Electronic structure methods (Density Functional Theory) used in industry from pharmaceuticals, materials and beyond

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Overview

1. Summary - Importance of computational chemistry methods in industry
2. Summary - Postulates of quantum mechanics/Hartree-Fock method
3. Density Functional Theory (DFT)

Computational chemistry

Computational chemistry/physics/materials science has become widely used because of:

- Dramatic **increase in computational power/speed** and the
- Design of **efficient quantum chemical algorithms**.

The computer calculations enable us to:

- **explain and rationalize known chemistry**.
- **explore new or unknown chemistry**.

The rise of computational chemistry in industry

More than 70% of the leading pharmaceutical companies have integrated specialized computational chemistry teams that drive strategic innovation.

- **Cost efficiency**: Advanced molecular simulations systematically minimize experimental iterations reducing R&D expenditures significantly.
- **Early stage virtual screening**: Computational protocols enable rapid identification of optimal candidates, expediting discovery and filtering ineffective molecules prior to experiment.
- **Enhanced prediction accuracy**: High-precision computational models improve the reliability of property predictions, guiding more effective experimental validation strategies.
- **Accelerated development**: Simulations expedite molecular design cycles, enabling rapid hypothesis testing and shortening product development timelines.

Benefits: **Speed**, **Cost** and **Accuracy**

Putting computational chemistry to work!

- Drug design
- Medicinal chemistry design
- Consumer packaged food
- Protein/antibody engineering
- Enzyme design
- Organic electronics
- Pharmaceutical formulations
- Catalysis design
- Polymer design
- Surface chemistry
- Energy capture and storage
- Semiconductors
- Peptide design
- Metals, alloys, and ceramics design

Postulates of quantum mechanics

1. Postulate 1
    - The state of a quantum system is described by the wavefunction $\Psi(\mathbf{r}, t)$.
    - $\Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t)\, d\tau$ gives the probability of finding the particle in volume $d\tau$ at $\mathbf{r}$.
    - Normalization: $\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t)\, \Psi(\mathbf{r}, t)\, d\tau = 1$
    - Wavefunction must be single-valued, continuous, finite, and normalized (also for many-particle systems).
2. Postulate 2
    - To every observable in classical mechanics there corresponds a linear, Hermitian operator in quantum mechanics.

Postulates of quantum mechanics

1. Postulate 3
   - Measurement of the observable associated to operator $\hat{A}$ yields only its eigenvalues a (eigenvalue equation):

$$\hat{A}\Psi(\mathbf{r},t) = a\Psi(\mathbf{r},t)$$

   - If the system is in an eigenstate of $\hat{A}$, with a single eigenvalue a, then any measurement will yield a.
2. Postulate 4
   - If a system is in a state described by a normalized wavefunction Ψ, then the expectation value of the observable corresponding to $\hat{A}$ is given by:

$$\langle A \rangle = \int_{-\infty}^{\infty} \Psi^*(\mathbf{r},t)\,\hat{A}\,\Psi(\mathbf{r},t)\,d\tau$$

Postulates of quantum mechanics

1. Postulate 5
    - The wavefunction or state function of a system evolves in time according to the time-dependent Schrödinger equation (the central equation of quantum mechanics):

$$\hat{H}\,\Psi(\mathbf{r},t) = i\hbar\,\frac{\partial}{\partial t}\Psi(\mathbf{r},t)$$

2. Postulate 6
    - The total wavefunction must be antisymmetric with respect to the interchange of all coordinates of one fermion with those of another.

The molecular Hamiltonian

Quantum chemistry is (typically) based on the **non-relativistic Schrödinger equation** within the Born–Oppenheimer approximation.

$$\hat{H}_{\text{tot}}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p})\,\Psi_{\text{tot}}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) = E(\mathbf{R}, \mathbf{P})\,\Psi_{\text{tot}}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p})$$

$\mathbf{r}, \mathbf{p} = \partial/\partial\mathbf{r}$: electronic collective coordinates.
$\mathbf{R}, \mathbf{P} = \partial/\partial\mathbf{R}$: nuclear collective coordinates.
E: allowed energy of the system.
Ψ_{tot}: function of the positions of all electrons and nuclei.
$\hat{H}_{tot}$: differential operator constructed from the classical Hamiltonian.

The molecular Hamiltonian

Due to Born-Oppenheimer approximation some terms coupling the electrons and nuclei can be neglected.

$$\Psi_{\text{tot}}(\mathbf{R},\mathbf{r}) = \Psi_{\text{nucl}}(\mathbf{R})\,\Psi_{\text{elec}}(\mathbf{r};\mathbf{R})$$

and

$$\hat{H}_{\text{tot}} = \hat{T}_{\text{nucl}}(\mathbf{P},\mathbf{R}) + \hat{H}_{\text{elec}}(\mathbf{p},\mathbf{r};\mathbf{R})$$

ignoring the dependence of $\hat{H}_{elec}$ on the momenta of the nuclei $\mathbf{P}$.

Solution of Schrödinger equation for the electrons, with fixed nuclei, indicated by $(;\mathbf{R})$:

$$\hat{H}_{\text{elec}}(\mathbf{p},\mathbf{r};\mathbf{R})\,\Psi_{\text{elec}}(\mathbf{r};\mathbf{R}) = E(\mathbf{R})\,\Psi_{\text{elec}}(\mathbf{r};\mathbf{R})$$

$V(\mathbf{R})$, potential energy surface: collection of all possible nuclear configurations, $\mathbf{R}$ together with the associated energies.

The nuclear Schrödinger equation

$V(\mathbf{R})$ is usually expanded to second order $\mathbf{R}$ about a stationary point $\mathbf{R}_0$:

$$V(\mathbf{R}) \approx V(\mathbf{R}_0) + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 V(\mathbf{R})}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right)(\mathbf{R}_i - \mathbf{R}_{0,i})(\mathbf{R}_j - \mathbf{R}_{0,j})$$

No need to solve the electronic Schrödinger equation at many $\mathbf{R}$'s. Only required:

- locate stationary point $\mathbf{R}_0$.
- evaluate energy and Hessian (second derivatives) at that $\mathbf{R}_0$.

The electronic Schrödinger equation

Pauli exclusion principle: Because electrons are indistinguishable fermions, any permutation of two electrons must change the sign of the wavefunction $\Psi_{elect}(\mathbf{r};\mathbf{R})$.

Slater determinant many-electron wavefunctions satisfy the Pauli principle.

$$\begin{aligned}\Psi_{\text{el}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = &\sum_{m_1,m_2,\ldots,m_N} C_{m_1,m_2,\ldots,m_N} \\ &\times \left|\phi_{m_1}(\mathbf{r}_1)\,\phi_{m_2}(\mathbf{r}_2)\,\cdots\,\phi_{m_N}(\mathbf{r}_N)\right|\end{aligned}$$

where

$$\left|\phi_{m_1}(\mathbf{r}_1)\,\phi_{m_2}(\mathbf{r}_2)\,\cdots\,\phi_{m_N}(\mathbf{r}_N)\right| = \frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_{m_1}(\mathbf{r}_1) & \phi_{m_2}(\mathbf{r}_1) & \cdots & \phi_{m_N}(\mathbf{r}_1)\\ \phi_{m_1}(\mathbf{r}_2) & \phi_{m_2}(\mathbf{r}_2) & \cdots & \phi_{m_N}(\mathbf{r}_2)\\ \vdots & \vdots & \ddots & \vdots\\ \phi_{m_1}(\mathbf{r}_N) & \phi_{m_2}(\mathbf{r}_N) & \cdots & \phi_{m_N}(\mathbf{r}_N)\end{vmatrix}$$

The electronic Schrödinger equation

$\phi_{m_i}(\mathbf{r}_i)$: one-electron molecular orbitals which are usually given as an expansion in "atomic orbitals", χ_n:

$$\phi_m(\mathbf{r}, s) = \sum_n D_{mn}\, \chi_n(\mathbf{r}) \otimes s$$

Coefficients D and C fully characterize the solution of the electronic Schrödinger equation for atoms and molecules.

Main topic of electronic structure methods

The development of approximated methods for the solution of the Schrödinger equation for the electrons (given by the coefficients D and C) for obtaining the potential for the nuclei dynamics $V(\mathbf{R})$.

Translation of this problem into a formulation suited for computation: choose an appropriate set of basis functions.

Basis functions in quantum chemistry

One or many-electron molecular wavefunctions are described in the basis of atom centered functions.

Simplified atomic orbitals: sum of Gaussians centered on the atoms times a polynomial, P_l, in the electron coordinates relative to that atom:

$$\chi_n(\mathbf{r}) = \sum_l N_n^l \exp\big(- \alpha_{nl} \, |\mathbf{r} - \mathbf{R}_I^n|^2 \big) \, P_l\big(\mathbf{r} - \mathbf{R}_I^n\big)$$

Basis sets: conventional sets of atomic orbitals that cover the polynomials up to a certain order with certain choices of "α".

Typical names: `6-31G`, `TZ2P` and `cc-pVQZ`.

Algorithmic procedure for the choice of basis sets: choose a basis, then vary coefficients D and C to approximate Ψ_{elec} that best solves the Schrödinger equation.

Hartree-Fock method

Hartree-Fock (HF) provides a mean-field approximation:

- Electrons do not interact with each other. The effect of other electrons is accounted for in a mean-field theory context.
- Wavefunction represented as a single Slater determinant made of one-electron molecular orbitals.

Hartree-Fock equations

$$h(x_1)\phi_i(x_1) + \sum_{j\neq i}\left[\int dx_2\,|\phi_j(x_2)|^2 r_{12}^{-1}\right]\phi_i(x_1) - \sum_{j\neq i}\left[\int dx_2\,\phi_j^*(x_2)\phi_i(x_2) r_{12}^{-1}\right]\phi_j(x_1) = \epsilon_i\phi_i(x_1)$$

where ϵ_i is the energy eigenvalue associated with orbital ϕ_i.

- First term: one-electron Hamiltonian $h(x_1)$.
- Second: Coulomb interaction of an electron in spin orbital ϕ_i with the average charge distribution of the other electrons. (**HF: a mean field theory**).
- Third: exchange term (it arises from the antisymmetry requirement of the wavefunction).

Hartree-Fock operator

$$f(x_1) = h(x_1) + \sum_j \big(J_j(x_1) - K_j(x_1)\big)$$

$$f(x_1)\phi_i(x_1) = \epsilon_i \phi_i(x_1)$$

- Self-consistent eigenvalue problem.
- Orbitals ϕ_i are eigenfunctions of f.

Self-consistent-field procedure

In matrix form:

$$\sum_{\nu} F_{\mu\nu} D_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} D_{\nu i}$$

More simple as matrices:

$$\mathbf{FD} = \mathbf{SD}\varepsilon$$

ε is a diagonal of the orbital energies ϵ_i.

- Generalized eigenvalue problem: $\mathbf{FD} = \mathbf{SD}\varepsilon$
- To simplify: transform to an orthogonal basis ($\mathbf{S} \rightarrow I$).
- Then it reduces to a standard eigenvalue problem for $\mathbf{F}$.
- But: $\mathbf{F}$ depends on the orbitals (and thus on $\mathbf{D}$).
- $\Rightarrow$ Must solve **iteratively** until self-consistency is reached.

Solution of Hartree-Fock-Roothaan equations are often called the self-consistent-field procedure.

Why Density Functional Theory (DFT)?

- DFT is one of the most popular and successful quantum-mechanical approaches to matter.
- Routinely used to compute:
    - Molecular binding energies
    - Band structures of solids
    - Widely applied across disciplines: from biology to materials science.
- **DFT bridges quantum mechanics and real materials — from atoms to solids.**

From wavefunction to density

All information about a system is contained in its wavefunction Ψ, the lowest-energy solution of the many-electron Schrödinger equation:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{I,i} \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_{I>J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \right.$$
$$\left. + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\mathbf{r},\mathbf{R}) = E_{\mathrm{el}} \Psi(\mathbf{r},\mathbf{R})$$

or, more compactly:

$$\left[\hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r},\mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})\right] \Psi(\mathbf{r},\mathbf{R}) = E_{\mathrm{el}} \Psi(\mathbf{r},\mathbf{R})$$

- External potential: $v(\mathbf{r},\mathbf{R})$ generated by the nuclei.
- For fixed nuclei: often written simply as $v(\mathbf{r})$.

Conventional quantum mechanical approach

- Standard sequence:

$$v(\mathbf{r}, \mathbf{R}) \implies \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \implies \text{Observables}$$

- One observable obtained this way is the electron density $\rho(\mathbf{r})$.
- Wavefunction-based methods (HF, CI, etc.) require massive computational effort:
  - Scales poorly with system size.
  - Full-CI impractical beyond a few electrons.
- **DFT provides a practical, accurate alternative** for medium (100 electrons) to large (thousands of electrons) systems.

The core idea of DFT

- **The electron density is at the center of DFT.**
- DFT recognizes that nonrelativistic Coulomb systems differ only by their potential $v(\mathbf{r}, \mathbf{R})$.
- The universal operators $\hat{T}_e$ (kinetic) and $\hat{V}_{ee}$ (electron–electron interaction) are treated once and for all.
- DFT provides a systematic way to map the **many-body problem** (with $\hat{V}_{ee}$) onto a **single-body problem** (without $\hat{V}_{ee}$).
- The calculation of the observables can be based on the electron density.

The density functional concept

Conceptual structure of DFT:

$$\rho(\mathbf{r}) \implies \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \implies v(\mathbf{r})$$

- Knowing the ground-state density $\rho(\mathbf{r})$ uniquely determines the wavefunction and potential and in turn all the observables.
- In practice, modern DFT calculations bypass explicit use of many-body wavefunctions.

The Hohenberg-Kohn theorem

- The **Hohenberg-Kohn (HK) theorem** is the foundation of DFT.
- It states that the ground-state density $\rho_0(\mathbf{r})$ uniquely determines:
  - the ground-state wavefunction $\Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)$,
  - and thus all ground-state observables.
- The theorem states that for the ground state the equation:

$$\rho(\mathbf{r}) = M \int \cdots \int \Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \Psi^*(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \, d\mathbf{r}_2 \cdots d\mathbf{r}_N$$

can be inverted.

The Hohenberg-Kohn theorem

- Given $\rho_0(\mathbf{r})$, one can in principle calculate Ψ_0.
- Therefore, all ground-state observables are functionals of ρ_0.
- This might seem impossible at first:
  - $\rho(\mathbf{r})$ depends on **3 variables**,
  - $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ depends on **3N variables**.
- The key: Ψ_0 is not an arbitrary function; it must not only reproduce ρ_0 but minimize the energy as well.

The Hohenberg-Kohn theorem

For a given ground-state density, the ground-state energy is:

$$E_{v,0} = \min_{\Psi \rightarrow \rho_0} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{eN} | \Psi \rangle$$

For an arbitrary density $\rho(\mathbf{r})$, we define:

$$E_v[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} + \hat{V}_{eN} | \Psi \rangle$$

- If ρ a density different from the ground state density ρ_0 in the external potential $v(r)$, then the Ψ that produces this density ρ is different from the ground state wavefunction Ψ_0, and according to the variational principle the minimum obtained from $E_v[\rho]$ is higher than (or equal to) the ground state energy $E_{v,0} = E_v[\rho_0]$.

The Hohenberg-Kohn theorem

The total energy functional can be written as:

$$E_v[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int d^3 r \, \rho(\mathbf{r}) \, v(\mathbf{r})$$

$$=: F[\rho] + V[\rho]$$

- $F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$: internal energy functional; independent of the external potential.
- The universality of the internal energy functional allows us to define the ground state wavefunction as that antisymmetric N-particle function that delivers the minimum of $F[\rho]$ and reproduces ρ_0.

The first Hohenberg-Kohn theorem

The nondegenerate ground-state wavefunction Ψ_0 is a unique functional of the ground state density $\rho_0(\mathbf{r})$.

$$\Psi_0(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \Psi[\rho_0(\mathbf{r})]$$

All ground-state observables $\hat{O}$ are also functionals of ρ_0:

$$O_0 = O[\rho_0] = \langle \Psi[\rho_0] | \hat{O} | \Psi[\rho_0] \rangle$$

The second Hohenberg-Kohn theorem

For the special case of the total energy observable:

$$E_{v,0} = E_v[\rho_0] = \langle \Psi[\rho_0] | \hat{H} | \Psi[\rho_0] \rangle$$

where $\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{eN}$.

The variational property holds:

$$E_v[\rho_0] \leq E_v[\rho']$$

Analogous to the standard variational principle for Ψ:

$$E_{v,0} = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \leq \langle \Psi' | \hat{H} | \Psi' \rangle = E_v[\Psi']$$

In exact DFT, if $E[\rho]$ for fixed v_{ext} is evaluated for a density that is not the ground state density of the system in potential v_{ext}, one never finds a result below the true ground state energy.

The second Hohenberg-Kohn theorem

In practice, $E_v[\rho]$ is minimized under the constraint that the total particle number N is fixed, by means of a Lagrange multiplier.

$$\frac{\delta E_v[\rho]}{\delta \rho(\mathbf{r})} = \mu = \frac{\partial E}{\partial N}$$

where μ is the chemical potential.

Universal and system-dependent functionals

Since kinetic and interaction energies of a nonrelativistic Coulomb system are described by universal operators:

$$E_v[\rho] = T[\rho] + V_{ee}[\rho] + V_{eN}[\rho] = F[\rho] + V_{eN}[\rho]$$

where $T[\rho]$ and $V_{ee}[\rho]$ are **universal** functionals.

The potential energy in a given potential $v(\mathbf{r})$ is the expectation value of the potential:

$$\hat{V}_{\text{ext}}(\mathbf{r}) = \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

which reads:

$$V_{\text{ext}}[\rho] = \int d^3r\, \rho(\mathbf{r})\, v_{\text{ext}}(\mathbf{r})$$

It is nonuniversal. **But if the system is specified, i.e., $v_{ext}(\mathbf{r})$ is known, the functional $V_{ext}[\rho]$ is known explicitly.**

DFT in practice

Once the external potential $v_{\text{ext}}(\mathbf{r})$ is known and reliable approximations for $T[\rho]$ and $V_{ee}[\rho]$ are available, the task reduces to minimizing the total energy functional:

$$E_v[\rho] = T[\rho] + V_{ee}[\rho] + V_{eN}[\rho] = T[\rho] + V_{ee}[\rho] + \int \rho(\mathbf{r})\, v_{\text{ext}}(\mathbf{r})\, d^3r$$

with respect to $\rho(\mathbf{r})$.

- The minimizing function $\rho_0(\mathbf{r})$ gives the ground state charge density.
- The minimum value $E_{v,0} = E_v[\rho_0]$ is the ground state energy.

Using DFT to explore physical properties

- Suppose $v_{\text{ext}}(\mathbf{r})$ depends on a parameter a:
  - e.g., lattice constant in a solid,
  - angle between two atoms in a molecule.
- Calculate $E_{v,0}(a)$ for various a values:
  - The minimum determines the equilibrium configuration a_0.
- From $E_{v,0}(a)$ one can compute:
  - Molecular geometries and lattice constants,
  - Unit cell volumes and charge distributions,
  - Total energies and potential energy surfaces.

Kohn-Sham DFT

- DFT can be implemented in many different ways.
- Minimizing an explicit energy functional $E_v[\rho]$ is possible, but often **computationally inefficient**.
- The most successful and widely used formulation is the **Kohn-Sham approach**.
- It combines the conceptual simplicity of DFT with the practical convenience of working with single-particle orbitals.

Key Idea of the Kohn-Sham method

This makes DFT look formally like a **single-particle theory**, but:

- many-body effects remain included, through the **exchange–correlation functional**.

This elegant combination of orbital-based and density-based ideas explains the **success and popularity** of the KS formalism.

The exchange-correlation energy

- Decomposition of the kinetic energy functional of interacting electrons, $T[\rho]$, into two parts:

$$T[\rho] = T_s[\rho] + T_c[\rho]$$

- $T_s[\rho]$: kinetic energy of a system of **noninteracting** particles with density ρ.
- $T_c[\rho]$: term accounting for **correlation effects**.
- Subscripts:
  - s = “single-particle” (noninteracting),
  - c = “correlation”.

The exchange-correlation energy

- $T_s[\rho]$ is not known as an explicit functional of ρ, but can be expressed in terms of the **Kohn–Sham orbitals** $\{\phi_i(\mathbf{r})\}$:

$$T_s[\rho] = -\frac{1}{2}\sum_{i=1}^{N}\int \phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r})\, d^3r$$

- Each orbital $\phi_i(\mathbf{r})$ corresponds to a single-particle state in an auxiliary noninteracting system.
- These orbitals reproduce the same total density.

The exchange-correlation energy

- The Kohn-Sham orbitals $\{\phi_i(\mathbf{r})\}$ are functionals of the density:

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

- Therefore, the kinetic energy can be written as:

$$T_s[\rho] = T_s[\{\phi_i[\rho]\}]$$

- This means:
  - T_s is an **explicit orbital functional**,
  - but only an **implicit density functional**.

The exchange-correlation energy

The exact energy functional can be rewritten as:

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{eN}[\rho] = T_s[\{\phi_i[\rho]\}] + V_H[\rho] + E_{xc}[\rho] + V_{eN}[\rho]$$

where:

- T_s – kinetic energy of the noninteracting system,
- V_H – classical Hartree (Coulomb) energy,
- E_{xc} – exchange–correlation energy functional,
- V_{eN} – electron–nuclear interaction.

The exchange–correlation term collects:

$$E_{xc} = (T - T_s) + (V_{ee} - V_H)$$

i.e. the difference between the noninteracting and interacting kinetic energies.

The exchange-correlation energy

- $E_{xc}[\rho]$ combines two key effects:

$$E_{xc} = E_x + E_c$$

  - E_x: exchange energy (from the Pauli principle),
  - E_c: due to electron correlation.
- The exchange energy can be expressed explicitly in terms of the single-particle orbitals:

$$E_x[\{\phi_i[\rho]\}] = -\frac{1}{2}\sum_{i,j}\int d^3r \int d^3r' \frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\phi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}$$

- E_{xc} is formally exact, but its **exact functional form** is **unknown**.

The Kohn-Sham equations

- Since T_s is an **orbital functional**, direct minimization with respect to ρ is not possible.
- Instead, Kohn and Sham proposed an **indirect minimization scheme** based on functional derivatives:

$$0 = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})}$$

The Kohn-Sham equations

- Expanding the functional derivative gives:

$$\frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_{\text{ext}}[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_H[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$
$$= \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

- $\frac{\delta V_{\text{ext}}[\rho]}{\delta \rho(\mathbf{r})} = v_{\text{ext}}(\mathbf{r})$: the 'external' potential the electrons move in (we use V_{ext} for V_{eN}).
- $\frac{\delta V_H[\rho]}{\delta \rho(\mathbf{r})}$: simply yields the Hartree potential.
- $\frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$: which can only be calculated explicitly once an approximation for E_{xc} has been chosen, one commonly writes v_{xc}.

The Kohn-Sham equations

- Consider a system of **noninteracting particles** moving in a potential $v_s(\mathbf{r})$.
- The corresponding minimization condition is:

$$0 = \frac{\delta E_s[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} + \frac{\delta V_s[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}$$

The Kohn-Sham equations

- For the noninteracting case, there are no Hartree or exchange-correlation terms.
- Thus, the minimization condition simplifies to:

$$0 = \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}$$

- The density that satisfies this equation is the noninteracting ground-state density $\rho_s(\mathbf{r})$.
- This defines the auxiliary system of noninteracting particles.

The Kohn-Sham equations

- Both minimizations lead to the condition:

$$\rho_s(\mathbf{r}) \equiv \rho(\mathbf{r}) \quad \text{if} \quad v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})$$

- The many-body interacting system in $v_{\text{ext}}(\mathbf{r})$ can thus be replaced by a noninteracting system in $v_s(\mathbf{r})$.

The Kohn-Sham equations

- The auxiliary noninteracting system is described by the Kohn–Sham (KS) single-particle Schrödinger equation:

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

- The density of the original system is obtained from the Kohn-Sham orbitals:

$$\rho(\mathbf{r}) \equiv \rho_s(\mathbf{r}) = \sum_{i=1}^{N} f_i\,|\phi_i(\mathbf{r})|^2$$

- f_i denotes the occupation of orbital i.

Kohn-Sham equations replace the problem of minimizing $E[\rho]$ by that of solving the Schrödinger equation for a non-interacting system.

The Kohn-Sham equations

- Solving the Kohn-Sham equations is a **nonlinear problem** because:
  - The potentials $v_H[\rho]$ and $v_{xc}[\rho]$ depend on the density $\rho(\mathbf{r})$,
  - $\rho(\mathbf{r})$ depends on the orbitals $\phi_i(\mathbf{r})$,
  - and the orbitals $\phi_i(\mathbf{r})$ depend on the potential $v_s(\mathbf{r})$.
- This circular dependence requires an iterative solution approach.
- The method used is known as the **self-consistent field (SCF)** procedure.

The Kohn-Sham equations

- Once the self-consistent density $\rho_0(\mathbf{r})$ has been obtained, the total energy can be evaluated.
- The most convenient expression is:

$$E_0 = \sum_{i=1}^{N} \epsilon_i - \frac{1}{2} \int d^3r \int d^3r' \, \frac{\rho_0(\mathbf{r})\, \rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d^3r \, v_{xc}(\mathbf{r})\, \rho_0(\mathbf{r}) + E_{xc}[\rho_0]$$

Exchange-correlation functionals

- Local functionals: LDA
- Semilocal functionals: GGA
- Meta-GGA
- Hybrid functionals