



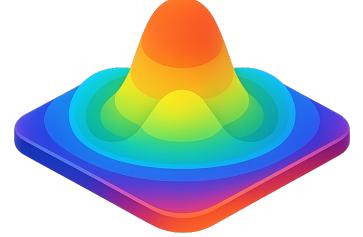
Computational Solid State Physics, part II

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Outline: Density Functional Theory



► Hohenberg-Kohn Theorems:

- Density as the basic variable.
- Variational Principle for the Energy Functional.

► Kohn-Sham Equations:

- Mapping the interacting electrons system on an effective non-interacting system.
- Contributions to the Total Energy.
- **Approximations** for the Exchange and Correlation Energy, Homogeneous Electron Gas and beyond

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**.

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

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

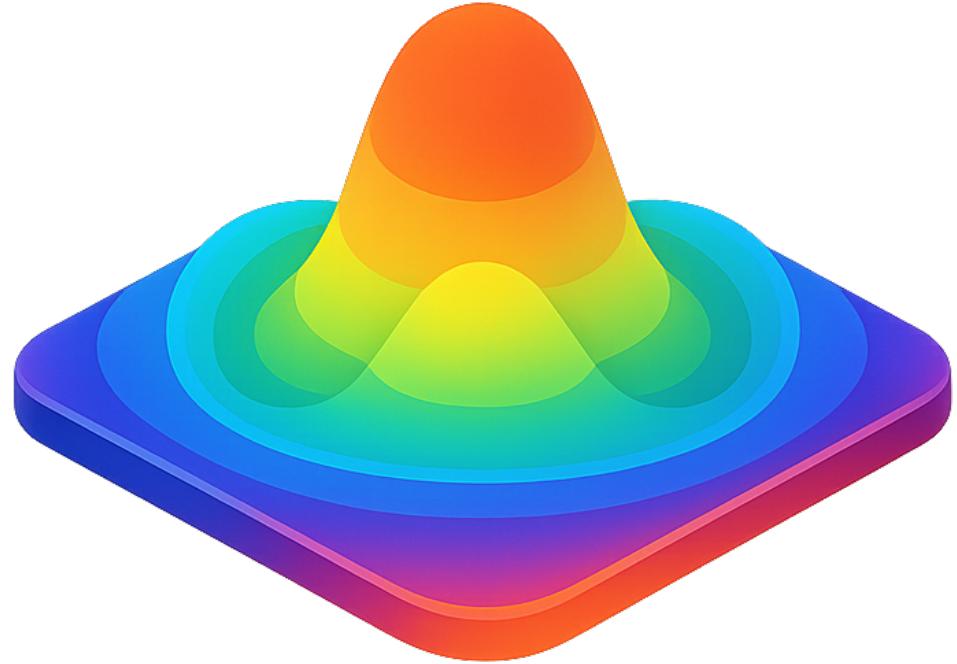
2) The **ground-state charge density** can be obtained solving a system of **self-consistent equations** for an **auxiliary system** of non-interacting quasi-particles (**Kohn-Sham electrons**):

$$n^0(\mathbf{r}) = \sum_{i \in \text{occ}} |\phi_i^{KS}(\mathbf{r})|^2$$

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

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

Hohemberg - Kohn Theorems:



Proofs & Derivations:

First Hohenberg-Kohn Theorem:

Given a system of interacting electrons subject to an external potential v_{ext} , there is a one-to-one correspondence between v_{ext} and its ground-state charge density:

$$v_{ext}(\mathbf{r}) \iff n_0(\mathbf{r})$$

$$\left(-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N v_{ext}(\mathbf{r}_i) + \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi_{el}^0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; R_\alpha) = E_0 \Psi_{el}^0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; R_\alpha)$$

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

$$v_{ext}(\mathbf{r}) = - \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|}$$

Properties of the Ground-State Density:

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

The ground-state average of any one-particle operator can be written as:

$$\left\langle \Psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \left| \sum_{i=1}^N f(\mathbf{r}_i) \right| \Psi_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \right\rangle = \int d\mathbf{r} n_0(\mathbf{r}) f(\mathbf{r})$$

Proof of the First Hohemberg-Kohn Theorem:

$$v_{ext}(\mathbf{r}) \implies n_0(\mathbf{r})$$

Follows from the definition of $n_0(\mathbf{r})$:

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

$$\hat{H}|\psi^{(0)}\rangle = E^{(0)}|\psi^{(0)}\rangle$$
$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext} = \hat{H}_{int} + \hat{V}_{ext}$$

External potential

Inferred to the electronic system

$$v_{ext}(\mathbf{r}) \Leftarrow n_0(\mathbf{r})$$

Not trivial, but can be shown *per absurdum*:

$$\hat{H}_{el} = \hat{H}_{int} + \hat{V}_{ext} = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_i^2 + v_{ext}(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$m(2), \bar{n}(2) \quad V_{ext}(2) \neq \bar{V}_{ext}(2) \quad |\psi_0\rangle, |\bar{\psi}_0\rangle$$

$$\langle \bar{\psi}^{(0)} | \hat{H} | \bar{\psi}^{(0)} \rangle = \bar{E}^{(0)}$$

$$= \langle \bar{\psi}^{(0)} | \hat{H}_{int} + \hat{V}_{ext} + \hat{V}_{ext} - \bar{V}_{ext} | \bar{\psi}^{(0)} \rangle \rightarrow E^{(0)}$$

$$\langle \psi^{(0)} | \hat{H} | \psi^{(0)} \rangle = \langle \psi^{(0)} | \hat{H}_{int} + \hat{V}_{ext} + \hat{V}_{ext} - V_{ext} | \psi^{(0)} \rangle \rightarrow \bar{E}^{(0)}$$

$$\bar{E}_+^{(0)} \bar{E}^{(0)} + \langle \bar{\psi}^{(0)} | \Delta V [\bar{\psi}^{(0)}] - \langle \psi^{(0)} | \Delta V | \psi^{(0)} \rangle$$

$$> E^{(0)} + \bar{E}^{(0)}$$

$$\Delta V = V_{\text{ext}} - \bar{V}_{\text{ext}} = \sum V_{\text{ext}}(\underline{z}) - \bar{V}_{\text{ext}}(\underline{z})$$

$$E^{(0)} + \bar{E}^{(0)} + \int d^3 r \bar{n}(\underline{z}) \cdot \Delta V + \\ - \int d^3 r n^{(0)}(\underline{z}) \Delta V > E^{(0)} + \bar{E}^{(0)}$$

If we assume that $n_0(\underline{z}) = \bar{n}_0(\underline{z})$ this is
 ————— \longrightarrow absurd!

Consequences of the First H-K Theorem:

It is trivial to prove that the ground-state averages of all terms of the Hamiltonian are functionals of v_{ext} :

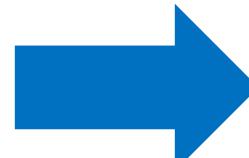
$$v_{\text{ext}}(\mathbf{r}) \Rightarrow \Psi^{(0)}(\mathbf{r}) \Rightarrow \begin{cases} E = E[v_{\text{ext}}(\mathbf{r})] \\ T = T[v_{\text{ext}}(\mathbf{r})] \\ V_{ee} = V_{ee}[v_{\text{ext}}(\mathbf{r})] \end{cases}$$

But due to the first Hohemberg-Kohn Theorem: $v_{\text{ext}}(\mathbf{r}) \iff n_0(\mathbf{r})$ this also means that they are functionals of the ground-state density:

$$E = E[n^{(0)}(\mathbf{r})]$$

$$T = T[n^{(0)}(\mathbf{r})]$$

$$V_{\text{ext}} = V_{\text{ext}}[n^{(0)}(\mathbf{r})]$$



$$V_{ee} = V_{ee}[n^{(0)}(\mathbf{r})]$$

Definition of the Energy Functional:

$$\hat{H}_{el} = \hat{H}_{int} + \hat{V}_{ext} = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_i^2 + v_{\text{ext}}(\mathbf{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$



$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + V_{\text{ext}}[n(\mathbf{r})] = T[n(\mathbf{r})] + V_{\text{ext}}[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})]$$



Universal
Internal Energy
Functional

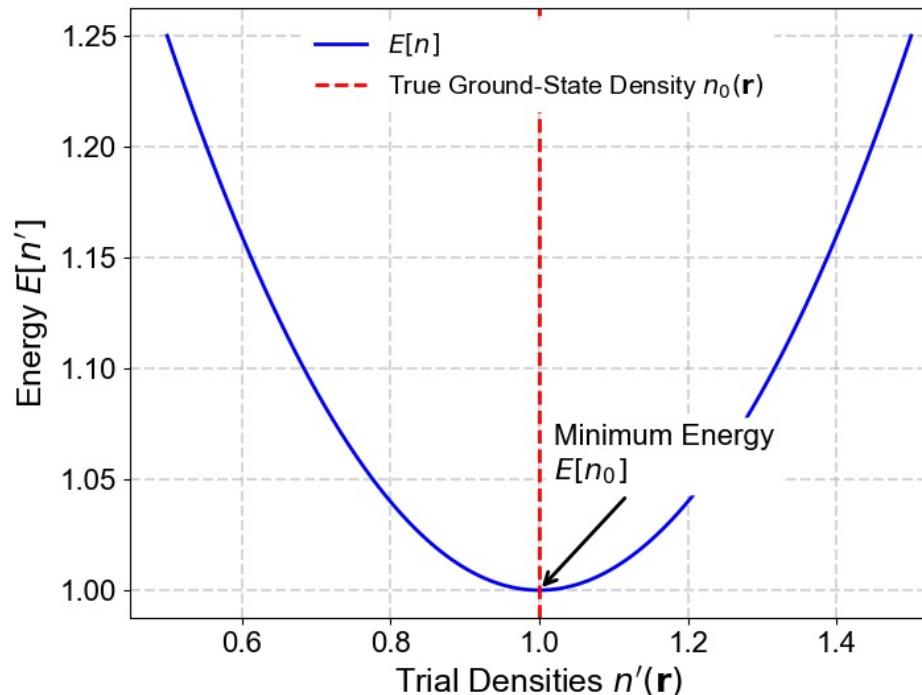
External Energy
Functional

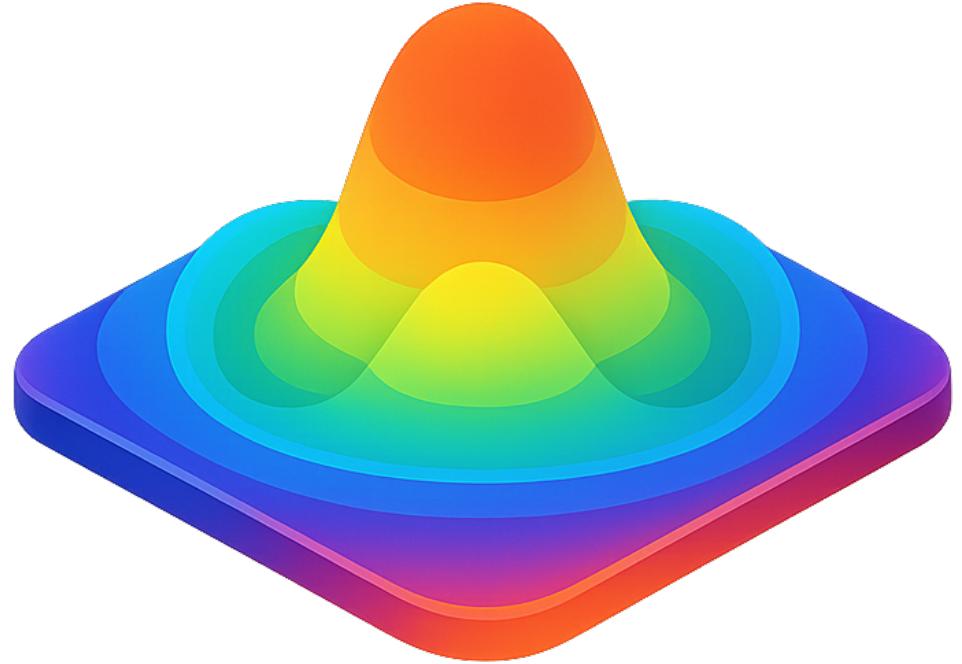
Second Hohenberg-Kohn Theorem:

Variational Principle: The ground-state charge density can be found **minimizing the total energy functional:**

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int d^3r n(\mathbf{r})v_{ext}(\mathbf{r})$$

$$\min_n(E[n(\mathbf{r})]) \Rightarrow E^0, n^0(\mathbf{r})$$





Kohn Sham Equations

Proofs & Derivations:

Kohn-Sham Equations:

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**) with the **same ground-state density**:

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

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

Kohn-Sham quasi-particles obey the single-particle equations:

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

Kohn-Sham Equations:

Kohn-Sham quasi-particles obey the **single-particle** equations:

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

Kohn-Sham Equations are in principle exact. The *effective potential* for the non-interacting quasi-particles is given by:

$$v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}[n](\mathbf{r})$$

External Potential Energy

Classical Electrostatic Repulsion (Hartree)

Exchange and Correlation Effects (Quantum)

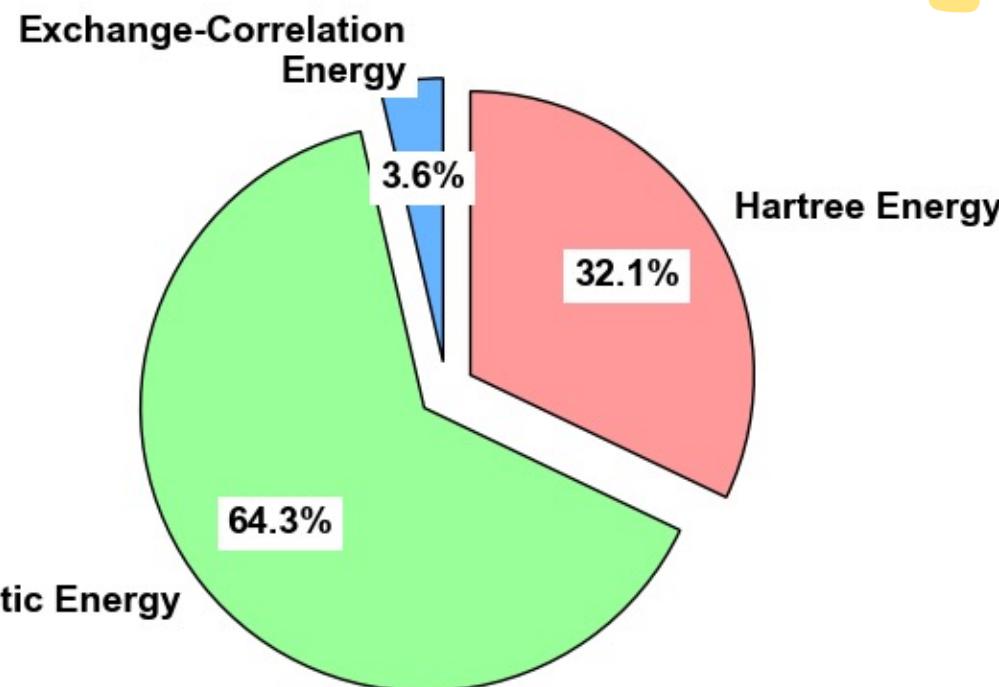
Kohn-Sham Equations, Contributions to the *internal* energy:

$$F[n(\mathbf{r})] = \underbrace{T[n(\mathbf{r})]}_{\text{Kinetic Energy}} + \underbrace{V_H[n(\mathbf{r})]}_{\text{Classical Electrostatic Repulsion}} + \underbrace{E_{xc}[n(\mathbf{r})]}_{\text{Exchange and Correlation}}$$

Kinetic
Energy

Classical
Electrostatic
Repulsion

Exchange and
Correlation



Derivation of Kohn-Sham Equations (1):

Kohn-Sham Equations are based on a **smart decomposition** of the total energy functional for the **non-interacting** system:

$$E[n_{int}(\mathbf{r})] = T[n_{int}(\mathbf{r})] + V_{ext}[n_{int}(\mathbf{r})] + V_H[n_{int}(\mathbf{r})] + E_{xc}[n_{int}(\mathbf{r})]$$

For a non-interacting systems, the first three terms can be written explicitly, and in particular:

$$T[n_{int}(\mathbf{r})] = -\frac{1}{2} \int \sum_{i=1}^N \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) d\mathbf{r}$$

$$V_H[n_{int}(\mathbf{r})] = \frac{1}{2} \int \int \frac{n_{int}(\mathbf{r}) n_{int}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

So, only the exchange & correlation part of the total energy functional is unknown.

Derivation of Kohn-Sham Equations (2):

The Exchange and Correlation Energy contains several many-body effects of electron-electron interaction:

$$E_{xc}[n_{int}(\mathbf{r})] = T[n_{int}(\mathbf{r})] - T[n_{nint}(\mathbf{r})] + V_{ee}[n(\mathbf{r})] - V_H[n(\mathbf{r})]$$

The **Total Energy** is given by:

$$E = 2 \sum_{j=1}^{N/2} \varepsilon_j + E_{xc}[n(\mathbf{r})] - \frac{e^2}{2} \iint \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - \int d\mathbf{r} v_{xc}(\mathbf{r}) n(\mathbf{r})$$

Derivation of Kohn-Sham Equations (3):

Kohn-Sham Equations are then obtained by variational minimization of the Kohn-Sham energy of the non-interacting system w.r.t. every possible choice of single-particle wfs:

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

1

The **exchange and correlation potential** is defined as:

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

And the **self-consistency** condition is given by:

$$n_0(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

2

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)

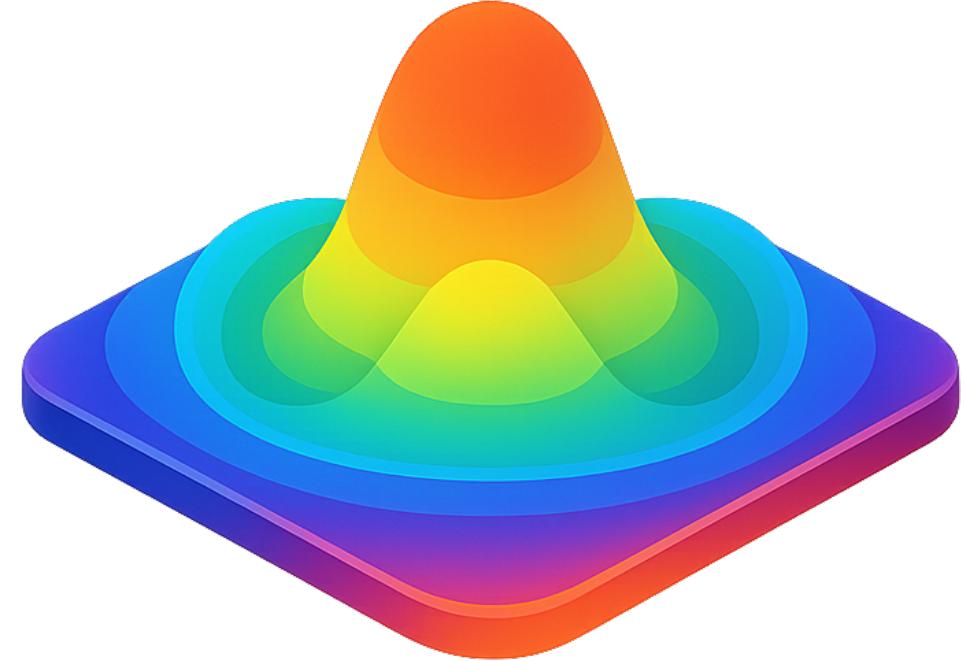
$$v_{\text{H}}[n(\mathbf{r})]$$

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)

Exchange and Correlation Potential



Local Density Approximation and Beyond

Exchange and Correlation Potential

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

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**:

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

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

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

Homogeneous Electron Gas

The Homogeneous (or uniform) Electron Gas is a model in which electrons move in a uniform positive background (jellium).

Properties:

- **Density** (electrons & nuclei) is **constant**: $n(\mathbf{r}) = n_0 = \text{const.}$

$$r_s = \left(\frac{3}{4\pi n_0} \right)^{1/3}$$

- **Total energy**: Electron-jellium interaction + Hartree terms cancel.

- **Kinetic Energy**:

$$\epsilon_T(n_0) = \frac{3}{10} (3\pi^2 n_0)^{2/3}$$

- **Exchange Energy**:

$$\epsilon_x(n_0) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n_0^{1/3}$$

- **Correlation Energy**: Not known analytically.

Homogeneous Electron Gas:

Ceperley, Adler (1980): DMC solution of the homogeneous electron gas vs r_s ; Tabulated energies for the spin-polarized/unpolarized Fermi fluid provided data to parametrize **correlation energy** for LDA.

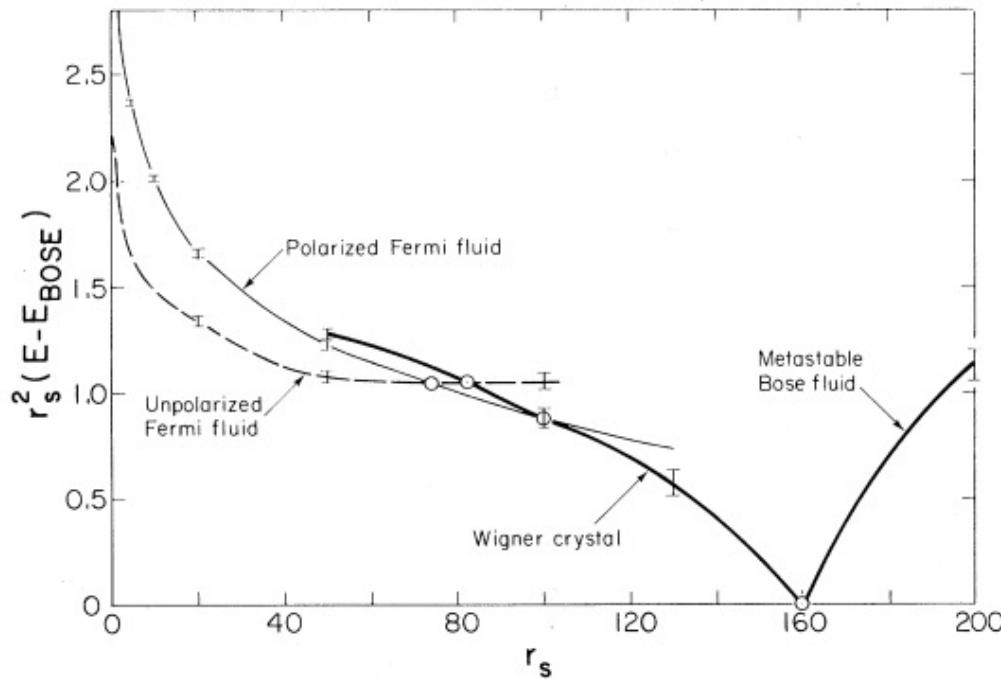


FIG. 2. The energy of the four phases studied relative to that of the lowest boson state times r_s^2 in rydbergs vs r_s in Bohr radii. Below $r_s = 160$ the Bose fluid is the most stable phase, while above, the Wigner crystal is most stable. The energies of the polarized and unpolarized Fermi fluid are seen to intersect at $r_s = 75$. The polarized (ferromagnetic) Fermi fluid is stable between $r_s = 75$ and $r_s = 100$, the Fermi Wigner crystal above $r_s = 100$, and the normal paramagnetic Fermi fluid below $r_s = 75$.

Homogeneous Electron Gas

Perdew-Zunger Parametrization:

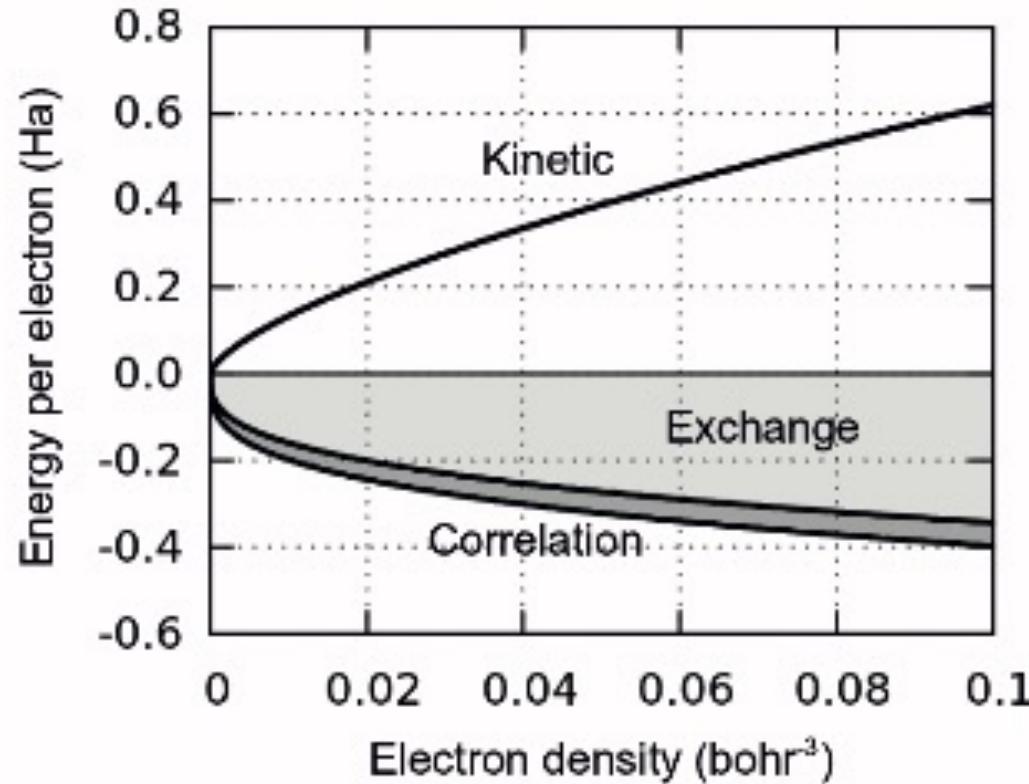
$$r_s(n) = \left(\frac{3}{4\pi n} \right)^{1/3}$$

$$\varepsilon_x(r_s) = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \frac{1}{r_s}$$

$$\varepsilon_c(n) = \begin{cases} A \ln r_s(n) + B + C r_s(n) \ln r_s(n) + D r_s(n), & r_s(n) < 1, \\ \frac{\gamma}{1 + \beta_1 \sqrt{r_s(n)} + \beta_2 r_s(n)}, & r_s(n) \geq 1, \end{cases}$$

J.P. Perdew and A. Zunger, “Self-interaction correction to density-functional approximations for many-electron systems”, Phys. Rev. B **23**, 5048 (1981).

Homogeneous Electron Gas



$$E(n) = \frac{3}{10} (3\pi^2 n)^{2/3} - \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} n^{1/3} + \varepsilon_c(n)$$

Local Density Approximation

Once a good approximation (analytical) for the exchange and correlation energy of the homogeneous electron gas is known, the exchange and correlation potential can be obtained as:

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \epsilon_{xc}(n(\mathbf{r})) + n(\mathbf{r}) \left. \frac{d\epsilon_{xc}(n)}{dn} \right|_{n=n(\mathbf{r})}$$

Since:

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

Beyond the Local Density Approximation

The local Density Approximation works «fine» for most systems where the local variation of the electronic charge density is «slow».

- **Generalized Gradient Approximation (GGA): (Kohn-Sham, 1965):**

Takes into account more explicitly the non-homogeneity of the charge density, including gradient corrections to the LDA.

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

«Famous» GGA functionals:

PW91 – Y. Wang and J. P. Perdew, Phys. Rev. B **43**, 8911 (1991).

PBE96 - J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett., 77, 3865 (1996).

Self-Consistent Solution of Kohn-Sham Equations:

