# Computational Solid State Physics, part II

- **Instructor:** Lilia Boeri

- **Email:** lilia.boeri@uniroma1.it

- **Webpage:** https://lboeri.wordpress.com

# Outline

**Single Particle Approximation:**

- Why is it useful?
- Wavefunction-based Methods: Hartree and Hartree-Fock Approximations

**Basics of Density Functional Theory:**

- Hohemberg-Kohn Theorems: Density is the basic Variable.
- Kohn Sham Equations: Practical recipe to derive single-particle equations.
- Approximations for the Exchange and Correlation Energy, Homogeneous
- Electron Gas and beyond

# Density Functional Theory

**Density Functional Theory (DFT)** is considered the **workhorse method** to compute the electronic and vibrational properties of solids, and their response to external perturbations.
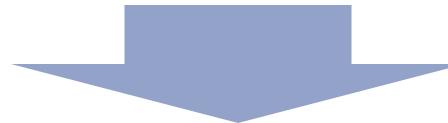
▶ **Based on two fundamental papers**:

- P. Hohenberg and W. Kohn, *Inhomogenous electron gas*, Phys. Rev. 136, B864 (1964).

   *"Density is the Basic Variable"*

- W. Kohn and L. J. Sham, *Self-Consistent Equations Including Exchange and Correlation Effects,* Phys. Rev. 140 A1133 (1965).

   *Practical recipe to write down (and solve) effective single-particle equations.*

# Main Concepts Behind DFT:

The **full quantum-many body** problem (electrons + nuclei) in solids and large molecules is **untractable** (too many degrees of freedom)...

    **1. Born-Oppenheimer Approximation:** Decouple ions & Electrons.

    **2. Self-Consistent Field** (Hartree 1926)**:** Single Particle Approximation

    (Effective single-particle equations).

**How to determine the «best» single-particle equations?**

**Wave-function-based methods:**

Hartree, Hartree-Fock, QMC

30's

**Density Functional Theory:** 60's

>80's

(Ground-state) Density is the main variable.
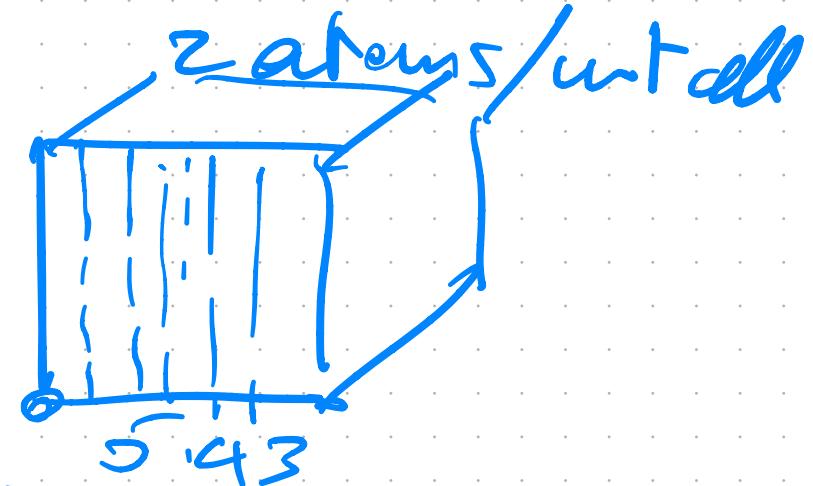
$Si$ $\quad\quad Z = 14 \quad Z_{val} = 4$

in the diamond lattice: $\quad\quad$ FCC lattice,

$a = 5.43\ \mathring{A} \quad\quad \Omega = \dfrac{(a^3)}{4}$

2 atoms/unit cell

5.43

$\Psi(\{\underline{R}\}, \{\underline{z}\})$

$N_{dim} = N_{at} + N_{el} = 2 + 8 = 10$

$\Delta x = 0.1\ \mathring{A}$

$\left[ \dfrac{1}{4}\left(\dfrac{a}{\Delta x}\right)^3 \right]^{10} = 10^{46}$ numbers → EXPONENTIAL WALL

$N_{dim}$ → $N_{points} = N_p$

# Independent - particle approximation:

$$(N_{points}) \cdot (N_{nuclei} + N_{e^-}) = 10^5 \rightarrow \text{Manageable}$$

# Fully interacting system:

$$(N_{points})^{(N_{nuclei} + N_e)} = 10^{46} \rightarrow \text{Undoable!}$$

# The Quantum-Many Body Problem:

All properties of a solid can be computed solving the **Quantum Many-Body Problem**, i.e. finding the eigenvalues and eigenstates of the Hamiltonian of interacting Nuclei and Electrons:

$$\hat{H}_{tot} = \hat{T}_N + \hat{T}_e + \hat{V}_{eN} + \hat{V}_{NN} + \hat{V}_{ee}$$

$$\hat{H}_{tot}\Phi(\mathbf{R}, \mathbf{r}) = E\Phi(\mathbf{R}, \mathbf{r}), \ \mathbf{R} = \{\mathbf{R}_\alpha\}, \ \mathbf{r} = \{\mathbf{r}_i\}$$

The size of the Hilbert space is **huge**!

# Born-Oppenheimer Approximation:

The **Quantum Many-Body Problem** of interacting nuclei and electrons:
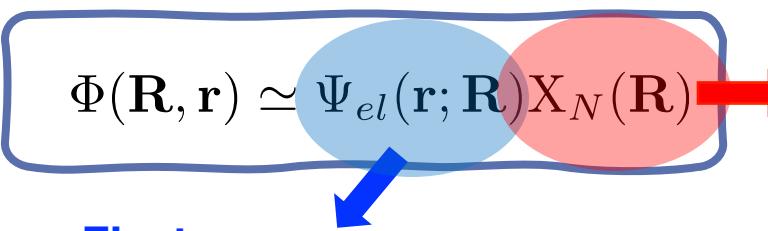
$$\hat{H}_{tot} = \hat{T}_N + \hat{T}_e + \hat{V}_{eN} + \hat{V}_{NN} + \hat{V}_{ee}$$

$$\hat{H}_{tot}\Phi(\mathbf{R}, \mathbf{r}) = E\Phi(\mathbf{R}, \mathbf{r}), \ \mathbf{R} = \{\mathbf{R}_\alpha\}, \ \mathbf{r} = \{\mathbf{r}_i\}$$

$10^{13} - 10^4$
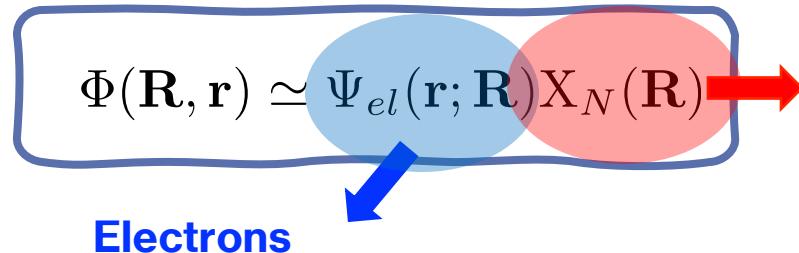
Can be **decoupled** due to the different characteristic scales of nuclear and electronic motion ($M_N >> m_{el}$):

**Factorization of the wavefunction:**

$$\Phi(\mathbf{R}, \mathbf{r}) \simeq \Psi_{el}(\mathbf{r}; \mathbf{R}) X_N(\mathbf{R})$$

**Nuclei**

**Electrons**

# Born-Oppenheimer Approximation:

▶ **Factorization of the wavefunction:**

$$\Phi(\mathbf{R}, \mathbf{r}) \simeq \Psi_{el}(\mathbf{r}; \mathbf{R}) X_N(\mathbf{R})$$ → **Nuclei**

**Electrons**

▶ **Effective Equations (Electrons + Nuclei)**

*clamped nuclei / ions*

$$\left[ -\frac{1}{2m_e} \nabla_{\mathbf{r}}^2 + V_{eN}(\mathbf{r}; \mathbf{R}) + V_{ee}(\mathbf{r}_{ij}) + V_{NN}(\mathbf{R}_{\alpha\beta}) \right] \Psi_{el}(\mathbf{r}; \mathbf{R}) = E_{El}^{(0)}(\mathbf{R}) \Psi_{el}(\mathbf{r}; \mathbf{R})$$

$$\left[ -\frac{1}{2M_N} \nabla_{\mathbf{R}}^2 + E_{el}(\mathbf{R}) \right] X_N(\mathbf{R}) = E_N X_N(\mathbf{R})$$ ← *Structrel Relaxation*

The electronic Schrodeinger's equation is **still too complicated** to solve analytically...

## **Self – Consistent Field Approximation (Hartree, 1926)**

Replace actual interacting electrons with effective non-interacting quasi-particles, **moving in an effective potential which incorporates the effect of all other (N-1) quasi-particles**.

$$H_{el} \simeq \sum_i h_i^{\text{eff}}$$

$$h_i^{\text{eff}} \phi_i = \varepsilon_i \phi_i$$

The original problem of solving a differential equation of 3N variables is recast into the manageable problem of solving a system of N equations of 3 variables, coupled self-consistently.

# How can we find the self-consistent field?

**1) Wavefunction based methods**

# Wavefunction-based methods:

**Trial wavefunction** + Minimization of the variational energy:

$$E_V[\Psi_T] = \frac{\left\langle \Psi_T | \hat{H}_{el} | \Psi_T \right\rangle}{\langle \Psi_T | \Psi_T \rangle}$$

**Hartree:** Trial wavefunction is a simple product of single-particle orbitals:

$$\Psi_{el}(\mathbf{r}; \mathbf{R}) \simeq \phi_1(\mathbf{r}_1; \mathbf{R})\phi_2(\mathbf{r}_2; \mathbf{R})...\phi_N(\mathbf{r}_N; \mathbf{R})$$

**Hartree-Fock:** Trial wavefunction is a properly antysimmetrized linear combination of Hartree's WFs:

$$\Psi_{HF}(x_1, ..., x_N) = \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^P \hat{P} \left[ \psi_\alpha(x_1)...\psi_\nu(x_N) \right] = \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^P \hat{P} \left[ \Psi_H^{\alpha,...,\nu} \right]$$

# Hartree's Approximation:

**Ansatz for the wavefunction:**

*(handwritten, red) # electron*
*(handwritten, blue) PAULI "S hed"*

$$\Psi_{el}(\mathbf{r};\mathbf{R}) \simeq \phi_1(\mathbf{r}_1;\mathbf{R})\phi_2(\mathbf{r}_2;\underline{\mathbf{R}})...\phi_N(\mathbf{r}_N;\underline{\mathbf{R}})$$

*(handwritten, blue) quantum state*

Variational minimization of the electronic energy yields a set of **N self-consistent equations**:

*(handwritten, red) e/i*

$$\left[-\frac{\nabla_i^2}{2m_e} + V_{eN}(\mathbf{r}_i) + V_{coul}(\mathbf{r}_i)\right]\phi_i(\mathbf{r}_i) = \varepsilon_i\phi_i(\mathbf{r}_i)$$
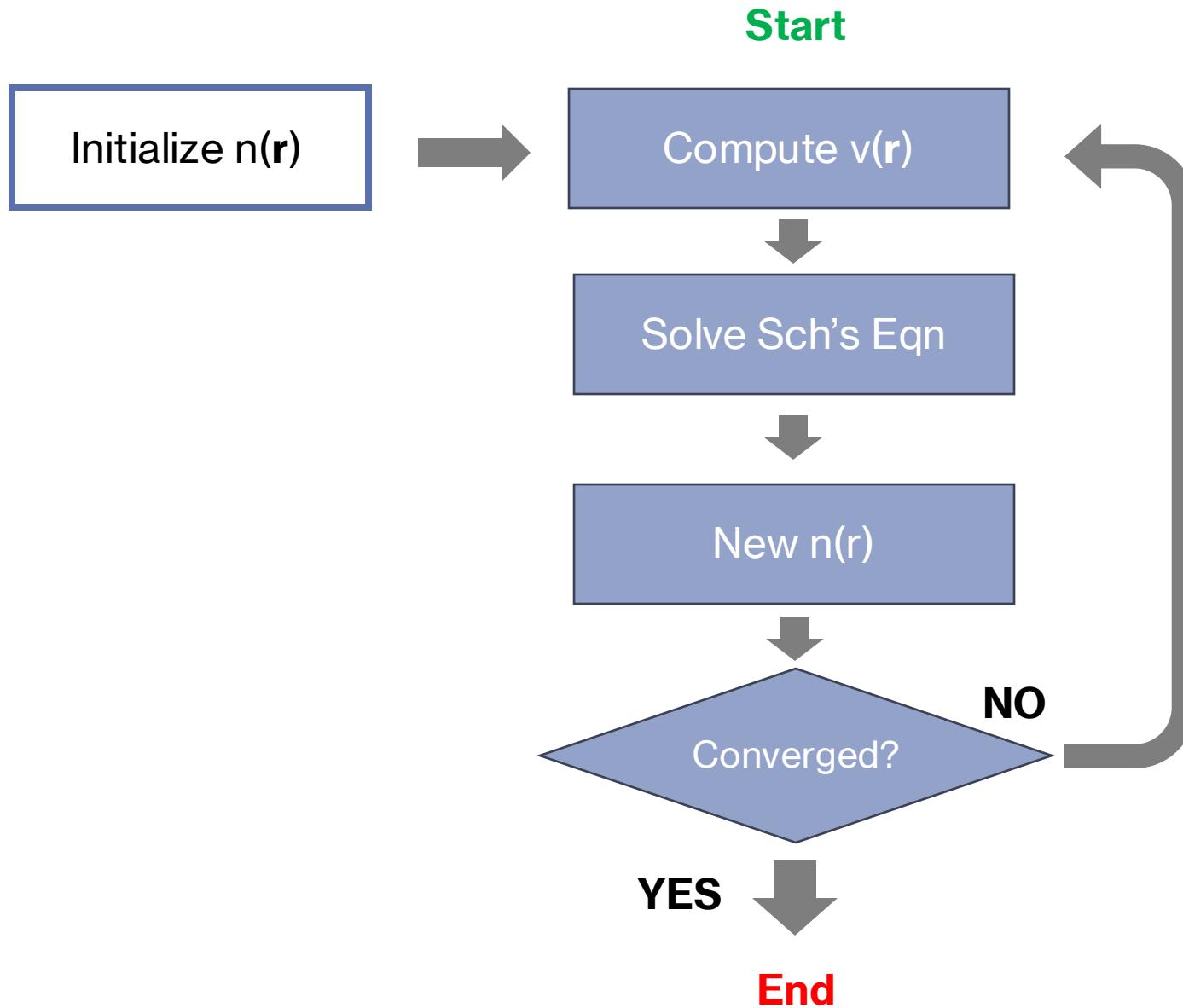
**Self-consistent potential**

$$V_{coul}(\mathbf{r}_i) = \sum_{j occ}\int d^3r' \frac{\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}_i|} - \int d^3r' \frac{\phi_i^*(\mathbf{r}')\phi_i(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}_i|}$$

*(handwritten) $n_j(\mathbf{r}_i)$*

**Average Electrostatic Repulsion**        **Self-interaction**

# Self-Consistent Field:

**Start**

Initialize n(**r**)

Compute v(**r**)

Solve Sch's Eqn

New n(r)

Converged?

**NO**

**YES**

**End**

# Hartree's Approximation:

## Ansatz for the wavefunction:

$$\Psi_{el}(\mathbf{r};\mathbf{R}) \simeq \phi_1(\mathbf{r}_1;\mathbf{R})\phi_2(\mathbf{r}_2;\mathbf{R})...\phi_N(\mathbf{r}_N;\mathbf{R})$$

### Properties of the Hartree wavefunction:

- The Pauli exclusion principle is enforced «by hand» (one particle in one orbital).

- Accounts for average (electrostatic) effect of the Coulomb interaction (screening).

- No **correlation** in the position of the effective (quasi)-particles.

### (Serious) Drawback:

- Enforcing the exclusion principle by hand does not respect symmetry properties of electronic (fermionic wavefunction).

# Hartree-Fock Approximation:

## Fermionic Statistics (Exchange):

Improve the quality of the trial wavefunction by accounting correctly for fermionic statistics :

$$\Psi(x_1, ..., x_j, ..., x_k, ..., x_N) = -\Psi(x_1, ..., x_k, ..., x_j, ..., x_N)$$

The HF **trial wavefunction** is a properly **antisymmetrized** and renormalized linear combination of Hartree's wavefunctions:

$$\Psi_{HF}(x_1, ..., x_N) = \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^P \hat{P} \left[ \psi_\alpha(x_1) ... \psi_\nu(x_N) \right] = \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^P \hat{P} \left[ \Psi_H^{\alpha,...,\nu} \right]$$

$$\Psi_H(x_1, ..., x_N) = \psi_\alpha(x_1) ... \psi_\nu(x_N)$$

# Hartree-Fock Approximation:

**Slater determinant** permits to write the trial wavefunction in compact and transparent form:

$$\Psi_{HF}(x_1, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_\alpha(x_1) & \psi_\alpha(x_2) & \ldots & \psi_\alpha(x_N) \\ \psi_\beta(x_1) & \psi_\beta(x_2) & \ldots & \psi_\beta(x_N) \\ \vdots & \vdots & \ddots & \\ \psi_\nu(x_1) & \psi_\nu(x_2) & \ldots & \psi_\nu(x_N) \end{vmatrix}$$

→ *orbitals*

*electron*
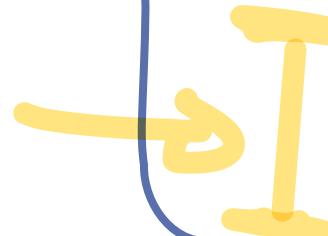
$$\psi_\alpha(x_i) = \psi_\alpha(\mathbf{r}_i, \sigma_i) = \phi_\alpha(\mathbf{r}_i)\chi_\alpha(\sigma_i)$$

- Putting two particles in the same spin-orbital is not allowed (determinant =0).

- Exchaning two particles the sign of the N-body wavefunction changes.

- There is a **correlation** between electrons with the **same spin.**

# Hartree-Fock Approximation:

Variational minimization with respect to a single orbital (γ) leads to the **effective single-particle** HF equations:

**Direct (Hartree) Term**

$$\left[-\frac{\hbar^2 \nabla_1^2}{2m} + v_{ei}(\mathbf{r}_1)\right]\psi_\gamma(x_1) + \left[\sum_\mu \int dx_2 \, \psi_\mu^*(x_2)\frac{1}{r_{12}}\psi_\mu(x_2)\right]\psi_\gamma(x_1)+$$

$$-\sum_\mu\left[\int dx_2\, \psi_\mu^*(x_2)\frac{1}{r_{12}}\psi_\gamma(x_2)\right]\delta_{\sigma_\gamma \sigma_\mu}\psi_\mu(x_1) = \varepsilon_\gamma \psi_\gamma(x_1)$$

**Exchange (Fock) Term**
**(couples e- with the same spin) – favours FM**

$$\hat{H}_{HF}|\psi_\gamma\rangle = \varepsilon_\gamma|\psi_\gamma\rangle$$

$$\hat{H}_{HF} = \hat{T}_e + \hat{v}_{ei} + \hat{v}_H\left[\{\psi_\gamma\}\right] + \hat{v}_x\left[\{\psi_\gamma\}\right]$$

# Hartree-Fock Approximation:

## Ansatz for the wavefunction:

$$\Psi_{HF}(x_1,...,x_N) = \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^P \hat{P} \left[\psi_\alpha(x_1)...\psi_\nu(x_N)\right] = \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^P \hat{P} \left[\Psi_H^{\alpha,...,\nu}\right]$$

### Advantages of the Hartree-Fock Approximation:

- Correctly accounts for fermionic anisymmetry of the wavefuction.
- Accounts for average (electrostatic) effect of the Coulomb interaction (screening) + effect of fermionic statistics (exchange).
- Koopman's theorem (HF orbital energies approximate ionization potentials).

### Drawbacks:

- **Scales very badly with system size (N$^4$).**
- Does not include **correlation effects** beyond excange **(dynamic e-e avoidance, strong correlation requires multiple determinants)**

# Effects of Electron-Electron Interaction:

**1) Average <u>Electrostatic Repulsion</u>**

                                           **Hartree**               **Classical**

*Screening* of ionic potentials

**2) Effect of Fermionic Statistics (<u>*Exchange*</u> Interaction)**       **Hartree-Fock**      **Quantum**

Magnetism

**3) Dynamic Interactions between all e- (<u>Correlation</u>)**           **Beyond H-F**      **Quantum**

Binding energy, cohesion of solids

CONFIGURATION INTERACTION
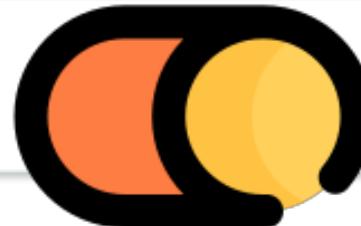
Improve Function → QMC

→ DENSITY FUNCTIONAL THEORY

# How can we find the self-consistent field?

2) Density Functional Theory

# Density Functional Theory:

**1) Density is the main variable:** the ground-state properties of a system of interacting electrons are uniquely determined by its **ground-state charge Density**.

$$n^0(\mathbf{r}) = N_{el} \int d^3r_2 ... d^3r_N |\Psi_{el}^0(\mathbf{r}, \mathbf{r}_2, ..., \mathbf{r}_N)|^2$$

P. Hohenberg and W. Kohn, *Inhomogenous electron gas*, Phys. Rev. **136**, B864 (1964).

2) The **ground-state charge density** can be obtained solving a system of **self-consistent equations** for an **auxiliary system** of non-interacting quasi-particles (**Kohn-Sham electrons**):

$$n^0(\mathbf{r}) = \sum_i |\phi_i^{KS}(\mathbf{r})|^2$$

$$h^{KS}\left[n^0(\mathbf{r})\right]\phi_i^{KS}(\mathbf{r}) = \varepsilon_i \phi_i^{KS}(\mathbf{r})$$

W. Kohn and L. J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, Phys. Rev. **140** A1133 (1965).

# Kohn-Sham Equations:

- **Single-Particle Equations (Kohn-Sham):**

$$\left(-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}[n(\mathbf{r})]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

- **Self-Consistency Condition:**
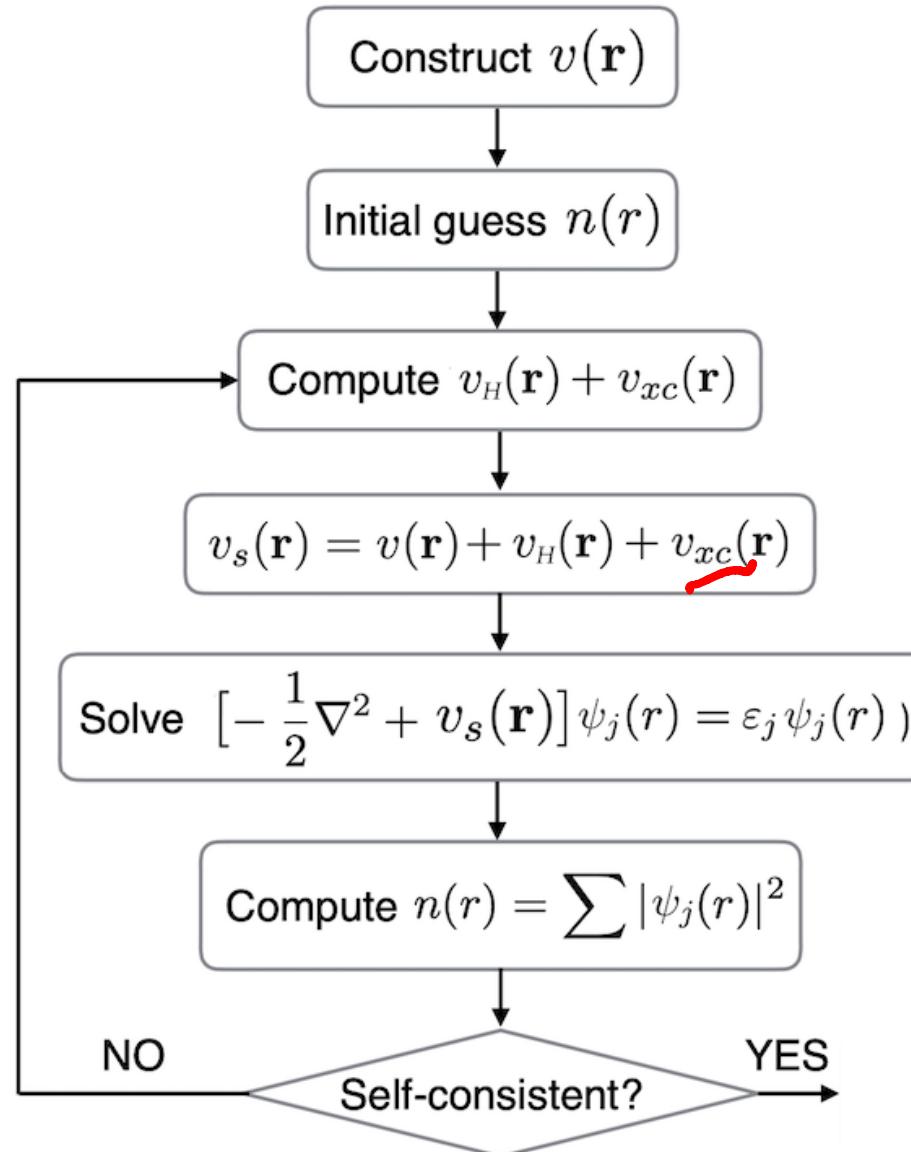
$$n_0(\mathbf{r}) = \sum_{i\ occ}|\phi_i(\mathbf{r})|^2$$

EXCHANGE AND correlation Potential

$$v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H[n(\mathbf{r})] + v_{xc}[n(\mathbf{r})]$$

# Self-Consistent Solution of Kohn-Sham Equations:

# Kohn-Sham Equations:

- **Effective Potential (Kohn-Sham)**

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}[n(\mathbf{r})] + v_{\text{xc}}[n(\mathbf{r})]$$

$v_{\text{ext}}(\mathbf{r})$ — **External Potential** (Nuclei + other external fields)

$v_{\text{H}}[n(\mathbf{r})]$ — **Hartree Potential** (Direct Electrostatic Repulsion)

$v_{\text{xc}}[n(\mathbf{r})]$ — **Exchange and Correlation Potential:** Contains all effects of e-e interaction beyond Hartree (unknown)

*IT EXISTS!*

# Exchange and Correlation Potential

$$v_{\mathrm{xc}}[n(\mathbf{r})]$$

**Exchange and Correlation Potential**: Contains all effects of e-e interaction beyond Hartree (unknown)

## Local Density Approximation:

Assume that the exchange and correlation energy of the real system is **locally** the same as that of the **homogeneous electron gas**:

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

$$E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r}))\, d\mathbf{r}$$

$$\epsilon_{xc}(n(\mathbf{r})) = \epsilon_x(n(\mathbf{r})) + \epsilon_c(n(\mathbf{r}))$$

*ANALYTICALLY* ↑

*NUMERICALLY* ↑

P. Hohenberg and W. Kohn, *Inhomogenous electron gas*, Phys. Rev. **136**, B864 (1964).