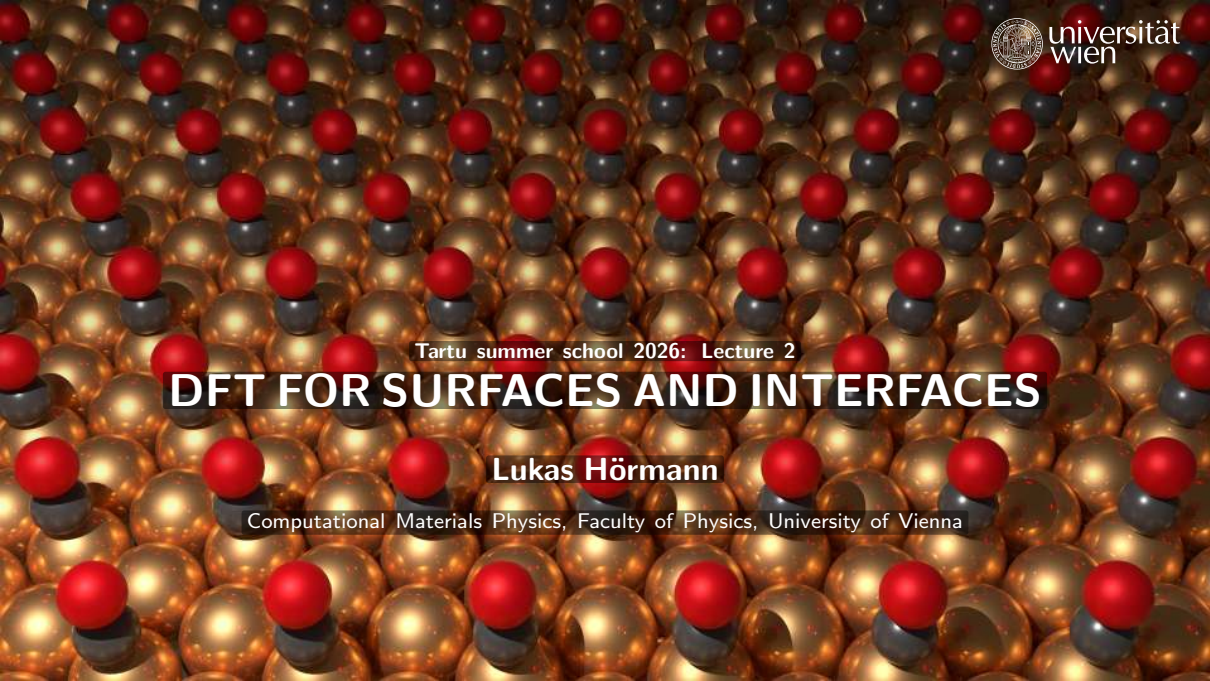

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Tartu summer school 2026: Lecture 2

DFT FOR SURFACES AND INTERFACES

Lukas Hörmann

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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

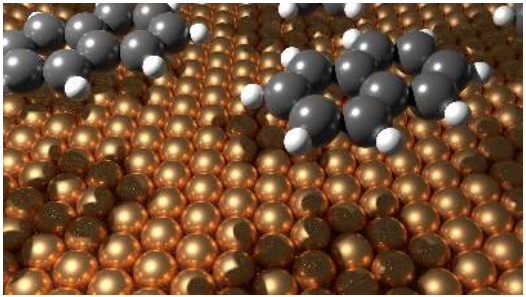
- The Bloch theorem
- Sampling the Brillouin zone

VdW corrections

How to run a calculation

Physics and chemistry at interface

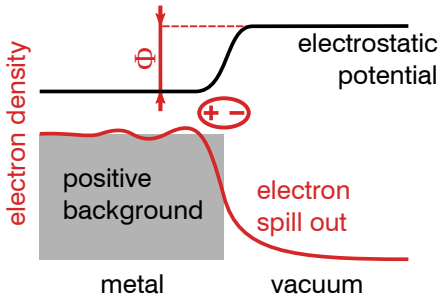
Before we dive into the actual simulation of the electronic structure, we need to define the physical problem:
What actually happens when a molecule meets a surface?



Let's break down the key interactions step by step...

Physics and chemistry at interface: Pristine surface

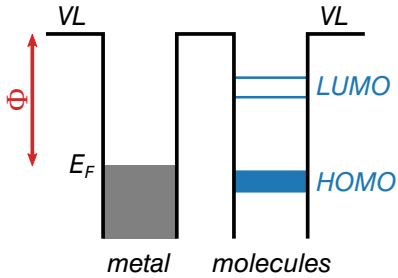
- **Discontinuity**: The periodic crystal lattice ends at the surface.
- **Electron spill-out**: Valence electron density extends into the vacuum, beyond the surface nuclei.
- **Surface dipole layer**: This charge redistribution creates a dipole at the interface.
- **Work function**: The dipole modifies the electrostatic potential, directly determining the work function.



Consequences

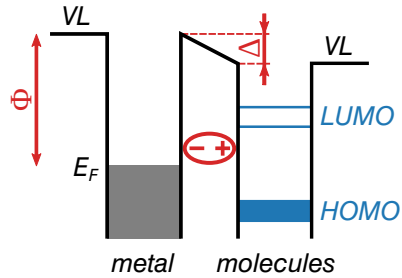
- Requires explicit **quantum-mechanical modeling**.
- Crucial for interpreting electron emission experiments (e.g., **UPS, XPS**).

Physics and chemistry at interface: Level alignment



Vacuum level alignment

- Large distance between molecules and substrate
- Molecule layer and substrate do not interact electronically



Push back

- Closer distance → electron density of molecule and substrate start overlapping
- Electron spill-out of the metal substrate is pushed back due to interaction with the electrons of a layer of molecules

Physics and chemistry at interface: Van der Waals

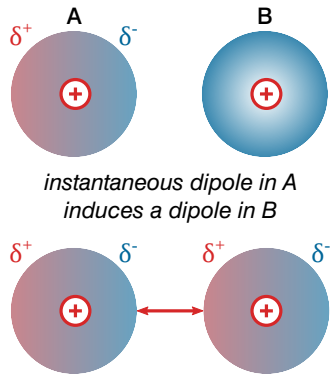
- **The physical origin:** Arises from non-local electron correlation, specifically the interaction between instantaneous fluctuating dipoles.

- **Strength :** Between two atoms, the leading-order interaction between two atoms is

$$V(r) = -\frac{C_6}{r^6}$$

with higher-order contributions $(C_8/r^8,\ C_{10}/r^{10}, \ldots)$.

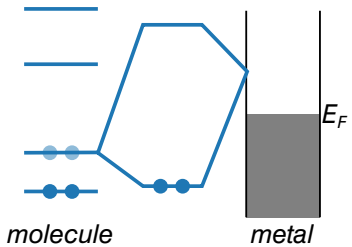
- **Role in adsorption:**
  - Sole driver of **physisorption**.
  - Critical for **chemisorption**: individually weak, but collectively substantial for large organic molecules.



instantaneous dipole in A induces a dipole in B

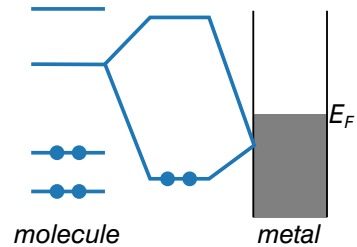
Physics and chemistry at interface: Hybridisation

Occupied molecular orbital interacts with unoccupied substrate state



- Bonding hybrid orbital one gets occupied → **Attractive interaction**

Unoccupied molecular orbital interacts with occupied substrate state



- Bonding hybrid orbital one gets occupied → **Attractive interaction**

Physics and chemistry at interface: Hybridisation

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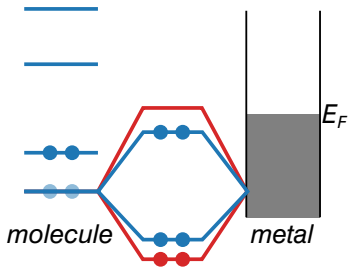
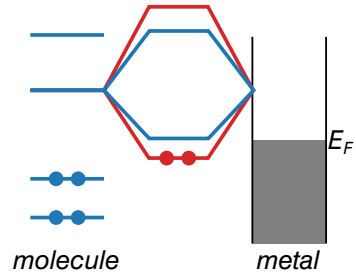
Occupied molecular orbital interacts with occupied substrate state



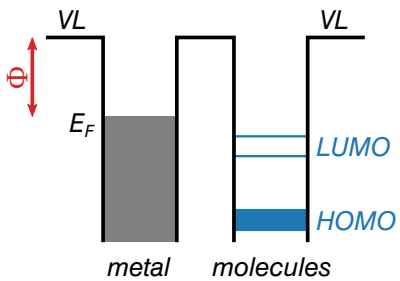
- Anti-bonding and bonding orbitals get occupied → **Repulsive interaction (Pauli repulsion**
- Anti-bonding orbital pushed above Fermi-level → dumps electrons and **makes interaction attractive**

Unoccupied molecular orbital interacts with unoccupied substrate state



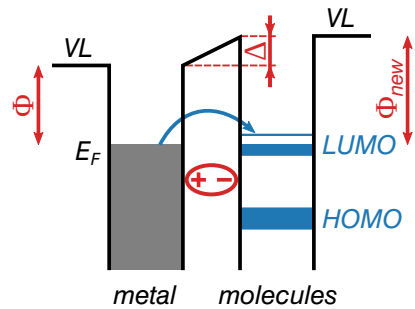
- No interaction
- Bonding orbital pushed below Fermi-level → get occupied and **makes interaction attractive**

Physics and chemistry at interface: Charge transfer



Large distance

- Molecule layer and substrate do not interact electronically
- LUMO of the molecules below the Fermi level



Closer distance

- Electron densities of subsystems overlap
- Electron transfer from the substrate to LUMO
- Dipole shifting the work-function
- Adsorbate may back-donate electrons via hybridisation of its lower-lying levels

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How to represent a surface in a calculation?

Structure of surfaces

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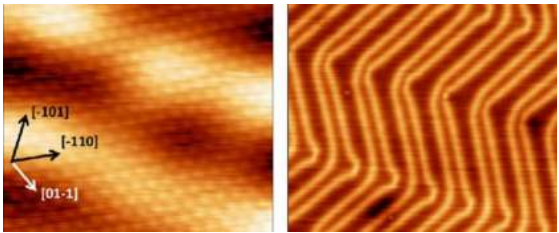
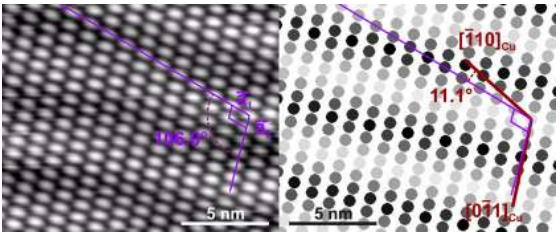
Surface reconstructions



Example: Au(111) surface reconstruction[1]

Commensurability



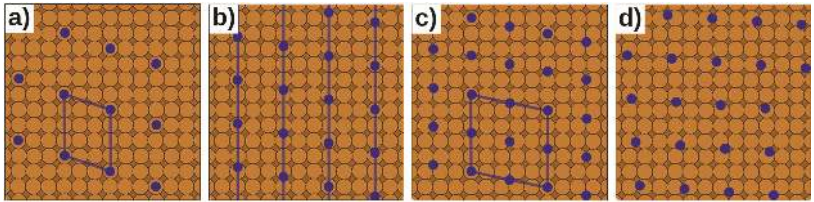
Example: Incommensurate Moire patterns of naphthalene on Cu(111)[2]

- **Lateral extension:** Effectively infinite in the x and y directions.
- **Long-range structural features:** Surfaces often exhibit patterns involving large numbers of atoms.
- **Periodicity:** Patterns on surface often repeat.

[1] Walen et al. J. Chem. Phys. 143.1 (2015).

[2] Forker et al. Langmuir 30.47 (2014): 14163-14170.

Commensurability



a) Commensurate structure

b) Point-on-line commensurate structure (commensurate in one direction, incommensurate in the other)

c) Higher order commensurate structure

d) Incommensurate structure

Clusters versus repeated slabs

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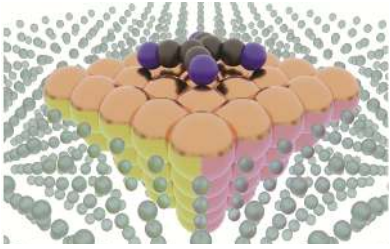
Cluster model

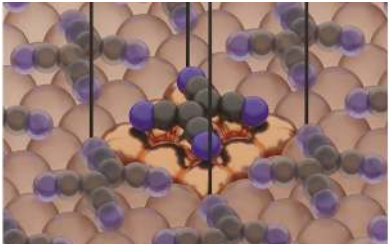


- Adsorbate + small substrate piece
- No periodicity

Properties

- Introduces new surface → unphysical artefacts
- Poor convergence of properties with regard to cluster size

Repeated slab model



- Adsorbate(s) + slab of several atomic layers
- Periodic in x, y, and z; vacuum gap in z

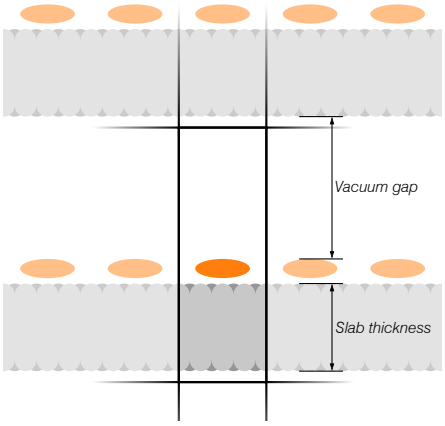
Properties

- Enforces (high-order) commensurability
- Better convergence of properties with number of atom layers

Repeated slab is usually preferred.

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

The repeated slab approach



Supercell

- Imposes (high-order) commensurability.
- Artefacts, such as lattice strain, remain.

Vacuum gap

- Must be sufficiently large (at least $10 - 15$ Å) to decouple periodic images along the z-axis.

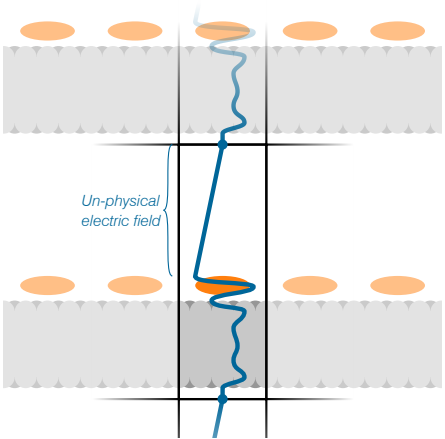
Slab thickness

- Must be thick enough to reproduce bulk-like properties.

Consequences

- System treated as **infinite lattice**.
- Good approximation for most surfaces.

The interface dipole



A consequence of periodic boundary conditions

- Asymmetric slabs create a net surface dipole.
- Periodic boundary conditions enforce the same potential at top and bottom of slab $V(z) = V(z + L)$.
- An **unphysical electric field** will automatically arise across the vacuum region to cancel the dipole.
- Electric field introduces a polarisation of the system, leading to artefacts $\rightarrow$ wrong work function, etc.

Dealing with the interface dipole

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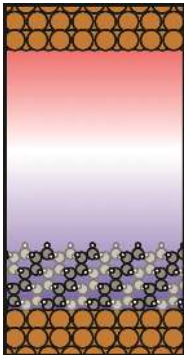
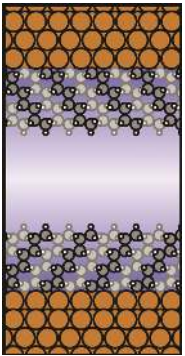
No correction



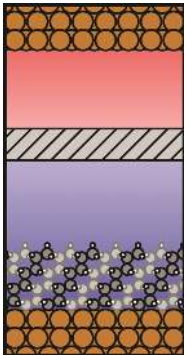
- Artificial field remains
- Outdated

Symmetric slab



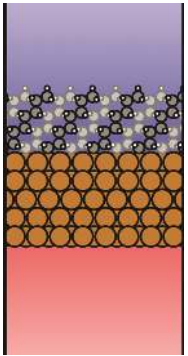
- System size doubled
- Limited by crystal symmetry

Electrostatic corr.



- Counter-dipole in vacuum
- Accurate and efficient
- Standard for surfaces

Mixed boundary



- Accurate: Non-periodic electrostatics
- Technically complex

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

Charged systems

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Isolated Clusters

- Electrostatics are straightforward ($V \sim 1/r$).
- Standard Poisson solvers apply; no artificial constraints.

Periodic Systems

- **Divergence problem:** The electrostatic energy of an infinitely periodic system is finite only if the unit cell is charge neutral. A net charge leads to a divergent Coulomb energy ($E \to \infty$).
- **Ewald summation:** Math necessarily assumes (and enforces) charge neutrality.
- **Homogeneous background charge:** Adding (or removing) electrons automatically gives rise to a homogeneous background charge that preserves charge neutrality.
- **Localised counter charges:** Ghost atoms, tuned nuclear charge

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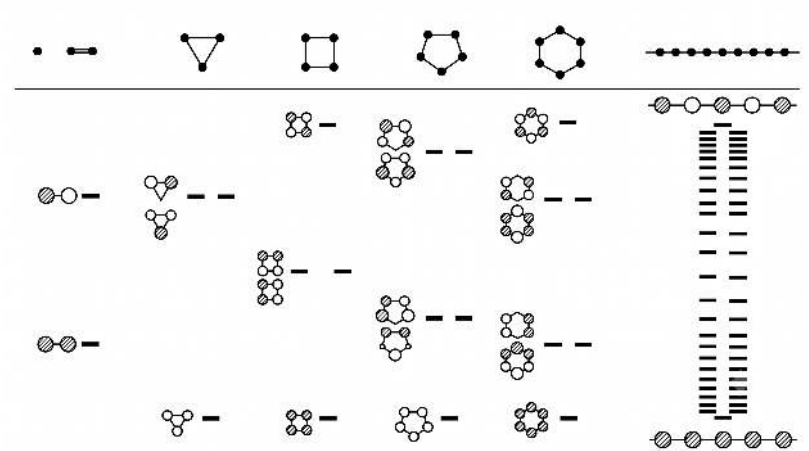
The wavefunction in a periodic system

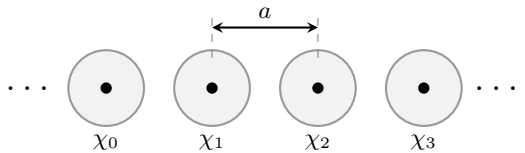
From discrete states to the band structure

- **Increasing states:** More interacting atoms $\rightarrow$ proportionally more molecular orbitals
- **Vanishing gap:** If $N \rightarrow \infty$ the energy spacing between adjacent states approaches zero
- **Band formation:** The discrete energy levels merge into continuous bands



The wavefunction in a periodic system

Consider an infinite 1D chain of atoms, each with a single s-orbital (χ), separated by a lattice constant a.



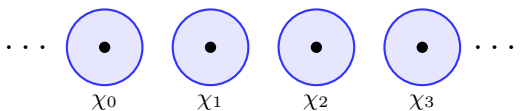
Bloch's formalism

$$\psi_k = \sum_n e^{ikna} \chi_n$$

- n: The unit cell index.
- k: The **wave vector**, which acts as a phase index.

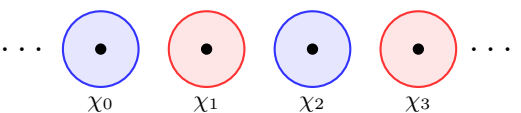
In-phase ($k = 0$)

$$e^{i(0)na} = 1 \implies \psi_0 = \chi_0 + \chi_1 + \chi_2 + \dots$$



Alternating phase ($k = \pi/a$)

$$e^{i(\frac{\pi}{a})na} = (-1)^n \implies \psi_{\frac{\pi}{a}} = \chi_0 - \chi_1 + \chi_2 - \dots$$

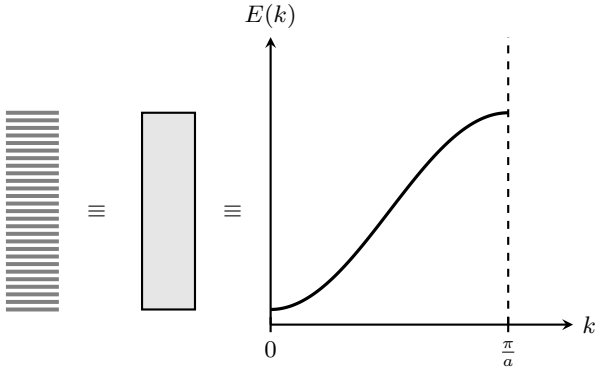


The band structure

- As the number of interacting atoms $N \to \infty$, discrete energy levels merge into continuous energy bands.
- The band energy is given by the dispersion relation $E(k)$, where k is the wave vector.

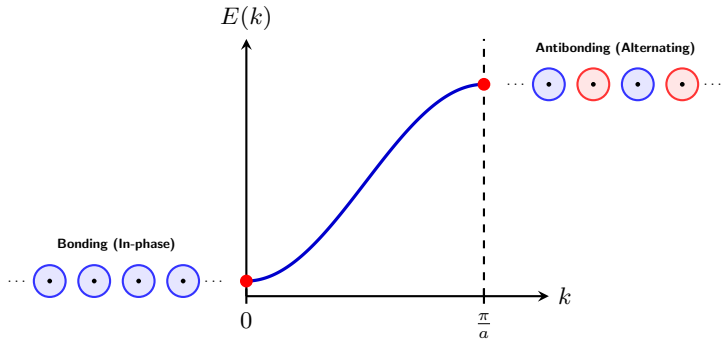
Brillouin Zone

The Brillouin zone is the primitive unit cell in reciprocal space. For a 1D lattice with constant a, the first Brillouin zone is $[-\pi/a, \pi/a]$. Since the dispersion is symmetric, $E(k) = E(-k)$, we typically plot $E(k)$ only for $k \in [0, \pi/a]$.



Band dispersion

- **Bonding states** ($k = 0$): In-phase orbitals, low energy.
- **Antibonding states** ($k = \pi/a$): Alternating phase, high energy.



- **Large orbital overlap**: Large energy difference between bonding and antibonding states → wide band dispersion.
- **Small orbital overlap**: Small energy difference → narrow (flat) bands.

The Bloch theorem

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How do we handle infinitely many atoms?

- **Periodic potential:** $V(\mathbf{r}+\mathbf{R}) = V(\mathbf{r})$
- **Bloch's theorem:** Solves the infinite crystal within a **single unit cell**.
- Crystal momentum $\mathbf{k}$ accounts for phase shifts between unit cells.

Plane wave basis functions

- Natural Bloch states:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

- **Truncation:** Size controlled by cutoff E_{cut}:

$$\frac{\hbar^2}{2m}|\mathbf{G}|^2 < E_{\text{cut}}$$

- **Spectral grid:** Given by unit cell size → **larger unit cells require a denser spectral grid**

Atom-centered basis functions

- Sum of local orbitals χ_α:

$$\psi_{n\mathbf{k}} = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\phi_{n\mathbf{R}} \quad \phi_{n\mathbf{R}}(\mathbf{r}) = \sum_{\alpha} c_{n\alpha}\chi_\alpha(\mathbf{r}-\mathbf{R})$$

- Substitute into $\hat{H}\psi = E\psi$ and project onto $\langle\phi_{n\mathbf{0}}|$:

$$\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\langle\phi_{n\mathbf{0}}|\hat{H}|\phi_{n\mathbf{R}}\rangle = E_{n\mathbf{k}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\langle\phi_{n\mathbf{0}}|\phi_{n\mathbf{R}}\rangle$$

- **Sparsity:** Interactions $\langle\phi_{n\mathbf{0}}|\hat{H}|\phi_{n\mathbf{R}}\rangle$ decay rapidly → Can truncated sum.

Sampling the Brillouin zone

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The need for k-space sampling
Physical observables require integration over the Brillouin zone (BZ):

Total Energy:

$$E = \sum_n \int_{\mathrm{BZ}} f_{n\mathbf{k}} E_n(\mathbf{k})\, d\mathbf{k}$$

Electron Density:

$$n(\mathbf{r}) = \sum_n \int_{\mathrm{BZ}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\mathbf{r})|^2\, d\mathbf{k}$$

→ **In practice, integrals are replaced by weighted discrete sums.**

Sampling the Brillouin zone: k-grid

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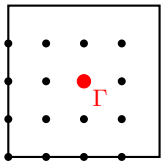
Brillouin zone

Given real-space lattice vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, the reciprocal vectors defining the Brillouin zone $\mathbf{b}_i$ are:

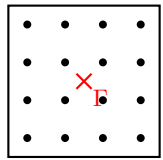
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

Γ-centered



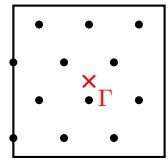
- Includes the origin ($\Gamma \to \mathbf{k} = \mathbf{0}$)
- Can be inefficient for highly elongated unit cells

Monkhorst-Pack



- Grid is shifted away from high-symmetry points
- Can allow reducing the number of k-points, slightly

Generalized Monkhorst-Pack



- Allows for arbitrary grid generation
- Samples BZ with optimally dense, isotropic spacing

Type and density of k-grid require careful testing!

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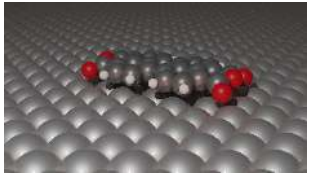
VdW corrections

Missing long-range interactions

Local and semi-local xc-functionals (LDA, GGA, hybrids) neglect **non-local electron correlation** (fluctuating dipoles), failing to capture vdW dispersion.

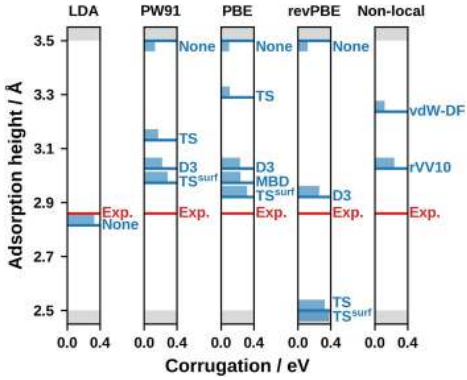
PTCDA on Ag(111): A case study

- **Molecule-substrate interaction**: O-Ag hybridisation, vdW forces, and Pauli repulsion.



- **GGA/Hybrids:** Underestimate energy; molecule fails to bind.
- **LDA:** Overbinds. Right geometry, wrong physics!

→ **Solution:** vdW corrections / vdW-DF.



[1] Hörmann et al., J. Chem. Phys. **153**, 10 (2020).

The zoo of vdW corrections

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Method	Density Dep.	Many-Body	Screening	Empiricism
DFT-D2	Fixed	Pairwise	None	High
DFT-D3	Geometry	+ 3-Body	Local	Medium
DFT-D4	Charges	+ 3-Body	Charge	Medium
TS	Atomic	Pairwise	None	Low
MBD	Atomic	All-order	Global	Low
MBD-NL	Atomic	All-order	Global	Low
vdW-DF	Continuous	Pairwise	None	None
VV10	Continuous	Pairwise	Short-range	Medium

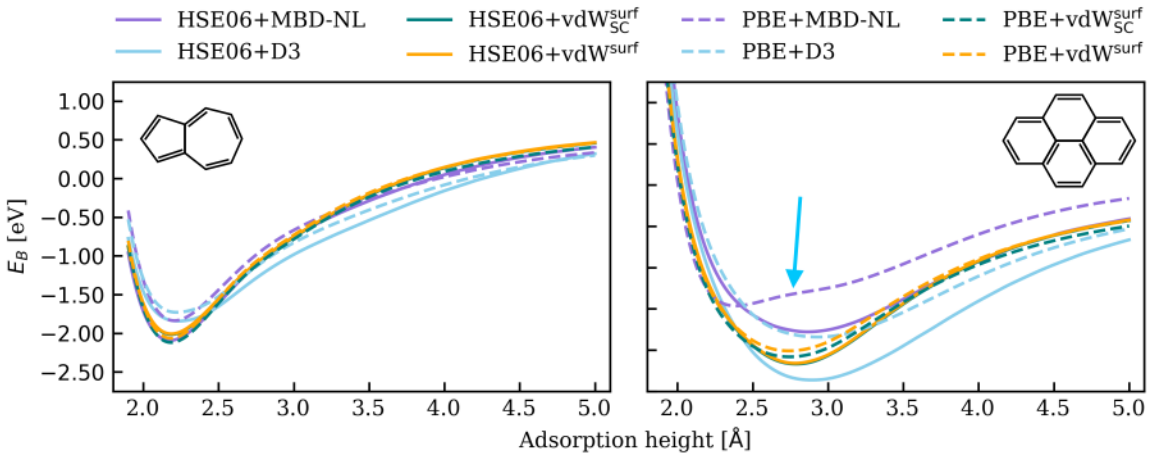
Advanced / First-Principles — Does the dispersion correction adapt to the local electronic environment?

Intermediate / Partial — Are interactions beyond simple two-atom pairs included?

Basic / Empirical / Missing — Is the polarizability correctly dampened by the surrounding medium?

You cannot just mix any functional and vdW-correction!

Some combinations of xc-functions and vdW corrections predict unphysical adsorption geometries. Example: **Binding energy curves** of organic molecules on Cu(111).



[1] Thake et al., in preparation.

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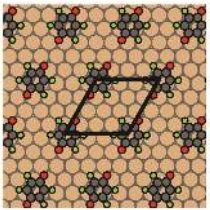
How to run a calculation

Wrong geometry → wrong property

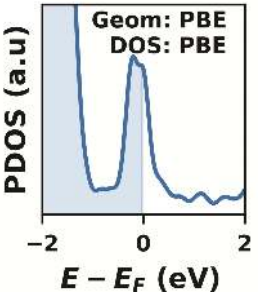
Example: Tetrafluorobenzoquinone on Cu(111)



Full PBE

PBE optimization + PBE electronic structure.

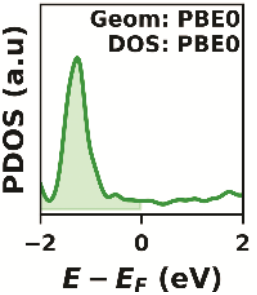
DOS projected onto adlayer



Full PBE0

PBE0 optimization + PBE0 electronic structure.

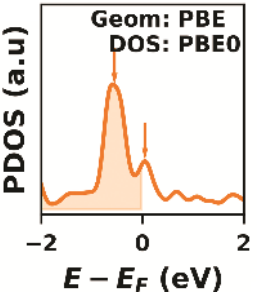
Qualitatively different



Mixed Approach

PBE geometry + PBE0 electronic structure.

Differs from full PBE0



Conclusion

- You need the correct geometry.
- Mixing different levels of theory, one for geometry and one for your target property, can backfire.

Convergence tests

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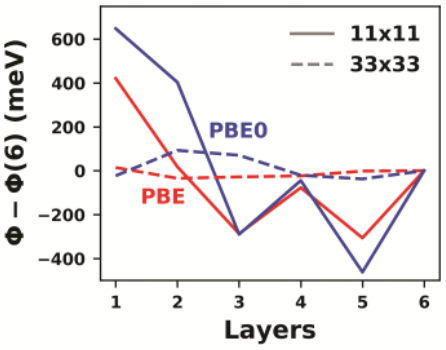
Best practices

Always ensure your physical observables becomes stable with respect to DFT settings.

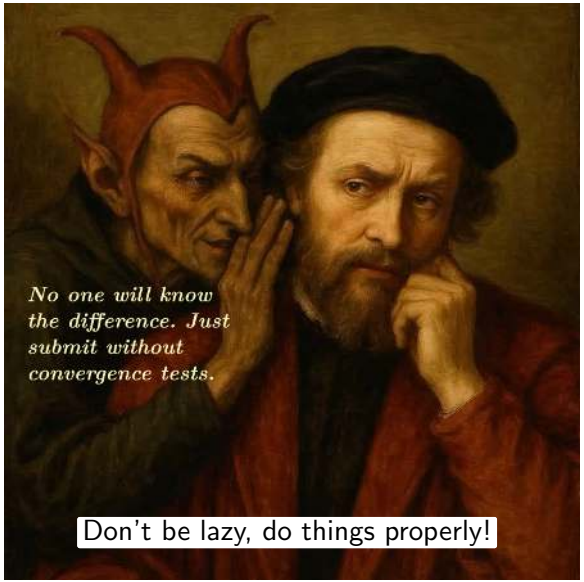
- Energies: Total, adsorption, surface, defect formation
- Electronic structure: Work function, band gap, magnetic moments
- **Your specific target property**

Most important settings for periodic boundary conditions:

- **Lattice constant**
- **K-grid**
- **Basis set** (number of basis functions, E_{cut})
- **Cell size** i.e., (x, y, z)-extension
  - *Cell size:* Ensure enough space to avoid interactions with the periodic image.
  - *Number of slab layers:* The slab must become bulk-like.
- **Functional** (LDA, GGA, Hybrids, vdW corrections, etc.)
- Etc.



Nobody likes convergence tests



Validate SCF convergence

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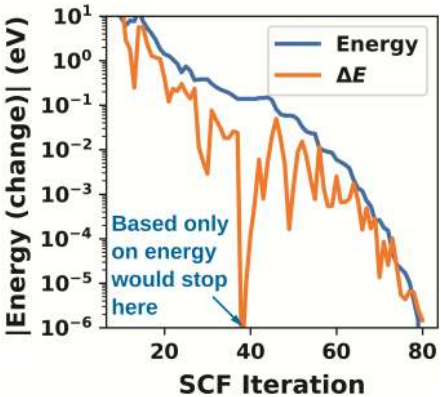
Spurious convergence

- Calculations can report a converged status by numerical chance.
- A converged energy is a *necessary*, but not *sufficient*, condition.

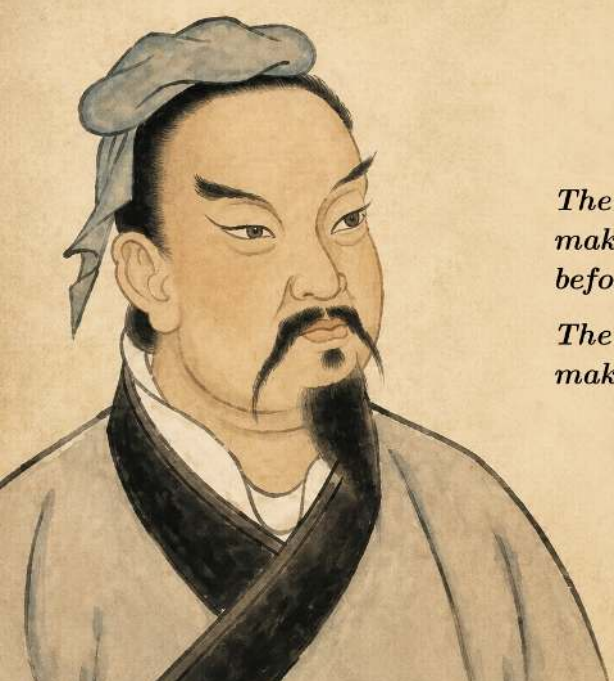


To ensure proper convergence, monitor multiple indicators:

- Total energy
- Charge density
- Sum of eigenvalues
- Your physical observable of interest (e.g., band gap, dipole).

Summary

- **Interface physics:** Account for work function shifts, level alignment, hybridization, and charge transfer.
- **Surface modeling:** Use repeated slabs with sufficient vacuum gaps and electrostatic dipole corrections.
- **Periodic Systems:** Apply Bloch's theorem and rigorously test k-point sampling in the Brillouin zone.
- **vdW interactions:** Standard local/semi-local DFT misses dispersion; apply appropriate vdW corrections.
- **Convergence:** Strictly test parameters (e.g., geometry, k-grid, basis set, etc.) and validate SCF convergence.



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The physicist who converges a calculation makes many tests in his temple before the calculation is submitted.

The physicist who loses CPU time makes but few tests beforehand.

Sun Tzu
famous Chinese general, 544 - 496 BC