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Review article

Density Functional Theory: From The Many-Body Schrödinger Equation to the Kohn–Sham Methodology

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Abstract
Density functional theory (DFT) describes the ground-state electron density and energy of matter. This paper traces the theoretical path from the many-body Schrödinger equation, which describes a system of nuclei and electrons completely but cannot be solved for any real system, to the Kohn-Sham methodology. We review the Born-Oppenheimer approximation, which fixes the nuclei and solves only for the motion of the electrons; the Hartree-Fock approximation, which uses a Slater determinant of individual spin-orbitals but neglects electron correlation; and the Hohenberg–Kohn theorems, which show that the electron density alone suffices to describe the system. The Kohn–Sham construction, based on a fictitious non-interacting system moving in an effective potential, confines all the unknown physics into the exchange–correlation energy, and the self-consistent field (SCF) loop used to solve the Kohn-Sham equations is described. Finally, approximations to the exchange–correlation energy are presented, from the local density approximation (LDA) through generalized gradient approximations (GGA, PBE), meta-GGA (SCAN) and hybrid functionals, including range-separated hybrids and the self-consistent choice of the mixing fraction, together with Jacob's ladder and a comparison of accuracy and computational cost. The assumptions underlying the Kohn–Sham scheme and the main limitations of current approximations — self-interaction and delocalization errors, strongly correlated systems and dispersion — are also discussed.
Keywords: Density Functional Theory, Born–Oppenheimer Approximation, Hartree–Fock, Kohn–Sham Equations.

Introduction

Why Do We Need a New Method to Describe Electrons?

The paper is organized in five parts: (i) general introduction — why we need a new theory to describe electrons in matter; (ii) the Born–Oppenheimer approximation — separating nuclear motion from electronic motion; (iii) the Hartree–Fock approximation — from a many-body wavefunction to independent orbitals; (iv) density functional theory (DFT) — from Hohenberg–Kohn to Kohn–Sham, including the assumptions on which the Kohn–Sham scheme rests, and exchange–correlation approximations; (v) the main limitations of present-day DFT.

An Equation That Describes Everything... and Cannot Be Solved

Any piece of matter around us - a crystal, a molecule, or even the human body - is, at its core, nothing but a collection of nuclei and electrons bound together by Coulomb forces. In principle, the Schrödinger- equation describes this system completely and exactly:

$$\hat{H}\Psi(r_1, r_2, \dots, r_N) = E\Psi(r_1, r_2, \dots, r_N) \quad (1)$$

The problem. The number of interacting variables is enormous: even for a medium-sized molecule, the wavefunction Ψ depends on thousands of entangled coordinates. The computational cost of solving this equation as it stands grows exponentially with the number of electrons itself, making a direct solution practically impossible for any real system beyond a few atoms.

This is why, over the past century, physicists have resorted to building a series of clever approximations - each simplifying the problem slightly at the cost of some accuracy - arriving at tools that can actually be applied to real crystals and molecules [1–3].

Three Milestones on This Journey

In this paper we will trace three theories, each built upon the previous one, each solving part of the problem left by the one before:

1. **Born–Oppenheimer.** We fix the nuclei in place (since they are far heavier than the electrons), focusing the solution on the motion of the electrons alone.
2. **Hartree–Fock.** We approximate the collective wavefunction using a Slater determinant of individual spin-orbitals, turning the *N*-electron problem into *N* coupled one-electron problems.
3. **Density functional theory.** We replace the fully complex wavefunction with a much simpler quantity: the electron density $\rho(r)$, drastically reducing computational complexity [1–3].

The Born–Oppenheimer Approximation

Step One: Freezing the Nuclear Motion

Why Can We Freeze the Nuclei?

The fundamental physical observation. Even the lightest nucleus (the proton) is about 1836 times heavier than the electron. This means the nuclei move far more slowly than the electrons - to the point that the electrons effectively "see" the nuclei as nearly stationary at every instant.

Born and Oppenheimer (1927) proposed splitting the problem into two independent parts:

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- **The electronic part.** We solve the Schrödinger equation for the electrons alone, assuming the nuclear positions are fixed (given as a parameter, not a variable).
- **The nuclear part.** We treat the nuclei as heavy classical particles, moving in a potential generated by the average distribution of the electrons [1–3].

The Full Hamiltonian of the System

Before any approximation, the Hamiltonian of the electron–nucleus system contains five terms [1–3]:

$$H = \sum_i \left(-\frac{\hbar^2 \nabla_i^2}{2m_e}\right) + \sum_k \left(-\frac{\hbar^2 \nabla_k^2}{2M_{noy}}\right) - \sum_k \sum_i \frac{Z_k e^2}{4\pi\varepsilon_0 r_{ik}} + \frac{1}{2}\sum_{i\neq j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \frac{1}{2}\sum_{k\neq h} \frac{Z_h Z_k e^2}{4\pi\varepsilon_0 r_{hk}} \quad (2)$$

where

V_{e-e}	Electrostatic repulsion between electrons;
T_e	Kinetic energy of the electrons;
$V_{noy-noy}$	Electrostatic repulsion between nuclei;
T_{noy}	Kinetic energy of the nuclei;
V_{e-noy}	Electrostatic attraction: electrons with nuclei.

Simplifying the Notation: Atomic Units

To avoid repeating physical constants in every equation, physicists adopt the atomic unit system, in which these quantities are set to a value of 1:

$4\pi\varepsilon_0 = 1$	Coulomb constant
$e = 1$	Elementary charge
$\hbar = 1$	Reduced Planck constant
$m_e = 1$	Electron mass

The benefit. With this choice, all physical constants disappear from the equations, making their formulation cleaner and easier to handle mathematically and computationally - this is the system used throughout the modern literature on DFT and electronic-structure calculations [1–3].

Separating the Wavefunction

By fixing the nuclei, their potential on the electrons becomes a given constant, so the Schrödinger equation for the total system separates into two equations: one for the nuclei within an average potential, and another for the electrons at given nuclear positions. The total wavefunction is then written as a product:

$$\Psi(r, R) = \Psi_R(r) \times \varphi(R) \quad (3)$$

where

$\phi(R)$	is the nuclear wavefunction, describing the motion of the nuclei within an average potential generated by the electrons;
$\Psi_R(r)$	is the electronic wavefunction, computed at a given fixed nuclear configuration R [1–3].

Why Isn't This Approximation Enough on Its Own?

The remaining obstacle. The electronic Hamiltonian contains three terms: the kinetic energy, the electrostatic attraction to the nuclei, and the electrostatic repulsion among the electrons themselves. This last term is a two-electron term (coupling every pair of electrons to each other), which prevents separating the *n*-electron equation into *n* simple one-electron equations.

Summary. The Born–Oppenheimer approximation solves the problem of the nuclei, but leaves the problem of electron–electron interaction unresolved. This is exactly what the next two theories - Hartree–Fock and then DFT - will each attempt to address, each in its own way [1–3].

The Hartree–Fock Approximation

From a Collective Wavefunction to Independent Orbitals

Hartree's Idea: Independent Particles

The idea. Even after the Born–Oppenheimer approximation, the mutual repulsion of the electrons remains an obstacle. Hartree proposed a bold simplification: instead of solving one complex equation for all the electrons together, we assume each electron moves independently, affected only by an average field generated by the rest of the electrons (rather than by the instantaneous details of their motion).

Under this assumption, the total wavefunction is written as a simple product of individual one-electron orbitals:

$$\Psi(1,2,\ldots,n) = \prod_i \varphi_i(i) \quad (4)$$

The result. The Schrödinger equation for *n* electrons separates into *n* much simpler one-electron equations, which can be solved numerically [2,4].

The Gap: The Pauli Exclusion Principle

Where does the flaw lie? Hartree's assumption (a wavefunction as a simple product of orbitals) does not account for the fact that electrons are fermions: the total wavefunction must be antisymmetric under the exchange of any two electrons. In

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other words, no two electrons can occupy exactly the same quantum state - this is the Pauli exclusion principle, which Pauli himself formulated through the concept of spin.

Why does this matter? Without this constraint, all electrons could in theory "collapse" into the lowest-energy orbital, which would contradict the stability of matter and the real shell structure of atoms. The Pauli principle is responsible for the gradual filling of electron shells, and therefore for the periodic table itself [2,4].

Fock's Contribution: The Slater Determinant

The solution. Fock introduced an elegant correction: instead of the simple product, the wavefunction is written as a Slater determinant - a matrix determinant of the individual orbitals, which automatically guarantees the required antisymmetry under the exchange of any two electrons:

$$\Psi_{1\dots n}(x_1, x_2, \dots, x_n) = \frac{1}{\sqrt{n!}} \det\left[\varphi_i(x_j)\right] \tag{5}$$

Note. The variable $x = (r, \sigma)$ combines the spatial position r and the spin state σ into a single variable — known as the spin-orbital [2,4].

The System's Energy: The Coulomb and Exchange Operators

Substituting the Slater determinant into the energy expression yields a sum containing two distinct terms in addition to the one-electron term:

- **K_i - the exchange operator.** A non-local operator arising from antisymmetry; it has no classical counterpart, and is known as the exchange energy.
- **J_i - the Coulomb operator.** Represents the average electrostatic potential generated by the remaining electrons; simply, the classical Coulomb repulsion between charges.

$$E_{HF} = \sum_i h\,(i) + \sum_{ij} \left[J_{ij} - K_{ij}\right] \tag{6}$$

Total electronic energy = the sum of the occupied orbital energies, corrected by the Coulomb and exchange energies [2,4].

From the Basic Integrals to the Correct Total Energy

To write the Hartree–Fock energy precisely, we define, in terms of the spin-orbitals ϕ_i, three integrals: $I(i)$ - the energy of a single electron in the nuclear potential, $J(i,j)$ - the classical Coulomb integral, and $K(i,j)$ - the exchange integral (with no classical counterpart, arising directly from the Pauli interaction):

$$I(i) = \langle\varphi_i(r)\left|-\frac{1}{2}\nabla^2 - \sum_a \frac{Z_a}{r_{ia}}\right|\varphi_i(r)\rangle, \quad J(i,j) = \langle\varphi_i\varphi_j\left|\frac{1}{r_{12}}\right|\varphi_i\varphi_j\rangle, \quad K(i,j) = \langle\varphi_i\varphi_j\left|\frac{1}{r_{12}}\right|\varphi_j\varphi_i\rangle \tag{7}$$

$$E^T = \sum_i E\,(i) - \sum_{ij}\left(2J_{ij} - K_{ij}\right) \tag{8}$$

Important note: the total energy is not simply the sum of the orbital energies ε_i. Adding them directly counts the repulsion interaction between every pair of electrons twice (once from the perspective of each electron in the pair), so the correction term $\Sigma(2J_{ij}-K_{ij})$ must be subtracted to remove this double-counting — this is exactly the subtle difference between the two equations above [2,4].

How Do We Find the Best Orbitals? The Variational Principle

The idea. We search for the orbitals ϕ_i that minimize the total energy of the system, subject to a fundamental constraint: these orbitals must remain orthonormal - otherwise they would lose their physical meaning as independent quantum states.

This constraint is imposed through the method of Lagrange multipliers $L = E_{HF} - \Sigma\lambda_{ij}(\langle\phi_i|\phi_j\rangle - \delta_{ij})$, and minimizing it with respect to the orbitals ($\delta L/\delta\phi_i = 0$) leads directly to an effective one-electron operator - the Fock operator $\hat{F}$ - defined as follows:

$$\hat{F} = \hat{h}(r) + \sum_j \left(2\hat{J}_j - \hat{K}_j\right) \tag{9}$$

$\hat{h}(r)$ is the one-electron Hamiltonian (kinetic energy + nuclear potential), and $\Sigma_j(2\hat{J}_j - \hat{K}_j)$ collects the Coulomb and exchange contributions from the rest of the electrons. Fully minimizing L leads to the eigenvalue equation $\hat{F}\phi_i = \varepsilon_i\phi_i$, given in Eq. (10) below [2,4].

The Hartree–Fock Equations

The canonical orbitals. With a suitable choice of linear combination of the orbitals, the Lagrange multipliers can be simplified to purely diagonal values ε_i, the canonical orbital energies:

$$\hat{F}\varphi_i = \varepsilon_i\varphi_i \tag{10}$$

Interpretation of the orbital energies. By Koopmans' theorem [2,5], $-\varepsilon_i$ equals an ionization energy only in the frozen-orbital approximation; orbital relaxation and correlation are neglected, so the ε_i are approximate, and the gap between occupied and empty orbital energies is greatly overestimated [2].

The Fock operator. Importantly, F depends on the very orbitals ϕ_i we are looking for — so the equation is nonlinear and must be solved iteratively (self-consistent field) [2,4].

The Practical Solution: SCF and LCAO

The LCAO basis. In practice, each orbital ϕ_i is written as a linear combination of known basis functions (usually atomic orbitals): $\phi_i = \Sigma\, c_{\mu i}\,\chi_\mu$. This turns the differential problem into an algebraic (matrix) problem that can be solved efficiently on a computer.

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The self-consistent field (SCF). Since the Fock operator *F* depends on the orbitals themselves, we solve the equation iteratively: we guess initial orbitals, build the Fock operator, solve for new orbitals, and repeat until the results no longer change between successive cycles (convergence).
This combination (SCF + LCAO) is what makes Hartree–Fock, despite its age, still used as a starting point in much of modern quantum chemistry software [2,4].

What's Still Missing?

Electron correlation energy. Hartree–Fock assumes that each electron moves in a fixed average field generated by the rest, ignoring the fact that the motion of each electron is instantaneously affected by the precise positions of the other electrons (avoiding getting close to them). This neglected instantaneous correlation is called the electron correlation energy:

$$E_c = E_{exact} - E_{HF} \quad (11)$$

Because Hartree–Fock ignores this correlation entirely, it always overestimates the total energy of the system ($E_{HF} \geq E_{exact}$) [2,4].

Summary Assessment of the Method

Table 1. Strengths and weaknesses of the Hartree–Fock method [2,4].

Strengths	Weaknesses
• A rigorous and straightforward theoretical foundation • Incorporates the Pauli principle exactly via the Slater determinant • A reliable starting point for more accurate methods (such as CI and Coupled-Cluster) • Computationally efficient for small and medium-sized molecules	• Completely neglects the electron correlation energy • Always overestimates the total energy • Its computational cost grows rapidly with system size • Insufficient for describing many properties of solids

Density Functional Theory

From Hohenberg–Kohn to Kohn–Sham, and Exchange–Correlation Approximations

The Revolutionary Idea: Density Instead of the Wavefunction

The radical shift. Even with Hartree–Fock, the wavefunction Ψ - the central quantity in quantum mechanics - remains highly complex: it depends on 3*N* spatial coordinates for *N* electrons. In the late 1960s, Hohenberg and Kohn proposed a radical idea: what if we replaced Ψ with a much simpler quantity - the electron density $\rho(r)$ - which depends on only 3 coordinates, regardless of the number of electrons? [1,2,6]

Table 2. Comparison between the electron density and the many-electron wavefunction.

Quantity	Description
$\rho(r)$	An electron density with only 3 coordinates, a quantity directly measurable experimentally.
$\Psi(r_1, \ldots, r_N)$	A complex wavefunction with 3*N* coordinates, not directly measurable.

Why Is This Simplification So Remarkable?

From the wavefunction to the density. The electron density is obtained from the wavefunction by partial integration over all electrons but one:

$$n(r) = N \int d^3r_2 \cdots d^3r_N \, |\Psi(r, r_2, \ldots, r_N)|^2 \quad (12)$$

The practical impact. With this transition, we move from a problem with 3*N*+1 coordinates (degrees of freedom) to a problem with only three spatial coordinates - an enormous simplification that makes calculating large systems (crystals, proteins) practically feasible, something that could never be achieved by working with Ψ directly [1,2,6].

The First Hohenberg–Kohn Theorem

The central idea. Since the charge and mass of the electron are universal constants, the only factor determining the shape of the ground-state electron density is the external potential $V(r)$ generated by the nuclei. Hohenberg and Kohn (1964) proved that this relationship is reversible: the density $\rho_0(r)$ alone - with no additional information - uniquely determines the external potential $V(r)$ (up to a trivial additive constant).

The profound consequence. Since $V(r)$ determines the full Hamiltonian, and therefore all the properties of the system, the ground-state density $\rho_0(r)$ determines - in principle - everything about the system: the energy, the wavefunction, and all observable properties [1,2,6].

A Glimpse of the Proof: By Contradiction

1. Suppose, for the sake of argument, that two different potentials $V(r)$ and $V'(r)$ (differing by more than an additive constant) produce the same ground-state density $\rho_0(r)$.
2. Each potential corresponds to a different Hamiltonian (*H* and *H'*), and therefore to two different wavefunctions (Ψ and Ψ') that share the same density $\rho_0(r)$.

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3. Using the variational principle, one can show that this leads to a contradiction in the ordering of the two energies E_0 and E_0' (each would have to be smaller than the other simultaneously).
4. The contradiction means the original assumption is false: two different potentials cannot produce the same ground-state density.

This proves that the relationship between $V(r)$ and $\rho_0(r)$ is one-to-one in both directions [1,2,6].

The Total Energy as a Functional of the Density

Since $\rho(r)$ determines everything, the total ground-state energy is written as a functional of the density, with three components [1,2,6]:

$T[\rho]$	The kinetic energy of the electrons;
$U[\rho]$	The mutual repulsion energy of the electrons;
$V[\rho]$	The interaction energy of the electrons with the external potential (the nuclei).

$$E[\rho] = T[\rho] + U[\rho] + V[\rho] = F[\rho] + \int V(r)\rho(r)\,dr \tag{13}$$

The Universal Functional F[ρ]

Why "universal"? Note that the terms $T[\rho]$ and $U[\rho]$ do not depend on the particular system being studied - they describe only the motion of the electrons and their mutual repulsion, regardless of whether the system is a hydrogen atom or a silicon crystal. For this reason we combine them into a single functional called the universal functional (or the Hohenberg–Kohn functional):

$$F[\rho] = T[\rho] + U[\rho] \tag{14}$$

Once $F[\rho]$ is known (the same functional for every system), it suffices to specify the $V(r)$ of any particular system to compute its total energy [1,2,6].

The Second Hohenberg–Kohn Theorem: The Variational Principle

The principle. For any valid trial density $\rho'(r)$ (representing an integer number of electrons), the resulting energy $E[\rho']$ is greater than or equal to the true ground-state energy E_0 - with equality only when $\rho' = \rho_0$ exactly:

$$E[\rho'] \geq E_0 = E[\rho_0] \tag{15}$$

The practical significance. This turns finding the ground state into an optimization (minimization) problem: we search for the density that minimizes $E[\rho]$, exactly as we did earlier with the wavefunction in Hartree–Fock - except this time, the varying quantity is much simpler [1,2,6].

Minimization Constrained by the Number of Electrons

The necessary constraint. When minimizing $E[\rho]$, the total number of electrons N must be kept fixed - otherwise the density would lose its physical meaning:

$$\int \rho(r)\,dr - N = 0 \tag{16}$$

The corresponding Lagrangian:

$$E[\rho] - \lambda\left(\int \rho(r)\,dr - N\right) \tag{17}$$

Minimizing this Lagrangian ($\delta/\delta\rho = 0$) leads to the Euler–Lagrange equation, from which λ is identified physically as the chemical potential of the electrons [1,2,6].

The Dilemma: The Functional Has an Unknown Form

The practical problem. The two Hohenberg–Kohn theorems proved that $F[\rho]$ exists, and that a variational principle governs the search for the ground state. But they did not tell us the explicit mathematical form of $F[\rho]$. There is no known analytical formula for computing the kinetic energy $T[\rho]$ or the repulsion energy $U[\rho]$ directly from the density alone, for any real interacting system.

The theory is entirely correct... but it is not practically applicable in this form. This is exactly what Kohn and Sham would solve just one year later, in 1965 [1,4,7].

Kohn and Sham's Idea: A Fictitious Auxiliary System

The ingenious trick. Instead of trying to find a formula for $T[\rho]$ of the real interacting system (an extremely difficult problem), Kohn and Sham imagined an auxiliary system made of fictitious, non-interacting electrons, moving in an effective potential specifically designed so that they produce exactly the same electron density $\rho(r)$ as the real interacting system.

Why is this useful? The kinetic energy of a non-interacting system (T_f) has an exact, known formula in terms of its individual orbitals - exactly as in Hartree–Fock. We now only need to compute the small remaining difference between the real and fictitious systems [1,4,7].

Decomposing the Functional Step by Step

We rewrite $F[\rho]$ by adding and subtracting the kinetic energy of the fictitious non-interacting system $T_f[\rho]$, without changing its value:

$$F[\rho] = T_f[\rho] + U[\rho] + \big(T[\rho] - T_f[\rho]\big) \tag{18}$$

The difference between the real and fictitious kinetic energies is relatively small, and we call it the kinetic correlation energy: $E_c[\rho] = T[\rho] - T_f[\rho]$.

Similarly, we add and subtract the classical electrostatic Hartree energy $U_H[\rho]$ from the repulsion term $U[\rho]$ [1,4,7]:

$$U[\rho] = U_H[\rho] + (U[\rho] - U_H[\rho]), \quad E_x[\rho] = U[\rho] - U_H[\rho] \tag{19}$$

Arriving at the Exchange–Correlation Energy

Collecting all the previous terms, the universal functional becomes:

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$$F[\rho] = T_f[\rho] + U_H[\rho] + E_c[\rho] + E_x[\rho] \quad (20)$$

We combine the last two terms, unknown analytically, into a single functional: the exchange–correlation energy $E_{xc}[\rho]$:

$$F[\rho] = T_f[\rho] + U_H[\rho] + E_{xc}[\rho], \quad E_{xc}[\rho] = E_c[\rho] + E_x[\rho] \quad (21)$$

With this step, we have confined everything unknown, whose exact form we do not know, into a single relatively small term: $E_{xc}[\rho]$. Within the assumptions above this is exact in principle, but in practice $E_{xc}[\rho]$ must be approximated. All that remains now is finding good approximations for this single term — and this is the focus of the next part of this paper (the section on exchange–correlation approximations) [1,4,7].

What Does the Exchange–Correlation Energy Contain?

E_c - correlation. The instantaneous correlation in the motion of the electrons (avoiding spatial proximity), together with the correction for the difference between the real and fictitious kinetic energies.

E_x - exchange. The effect of the Pauli principle: it prevents two electrons of the same spin from occupying the same position, keeping them apart and lowering their mutual repulsion energy.

Why is this term relatively small? Because we have already separated out the bulk of the kinetic energy (T_f) and the classical repulsion energy (U_H) using exact, known formulas. What remains in E_{xc} is only fine quantum corrections - which makes it far easier to approximate than approximating $F[\rho]$ as a whole at once [1,4,7].

The Total Energy in Kohn–Sham Form

Adding the electrons' interaction with the external potential, the total energy of the system becomes:

$$E[\rho] = T_f[\rho] + U_H[\rho] + E_{xc}[\rho] + \int V(r)\rho(r)\,dr \quad (22)$$

Applying the variational principle. We minimize this energy with respect to the density $\rho(r)$ (or equivalently, in terms of the orbitals of the auxiliary system), while keeping the total number of electrons N fixed. The Hohenberg–Kohn variational principle guarantees that the density obtained at the minimum is the true ground-state density of the real interacting system - even though we work in practice with a fictitious non-interacting system [1,4,7].

The Kohn–Sham Effective Potential

From minimization to the potential. Minimizing the energy leads to an equation for a single effective potential $V_{KS}(r)$, felt by every electron in the fictitious system, which encapsulates all the complex physics of the real system:

$$V_{KS}(r) = V(r) + \int \frac{\rho(r')}{|r-r'|}\,dr' + \frac{\delta E_{xc}[\rho]}{\delta\rho(r)} \quad (23)$$

where the three terms are, respectively [1,4,7]:

$V(r)$	the external potential (the nuclei);
$\int \frac{\rho(r')}{\lvert r-r'\rvert}\,dr'$	the classical Hartree potential;
$\frac{\delta E_{xc}[\rho]}{\delta\rho(r)}$	the exchange–correlation potential.

The Kohn–Sham Equations

With this effective potential, the problem reduces to a single-particle Schrödinger equation - exactly as in Hartree–Fock, but with a simpler potential:

$$\left[-\frac{\hbar^2\nabla^2}{2m_e} + V_{KS}(r)\right]\varphi_i(r) = \varepsilon_i\varphi_i(r) \quad (24)$$

The Kohn–Sham orbitals ϕ_i. Fundamentally fictitious, mathematical orbitals (not necessarily representing real orbitals), but they are the tool from which we construct the density [1,4,7]:

$$\rho(r) = \sum_i |\varphi_i(r)|^2 \quad (25)$$

The Self-Consistent Field (SCF) Loop

What is SCF? An iterative loop used to find a system's stable, ground-state electron density and energy.

Why do we need it?

- Kohn–Sham equations require the electron density to build the potential.
- However, the electron density is calculated from the wavefunctions (orbitals) generated by those exact equations.
- To solve this mathematical circular dependency, we must use a back-and-forth guessing and refining loop.

The five-step SCF cycle. The five steps are summarized in Table 3.

Table 3. The five-step SCF cycle.

Step	Name	Description	Equation
1	Initial Guess	Construct a starting trial electron density (e.g., from isolated atoms).	$\rho_{\text{in}}(\mathbf{r})$
2	Build Potential	Calculate the effective potential (nuclear, Coulomb repulsion, and exchange-correlation).	$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})$

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Step	Name	Description	Equation
3	Solve Kohn–Sham	Compute the new wavefunctions and single-particle energy levels.	$\widehat{H}_{\mathrm{KS}}\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r})$
4	Update Density	Generate a brand-new output electron density from these wavefunctions.	$\rho_{\mathrm{out}}(\mathbf{r}) = \sum_i \lvert\varphi_i(\mathbf{r})\rvert^2$
5	Check Convergence	Compare input vs. output density.	$\lvert\rho_{\mathrm{out}}^{(n)} - \rho_{\mathrm{in}}^{(n)}\rvert < \delta$

If the difference is below the convergence threshold, the loop stops; if not, mix the densities and repeat from Step 2:

$$\rho_{\mathrm{in}}^{(n+1)} = (1-\alpha)\rho_{\mathrm{in}}^{(n)} + \alpha\rho_{\mathrm{out}}^{(n)} \quad (26)$$

Once converged: the density is self-consistent → calculate physical properties [1,4,7].

What Is Exact and What Is Approximate in Kohn–Sham DFT?

The Kohn–Sham scheme is exact in principle only if (i) the nuclei are fixed and the Hamiltonian is non-relativistic [1]; (ii) only ground-state quantities are considered, the Kohn–Sham orbitals and eigenvalues being auxiliary [1,2,6]; and (iii) the exact density can be reproduced by non-interacting electrons in a local effective potential (non-interacting V-representability), which is assumed and not rigorously proved [2,7]. In practice it is approximate, because $E_{xc}[\rho]$ is unknown and because of numerical approximations (basis set and cutoff, k-points, pseudopotentials, SCF convergence) [1,4].

The Complete Roadmap So Far

Table 4. The theoretical roadmap from the Schrödinger equation to the exchange–correlation energy.

Step	Description
Schrödinger	A many-body equation, impossible to solve
Born–Oppenheimer	Freezing the nuclei
Hohenberg–Kohn	The density $\rho(r)$ suffices to describe the system
Kohn–Sham	A fictitious system + an effective potential V_{KS}
$E_{xc}[\rho]$	The only term left to approximate (exact in principle, approximate in practice)

Where do we stand now? We have arrived at a formulation that is exact in principle, within the assumptions above, with a single relatively small unknown term: the exchange–correlation energy $E_{xc}[\rho]$, which in practice must be approximated. Finding good, practical approximations for this term has, since the 1960s, been the focus of active research in DFT — and it is the subject of the next part of this paper: from the simplest approximation (LDA) to the most advanced approximations (hybrids).

Exchange–Correlation Approximations

The Local Density Approximation (LDA)

The idea. The simplest possible approximation: we assume that every point r in the material behaves locally as if it were part of a homogeneous electron gas (with exactly the same density $\rho(r)$ at that point). Since the exact properties of the homogeneous electron gas are known analytically, we can borrow its formula to compute E_{xc} locally at each point, then integrate the contributions over all space:

$$E_{xc}^{LDA}[\rho] = \int \rho(r)\, \varepsilon_{xc}^{hom}\big(\rho(r)\big)\, dr \quad (27)$$

Here $\varepsilon_{xc}^{hom}(\rho)$ is the exchange–correlation energy per electron in a homogeneous gas of density ρ — a quantity known precisely from quantum Monte Carlo calculations [2,4].

The Exchange and Correlation Terms in LDA

The correlation term. It has no simple analytical formula; it is computed numerically with high precision via quantum Monte Carlo simulations of the homogeneous electron gas (Ceperley and Alder, 1980), and the numerical results are then fit with suitable analytical formulas (such as VWN).

The exchange term (Dirac formula). It has an exact analytical formula, known since the 1930s:

$$\varepsilon_x = -\frac{3}{4}\left(\frac{3\rho}{\pi}\right)^{1/3} \quad (28)$$

Adding the two terms together gives the first practical, complete approximation for the exchange–correlation energy, usable in real DFT calculations [2,4].

The VWN Functional: The Analytical Approximation of the Correlation Term

The idea. We saw that the correlation term ε_{xc}^{hom} has no simple analytical formula, and is computed numerically via quantum Monte Carlo simulations of a homogeneous electron gas (Ceperley and Alder, 1980). Vosko, Wilk, and Nusair (VWN, 1980) provided a precise analytical formula that fits these numerical results, and it remains the most widely used in practical LDA applications to this day:

$$\varepsilon_c^{VWN}(x) = \frac{A}{2}\left\{\ln\left[\frac{x^2}{X(x)}\right] + \frac{2b}{Q}\tan^{-1}\left(\frac{Q}{2x+b}\right) - \frac{bx_0}{X(x_0)}\left[\ln\left(\frac{(x-x_0)^2}{X(x)}\right) + \frac{2(b+2x_0)}{Q}\tan^{-1}\left(\frac{Q}{2x+b}\right)\right]\right\} \quad (29)$$

where $x = \sqrt{r_s}$, $X(x) = x^2 + bx + c$, $Q = \sqrt{(4c - b^2)}$, and $r_s = (3/4\pi\rho)^{1/3}$ is the Wigner–Seitz radius. The constants (unpolarized case): $A = 0.0621814$, $x_0 = -0.409286$, $b = 13.0720$, $c = 42.7198$ [2,4].

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When Does LDA Succeed and When Does It Fail?

Table 5. Strengths and weaknesses of the local density approximation [2,4].

Strengths	Weaknesses
• Extremely computationally efficient • Surprisingly accurate for metals and covalent bonds • Gives crystal structures and lattice constants close to experiment • Still the foundation for many more recent approximations	• Assumes $\rho(r)$ varies slowly — not true near nuclei or in vacuum • Limited for van der Waals bonds (non-local correlation) • Typically underestimates the band gap • Does not distinguish well between states of different spin

The Generalized Gradient Approximation (GGA)

Beyond the homogeneity assumption. LDA assumes the density varies slowly - but this is not true in many molecules and surfaces. GGA improves on this by including not only the value of the density $\rho(r)$, but also its gradient (shown below). The formula is sometimes written in terms of the two separate spin densities when generalized to the spin-polarized case:

$$E_{xc}^{GGA}[\rho] = \int f\big(\rho(r), \nabla\rho(r)\big)\, dr \tag{30}$$

$$s(r) = \frac{|\nabla\rho(r)|}{2K_F\rho(r)} = \frac{|\nabla\rho(r)|}{2(3\pi^2)^{1/3}\rho^{4/3}(r)}, \quad K_F = (3\pi^2\rho)^{1/3} \tag{31}$$

The necessary limiting condition: when the gradient vanishes ($s \to 0$), the GGA approximation automatically reduces to the local density approximation LDA - a physical requirement that any consistent GGA functional must satisfy [2,4].

The Most Popular GGA Functional: PBE (1996)

PBE — Perdew, Burke, Ernzerhof. The most widely used functional in solid-state calculations today; it contains no empirically fitted parameters (parameter-free) - all of its constants are derived from strict physical conditions that the functional must satisfy. Several related functionals are listed in Table 6 [2,4].

Table 6. PBE and related GGA functionals.

Functional	Year published	Notes
PBE	1996	General-purpose, excellent for molecules and extended systems
PBEsol	2008	Tailored for solids and surfaces (modification μ = 10/81)
WC (Wu–Cohen)	2006	Improved equilibrium volumes for close-packed solids
BLYP	1988	Very popular in molecular chemistry (Becke exchange + LYP correlation)
AM05	2005	Excellent for surfaces and crystalline systems, based on the jellium model

The Complete Formula for the PBE Functional (Exchange)

PBE's constants and variables. κ = 0.804 (ensures a strict physical upper bound), μ = 0.2195 (derived from $\beta\cdot\pi^2/3$, where β = 0.066725). As for s (Eq. (31)), it is the reduced gradient, which measures the local degree of inhomogeneity of the density; it depends on $k_F = (3\pi^2\rho)^{1/3}$.

The exchange term $F_x(s)$. An enhancement factor multiplying the LDA exchange:

$$F_x(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa} \tag{32}$$

PBE contains no empirically fitted parameter whatsoever (fully parameter-free) - all of its constants are derived from strict physical conditions that the functional must satisfy. The corresponding correlation term E_c^{PBE} similarly adds a gradient correction H on top of the LDA correlation, with coefficient γ = 0.031091 [2,4].

The Correlation Energy in the GGA Approximation

The correlation energy in the GGA approximation is written as:

$$E_C^{GGA}[\rho_\uparrow, \rho_\downarrow] = \int d^3r\, \rho\big[E_C^{unif}(r_s, \zeta) + H(r_s, \zeta, t)\big] \tag{33}$$

The fundamental physical variables. The local Seitz radius (r_s) measures the local electron density:

$$\rho = \frac{3}{4\pi r_s^3} \tag{34}$$

The relative spin polarization (ζ):

$$\zeta = \frac{\rho_\uparrow - \rho_\downarrow}{\rho} \tag{35}$$

The reduced density gradient for correlation (t):

$$t = \frac{|\nabla\rho|}{2\phi k_s \rho} \tag{36}$$

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A Deeper Step: The Meta-GGA Approximation

The idea. Meta-GGA adds a third variable beyond the density and its gradient: the orbital kinetic energy density $\tau(r)$ (or the Laplacian of the density):

$$\tau(r) = \frac{1}{2}\sum_{i}^{occ} |\nabla\varphi_i(r)|^2 \quad (37)$$

This quantity gives the functional the ability to distinguish precisely between different types of chemical bonds (covalent, metallic, or weak).

A prominent example: SCAN (2015). The "Strongly Constrained and Appropriately Normed" method — it satisfies all 17 known strict physical constraints for this class of functionals, and delivers accuracy close to hybrid methods at a much lower computational cost [2,4,8].

Hybrid Approximations

The idea. The exact exchange energy is fully known from Hartree–Fock theory. Why not borrow part of it and combine it with the exchange and correlation of density functional theory? This is exactly what hybrid functionals do: they mix a fraction α of exact Hartree–Fock exchange with the remainder from GGA or Meta-GGA:

$$E_{xc}^{hyb} = \alpha E_x^{HF} + (1-\alpha)E_x^{GGA} + E_c^{GGA} \quad (38)$$

- **B3LYP (1994).** A very popular mix in molecular chemistry, with empirically fitted coefficients.
- **PBE0 (1999).** α = 0.25 of Hartree–Fock exchange combined with PBE [2,4].

Range-Separated Hybrid Exchange (RSH)

The idea. Instead of a fixed fraction α of Hartree–Fock exchange at all distances, range-separated hybrids split the same Coulomb interaction into a short-range part and a long-range part via the separation parameter ω, giving each part its own fraction of exact exchange: β for the short range and α for the long range — this allows the near- and far-field electron dynamics to be tuned separately and precisely:

$$V_{xc}(r,r') = \beta V_x^{sr-ex}(r,r';\omega) + \alpha V_x^{lr-ex}(r,r';\omega) + (1-\beta)V_x^{sr}(r;\omega) + (1-\alpha)V_x^{lr}(r;\omega) + V_c(r) \quad (39)$$

The separation itself is based on partitioning the Coulomb potential: $1/|r-r'| = \mathrm{erfc}(\omega|r-r'|)/|r-r'| + \mathrm{erf}(\omega|r-r'|)/|r-r'|$ — the first term (short-range) and the second (long-range, via the error function erf), with ω controlling the position of the crossover between the two ranges [2,4].

Choosing α Self-Consistently: The GKS Approach

The idea. The mixing fraction α from the previous subsection is not determined on its own. The Generalized Kohn–Sham (GKS) formulation proposes determining it self-consistently rather than choosing it by hand: by linking it to the static dielectric constant of the material ε_∞ through the following relation:

$$\alpha = \varepsilon_\infty^{-1} \quad (40)$$

The physical basis: non-metallic materials screen the long-range Coulomb interaction inversely proportional to ε_∞. The self-consistency loop: an initial guess for α → compute V_{xc} and solve the Kohn–Sham equations → compute the resulting ε_∞ from the solution → check for convergence; if convergence is not reached, α is updated using the relation above and the loop repeats, otherwise the output is the final hybrid functional [2,4].

Jacob's Ladder: A Map of All the Approximations

Each higher rung adds greater accuracy — at a higher computational cost (Table 7).

Table 7. Jacob's ladder of exchange–correlation approximations.

Rung	Approximation	Ingredient
1	LDA	Density only ρ
2	GGA	+ Density gradient ρ
3	Meta-GGA	+ Kinetic energy density τ
4	Hybrids	+ Partial Hartree–Fock exchange
5	RPA and beyond	+ Full exact correlation

Accuracy versus Computational Cost

Table 8. Accuracy versus computational cost of the main approximations.

Approximation	Computational cost	Accuracy	Typical use
LDA	Very low	Low	Very large systems, quick initial screening
GGA (PBE)	Low	Good	General-purpose use in solids
Meta-GGA (SCAN)	Low–Moderate	Very good	Higher accuracy at reasonable cost
Hybrid (PBE0)	High	Very good	Molecules, improved band gaps

Limitations of Density Functional Theory

The main systematic limitations of approximate functionals are summarized below and in Table 9.

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Self-Interaction Error

The Hartree energy contains an unphysical repulsion of each electron with itself; exact exchange cancels it in Hartree–Fock and would do so in the exact functional, but not in approximate ones [2,4]. This self-interaction error (SIE) is clearest in stretched H_2^+ [4,8] and affects localized d and f states (NiO, for example, is described as a metal) [4]. Remedies are the Perdew–Zunger correction [9], hybrid functionals and DFT+U [4].

Delocalization Error and the Band-Gap Problem

The exact energy is piecewise linear in the fractional electron number [10]; LDA and GGAs are convex, which favors spread-out charge (delocalization error) [11]. A related problem is that the Kohn–Sham gap is not the true gap of the material and is usually underestimated [1,4].

Strongly Correlated Systems

Because Kohn–Sham electrons are non-interacting, materials with partially filled d or f shells, such as cuprates, are poorly described [1]; static correlation appears when configurations are nearly degenerate [11]. Remedies include DFT+U [4], GW and DFT+DMFT [1].

Dispersion (van der Waals) Interactions

Semilocal functionals cannot capture the long-range C/r^6 dispersion [4,8]; for example, a GGA overestimated molecular-crystal volumes by about 20% [4]. Remedies are DFT-D corrections such as D3 [4,12] and non-local functionals such as vdW-DF [13].

Table 9. Summary of the main limitations of approximate density functionals [1,4,11].

Limitation	Physical origin	Typical consequences	Common remedies
Self-interaction error	Incomplete cancellation of the Hartree self-repulsion	Over-delocalized electrons; errors for d and f states	Hybrids; Perdew–Zunger; DFT+U
Delocalization error	Energy convex in fractional electron number	Charge delocalization; underestimated gaps	Hybrid functionals
Strong correlation	Non-interacting Kohn–Sham description	Failures for d/f shells and cuprates	DFT+U; GW; DFT+DMFT
Dispersion	No long-range non-local correlation	Overestimated molecular-crystal volumes	DFT-D (D3); vdW-DF

Conclusion: The Complete Roadmap

1. **Schrödinger:** an equation describing everything, but impossible to solve for any real system
2. **Born–Oppenheimer:** we fix the nuclei, and solve only for the motion of the electrons
3. **Hartree–Fock:** we approximate the wavefunction with a Slater determinant - it resolves Pauli, but neglects correlation
4. **Hohenberg–Kohn:** the density $\rho(r)$ alone suffices to fully describe the system
5. **Kohn–Sham:** a fictitious non-interacting system + an effective potential, confining the unknown many-body physics into $E_{xc}[\rho]$ (exact in principle, approximate in practice)
6. **From LDA to hybrid functionals:** a series of increasingly accurate approximations for $E_{xc}[\rho]$

These approximations have systematic limitations (self-interaction and delocalization errors, strongly correlated systems, dispersion), discussed above.

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