substitute this decomposition in the stationarity condition eqn. (12)

$$\frac{\delta T_S[n]}{\delta n(\vec{r})} = -V(\vec{r}) - V_H(\vec{r}) - V_{xc}(\vec{r}), \quad \text{--- (22)}$$

where  $V_H(\vec{r}) = \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}'$  is the

Hartree potential and

$$V_{xc}(\vec{r}) \equiv \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} \quad \text{--- (23)}$$

is the exchange-correlation (xc) potential.

Comparing eqns. (19) and (22), we obtain an expression for the Kohn-Sham potential

$$V_{KS}(\vec{r}) = V(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}), \quad \text{--- (24)}$$

Observe that minimizing  $E_{KS}^{(0)}[n]$  is equivalent to finding the ground-state density of a non-interacting electron system in the presence of the Kohn-Sham potential  $V_{KS}(\vec{r})$ .

Now to compute the ground-state density, we can solve the Kohn-Sham equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}) \right] \phi_\alpha(\vec{r}, s) = \varepsilon_\alpha \phi_\alpha(\vec{r}, s), \quad \text{--- (25)}$$

for the orbitals  $\phi_\alpha(\vec{r})$  with  $\alpha=1, \dots, N$ ,  $\varepsilon_1 < \varepsilon_2 \dots < \varepsilon_N$ .

The ground state density is given by

$$n(\vec{r}) = \sum_{\alpha=1}^N \sum_s |\phi_\alpha(\vec{r}, s)|^2. \quad \text{--- (26)}$$