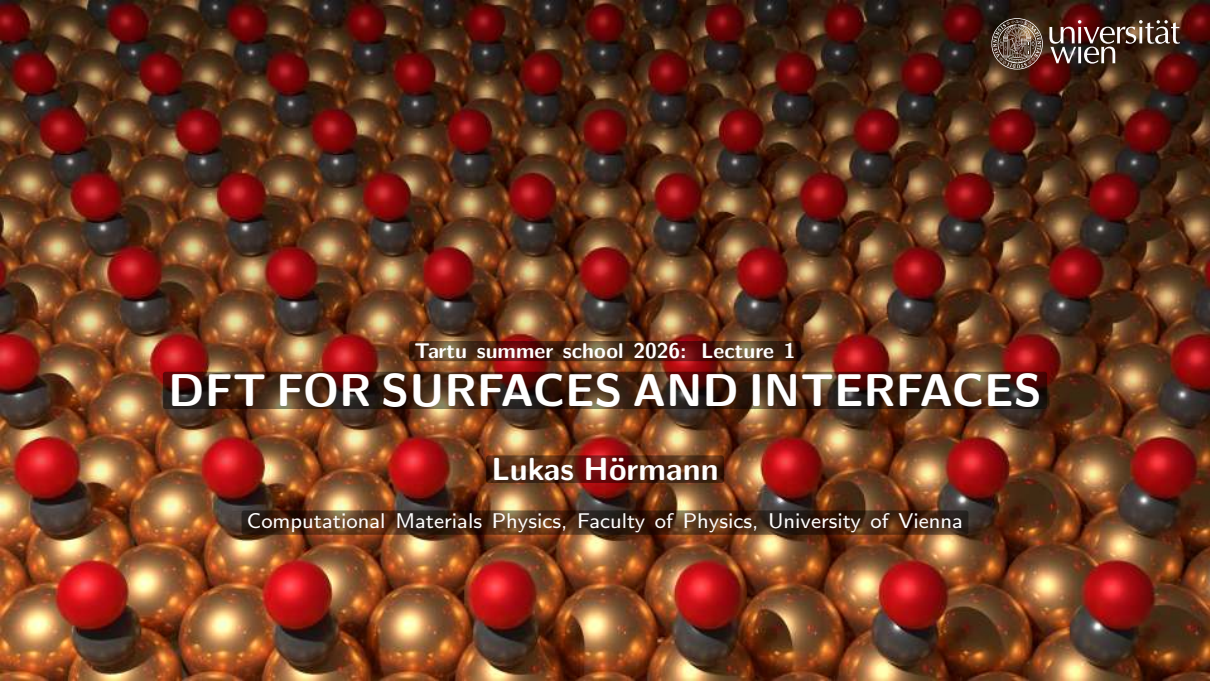

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Tartu summer school 2026: Lecture 1

DFT FOR SURFACES AND INTERFACES

Lukas Hörmann

Computational Materials Physics, Faculty of Physics, University of Vienna

Define your problem!

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What property do you want to model?

Geometry | Energy | Band gap | Work function | Dielectric constant | XPS spectrum

How do you describe the relevant physics?

Level of sophistication and methodological challenge

How do you actually calculate it?

Numerical strategies and the specific settings for solving the system of equations

What I will cover

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Lecture 1

The electronic structure method

- Material classes and properties
- A brief introduction to Kohn-Sham DFT

Exchange-correlation functionals

- Different types of xc-functionals
- Self-interaction error

Basis functions

- Basis sets
- Basis set superposition error

Self-consistent field procedure

Lecture 2

Physics and chemistry at interface

- Work function
- Level alignment, hybridisation, charge transfer
- VdW interactions

How to represent a surface in a calculation?

- Clusters versus repeated slabs
- Dipoles and charges

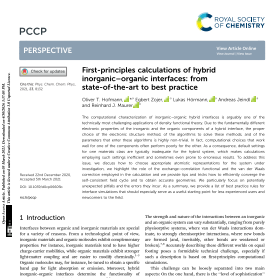
The wavefunction on a periodic system

- The Bloch theorem
- Sampling the Brillouin zone

VdW corrections

How to run a calculation

Literature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PERSPECTIVE

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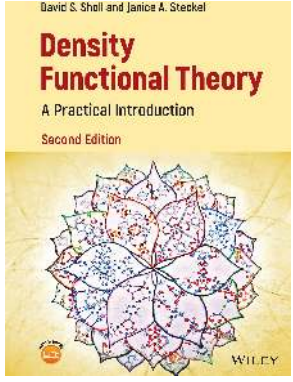
First-principles calculations of hybrid inorganic–organic interfaces: from state-of-the-art to best practice

Oliver T. Hofmann, Egbert Zojer, Lukas Hörmann, Andreas Jeindl and Reinhard J. Maurer

1 Introduction

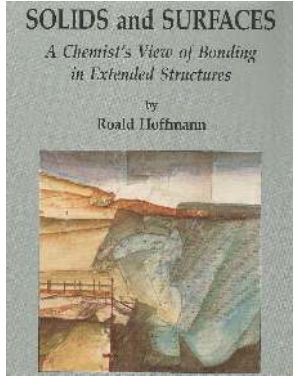

David S. Sholl and Janice A. Steckel

Density Functional Theory

A Practical Introduction

Second Edition

WILEY


SOLIDS and SURFACES

A Chemist's View of Bonding in Extended Structures

by

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DOI: 10.1039/d0cp06605b

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Solids and surfaces: A chemist's view of bonding in extended structures.
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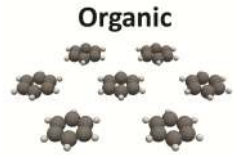
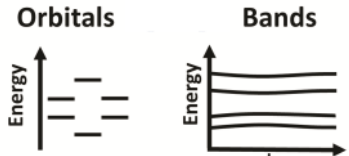
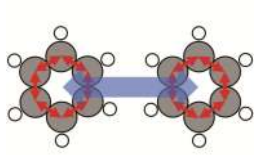
The challenge of organic-inorganic interfaces







Inorganic substrate
- Extended 3D periodic structures

Organic adsorbate
- Localized molecular units

Metals and semiconductors
- Large wave-function overlap
- Bands with large dispersion

Organic materials (and insulators)
- Small wave-function overlap
- Flat bands

Metals and semiconductors
- Uniform electron density
- Large screening

Organic molecules
- Strongly varying electron density

Metals and insulators
- High coordination numbers
- Isotropic forces

Organic molecules (and semiconductors)
- Covalent forces
- Strongly anisotropic

[1] Hofmann et al. Phys. Chem. Chem. Phys. 23.14 (2021): 8132-8180.

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The electronic structure method

The many-particle problem

Time independent Schrödinger equation:

$$H\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R})$$

Total Hamiltonian

$$H = \underbrace{T_e + T_N}_{\text{Kinetic}} + \underbrace{V_{ee} + V_{eN} + V_{NN}}_{\text{Potential}}$$

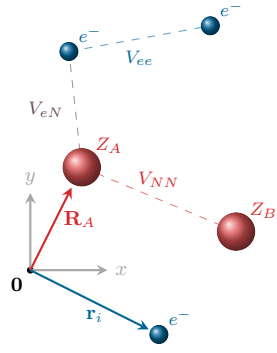
Kinetic Energy (T)

- $T_e = -\frac{1}{2}\sum_i \nabla_i^2$ (Electrons)
- $T_N = -\sum_A \frac{1}{2M_A}\nabla_A^2$ (Nuclei)

Potential Energy (V)

- $V_{ee} = \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$ (Electron-electron repulsion)
- $V_{eN} = -\sum_{i,A} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}$ (Electron-nucleus attraction)
- $V_{NN} = \sum_{A<B} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$ (Nucleus-nucleus repulsion)

Working in **atomic units** *($m_e = e = \hbar = 4\pi\epsilon_0 = 1$) simplifies the expressions.*



The Born-Oppenheimer approximation

We can expand the exact total wavefunction as a superposition of products (**Born-Huang Expansion**), using the complete set of electronic (ϕ_n) and nuclear (χ_n) eigenfunctions:

$$\psi(\mathbf{r}, \mathbf{R}) = \sum_n \chi_n(\mathbf{R})\phi_n(\mathbf{r}; \mathbf{R})$$

Born-Oppenheimer ansatz

Assuming the motion of electrons and nuclei decouple, we use a single-product ansatz for the wavefunction:

$$\psi(\mathbf{r}, \mathbf{R}) \approx \chi(\mathbf{R})\phi(\mathbf{r}; \mathbf{R})$$

Separation of scales ($M_N \gg m_e$)

- Electrons move so fast they respond *instantaneously* to nuclear motion.
- From the electrons' perspective, the nuclei are frozen at coordinates $\mathbf{R}$.

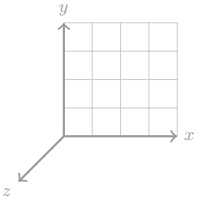
Electronic Schrödinger equation

- V_{eN} acts as the external potential (V_{ext}).
- $V_{NN}(\mathbf{R})$ becomes a constant energy shift (dropped from the operator, added back for total energy).

$$[T_e + V_{ee} + V_{ext}]\phi(\mathbf{r}; \mathbf{R}) = E_{elec}(\mathbf{R})\phi(\mathbf{r}; \mathbf{R})$$

The dimensionality problem

To evaluate the electronic wavefunction $\psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ computationally (before it was ϕ), we must discretise space. Assume a very modest grid of just $M = 100$ points per spatial axis:



1 electron (3D): $100^3 = 10^6$ values $\approx$ **8** MB

2 electrons (6D): $100^6 = 10^{12}$ values $\approx$ **8** TB

10 electrons (30D): $100^{30} = 10^{60}$ values $\rightarrow$ **Intractable**

How to overcome this: The variational principle

Because solving the $3N$-dimensional Schrödinger equation is impossible for real systems, we must rely on approximations. The variational principle guarantees that any trial wavefunction $|\psi\rangle$ yields an energy higher than or equal to the true ground state energy E_0:

$$E = \frac{\langle\psi| H |\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

The state that minimises this energy is the exact ground state $|\psi_0\rangle$.

The Hohenberg-Kohn theorems

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If we have a system with a Hamiltonian that looks like:

$$H = T + V_{ee} + V_{ext} \quad \rightarrow \quad H\psi = E\psi$$

Hohenberg-Kohn theorems

- **Theorem 1:** The ground-state electron density $n_0(\mathbf{r})$ uniquely determines the external potential $V_{\text{ext}}(\mathbf{r})$ (up to an additive constant). In other words, **two different external potentials cannot give rise to the same ground-state electron density.**
- **Theorem 2:** The electron density that minimises the energy is the ground-state density $n_0(\mathbf{r})$.

These theorems allow us to express the variational approach by formulating the ground state as a functional of the electron density $n(\mathbf{r})$ rather than the wavefunction:

$$\psi_0 = \psi[n_0]$$

Consequently, the **ground state energy is uniquely determined by the density**:

$$E[n_0] = \langle \psi[n_0] | \left[T + V_{ext} + V_{ee} \right] | \psi[n_0] \rangle$$

→ **We move from a $3N$-dimensional problem to a much more tractable 3-dimensional problem.**

The Kohn-Sham ansatz

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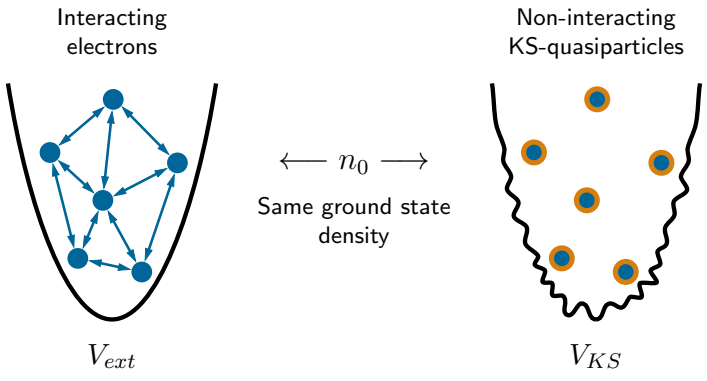
To make the energy functional tractable, we map the interacting system onto a system of **non-interacting Kohn-Sham quasiparticles** $\phi_i(\mathbf{r})$. We define the density using Kohn-Sham quasiparticles:

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



The Kohn-Sham ansatz

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Using Kohn-Sham quasiparticles $\phi_i(\mathbf{r})$ and density $n(\mathbf{r})$, we write the energy functional $E[n]$, partitioned into:

- Terms we know: kinetic, Hartree, external potential
- **Exchange-correlation components:** all the complicated physics

$$E[n] = \underbrace{-\frac{1}{2}\sum_i \int \phi_i^*(\mathbf{r})\nabla^2\phi_i(\mathbf{r})d\mathbf{r}}_{E_T} + \underbrace{\frac{1}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'}_{E_H} + \int d\mathbf{r}\ n(\mathbf{r})V(\mathbf{r}) + E_{xc}[n]$$

Vary energy $E[n]$ with respect to ϕ_i to minimise E; constrain orthonormality of orbitals:

$$\mathcal{L}[\phi_i] = E[n] - \sum_{ij}\epsilon_{ij}(\delta_{ij} - \langle\phi_j|\phi_i\rangle) \quad \rightarrow \quad \frac{\partial\mathcal{L}}{\partial\phi_s^*} = 0$$

Constrained minimisation yields the effective single-particle **Kohn-Sham equations**:

$$\left(-\frac{1}{2}\nabla^2 + V_H(\mathbf{r}) + V(\mathbf{r}) + V_{xc}(\mathbf{r})\right)\phi_s(\mathbf{r}) = \epsilon_s\ \phi_s(\mathbf{r})$$

$$h_{KS}\ \phi_s(\mathbf{r}) = \epsilon_s\ \phi_s(\mathbf{r})$$

Ingredients to numerically solve this: **xc-functional $V_{xc}(\mathbf{r})$** and **basis function for $\phi_s(\mathbf{r})$**

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Exchange-correlation functionals

or the bucket of insufficiently understood and complicated physics

Exchange-correlation functionals: Jacob's ladder

Local and semi-local functionals

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LDA $E_{xc}^{\text{LDA}} = \int n(\mathbf{r})\epsilon_{xc}(n)\, d\mathbf{r}$

- **Local functional:** Depends only on local density ($n(\mathbf{r})$)
- Overbinds adsorbates.

GGA $E_{xc}^{\text{GGA}} = \int n(\mathbf{r})\epsilon_{xc}(n, \nabla n)\, d\mathbf{r}$

- **Semi-local functional:** Depends on local density ($n(r)$) and it's curvature ($\nabla n(r)$)
- Blind to long-range interactions such as van der Waals ($\rightarrow$ lecture 2).

Meta-GGA $E_{xc}^{\text{mGGA}} = \int n(\mathbf{r})\epsilon_{xc}(n, \nabla n, \tau)\, d\mathbf{r}$

- Adds kinetic energy density (τ)
- Captures intermediate-range interactions; Can yield accurate surface energies


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exact functional
Beware, this is no ordinary rabbit!

Self-interaction

Let's examine the energy integrals for a **single electron** in orbital $\phi_i(\mathbf{r})$. An electron cannot interact with itself $\rightarrow$ **self-interaction energy must be zero**.

In **Hartree-Fock** theory, this cancellation is perfect:

$$F(\mathbf{r}) = h(\mathbf{r}) + \sum_j [J_j(\mathbf{r}) - K_j(\mathbf{r})] \qquad F(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

Coulomb term: Electrostatic repulsion of the electron's density ($n_i = |\phi_i|^2$) interacting with itself:

$$\langle \phi_i | J_i | \phi_i \rangle = \iint \frac{|\phi_i(\mathbf{r})|^2 |\phi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Exchange term : Non-local exchange interaction required by the antisymmetry of the wavefunction:

$$\langle \phi_i | K_i | \phi_i \rangle = \iint \frac{\phi_i^*(\mathbf{r})\phi_i(\mathbf{r}')\phi_i^*(\mathbf{r}')\phi_i(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

Coulomb and Exchange terms cancel exactly for the same electron

For the same electron, the integrands are identical ($|\phi_i(\mathbf{r})|^2 |\phi_i(\mathbf{r}')|^2$) and the exact self-interaction cancels:

$$\langle \phi_i | J_i - K_i | \phi_i \rangle = 0$$

Self-interaction error in DFT

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In **Kohn-Sham DFT**, exchange and correlation are approximated as a functional of the local electron density, $n(\mathbf{r})$.

The **Kohn-Sham Hamiltonian** uses effective local potentials:

$$h_{KS}(\mathbf{r}) = h(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \qquad h_{KS}(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

Coulomb energy: The exact unphysical self-repulsion energy of a single electron ($n_i = |\phi_i|^2$):

$$E_H[n_i] = \frac{1}{2}\langle \phi_i | V_H | \phi_i \rangle = \frac{1}{2} \iint \frac{|\phi_i(\mathbf{r})|^2 |\phi_i(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}'$$

Exchange-correlation energy: DFT approximates the xc-energy with a functional based on the local density:

$$E_{xc}[n_i] = \int |\phi_i(\mathbf{r})|^2 \epsilon_{xc}(n_i(\mathbf{r}))\, d\mathbf{r} \qquad V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \epsilon_{xc}(n) + n\frac{\partial \epsilon_{xc}(n)}{\partial n}$$

Approximate exchange fails to cancel self-Coulomb repulsion

Because E_{xc} is an approximation, it cannot perfectly cancel the Coulomb energy. For a single electron:

$$E_H[n_i] + E_{xc}[n_i] \neq 0$$

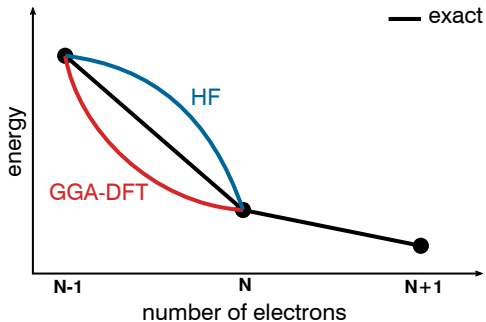
Consequences of the self-interaction error: Delocalisation error

For many-electron systems, the self-interaction error (SIE) acts as a **delocalisation error**. This is best understood via fractional charges.

The straight-line condition
Energy of an open system with a fractional number of electrons must be a **strict linear interpolation** between integer states N and $N + 1$.

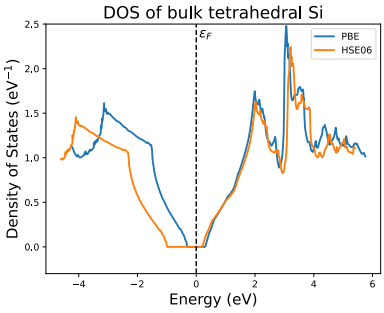
Deviation from the straight line

- **LDA-DFT and GGA-DFT**
  Underestimates the energy for fractional electron numbers $\rightarrow$ electrons get over-delocalised
- **Hartree-Fock**
  Overestimates the energy of fractional electron numbers.



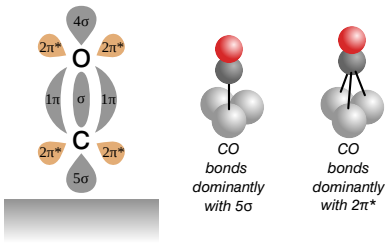
Consequences of the self-interaction error: Examples

Underestimation of band gaps



- The SIE raises the energy of localised occupied states (Valence Band) and lowers the energy of unoccupied states (Conduction band).
- LDA and GGA systematically underestimate band gaps. Can even predict insulating systems as metallic.

The CO adsorption puzzle



- In experiment 5σ-bonding to top site.
- SIE shifts the metal d-band up in energy and the empty CO $2\pi^*$ orbital down. Stronger $2\pi^*$-d bonding $\rightarrow$ prefers hollow site that maximises $2\pi^*$-d bonding.
- Wrong adsorption site.

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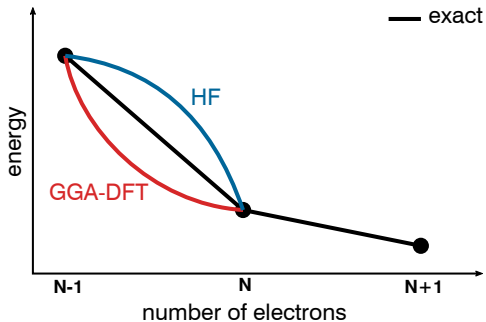

The solution: Hybrid functionals?

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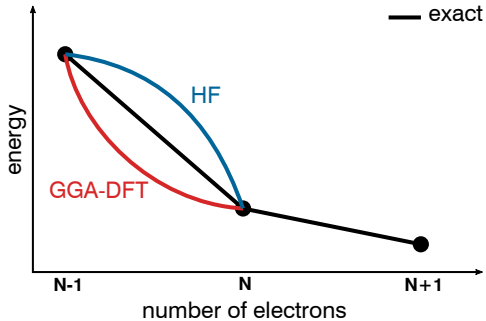
Mix GGA and HF to cancel errors

$$E_{xc}^{\text{hybrid}} = \alpha E_x^{\text{HF}} + (1-\alpha) E_x^{\text{GGA}} + E_c^{\text{GGA}}$$

- Mixes in exact (Hartree-Fock) exchange, via an empirical parameter α
- Mitigates Self-Interaction Error (by harnessing fortuitous cancellation of errors)
- Computationally expensive
- **But they do work quite well.**



Higher Rungs of Jacob's Ladder

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- **GW approximation:** Calculates quasiparticle self-energy dynamically. Corrects standard DFT eigenvalue errors to produce highly accurate **band structures** and band gaps.

- **BSE (Bethe-Salpeter equation):** Evaluates the two-particle Green's function to capture electron-hole interactions. Essential for calculating optical **spectra with bound quasiparticles** (e.g., excitons).

- **RPA (Random phase approximation):** Combines exact exchange with fully non-local correlation, capturing **vdW interactions automatically**.
  Drawback: Prone to severe Basis Set Superposition Error (BSSE).

Computational expense

These methods scale poorly ($O(N^4)$ or worse). Not used routinely.

Jacob's ladder, when you don't know what you're doing

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Basis functions

Basis set expansions

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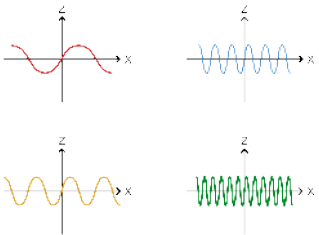
To solve the Kohn-Sham equations, we expand the unknown wavefunctions $\phi_i(\mathbf{r})$ as a linear combination of **basis functions** $\chi_\alpha(\mathbf{r})$.

$$\phi_i(\mathbf{r}) = \sum_\alpha c_{i\alpha}\chi_\alpha(\mathbf{r})$$

The Variational Principle: The **coefficients $c_{i\alpha}$ are optimised** to minimise the total energy. Adding more basis functions expands the variational space, lowering the calculated energy toward the true ground state.

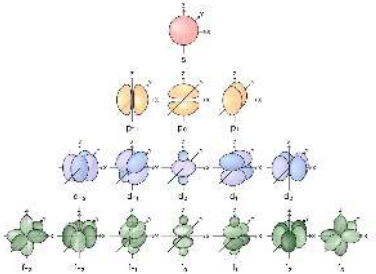
Delocalised basis functions (plane waves)

$$\chi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}\cdot\mathbf{r}}$$



Atom-centred basis functions

e.g. $\chi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\theta,\phi)$



Plane waves

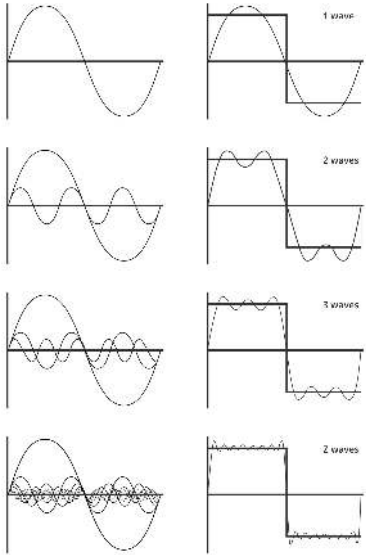
- **Intrinsically periodic and fill all space** → ideal when describing a material's uniform electron density.

$$\chi_{\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}\cdot\mathbf{r}}$$

- **Systematic convergence** via cutoff energy:

$$E_{\text{cut}} = \frac{\hbar^2 |\mathbf{G}|^2}{2m_e}$$

- **Surfaces and interfaces are all but uniform!** The electron density fundamentally changes at the boundary, analogous to a step function. Describing such a boundary requires many plane waves, i.e., a large E_{cut}.



Plane waves and pseudo-potentials

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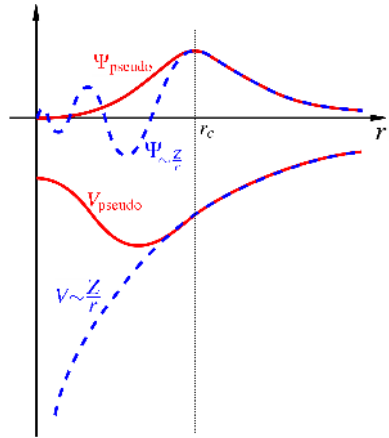
Plane waves struggle with rapidly changing electron density

- Close to nucleus: Divergent Coulomb potential
- Wavefunctions oscillate rapidly
- Would require massive E_{cut}

Cutting out the core states

- Inside the core radius ($r < r_c$):
  - Replace the true Coulomb potential with **pseudopotential** (nucleus + core electrons)
  - Pseudo-wavefunction is smooth
- Outside the core ($r > r_c$): Wave function matches the true all-electron wavefunction.



Atom-centred basis functions

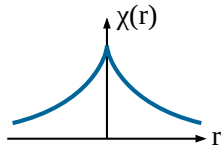
Inspired by atomic orbitals → Multiple basis functions on each atom:

$$\chi_{nlm}(\mathbf{r} - \mathbf{R}_I) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

Major advantage: Naturally supports all-electron calculations.

Slater-type (STOs)

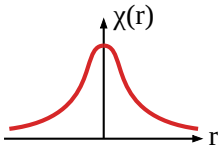
$$R(r) \propto r^{n-1} e^{-\zeta r}$$



- Correct physical shape (cusp at $r = 0$, e^{-r} tail).
- Numerically expensive.

Gaussian-type (GTOs)

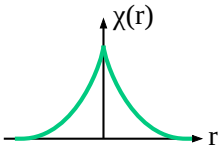
$$R(r) \propto r^{n-1} e^{-\alpha r^2}$$



- Cheap, but wrong shape.
- *Solution:* Combine multiple GTOs to mimic STOs.

Numeric (NAOs)

$$R(r) \propto u(r)$$



- $u(r)$ is not analytical; computed on a 1D grid.
- Zero beyond a cutoff radius.

Downsides: No systematic convergence, **Basis set superposition error**

Basis Set Superposition Error (BSSE)

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- **Finite basis sets are incomplete**

  In a dimer, fragment A borrows B's basis functions $\rightarrow$ Artificially expands variational space, falsely lowering E_{AB}.

  $$E_{AB}^{A\cup B} < E_{AB}^{A}, \quad E_{AB}^{B}$$

- **Overestimated binding**

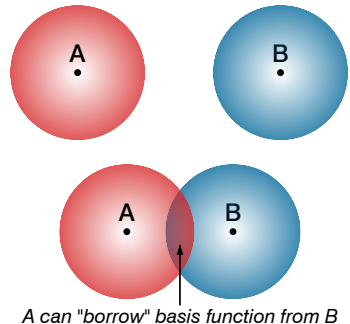
  Isolated fragments lack this expanded basis, resulting in mathematically exaggerated binding energies:

  $$E_{\text{ads}} = E_{AB}^{A\cup B} - E_{A}^{A} - E_{B}^{B} < E_{\text{ads}}^{\text{true}}$$

- **Counterpoise correction**

  Calculate isolated fragments using empty **"ghost atoms"** to introduce full variational space.

- **In standard DFT, tight basis sets mostly fix BSSE**



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Self-consistent field procedure

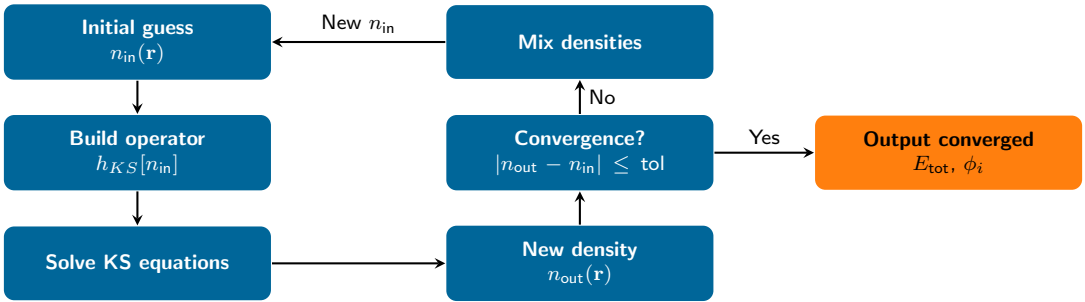
Solving the Kohn-Sham equations: Self-consistent field

The **Kohn-Sham Hamiltonian** is a functional of the electron density:

$$h_{KS}[n] = h + V_H[n] + V_{xc}[n] \qquad h_{KS}[n]\phi_i = \epsilon_i \phi_i$$

- The density is calculated through $n(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2$
- To calculate ϕ_i we need $h_{KS}[n]$, which inherently requires $n(\mathbf{r})$.

Iterative solution $\rightarrow$ **self-consistent field (SCF)**



Density update algorithms

Direct density insertion ($n_{\text{in}}^{(k+1)} = n_{\text{out}}^{k}$) often causes numerical instabilities. $\rightarrow$ mix input and output densities

Standard Mixing Algorithms

- **Linear mixing:** Simplest approach. Blends a fraction α of the new density with the old. (Often slow or unstable for metals).

$$n_{\text{in}}^{(k+1)} = \alpha n_{\text{out}}^{(k)} + (1-\alpha) n_{\text{in}}^{(k)}$$

- **Pulay mixing (DIIS):** The modern standard. Uses a history of previous steps to minimise the residual error ($R_i = n_{\text{out}}^{(i)} - n_{\text{in}}^{(i)}$):

$$n_{\text{in}}^{(k+1)} = \sum_i c_i \left(n_{\text{in}}^{(i)} + \alpha R_i \right) \quad \text{subject to} \quad \sum c_i = 1$$

- **Broyden mixing:** Quasi-Newton method updating an approximate Jacobian. Highly robust for complex metallic and magnetic systems.

Solving the Kohn-Sham equations: Self-consistent field

The **Kohn-Sham Hamiltonian** is a functional of the electron density:

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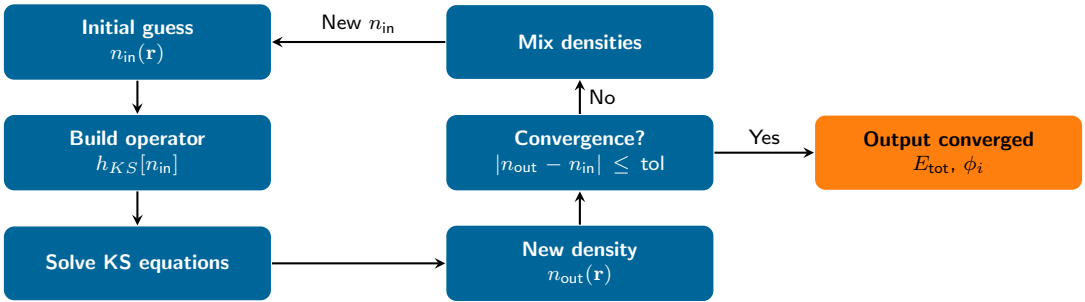
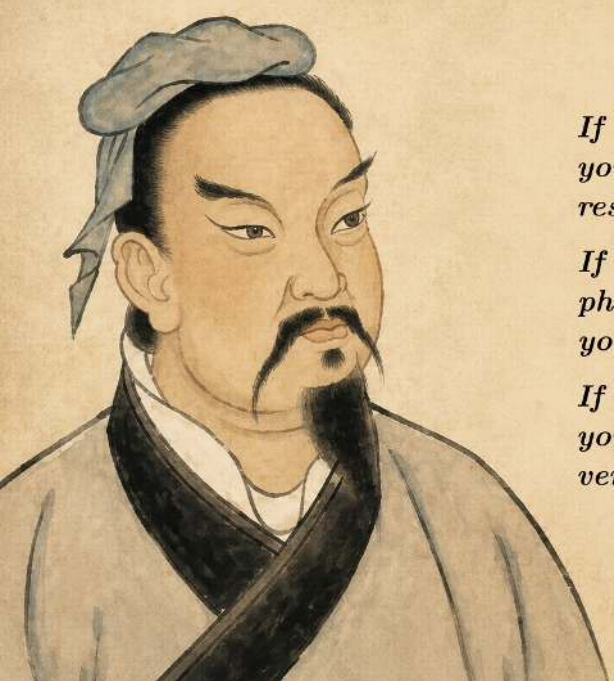


Summary

- **Kohn-Sham DFT:** Maps interacting electrons to a non-interacting system.
- The unknown physics is hidden in V_{xc}.
- **Known limits:** LDA/GGA approximations suffer from self-interaction error (SIE), causing artificial electron delocalisation.
- **Basis sets:**
  - *Plane waves:* Systematic, but struggle with discontinuity at surfaces.
  - *Atom-centred:* Efficient for surfaces/molecules, but prone to BSSE.
- **SCF cycle:** KS equations are solved iteratively.



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If you know the physics and know your method, you need not fear the result of a hundred calculations.

If you know your method but not the physics, for every convergence gained you will also suffer a crash.

If you know neither the physics nor your method, you will only produce very expensive random numbers.

Sun Tzu
famous Chinese general, 544 - 496 BC

Bonus material 1: Proof of Hohenberg-Kohn theorem 1

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Proof by contradiction

Assume two different external potentials, V_1 and V_2 (differing by more than a constant), yield the *same* ground-state density $n_0(\mathbf{r})$. They correspond to different Hamiltonians $\hat{H}_1 = T + U + V_1$ and $\hat{H}_2 = T + U + V_2$, and different ground-state wavefunctions ψ_1 and ψ_2.

By the variational principle, evaluating $\hat{H}_1$ with the trial wavefunction ψ_2 gives a strictly higher energy:

$$E_1 < \langle\psi_2|\,\hat{H}_1\,|\psi_2\rangle = \langle\psi_2|\,\hat{H}_2 + (\hat{H}_1 - \hat{H}_2)\,|\psi_2\rangle$$

Since $\hat{H}_1$ and $\hat{H}_2$ only differ by their external potentials, this becomes:

$$E_1 < E_2 + \int n_0(\mathbf{r})\,[V_1(\mathbf{r}) - V_2(\mathbf{r})]\,d\mathbf{r} \qquad \textbf{(1)}$$

Reversing the roles (evaluating $\hat{H}_2$ with trial wavefunction ψ_1) yields:

$$E_2 < E_1 + \int n_0(\mathbf{r})\,[V_2(\mathbf{r}) - V_1(\mathbf{r})]\,d\mathbf{r} \qquad \textbf{(2)}$$

Adding **(1)** and **(2)** gives a strict contradiction:

$$E_1 + E_2 < E_2 + E_1$$

Conclusion: The initial assumption must be false. The external potential is uniquely determined by the ground-state density $n_0(\mathbf{r})$.