Professional Certificate in Density Functional Theory Calculations

Electron Density And Exchange Correlation

Adiabatic Connection

Related terms: Kohn-Sham system, exchange-correlation energy, coupling constant

Explanation: The adiabatic connection is a conceptual pathway that links a non-interacting reference system to the fully interacting physical system by continuously scaling the electron-electron interaction strength with a coupling constant λ ranging from 0 to 1. At $\lambda = 0$ the system reduces to the Kohn-Sham non-interacting electrons, while $\lambda = 1$ corresponds to the real interacting electrons. The exchange-correlation energy can be expressed as an integral over λ of the exchange-correlation hole contribution, providing a rigorous foundation for constructing approximate functionals.

Example: In the popular hybrid functional B3LYP, the adiabatic connection is invoked to mix a fixed fraction of exact Hartree-Fock exchange ($\lambda \approx 0.20$) with DFT exchange-correlation.

Practical application: Enables the design of hybrid and range-separated functionals that balance accuracy and computational cost for molecules and solids.

Challenges: Accurate evaluation of the λ-dependent integrand requires knowledge of the exchange-correlation hole, which is not directly accessible; approximations can lead to systematic errors in reaction barriers and charge-transfer excitations.

Atomic Orbital

Related terms: basis set, Gaussian functions, plane-wave expansion

Explanation: An atomic orbital (AO) is a mathematical function that describes the spatial distribution of an electron bound to a single atom. In quantum-chemical calculations, AOs serve as building blocks for molecular orbitals through linear combinations. They are typically represented by contracted Gaussian functions because of their favorable integral properties, although Slater-type orbitals are sometimes used for higher accuracy.

Example: The 2p_z AO of carbon in a benzene molecule contributes to the π-system that determines aromaticity.

Practical application: Choice of AO basis set (e.g., STO-3G, 6-31G*, cc-pVTZ) directly influences the quality of the electron density and hence the computed exchange-correlation energy.

Challenges: Larger and more flexible basis sets increase computational cost and may introduce linear-dependency problems; selecting an optimal basis for a given system remains a nuanced task.

Band Gap

Related terms: Kohn-Sham eigenvalues, exchange-correlation functional, semiconductor

Explanation: The band gap is the energy difference between the highest occupied and lowest unoccupied electronic states in a solid. In Kohn-Sham DFT, the eigenvalue gap (the difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital) often underestimates the experimental band gap because the exchange-correlation potential lacks the derivative discontinuity.

Example: For silicon, a local-density approximation (LDA) predicts a gap of ~0.6 eV, whereas the experimental value is about 1.1 eV.

Practical application: Accurate band-gap predictions are essential for designing optoelectronic materials, photovoltaic cells, and semiconductor devices. Hybrid functionals or many-body perturbation methods (GW) are employed to improve gap estimates.
Challenges: Balancing computational expense with accuracy; hybrid functionals increase cost, while GW requires a costly many-body treatment.

Becke Exchange
Related terms: B88 functional, gradient-corrected exchange, hybrid functional
Explanation: The Becke exchange functional, commonly denoted B88, introduces a gradient correction to the local-density approximation (LDA) exchange energy. It accounts for the inhomogeneity of the electron density by incorporating the reduced density gradient, improving the description of exchange effects in molecules and solids.
Example: In the B3LYP hybrid functional, 20 % of the exact Hartree-Fock exchange is mixed with 80 % of the Becke exchange component.
Practical application: Widely used in quantum chemistry for geometry optimizations, vibrational frequency calculations, and reaction-energy predictions due to its balanced accuracy.
Challenges: The functional parameters are empirically fitted; transferring them to exotic systems (e.g., transition-metal complexes) can lead to systematic errors.

Correlation Functional
Related terms: LDA correlation, GGA correlation, meta-GGA
Explanation: A correlation functional quantifies the contribution to the total energy arising from electron-electron interactions beyond the mean-field exchange term. In the local-density approximation, correlation depends only on the local electron density, while generalized gradient approximations (GGAs) incorporate density gradients to capture non-uniform effects. Meta-GGAs further include kinetic-energy density or Laplacian terms for enhanced accuracy.
Example: The Perdew-Burke-Ernzerhof (PBE) functional pairs a GGA exchange with a GGA correlation term, forming a widely adopted functional for solid-state calculations.
Practical application: Determines the accuracy of thermochemical predictions, bulk moduli, and surface energies.
Challenges: Correlation functionals often struggle with strong-correlation regimes (e.g., bond dissociation, Mott insulators), requiring more sophisticated approaches such as DFT+U or hybrid methods.

Density Functional
Related terms: Hohenberg-Kohn theorem, Kohn-Sham equations, exchange-correlation functional
Explanation: A density functional is a mathematical mapping that assigns a scalar energy value to a given electron density distribution $\rho(r)$. The foundational Hohenberg-Kohn theorems guarantee that the ground-state energy is a unique functional of the ground-state density, enabling the replacement of the many-electron wavefunction by the much simpler density variable.
Example: The total energy functional $E[\rho] = T_s[\rho] + V_{ext}[\rho] + J[\rho] + E_{xc}[\rho]$ comprises kinetic, external, Hartree, and exchange-correlation contributions.
Practical application: Forms the backbone of DFT calculations across chemistry, materials science, and condensed-matter physics.

Challenges: The exact form of $E_{xc}[\rho]$ is unknown; approximations introduce systematic biases that must be understood and mitigated.

Density Gradient

Related terms: reduced density gradient, GGA, exchange-correlation hole

Explanation: The density gradient $\nabla\rho(r)$ measures how rapidly the electron density changes in space. In generalized gradient approximations, the reduced density gradient $s = |\nabla\rho|/(2(3\pi^2)^{1/3}\rho^{4/3})$ is used as a dimensionless parameter to modulate the exchange-correlation energy, allowing the functional to respond to inhomogeneities.

Example: In regions of low density (e.g., interstitial spaces), s becomes large, and GGA functionals adjust the exchange-correlation contribution accordingly.

Practical application: Improves predictions of molecular geometries, reaction barriers, and non-covalent interactions.

Challenges: Over-emphasis on gradient terms can lead to spurious exchange-correlation holes, causing over-binding or under-binding in certain systems.

Exchange Hole

Related terms: exchange-correlation hole, pair density, Fermi hole

Explanation: The exchange hole describes the depletion of electron probability around a reference electron due to the antisymmetry of the many-electron wavefunction (Pauli exclusion). It represents the reduction in the probability of finding another electron with the same spin in the vicinity of a given electron. Mathematically, it appears in the pair density as a negative contribution that integrates to –1 for each electron.

Example: In a homogeneous electron gas, the exchange hole is spherical and its depth is determined solely by the local density.

Practical application: Forms the basis for constructing exchange functionals; accurate modeling of the exchange hole leads to better predictions of exchange energies.

Challenges: Capturing the full spatial dependence of the exchange hole in inhomogeneous systems is difficult; approximations often rely on local or semi-local descriptors.

Exchange-Correlation Functional

Related terms: LDA, GGA, meta-GGA, hybrid functional

Explanation: The exchange-correlation (XC) functional, denoted $E_{xc}[\rho]$, encapsulates all many-body effects beyond the classical electrostatic (Hartree) interaction. It is the only term in Kohn-Sham DFT that must be approximated, and its quality determines the overall accuracy of the calculation. XC functionals are classified by their level of sophistication: local (LDA), gradient-corrected (GGA), meta-GGA, hybrid (mixing exact exchange), and range-separated hybrids.

Example: The PBE functional combines a GGA exchange (PBE-X) with a GGA correlation (PBE-C) to give a balanced description for a broad range of systems.

Practical application: Used to predict thermochemistry, structures, spectroscopic properties, and phase stability.

Challenges: No universal functional exists; each functional may excel for certain properties while failing for others, necessitating careful selection and benchmarking.

Exchange-Correlation Hole

Related terms: exchange hole, correlation hole, adiabatic connection

Explanation: The exchange-correlation hole combines the exchange hole (stemming from Pauli exclusion) and the correlation hole (arising from electron-electron Coulomb repulsion) into a single entity that describes the net reduction in electron probability around a reference electron. Its integral over all space equals -1, reflecting the removal of one electron's charge. Accurate modeling of the XC hole is central to developing reliable XC functionals.

Example: In the uniform electron gas, the XC hole can be derived analytically, providing a reference for constructing LDA functionals.

Practical application: Provides physical insight for designing non-local functionals such as those based on the random-phase approximation (RPA).

Challenges: The exact XC hole is a high-dimensional object; approximations must balance computational tractability with physical realism.

Fermi Hole

Related terms: exchange hole, spin density, Pauli principle

Explanation: The Fermi hole is another name for the exchange hole, emphasizing its origin in the antisymmetry of the fermionic wavefunction. It is present only for electrons of the same spin and leads to a depletion of same-spin electron density around a reference electron.

Example: In a spin-polarized system, the Fermi hole for up-spin electrons differs from that for down-spin electrons, affecting magnetic properties.

Practical application: Influences the spin-dependent part of the XC functional, crucial for magnetic materials and open-shell molecules.

Challenges: Capturing spin-dependent variations of the Fermi hole within simple functionals can be inadequate for strongly correlated magnetic systems.

Generalized Gradient Approximation

Related terms: GGA, PBE, exchange-correlation functional

Explanation: The GGA improves upon the LDA by incorporating the reduced density gradient s into the functional form. This semi-local approach allows the XC energy density to respond to variations in the electron density, leading to better predictions of molecular geometries, reaction energies, and surface properties.

Example: The PBE functional is a non-empirical GGA that satisfies known exact constraints, making it a standard choice for solid-state calculations.

Practical application: Widely used for bulk modulus, lattice constants, and adsorption energies on surfaces.

Challenges: GGAs may over-delocalize electrons, causing errors in band gaps and reaction barrier heights; they also lack the derivative discontinuity required for accurate excitation energies.

Hartree Potential

Related terms: $J[\rho]$, electrostatic energy, Kohn-Sham equation

Explanation: The Hartree potential $V_H(r) = \int \rho(r')/|r-r'|\, dr'$ represents the classical Coulomb repulsion of the electron density with itself. It is a functional of the electron density and appears as the $J[\rho]$ term in the total energy expression.

Example: In a hydrogen atom, the Hartree potential vanishes because there is only one electron; in multi-electron atoms, it contributes significantly to the total potential felt by each electron.
Practical application: Provides the mean-field electrostatic environment in Kohn-Sham equations; accurate evaluation is essential for self-consistent field convergence.
Challenges: The Hartree potential includes a self-interaction error for each electron; correcting this error requires additional terms such as self-interaction corrections (SIC).

Hybrid Functional
Related terms: B3LYP, exact exchange, range-separated functional
Explanation: Hybrid functionals mix a fraction of exact Hartree-Fock exchange with a DFT exchange-correlation component. The mixing coefficient is often empirically determined but can be derived from the adiabatic connection. This approach reduces self-interaction error and improves the description of exchange, leading to better thermochemical and kinetic predictions.
Example: B3LYP combines 20 % exact exchange, 80 % Becke exchange, and the Lee-Yang-Parr correlation functional.
Practical application: The default choice for many organic and organometallic chemistry studies, providing a good balance between accuracy and computational cost.
Challenges: The exact exchange portion increases computational scaling (O(N^4) for conventional implementations); hybrid functionals may still fail for strongly correlated systems and periodic solids unless a screened Coulomb operator is employed.

Hartree-Fock Exchange
Related terms: exact exchange, non-local operator, self-interaction error
Explanation: Hartree-Fock exchange is the non-local exchange term obtained from the Slater determinant of occupied orbitals. It accounts exactly for the antisymmetry of the wavefunction but neglects electron correlation. In hybrid DFT, a portion of this term is mixed with DFT exchange to improve accuracy.
Example: In B3LYP, the exact exchange contribution is evaluated using the occupied Kohn-Sham orbitals and added to the DFT exchange energy.
Practical application: Reduces delocalization error, improves band-gap predictions, and yields better reaction barrier heights.
Challenges: Computationally demanding for large systems; the non-local nature complicates implementation in plane-wave codes, prompting the use of screened hybrids (e.g., HSE06).

Hartree-Fock Theory
Related terms: self-consistent field, exchange energy, correlation energy
Explanation: Hartree-Fock (HF) theory provides a mean-field description of electrons by constructing a single Slater determinant that minimizes the total energy. It yields exact exchange but omits electron correlation, making HF energies typically higher than the exact ground-state energy. HF solutions serve as a reference for post-HF methods and as a source of exact exchange in hybrid functionals.
Example: The HF calculation of water predicts a bond length slightly longer than the experimental value due to missing correlation.
Practical application: Provides initial guesses for Kohn-Sham orbitals, a benchmark for assessing DFT performance, and a component of hybrid functionals.

Challenges: Inapplicable for systems with strong static correlation (e.g., bond breaking) where a single determinant is insufficient.

Kohn-Sham Equations
Related terms: effective potential, orbitals, self-consistent field
Explanation: The Kohn-Sham (KS) equations are a set of one-electron Schrödinger-like equations that generate a set of non-interacting orbitals whose density reproduces the exact ground-state electron density of the interacting system. The KS Hamiltonian includes the kinetic energy of non-interacting electrons, the external potential, the Hartree potential, and the exchange-correlation potential v_xc(r) = δE_xc/δρ(r). Solving these equations self-consistently yields the KS orbitals and the electron density.
Example: In a silicon crystal, the KS equations produce Bloch orbitals that form valence and conduction bands.
Practical application: Forms the computational core of all DFT codes; the quality of the XC functional determines the accuracy of the resulting KS eigenvalues and densities.
Challenges: Convergence can be difficult for metallic systems, large unit cells, or when the XC potential exhibits discontinuities.

Kohn-Sham Kinetic Energy
Related terms: T_s[ρ], non-interacting kinetic energy, orbital-dependent functional
Explanation: T_s[ρ] denotes the kinetic energy of the fictitious non-interacting electron system that reproduces the exact electron density. It is expressed as a sum over the occupied KS orbitals: T_s = −½ Σ_i ⟨ψ_i|∇^2|ψ_i⟩. Unlike the interacting kinetic energy, T_s can be evaluated exactly from the KS orbitals, making it a known quantity in the DFT energy expression.
Example: In the LDA, T_s is computed from the KS orbitals but the XC functional assumes a uniform electron gas for the remaining kinetic correlation.
Practical application: Accurate evaluation of T_s is essential for orbital-dependent functionals such as meta-GGAs and hybrid functionals.
Challenges: For orbital-free DFT, approximating T_s directly from the density without orbitals remains an open research area.

Local Density Approximation
Related terms: LDA, uniform electron gas, exchange-correlation functional
Explanation: LDA assumes that the exchange-correlation energy density at each point in space depends only on the local electron density, as if the electrons formed a homogeneous electron gas (HEG) at that density. The functional is derived from quantum Monte Carlo data for the HEG, providing analytic expressions for both exchange and correlation.
Example: The Perdew-Zunger LDA correlation functional combines the Ceperley-Alder HEG data with the Dirac exchange formula.
Practical application: Offers a simple, computationally cheap functional that works surprisingly well for bulk metals and simple solids.
Challenges: LDA tends to overbind molecules, underestimate bond lengths, and poorly describe van der Waals interactions due to its lack of gradient information.

Meta-GGA
Related terms: TPSS, kinetic-energy density, higher-rung functional
Explanation: Meta-GGAs extend the GGA framework by incorporating additional ingredients such as the kinetic-energy density $\tau(r) = \frac{1}{2} \Sigma_i |\nabla\psi_i(r)|^2$ or the Laplacian of the density $\nabla^2\rho(r)$. These extra terms enable a more nuanced description of the local electronic environment, allowing meta-GGAs to approach hybrid-functional accuracy without explicit exact exchange.
Example: The TPSS functional uses $\tau(r)$ to satisfy exact constraints and yields improved thermochemistry compared to PBE.
Practical application: Provides a good compromise for large systems where hybrid functionals are too costly, delivering accurate lattice constants and reaction energies.
Challenges: The increased complexity can cause numerical instability; meta-GGAs may still struggle with long-range dispersion unless supplemented with empirical corrections.

Non-Local Correlation
Related terms: van der Waals functional, RPA, dispersion correction
Explanation: Non-local correlation accounts for electron-correlation effects that depend on electron density at two distinct points, r and r′. This is essential for describing long-range dispersion (van der Waals) interactions, which are absent in local or semi-local functionals. The non-local term is typically expressed as an integral over a kernel $\Phi(r,r')$ that couples densities at different locations.
Example: The vdW-DF family adds a non-local correlation term to a GGA exchange to capture dispersion between layered graphene sheets.
Practical application: Enables accurate modeling of physisorption, molecular crystals, and biomolecular interactions.
Challenges: The kernel evaluation is computationally demanding; approximations may introduce errors in binding energies and equilibrium distances.

Orbital-Dependent Functional
Related terms: meta-GGA, exact exchange, Optimized Effective Potential
Explanation: An orbital-dependent functional explicitly depends on the Kohn-Sham orbitals rather than solely on the electron density. Examples include exact exchange (as in hybrids) and certain meta-GGAs that use kinetic-energy density. To obtain a corresponding XC potential, one must solve the Optimized Effective Potential (OEP) equations, which are more complex than the simple functional derivative used for density-only functionals.
Example: The exact-exchange OEP method yields an XC potential that reproduces the Hartree-Fock exchange energy while remaining within the KS framework.
Practical application: Provides higher accuracy for systems where density-only functionals fail, such as in the description of charge-transfer excitations.
Challenges: OEP calculations are computationally intensive; approximations like the Krieger-Li-Iafrate (KLI) scheme are employed to reduce cost but may sacrifice precision.

Optimized Effective Potential
Related terms: OEP, orbital-dependent functional, exchange potential
Explanation: The OEP method determines a local, multiplicative potential $v_{xc}(r)$ that yields the same

electron density as an orbital-dependent functional. It involves solving an integral equation derived from the functional derivative of the energy with respect to the orbitals. The resulting potential incorporates the effects of exact exchange and, in some cases, correlation.
Example: In the exact-exchange OEP, the resulting potential reproduces the Hartree-Fock exchange energy while maintaining a KS-type orbital picture.
Practical application: Allows the use of orbital-dependent functionals within standard KS codes, enabling improved band-gap predictions and better description of response properties.
Challenges: The OEP equation is numerically demanding; iterative solvers may suffer from convergence issues, especially for large or metallic systems.

Pair Density
Related terms: exchange-correlation hole, two-electron density, reduced density matrix
Explanation: The pair density $\rho_2(r_1,r_2)$ gives the probability of simultaneously finding one electron at r_1 and another at r_2. It contains information about both exchange and correlation effects. The exchange-correlation hole is derived from the difference between the pair density and the product of individual densities.
Example: In a single-determinant wavefunction, the pair density can be expressed analytically in terms of occupied orbitals, revealing the Fermi hole structure.
Practical application: Provides a route to construct non-local XC functionals and to analyze electron-pair correlations in chemical bonding.
Challenges: Direct computation of the full pair density scales poorly with system size; approximations are required for practical DFT calculations.

Plane-Wave Basis
Related terms: periodic boundary conditions, cutoff energy, FFT
Explanation: Plane-wave basis sets expand the Kohn-Sham orbitals as a sum of plane waves, ψ_k(r) = Σ_G c_G e^{i(k+G)·r}, where G are reciprocal lattice vectors. This representation is natural for periodic systems (crystals) and enables efficient evaluation of kinetic energy and the Hartree potential via Fast Fourier Transforms (FFT). The basis is controlled by a kinetic-energy cutoff, which determines the number of plane waves included.
Example: A cutoff of 500 eV is typical for accurate calculations of silicon using the PBE functional.
Practical application: Dominant in solid-state DFT codes (VASP, Quantum ESPRESSO) for computing band structures, phonons, and surface energies.
Challenges: Requires pseudopotentials or projector-augmented waves to treat core electrons; high cutoffs increase memory and CPU demands.

Potential Functional
Related terms: v_xc(r), functional derivative, Kohn-Sham potential
Explanation: The potential functional v_xc[ρ](r) is obtained by taking the functional derivative of the exchange-correlation energy with respect to the electron density: v_xc(r) = δE_xc[ρ]/δρ(r). This potential enters the KS equations and determines how the electrons experience exchange-correlation effects. For semi-local functionals, the derivative is straightforward; for orbital-dependent functionals, the OEP method is required.
Example: In LDA, v_xc(r) depends only on ρ(r) and can be expressed analytically using the derivative of the

uniform-electron-gas XC energy per particle.

Practical application: Determines the shape of the KS potential, influencing orbital energies, density distribution, and response properties.

Challenges: Accurate functional derivatives are essential for obtaining reliable forces and vibrational frequencies; numerical noise can affect convergence.

Reduced Density Gradient

Related terms: s, GGA, exchange-correlation enhancement factor

Explanation: The reduced density gradient $s = |\nabla\rho|/(2(3\pi^2)^{1/3}\rho^{4/3})$ provides a dimensionless measure of density inhomogeneity. GGA functionals use s to modulate the exchange-correlation energy density via an enhancement factor F(s), which smoothly interpolates between the homogeneous limit $(s \to 0)$ and the rapidly varying limit (large s).

Example: In the B88 exchange functional, the enhancement factor grows as s^2, improving the description of exchange in regions of low density.

Practical application: Determines the shape of the exchange-correlation energy surface; essential for accurate geometry optimizations and reaction-energy predictions.

Challenges: Excessive growth of F(s) can lead to over-binding or spurious long-range interactions; constraints are imposed to keep the functional well-behaved.

Self-Interaction Error

Related terms: SIC, LDA, exact exchange

Explanation: Self-interaction error (SIE) arises when an approximate XC functional does not fully cancel the spurious interaction of an electron with itself present in the Hartree term. In exact theory, the exchange term exactly cancels this self-interaction, but most semi-local functionals (LDA, GGA) leave a residual error, leading to overly delocalized electron densities and inaccurate ionization potentials.

Example: The LDA predicts a too low ionization energy for the hydrogen atom because of SIE.

Practical application: Impacts charge-transfer excitations, band-gap predictions, and the description of localized states (e.g., d- or f-electrons).

Challenges: Correcting SIE requires more sophisticated functionals (hybrids, SIC methods) or explicit self-interaction corrections, which increase computational effort.

Spin Density

Related terms: magnetization, spin-polarized DFT, exchange-correlation functional

Explanation: Spin density $\rho_\sigma(r)$ ($\sigma = \uparrow$ or $\downarrow$) describes the spatial distribution of electrons with a given spin orientation. In spin-polarized DFT, separate densities for up- and down-spin electrons are used, allowing the treatment of magnetic materials and open-shell molecules. The total density is $\rho = \rho_\uparrow + \rho_\downarrow$, while the spin magnetization is $m = \rho_\uparrow - \rho_\downarrow$.

Example: In ferromagnetic iron, the spin density shows a surplus of up-spin electrons, leading to a net magnetic moment.

Practical application: Enables calculation of magnetic moments, spin-dependent band structures, and exchange splittings.

Challenges: Accurate spin-dependent XC functionals are required; many GGAs perform reasonably, but hybrid functionals may be needed for quantitative magnetism.

Thomas-Fermi Model

Related terms: orbital-free DFT, kinetic-energy functional, electron gas

Explanation: The Thomas-Fermi (TF) model is the earliest density-only approach, approximating the kinetic energy as a functional of the local electron density alone, based on the uniform electron gas. It yields a simple expression T_TF[ρ] = C_F ∫ ρ(r)^{5/3} dr, where C_F is a constant. While qualitatively capturing overall trends, TF lacks shell structure and fails to describe chemical bonding.

Example: TF predicts a smooth electron density for an atom, missing the characteristic nodal structure of atomic orbitals.

Practical application: Serves as a foundation for orbital-free DFT, where more sophisticated kinetic-energy functionals are built upon the TF baseline.

Challenges: The TF kinetic functional is too crude for most chemistry applications; developing accurate orbital-free kinetic functionals remains an active research area.

Van der Waals Functional

Related terms: non-local correlation, vdW-DF, dispersion interactions

Explanation: Van der Waals (vdW) functionals augment conventional GGAs with a non-local correlation term that captures long-range dispersion forces. The functional typically takes the form E_c^{nl}[ρ] = ½ ∫∫ ρ(r) Φ(r,r′) ρ(r′) dr dr′, where Φ is a kernel derived from the response of the electron gas. The vdW-DF family (e.g., vdW-DF1, vdW-DF2) combines a specific exchange component with this correlation term.

Example: Applying vdW-DF2 to the adsorption of benzene on graphite yields binding energies in close agreement with experiment.

Practical application: Essential for modeling layered materials, molecular crystals, and biomolecular complexes where dispersion governs structure and stability.

Challenges: The choice of exchange partner influences accuracy; some vdW functionals may over-estimate binding distances, requiring empirical re-parameterization.

Weighted Density Approximation

Related terms: WDA, non-local functional, average density

Explanation: The weighted density approximation (WDA) replaces the local density in the XC functional with a weighted average over a finite region, effectively introducing non-locality. The weighting function is chosen to satisfy known sum rules and to reproduce the exchange-correlation hole of the uniform electron gas. WDA aims to improve upon LDA by incorporating some degree of density inhomogeneity without full gradient dependence.

Example: WDA has been applied to semiconductor band-gap calculations, yielding modest improvements over LDA.

Practical application: Provides an alternative route to incorporate non-local effects while retaining computational simplicity relative to full GGA.

Challenges: Determining an optimal weighting function is non-trivial; WDA may still miss important gradient-dependent physics.

XC Kernel

Related terms: linear response, time-dependent DFT, f_xc

Explanation: The exchange-correlation kernel f_xc(r,r′,ω) is the functional derivative of the XC potential with

respect to the density, $f_{xc} = \delta v_{xc}(r)/\delta\rho(r')$. In time-dependent DFT (TDDFT), the kernel governs the response of the system to external perturbations and determines excitation energies. Approximate kernels (e.g., adiabatic LDA) are often used, but they may miss important frequency-dependent and non-local effects.
Example: The adiabatic PBE kernel provides reasonable excitation energies for valence excitations but fails for charge-transfer states.
Practical application: Enables calculation of optical spectra, polarizabilities, and excited-state properties.
Challenges: Developing accurate, frequency-dependent kernels remains a central challenge for TDDFT, especially for long-range charge-transfer and double excitations.

Zero-Point Energy

Related terms: vibrational correction, thermochemistry, DFT
Explanation: Zero-point energy (ZPE) is the quantum mechanical energy remaining in a system at absolute zero due to vibrational motion. In DFT thermochemistry, ZPE corrections are added to electronic energies to obtain more accurate reaction enthalpies and free energies. ZPE is computed from harmonic vibrational frequencies obtained from the Hessian of the DFT energy surface.
Example: For the H_2 molecule, the ZPE is approximately 0.27 eV, which must be added to the electronic energy when comparing to experimental dissociation energies.
Practical application: Essential for high-accuracy thermodynamic predictions, isotope effect studies, and benchmarking DFT functionals.
Challenges: Harmonic approximation may be insufficient for floppy molecules; anharmonic corrections increase computational cost.

Charge Density

Related terms: electron density, $\rho(r)$, observable
Explanation: The charge density $\rho(r)$ describes the distribution of electronic charge in space and is the primary variable in DFT. It is obtained by summing the squared magnitudes of the occupied Kohn-Sham orbitals: $\rho(r) = \Sigma_i |\psi_i(r)|^2$. The density uniquely determines the ground-state energy and all observable properties according to the Hohenberg-Kohn theorems.
Example: In a water molecule, the electron density shows high concentration around the oxygen atom and along the O-H bonds.
Practical application: Visualization of charge density aids in interpreting chemical bonding, reactivity, and electrostatic potentials.
Challenges: Accurate density requires a converged basis set and a reliable XC functional; errors propagate to derived properties such as dipole moments and reaction barriers.

Exchange-Correlation Energy

Related terms: $E_{xc}[\rho]$, XC functional, adiabatic connection
Explanation: The exchange-correlation energy $E_{xc}[\rho]$ is the component of the total electronic energy that accounts for all many-body effects beyond the classical electrostatic (Hartree) term and the kinetic energy of non-interacting electrons. It includes both exchange (due to antisymmetry) and correlation (dynamic electron–electron interactions). Because its exact form is unknown, approximations are employed.
Example: In the PBE functional, E_{xc} is split into an exchange part E_x^{PBE} and a correlation part

E_c^{PBE}, each expressed in terms of ρ and its gradients.
Practical application: Determines the accuracy of computed bond energies, geometries, and electronic properties across chemistry and materials science.
Challenges: Balancing accuracy for diverse properties; no single functional performs optimally for all systems, leading to ongoing development of new XC approximations.

Hartree–Fock–DFT Hybrid
Related terms: mixing parameter, exact exchange fraction, global hybrid
Explanation: A Hartree–Fock–DFT hybrid combines a fixed proportion