

# DFT Foundations

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## Abstract

These notes are written as a *solutionary* to accompany a first lecture on DFT. The Hartree–Fock and Kohn–Sham working equations are derived in the following way: we show how the Slater–Condon results follow from the reduced density matrices of a Slater determinant, and we write the constrained variation term-by-term until the final Euler–Lagrange equations appear. We also include verbose, step-by-step proofs of the two Hohenberg–Kohn (HK) theorems, following the standard literature.

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## 1 Setup: electronic Hamiltonian and notation

We work in *atomic units* ( $\hbar = m_e = e = 4\pi\epsilon_0 = 1$ ). For fixed nuclei (Born–Oppenheimer),

$$\hat{H}[v] = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i), \quad (1)$$

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2, \quad \hat{V}_{ee} = \sum_{i < j} \frac{1}{r_{ij}}, \quad v(\mathbf{r}) \equiv v_{\text{ext}}(\mathbf{r}) = - \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}. \quad (2)$$

The wavefunction depends on space+spin  $\mathbf{x} = (\mathbf{r}, \sigma)$ :  $\Psi = \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$ . The density is

$$\rho(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\sigma_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N, \quad \int \rho(\mathbf{r}) d\mathbf{r} = N. \quad (3)$$

## 2 Variational principle (Rayleigh–Ritz)

The central mathematical tool behind Hartree–Fock and Kohn–Sham DFT is the **variational principle**. The idea is simple: if we can write the energy as an expectation value of the Hamiltonian, then the ground state is obtained by minimizing that expectation value.

**Energy functional.** For any (normalizable) antisymmetric trial wavefunction  $\Psi$ , define the Rayleigh quotient

$$E[\Psi] \equiv \frac{\langle \Psi | \hat{H}[v] | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (4)$$

If we enforce normalization  $\langle \Psi | \Psi \rangle = 1$ , then  $E[\Psi] = \langle \Psi | \hat{H}[v] | \Psi \rangle$ .

**Why the minimum is the ground-state energy.** Let  $\{\Psi_n\}$  be a complete orthonormal eigenbasis of  $\hat{H}[v]$  with  $\hat{H}[v]\Psi_n = E_n\Psi_n$  and  $E_0 \leq E_1 \leq \dots$ . Expand any normalized trial state as  $\Psi = \sum_n c_n \Psi_n$ , with  $\sum_n |c_n|^2 = 1$ . Then

$$E[\Psi] = \langle \Psi | \hat{H}[v] | \Psi \rangle = \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2 = E_0. \quad (5)$$

So the variational principle states that *every* trial wavefunction has energy above the true ground state, and the minimum equals  $E_0$ .

**Stationarity condition: how an eigenvalue problem appears.** Minimizing the Rayleigh quotient can be written as a constrained minimization problem: minimize  $\langle \Psi | \hat{H}[v] | \Psi \rangle$  under the constraint  $\langle \Psi | \Psi \rangle = 1$ . Introduce a Lagrange multiplier  $\lambda$  and define the Lagrangian

$$\mathcal{L}[\Psi] = \langle \Psi | \hat{H}[v] | \Psi \rangle - \lambda (\langle \Psi | \Psi \rangle - 1). \quad (6)$$

Requiring  $\delta\mathcal{L} = 0$  for arbitrary variations  $\delta\Psi^*$  gives

$$\hat{H}[v]\Psi = \lambda\Psi. \quad (7)$$

Therefore, stationary points of the energy functional are eigenstates of the Hamiltonian, and the *lowest* stationary value is the ground state. This is the mathematical template we will reuse below:

- Hartree–Fock: same variational idea, but the trial space is restricted to *Slater determinants*.
- Kohn–Sham: same variational idea, but the unknown universal functional is handled via the Kohn–Sham decomposition and orbital constraints.

## 3 Hohenberg–Kohn theorems

We now switch perspective: instead of varying over wavefunctions (HF), DFT aims to work with the density  $\rho(\mathbf{r})$ . The HK theorems justify why the density is enough for ground-state properties.

**Assumptions used in the standard HK proofs.** Lets assume:

- the ground state is *non-degenerate* (degenerate cases require ensemble generalizations);
- $v(\mathbf{r})$  is such that a well-defined ground state exists (typically  $v$  is bounded from below and grows suitably at infinity);

- densities considered are ground-state densities of some external potential (the  $v$ -representability subtlety).

**HK Theorem 1 (uniqueness of the external potential).**

**Statement.** For a non-degenerate ground state, the ground-state density  $\rho_0(\mathbf{r})$  determines the external potential  $v(\mathbf{r})$  up to an additive constant. Consequently, it determines the Hamiltonian  $\hat{H}[v]$ , the ground-state wavefunction  $\Psi_0$ , and all ground-state observables.

**Proof (by contradiction; all inequalities shown).** Assume there exist two different external potentials  $v$  and  $v'$  that are *not* equal up to a constant, but that nonetheless produce the *same* ground-state density  $\rho_0(\mathbf{r})$ .

Define the two Hamiltonians

$$\hat{H} \equiv \hat{H}[v] = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i), \quad \hat{H}' \equiv \hat{H}[v'] = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^N v'(\mathbf{r}_i). \quad (8)$$

Let their (non-degenerate) ground states and energies be  $(\Psi_0, E_0)$  and  $(\Psi'_0, E'_0)$ .

**First variational inequality.** Because  $\Psi_0$  is the ground state of  $\hat{H}$ , using  $\Psi'_0$  as a trial state gives

$$E_0 < \langle \Psi'_0 | \hat{H} | \Psi'_0 \rangle. \quad (9)$$

Now rewrite  $\hat{H}$  in terms of  $\hat{H}'$ :

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_i v(\mathbf{r}_i) = \left( \hat{T} + \hat{V}_{ee} + \sum_i v'(\mathbf{r}_i) \right) + \sum_i (v(\mathbf{r}_i) - v'(\mathbf{r}_i)) = \hat{H}' + \sum_i (v - v'). \quad (10)$$

Insert into (9):

$$E_0 < \langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle + \left\langle \Psi'_0 \left| \sum_i (v - v') \right| \Psi'_0 \right\rangle. \quad (11)$$

Since  $\Psi'_0$  is an eigenstate of  $\hat{H}'$ ,

$$\langle \Psi'_0 | \hat{H}' | \Psi'_0 \rangle = E'_0. \quad (12)$$

For the remaining term, use the one-body identity:

$$\left\langle \Psi \left| \sum_i w(\mathbf{r}_i) \right| \Psi \right\rangle = \int \rho_\Psi(\mathbf{r}) w(\mathbf{r}) d\mathbf{r}. \quad (13)$$

Applying this with  $w = v - v'$  and using the assumption that  $\rho_{\Psi'_0} = \rho_0$  gives

$$\left\langle \Psi'_0 \left| \sum_i (v - v') \right| \Psi'_0 \right\rangle = \int \rho_0(\mathbf{r}) (v(\mathbf{r}) - v'(\mathbf{r})) d\mathbf{r}. \quad (14)$$

Therefore,

$$E_0 < E'_0 + \int \rho_0(\mathbf{r}) (v(\mathbf{r}) - v'(\mathbf{r})) d\mathbf{r}. \quad (15)$$

**Second variational inequality (swap roles).** Now repeat the same reasoning with roles reversed:

$$E'_0 < \left\langle \Psi_0 \left| \hat{H}' \right| \Psi_0 \right\rangle = \left\langle \Psi_0 \left| \hat{H} \right| \Psi_0 \right\rangle + \left\langle \Psi_0 \left| \sum_i (v' - v) \right| \Psi_0 \right\rangle = E_0 + \int \rho_0(\mathbf{r}) (v'(\mathbf{r}) - v(\mathbf{r})) d\mathbf{r}. \quad (16)$$

**Contradiction.** Add (15) and (16). The integrals cancel:

$$E_0 + E'_0 < E'_0 + E_0, \quad (17)$$

which is impossible. Hence our assumption was false;  $v$  is uniquely determined by  $\rho_0$  up to a constant. This proves HK1.

**HK Theorem 2 (density variational principle).**

**Statement.** There exists a universal functional  $F[\rho]$  such that

$$E_v[\rho] \equiv F[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \quad (18)$$

is minimized by the exact ground-state density  $\rho_0$ , and the minimum equals the ground-state energy  $E_0$ .

**Proof.** Define

$$F[\rho] \equiv \min_{\Psi \rightarrow \rho} \left\langle \Psi \left| \hat{T} + \hat{V}_{ee} \right| \Psi \right\rangle, \quad (19)$$

and let  $\Psi_\rho$  be a minimizer. Then

$$E_v[\rho] = F[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} = \left\langle \Psi_\rho \left| \hat{T} + \hat{V}_{ee} \right| \Psi_\rho \right\rangle + \left\langle \Psi_\rho \left| \sum_i v(\mathbf{r}_i) \right| \Psi_\rho \right\rangle = \left\langle \Psi_\rho \left| \hat{H}[v] \right| \Psi_\rho \right\rangle. \quad (20)$$

By the wavefunction variational principle,

$$E_v[\rho] = \left\langle \Psi_\rho \left| \hat{H}[v] \right| \Psi_\rho \right\rangle \geq \left\langle \Psi_0 \left| \hat{H}[v] \right| \Psi_0 \right\rangle = E_0. \quad (21)$$

For  $\rho = \rho_0$ ,  $\Psi_0$  is an admissible state in the constrained search, so equality is achieved:  $E_v[\rho_0] = E_0$ . Thus  $E_v[\rho]$  is minimized by  $\rho_0$ . This proves HK2.

## 4 Hartree–Fock: from a Slater determinant to the HF equations

Hartree–Fock restricts the trial wavefunction to a single Slater determinant of *orthonormal* spin-orbitals  $\{\chi_i(\mathbf{x})\}_{i=1}^N$ :

$$\Phi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det [\chi_i(\mathbf{x}_j)], \quad \langle \chi_i | \chi_j \rangle = \delta_{ij}. \quad (22)$$

We minimize  $\left\langle \Phi \left| \hat{H}[v] \right| \Phi \right\rangle$  over  $\{\chi_i\}$  under the orthonormality constraint (22).

**A brief description of the Slater–Condon formulas.**

Write the Hamiltonian as a sum of one- and two-body operators:

$$\hat{H}[v] = \sum_{i=1}^N \hat{h}(i) + \sum_{i < j} \hat{g}(i, j), \quad \hat{h}(i) = -\frac{1}{2} \nabla_i^2 + v(\mathbf{r}_i), \quad \hat{g}(i, j) = \frac{1}{r_{ij}}. \quad (23)$$

The *key idea* behind Slater–Condon is that expectation values over a Slater determinant can be written using reduced density matrices (RDMs). For a normalized  $N$ -electron state  $\Psi$ :

$$\gamma(\mathbf{x}, \mathbf{x}') \equiv N \int \Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N) \Psi^*(\mathbf{x}', \mathbf{x}_2, \dots, \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N \quad (\text{1-RDM}), \quad (24)$$

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) \equiv N(N-1) \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots) \Psi^*(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \dots) d\mathbf{x}_3 \cdots \quad (\text{2-RDM}). \quad (25)$$

The objects in Eqs. above are the *kernels* of the one- and two-particle reduced density matrices (RDMs).

- $\gamma(\mathbf{x}, \mathbf{x}')$  is the **one-particle RDM**. It is a two-point quantity: it correlates the amplitude of finding one electron at  $\mathbf{x}$  with the amplitude at  $\mathbf{x}'$ , after integrating out (“tracing over”) all other electrons. Its diagonal gives the density (including spin):  $\gamma(\mathbf{x}, \mathbf{x})$  is the probability density in  $(\mathbf{r}, \sigma)$ . If we sum over spin, we recover the usual spatial density:

$$\rho(\mathbf{r}) = \sum_{\sigma} \gamma((\mathbf{r}, \sigma), (\mathbf{r}, \sigma)).$$

- $\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2)$  is the **two-particle RDM**. It contains information about pair correlations: it tells us about the joint probability amplitudes for finding *two* electrons at  $(\mathbf{x}_1, \mathbf{x}_2)$  and at  $(\mathbf{x}'_1, \mathbf{x}'_2)$ , again after tracing out the remaining  $N-2$  electrons.

The prefactors  $N$  and  $N(N-1)$  come from *counting how many equivalent choices* there are when we “single out” one electron (or a pair of electrons) from an  $N$ -electron wavefunction:

- In the 1-RDM, there are  $N$  equivalent ways to choose which electron is labeled “1” (the one whose coordinate becomes  $\mathbf{x}$ ). The factor  $N$  ensures the correct normalization:

$$\int d\mathbf{x} \gamma(\mathbf{x}, \mathbf{x}) = N.$$

- In the 2-RDM, there are  $N(N-1)$  ordered ways to choose two distinct electrons (1, 2) out of  $N$ . The factor  $N(N-1)$  ensures

$$\iint d\mathbf{x}_1 d\mathbf{x}_2 \Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1, \mathbf{x}_2) = N(N-1).$$

This normalization is what makes the RDMs the natural objects for computing expectation values of one- and two-body operators. Then, for any one-body operator  $\hat{O} = \sum_i \hat{o}(i)$  and any symmetric two-body operator  $\hat{W} = \sum_{i < j} \hat{w}(i, j)$ :

$$\langle \Psi | \hat{O} | \Psi \rangle = \int d\mathbf{x} d\mathbf{x}' \gamma(\mathbf{x}', \mathbf{x}) o(\mathbf{x}, \mathbf{x}'), \quad (26)$$

$$\langle \Psi | \hat{W} | \Psi \rangle = \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 d\mathbf{x}'_1 d\mathbf{x}'_2 \Gamma(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x}_1, \mathbf{x}_2) w(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2). \quad (27)$$

For a Slater determinant of orthonormal orbitals, the 1-RDM is

$$\gamma(\mathbf{x}, \mathbf{x}') = \sum_{i=1}^N \chi_i(\mathbf{x}) \chi_i^*(\mathbf{x}'), \quad (28)$$

and the 2-RDM is

$$\Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = \gamma(\mathbf{x}_1, \mathbf{x}'_1) \gamma(\mathbf{x}_2, \mathbf{x}'_2) - \gamma(\mathbf{x}_1, \mathbf{x}'_2) \gamma(\mathbf{x}_2, \mathbf{x}'_1). \quad (29)$$

For a Slater determinant, the 2-RDM can be written explicitly as a sum over occupied orbitals. A standard (and very instructive) form is:

$$\Gamma(1, 2; 1', 2') = \sum_{i=1}^N \sum_{j=1}^N \left[ \chi_i(1) \chi_j(2) \chi_i^*(1') \chi_j^*(2') - \chi_i(1) \chi_j(2) \chi_j^*(1') \chi_i^*(2') \right],$$

where we use the short notation  $1 \equiv \mathbf{x}_1$ ,  $1' \equiv \mathbf{x}'_1$ , etc.

There are two important messages in this expression:

- The *first term* (sometimes called the “direct” contraction) corresponds to pairing  $\chi_i(1)$  with  $\chi_i^*(1')$  and  $\chi_j(2)$  with  $\chi_j^*(2')$ .
- The *second term* swaps the primed labels between the orbitals. This is the **exchange** structure and it appears because the determinant is antisymmetric: swapping two electron labels changes the sign of the wavefunction, and that sign survives in the two-particle object.

Now the crucial observation: using the determinant 1-RDM in Eq. (28),

$$\gamma(1, 1') = \sum_{i=1}^N \chi_i(1) \chi_i^*(1'), \quad \gamma(2, 2') = \sum_{j=1}^N \chi_j(2) \chi_j^*(2'),$$

the product  $\gamma(1, 1') \gamma(2, 2')$  expands to

$$\gamma(1, 1') \gamma(2, 2') = \sum_{i,j} \chi_i(1) \chi_j(2) \chi_i^*(1') \chi_j^*(2'),$$

which matches *exactly* the first (direct) term of  $\Gamma$  above. Similarly,

$$\gamma(1, 2') = \sum_i \chi_i(1) \chi_i^*(2'), \quad \gamma(2, 1') = \sum_j \chi_j(2) \chi_j^*(1'),$$

so

$$\gamma(1, 2') \gamma(2, 1') = \sum_{i,j} \chi_i(1) \chi_j(2) \chi_i^*(2') \chi_j^*(1'),$$

which matches the second (exchange) term. Putting both pieces together yields Eq. (29):

$$\Gamma(1, 2; 1', 2') = \gamma(1, 1') \gamma(2, 2') - \gamma(1, 2') \gamma(2, 1').$$

**Physical interpretation.** The minus sign is the mathematical signature of the Pauli principle at the two-particle level. Even before we do any energy minimization, the *structure* of the determinant

automatically builds in an “exchange hole”: same-spin electrons avoid each other, which lowers the energy relative to the naive classical (direct) Coulomb picture.

Equation (29) is the origin of exchange.

**One-body operator expectation (derivation).** For a local one-body operator,  $o(\mathbf{x}, \mathbf{x}') = o(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')$ ,

$$\left\langle \Phi \left| \sum_i \hat{o}(i) \right| \Phi \right\rangle = \int d\mathbf{x} d\mathbf{x}' \gamma(\mathbf{x}', \mathbf{x}) o(\mathbf{x}) \delta(\mathbf{x} - \mathbf{x}') = \int d\mathbf{x} \gamma(\mathbf{x}, \mathbf{x}) o(\mathbf{x}) \quad (30)$$

$$= \sum_{i=1}^N \int d\mathbf{x} \chi_i^*(\mathbf{x}) o(\mathbf{x}) \chi_i(\mathbf{x}) = \sum_{i=1}^N \langle \chi_i | \hat{o} | \chi_i \rangle. \quad (31)$$

**Two-body operator expectation (derivation).** For the Coulomb interaction,  $w(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = r_{12}^{-1}\delta(\mathbf{x}_1 - \mathbf{x}'_1)\delta(\mathbf{x}_2 - \mathbf{x}'_2)$ ,

**Shorthand notation.** From here on we use compact labels for electron coordinates:

$$1 \equiv \mathbf{x}_1, \quad 2 \equiv \mathbf{x}_2, \quad 1' \equiv \mathbf{x}'_1, \quad 2' \equiv \mathbf{x}'_2, \quad d1 \equiv d\mathbf{x}_1, \quad d2 \equiv d\mathbf{x}_2, \quad r_{12} \equiv |\mathbf{r}_1 - \mathbf{r}_2|.$$

This keeps the algebra readable while preserving the full space+spin dependence.

$$\left\langle \Phi \left| \sum_{i < j} \frac{1}{r_{ij}} \right| \Phi \right\rangle = \frac{1}{2} \int d1 d2 \Gamma(1, 2; 1, 2) \frac{1}{r_{12}} \quad (32)$$

$$= \frac{1}{2} \int d1 d2 \left( \gamma(1, 1)\gamma(2, 2) - \gamma(1, 2)\gamma(2, 1) \right) \frac{1}{r_{12}}. \quad (33)$$

Substitute (28) and expand the sums to obtain the direct-minus-exchange structure:

$$\left\langle \Phi \left| \sum_{i < j} \frac{1}{r_{ij}} \right| \Phi \right\rangle = \frac{1}{2} \sum_{i,j} J_{ij} - \frac{1}{2} \sum_{i,j} K_{ij}, \quad (34)$$

with

$$J_{ij} = \iint \frac{|\chi_i(1)|^2 |\chi_j(2)|^2}{r_{12}} d1 d2, \quad (35)$$

$$K_{ij} = \iint \frac{\chi_i^*(1)\chi_j^*(2)\chi_j(1)\chi_i(2)}{r_{12}} d1 d2. \quad (36)$$

**HF energy and its physical meaning.** Therefore,

$$E_{\text{HF}}[\{\chi\}] = \sum_{i=1}^N \left\langle \chi_i \left| \hat{h} \right| \chi_i \right\rangle + \frac{1}{2} \sum_{i,j} (J_{ij} - K_{ij}). \quad (37)$$

The one-electron term is kinetic + electron–nucleus. The  $J$  term is classical Coulomb repulsion between charge clouds. The  $K$  term is exchange (a nonlocal quantum effect of antisymmetry).

**Constrained minimization: deriving the HF equations.**

Introduce Lagrange multipliers  $\varepsilon_{ij}$  and define

$$\mathcal{L}[\{\chi\}] = E_{\text{HF}}[\{\chi\}] - \sum_{i,j} \varepsilon_{ij} (\langle \chi_i | \chi_j \rangle - \delta_{ij}). \quad (38)$$

Compute  $\delta\mathcal{L}$  under  $\chi_i^* \rightarrow \chi_i^* + \delta\chi_i^*$ .

Using the variations derived in the text and writing the constraint variation explicitly, the full variation can be written as

$$\delta\mathcal{L} = \sum_{i=1}^N \int d1 \delta\chi_i^*(1) \left[ \hat{h}(1)\chi_i(1) + \sum_{j=1}^N ((\hat{J}_j\chi_i)(1) - (\hat{K}_j\chi_i)(1)) - \sum_{j=1}^N \varepsilon_{ij}\chi_j(1) \right]. \quad (39)$$

Since each  $\delta\chi_i^*(1)$  is arbitrary, the bracket must vanish:

$$\hat{h}(1)\chi_i(1) + \sum_{j=1}^N (\hat{J}_j - \hat{K}_j)\chi_i(1) = \sum_{j=1}^N \varepsilon_{ij}\chi_j(1). \quad (40)$$

Define the Fock operator  $\hat{f} \equiv \hat{h} + \sum_j (\hat{J}_j - \hat{K}_j)$ , so  $\hat{f}\chi_i = \sum_j \varepsilon_{ij}\chi_j$ . Diagonalizing the Hermitian multiplier matrix yields the canonical Hartree–Fock equations

$$\hat{f}\chi_i = \varepsilon_i\chi_i. \quad (41)$$

### Hartree–Fock (HF) working equation.

The canonical Hartree–Fock equations are the single-particle eigenvalue problem

$$\boxed{\hat{f}\chi_i = \varepsilon_i\chi_i}, \quad \hat{f} = \hat{h} + \sum_{j=1}^N (\hat{J}_j - \hat{K}_j),$$

with  $\hat{h} = -\frac{1}{2}\nabla^2 + v(\mathbf{r})$  and  $\hat{J}_j, \hat{K}_j$  the Coulomb and exchange operators built from the occupied orbitals. The equations are solved self-consistently because  $\hat{f}$  depends on  $\{\chi_j\}$ .

## 5 Kohn–Sham DFT: variational derivation.

The HK theorems guarantee that the exact ground-state energy can be obtained by minimizing

$$E_v[\rho] = F[\rho] + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r},$$

where the *universal* functional  $F[\rho]$  contains the kinetic energy and the electron–electron interaction:

$$F[\rho] = T[\rho] + E_{ee}[\rho].$$

The difficulty is that  $F[\rho]$  is not known in closed form. Kohn and Sham introduced a clever decomposition that (i) keeps the dominant pieces explicit and computable, and (ii) bundles the remaining unknown part into a single functional.

**How the Kohn–Sham decomposition is constructed.** Start by adding and subtracting two quantities that we *can* write explicitly:

- $T_s[\rho]$ , the kinetic energy of a fictitious *non-interacting* system that reproduces the same density  $\rho$ ;
- $J[\rho]$ , the classical (Hartree) Coulomb energy of the density  $\rho$ .

Formally,

$$\begin{aligned} F[\rho] &= T[\rho] + E_{ee}[\rho] \\ &= T_s[\rho] + \underbrace{(T[\rho] - T_s[\rho])}_{\text{"kinetic correlation"}} + J[\rho] + \underbrace{(E_{ee}[\rho] - J[\rho])}_{\text{exchange + correlation}}. \end{aligned}$$

All the complicated remainder is then defined as the exchange–correlation functional:

$$E_{xc}[\rho] \equiv (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]).$$

With this *definition*, the exact energy functional becomes

$$E[\rho] = T_s[\rho] + J[\rho] + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho],$$

which is the central Kohn–Sham form written below as Eq. (42).

**What each term represents physically.**  $T_s$  is a kinetic-energy model that we can compute from single-particle orbitals;  $J$  is classical electrostatics;  $\int \rho v$  is electron–nucleus (or, more generally, external) potential energy;  $E_{xc}$  corrects both the kinetic and interaction pieces beyond these simple forms.

We start from the Kohn–Sham decomposition of the exact energy:

$$E[\rho] = T_s[\rho] + J[\rho] + \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} + E_{xc}[\rho], \quad (42)$$

with

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (43)$$

The density is represented by orthonormal Kohn–Sham orbitals  $\{\varphi_i\}$ :

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2, \quad \langle \varphi_i | \varphi_j \rangle = \int d\mathbf{r} \varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r}) = \delta_{ij}. \quad (44)$$

The non-interacting kinetic energy is

$$T_s[\rho] = -\frac{1}{2} \sum_{i=1}^N \int d\mathbf{r} \varphi_i^*(\mathbf{r})\nabla^2\varphi_i(\mathbf{r}). \quad (45)$$

We minimize  $E[\rho]$  with respect to  $\{\varphi_i^*\}$  under (44).

**Goal of the Kohn–Sham variational step.** At this stage,  $E[\rho]$  is a functional of the density, and the density is a functional of the orbitals via

$$\rho(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2.$$

Therefore, minimizing  $E[\rho]$  with respect to the orbitals is a *constrained functional minimization problem*: we must vary  $\{\varphi_i^*\}$  while preserving orthonormality (44).

**HF vs KS: what is the difference?** In Hartree–Fock, the energy is an explicit functional of the occupied orbitals (through Coulomb and exchange operators), so the variational problem is “orbital-only”. In Kohn–Sham DFT, the fundamental functional is written in terms of the density, and the orbitals enter because we represent  $\rho$  as  $\rho = \sum_i |\varphi_i|^2$ . In both cases the *same mathematical constraint* appears: the orbitals must remain orthonormal, which is enforced with Lagrange multipliers.

The orthonormality conditions are a set of  $N^2$  constraints:

$$\langle \varphi_i | \varphi_j \rangle - \delta_{ij} = \int d\mathbf{r} \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) - \delta_{ij} = 0, \quad i, j = 1, \dots, N. \quad (46)$$

We enforce them with a Hermitian matrix of Lagrange multipliers  $\varepsilon_{ij}$ .

**We now compute  $\delta\mathcal{L}_{KS}/\delta\varphi_i^*$  term-by-term.** To make the logic transparent, we first write the variation of each energy component *before* assembling the final bracket.

**Kinetic term  $T_s$ .** Start from

$$T_s[\rho] = -\frac{1}{2} \sum_i \int d\mathbf{r} \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}).$$

Varying  $\varphi_i^* \rightarrow \varphi_i^* + \delta\varphi_i^*$  gives

$$\delta T_s = -\frac{1}{2} \sum_i \int d\mathbf{r} \delta\varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}),$$

so the functional derivative is

$$\frac{\delta T_s}{\delta\varphi_i^*(\mathbf{r})} = -\frac{1}{2} \nabla^2 \varphi_i(\mathbf{r}).$$

**External potential term  $\int \rho v$ .** Using  $\rho = \sum_k |\varphi_k|^2$ ,

$$\int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} = \sum_k \int d\mathbf{r} \varphi_k^*(\mathbf{r}) v(\mathbf{r}) \varphi_k(\mathbf{r}).$$

Varying with respect to  $\varphi_i^*$  selects the  $k = i$  term:

$$\delta \left( \int \rho v \right) = \int d\mathbf{r} \delta\varphi_i^*(\mathbf{r}) v(\mathbf{r}) \varphi_i(\mathbf{r}),$$

hence

$$\frac{\delta}{\delta\varphi_i^*(\mathbf{r})} \left( \int \rho v \right) = v(\mathbf{r}) \varphi_i(\mathbf{r}).$$

**Hartree term**  $J[\rho]$ . Start from

$$J[\rho] = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

A standard functional-derivative calculation gives

$$\frac{\delta J}{\delta \rho(\mathbf{r})} = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \equiv v_H(\mathbf{r}).$$

Now use the chain rule: under a variation of  $\varphi_i^*$ , the induced density variation is

$$\delta\rho(\mathbf{r}) = \delta(|\varphi_i(\mathbf{r})|^2) = \delta\varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r}) + \underbrace{\varphi_i^*(\mathbf{r})\delta\varphi_i(\mathbf{r})}_{\text{independent variation}}.$$

Keeping only the  $\delta\varphi_i^*$  part (because we take  $\delta/\delta\varphi_i^*$ ),

$$\delta J = \int d\mathbf{r} \frac{\delta J}{\delta \rho(\mathbf{r})} \delta\rho(\mathbf{r}) = \int d\mathbf{r} v_H(\mathbf{r}) \delta\varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}),$$

so

$$\frac{\delta J}{\delta\varphi_i^*(\mathbf{r})} = v_H(\mathbf{r}) \varphi_i(\mathbf{r}).$$

**Exchange–correlation term**  $E_{xc}[\rho]$ . By definition,

$$v_{xc}(\mathbf{r}) \equiv \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}.$$

Using the same chain rule as above,

$$\delta E_{xc} = \int d\mathbf{r} v_{xc}(\mathbf{r}) \delta\rho(\mathbf{r}) \Rightarrow \frac{\delta E_{xc}}{\delta\varphi_i^*(\mathbf{r})} = v_{xc}(\mathbf{r}) \varphi_i(\mathbf{r}).$$

**Constraint term.** The constraint contribution is

$$-\sum_{i,j} \varepsilon_{ij} (\langle \varphi_i | \varphi_j \rangle - \delta_{ij}) = -\sum_{i,j} \varepsilon_{ij} \left( \int d\mathbf{r} \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) - \delta_{ij} \right).$$

Varying with respect to  $\varphi_i^*(\mathbf{r})$  yields

$$\frac{\delta}{\delta\varphi_i^*(\mathbf{r})} \left[ -\sum_{k,j} \varepsilon_{kj} \int d\mathbf{r} \varphi_k^*(\mathbf{r}) \varphi_j(\mathbf{r}) \right] = -\sum_j \varepsilon_{ij} \varphi_j(\mathbf{r}).$$

The important point is that the multiplier matrix couples orbital  $i$  to all orbitals  $j$ .

With these pieces in hand, we now assemble the full  $\delta\mathcal{L}_{KS}$  and set its bracket to zero.

Introduce Lagrange multipliers  $\varepsilon_{ij}$  and define the constrained functional

$$\mathcal{L}_{KS}[\{\varphi\}] = E[\rho] - \sum_{i,j} \varepsilon_{ij} (\langle \varphi_i | \varphi_j \rangle - \delta_{ij}). \quad (47)$$

Vary  $\varphi_i^* \rightarrow \varphi_i^* + \delta\varphi_i^*$  and collect the result into the standard “variation equals arbitrary test function times a bracket” form:

$$\delta\mathcal{L}_{KS} = \sum_i \int d\mathbf{r} \delta\varphi_i^*(\mathbf{r}) \left[ -\frac{1}{2}\nabla^2\varphi_i(\mathbf{r}) + (v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}))\varphi_i(\mathbf{r}) - \sum_j \varepsilon_{ij}\varphi_j(\mathbf{r}) \right]. \quad (48)$$

Because the variations  $\delta\varphi_i^*(\mathbf{r})$  are arbitrary test functions, the only way for Eq. (48) to hold for *all* variations is that the bracket multiplying each  $\delta\varphi_i^*(\mathbf{r})$  vanishes pointwise. In other words, we impose the Euler–Lagrange condition by setting

$$\left[ -\frac{1}{2}\nabla^2\varphi_i(\mathbf{r}) + (v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}))\varphi_i(\mathbf{r}) - \sum_j \varepsilon_{ij}\varphi_j(\mathbf{r}) \right] = 0 \quad \text{for each } i.$$

Rearranging this expression yields the Kohn–Sham equation in its general (matrix) form:

$$\left[ -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \sum_j \varepsilon_{ij}\varphi_j(\mathbf{r}). \quad (49)$$

As in Hartree–Fock, the multiplier matrix  $\varepsilon_{ij}$  is Hermitian and can be diagonalized by a unitary rotation among orbitals. In the corresponding (canonical) orbital basis, the equations become

$$\left[ -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}). \quad (50)$$

### Kohn–Sham (KS) working equation.

The Kohn–Sham equations are the single-particle eigenvalue problem

$$\boxed{\left[ -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})}.$$

The effective terms  $v_H$  and  $v_{xc}$  are *functionals of the density*  $\rho(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2$ , so the KS problem is solved self-consistently: orbitals  $\rightarrow$  density  $\rightarrow$  potentials  $\rightarrow$  new orbitals.