

Electronic structure of surfaces: simple models, specific features, calculations

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NEVF 514 Surface Physics
III.

<http://crysa.fzu.cz/ondra/teor-surf-phys>

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Outline

What matters at surfaces: the barrier

Electronic states at surfaces: formal description

Specific features at surfaces

Computational approaches

Outline

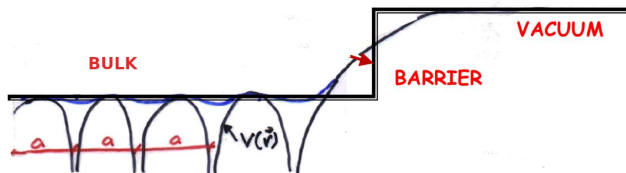
What matters at surfaces: the barrier

Electronic states at surfaces: formal description

Specific features at surfaces

Computational approaches

Surface termination



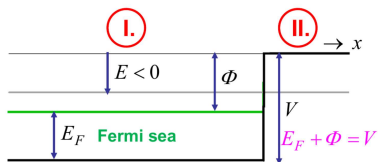
B. Velický

- ▶ One-electron Schrödinger equation in 1D

$$\left[-\frac{d^2}{dx^2} + V(x) \right] \psi_\alpha(x) = E_\alpha \psi_\alpha(x) \quad \hbar = 1, m = 1/2$$

- ▶ Termination: translation periodicity of the bulk stops abruptly.
- ▶ Neglect the atomic structure in the bulk: consider just the barrier separating two constant potentials.

Electron wave function in the presence of barrier



Solutions of Schrödinger equation in regions I. and II.

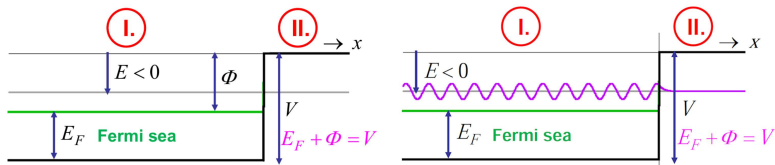
$$\text{I. } \psi = \alpha e^{ikx} + \beta e^{-ikx} \quad k^2 = E + V$$

$$\text{II. } \psi = \gamma e^{-i\kappa x} \quad \kappa^2 = -E$$

Matching the wave functions and their derivatives:

$$\begin{aligned} \psi(0^-) = \psi(0^+) & \quad \alpha + \beta = \gamma & \quad \alpha = |\alpha| e^{i\Delta} & \quad \gamma = 2|\alpha| \cos \Delta \\ \psi'(0^-) = \psi'(0^+) & \quad \alpha - \beta = \gamma i\kappa/k & \quad \beta = |\alpha| e^{-i\Delta} & \quad \tan \Delta = \kappa/k \end{aligned}$$

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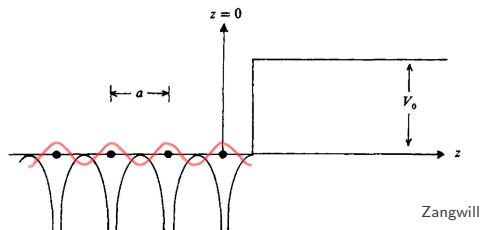
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Wave function is **decays in the vacuum** but **oscillates in the bulk**.

No restrictions on the energy.

Surface states in a simple model (1)



One-dimensional
nearly-free electron model.

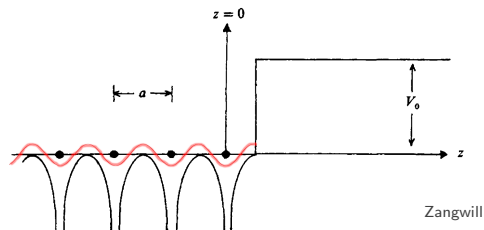
Reasonable for *metals*.
Recall the pseudopotentials.

$$\left[-\frac{d^2}{dz^2} + V(z) \right] \psi(z) = E \psi(z)$$

Weak periodic potential: $V(z) = -V_0 + 2V_K \cos(Kz)$.

$K = \frac{2\pi}{a}$ is the shortest 1D reciprocal lattice vector. V_K is **small**.

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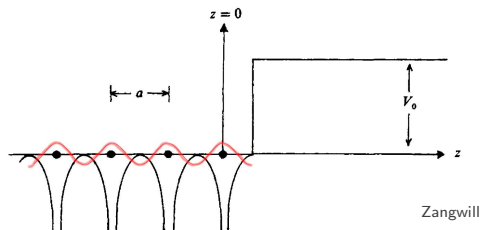
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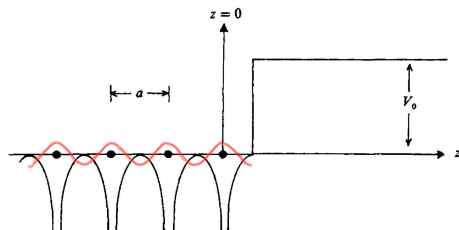
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Surface states in a simple model (2)



Oscillatory part of the potential V_K is small.

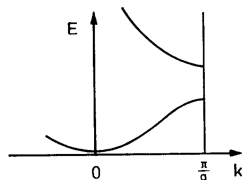
Trial wave function combines just two plane waves:

$$\psi_k(z) = \alpha e^{ikz} + \beta e^{i(k-K)z} .$$

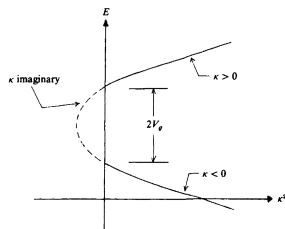
Substitute $\psi_k(z)$ into Schrödinger equation, neglect terms which contain components other than e^{ikz} and $e^{i(k-K)z}$ to get

$$\begin{bmatrix} k^2 - V_0 - E & V_K \\ V_K & (k - K)^2 - V_0 - E \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = 0$$

Surface states in a simple model (3)



Forstmann



Zangwill

Interesting things happen at the **Brillouin zone boundary**, which is at $k = K/2$.

Wave vector k in terms of deviation from the BZ boundary: $k = K/2 + \kappa$.

Gap at $\kappa = 0$:

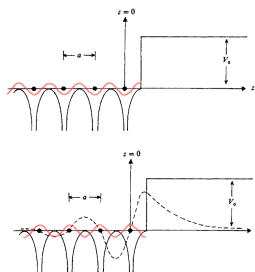
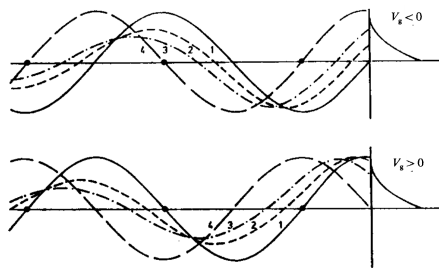
$$E = -V_0 + \left(\frac{K}{2}\right)^2 + \kappa^2 \pm \sqrt{K^2\kappa^2 + V_K^2}$$

$$\psi_k = e^{i\kappa z} \cos\left(\frac{K}{2}z + \delta\right)$$

For negative κ^2 , i.e., **complex κ** , there are solutions of the Schrödinger equation also **within the gap**.

However, they **grow exponentially**, hence are not normalizable for a periodic bulk.

Surface states in a simple model (4)



Semi-infinite problem:

$$\psi(z) = e^{\kappa z} \cos\left(\frac{K}{2}z + \delta\right) \quad z < \frac{a}{2}$$

$$\psi(z) = e^{-q\kappa z} \quad z > \frac{a}{2}$$

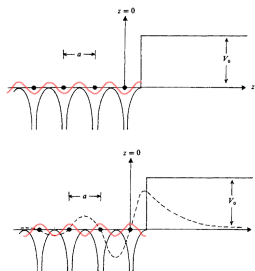
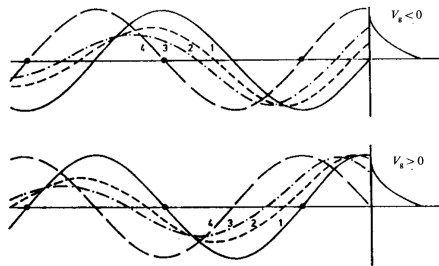
with $q = \sqrt{V_0 - E}$.

Smooth matching of the wave function across the interface requires

$$\frac{\psi'(a/2 - 0)}{\psi(a/2 - 0)} = \frac{\psi'(a/2 + 0)}{\psi(a/2 + 0)}$$

For the current model, this matching is possible **only for $V_K > 0$** .

Surface states in a simple model (4)

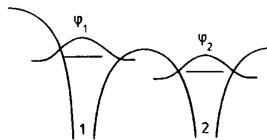
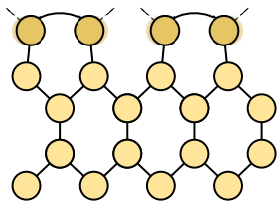


Whether a surface state exists or not depends on fine details of the electronic structure.

There is no entitlement to a surface state. It may exist or not.

Surface states generated in this way are sometimes called Shockley states.

Dangling bonds and surface states



Potential of surface atom **deviates** from potentials of bulk atoms.

Dangling bond: an **unsatisfied valence** on an atom.

Often at **surfaces of semiconductors**.

- ▶ Tight-binding model: nearest-neighbor interaction only.
- ▶ Wave functions expressed as linear combinations of atomic orbitals.
- ▶ **Mixing of wave functions** based on the surface atom and on the bulk atom may lead to a **surface state**.

Surface states generated through this mechanism are often called Tamm states.

The distinction between Shockley and Tamm states is *somewhat arbitrary*.

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How to modify Bloch wave functions (1)

Bloch functions in the bulk:

$$\psi_{\mathbf{k}}^n(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}^n(\mathbf{r}) .$$

Wave function may not grow exponentially (must be normalizable)
 $\Rightarrow \mathbf{k}$ has to be **real**.

Presence of surface does not affect bulk Bloch states significantly (surface represents only a tiny fraction of the crystal).

However, **new solutions, previously forbidden, may arise:**

If \mathbf{k} is complex, we have a solution that grows exponentially for either " $\mathbf{r} \rightarrow \infty$ " or " $\mathbf{r} \rightarrow -\infty$ " (think in 1D...).

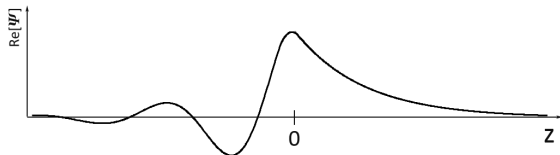
This makes it unusable **for the bulk**. However, ...

How to modify Bloch wave functions (2)

Exponentially growing solutions are unusable in the bulk.

If presence of a surface is taken into account:

In the bulk region, we can take an exponentially growing solution and at the surface (before it grows to infinity...) **match it** with another solution, which will decay exponentially with the distance from the surface.



Such solutions are called **surfaces states**.

Description of surface states

Translation periodicity perpendicular to the surface is broken. It is retained in the direction parallel to the surface.

bulk

surface

$$\psi_{\mathbf{k}}^n(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}^n(\mathbf{r}) \quad \longrightarrow \quad \psi_{\mathbf{k}_{\parallel}}^n(\mathbf{r}) = e^{i\mathbf{k}_{\parallel}\cdot\mathbf{r}_{\parallel}} e^{-\kappa\cdot r_{\perp}} u_{\mathbf{k}_{\parallel}}^n(\mathbf{r}_{\parallel})$$

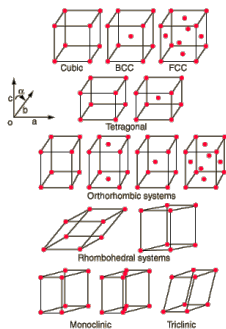
$u_{\mathbf{k}_{\parallel}}^n(\mathbf{r}_{\parallel})$ has the periodicity of the surface (in 2D).

Quantum number \mathbf{k}_{\parallel} is restricted to the first 2D Brillouin zone.

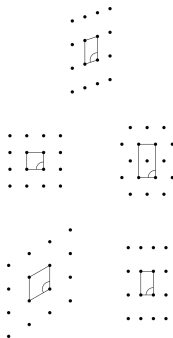
The energy of a surface state $\varepsilon_{\mathbf{k}_{\parallel}}^n$ is different from the bulk energy $\varepsilon_{\mathbf{k}}^n$ for the same \mathbf{k}_{\parallel} (because it has different [complex] k_{\perp}).

Surface states appear where there are no bulk states.

3D \rightarrow 2D: Use \mathbf{r}_{\parallel} instead of \mathbf{r} , \mathbf{k}_{\parallel} instead of \mathbf{k}



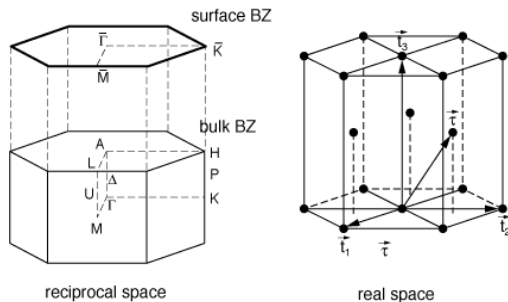
Bravais lattices in 3D



Bravais lattices in 2D

For surface states, \mathbf{k}_{\parallel} is conserved **up to** a 2D reciprocal lattice vector.

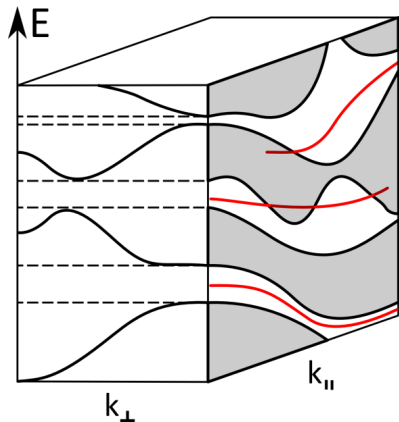
Projecting Brillouin zones from 3D to 2D



To explore surface states, it is useful to project the bulk band structure $\varepsilon_{\mathbf{k}}^n = \varepsilon_{\mathbf{k}_{\parallel}, k_{\perp}}^n$ from the 3D Brillouin zone into the corresponding 2D Brillouin zone.

The k_{\perp} direction thus collapses.

Bulk band structure $\varepsilon_{\mathbf{k}}^n$ projected into a 2D BZ

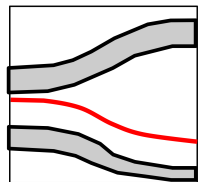


Grey shaded areas correspond to regions where there are bulk states with energy $\varepsilon_{\mathbf{k}_{||}, k_{\perp}}^n$, with k_{\perp} arbitrary.

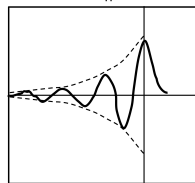
Red lines describe **surface bands**.

The **energy** of a surface state $\varepsilon_{\mathbf{k}_{||}}^n$ is **different** from the bulk energy $\varepsilon_{\mathbf{k}}^n$ for the same $\mathbf{k}_{||}$ (because it has different [complex] k_{\perp}).

Surface states and surface resonances



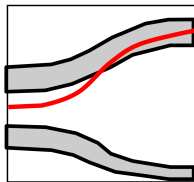
Γ $k_{\parallel} \rightarrow$



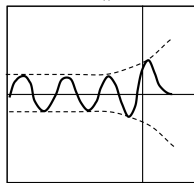
$x_{\perp} \rightarrow 0$

Surface state:

Energy in the gap in \mathbf{k}_{\parallel} space.
Exponential decay into bulk.



Γ $k_{\parallel} \rightarrow$



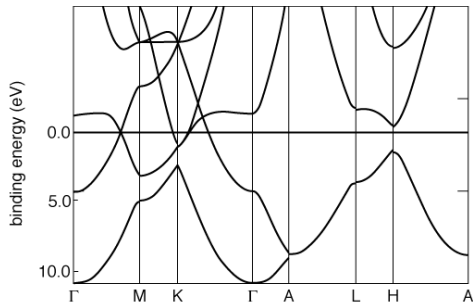
$x_{\perp} \rightarrow 0$

Surface resonance:

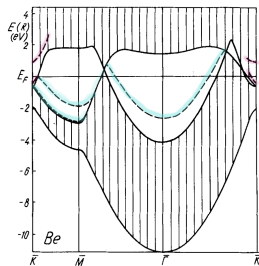
Energy overlaps with $\varepsilon_{\mathbf{k}_{\parallel}, k_{\perp}}^n$ of bulk.
Merges a Bloch wave function.

J. Phys. C: Solid State
Phys. **9**, 169 (1976)

Example: surface states of Be(0001)



Bulk $\varepsilon_{\mathbf{k}}^n$



Surf. Sci. **188**, 287 (1987)

Projected $\varepsilon_{\mathbf{k}_{\parallel}, \mathbf{k}_{\perp}}^n$
plus surface states
and resonances

Outline

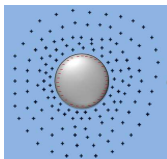
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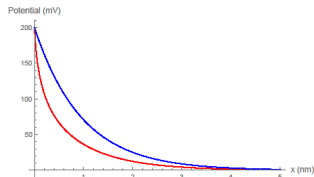
Computational approaches

Screening of charge: classically



In classical electrostatics, a charge impurity in a pool of moving charges is screened (e.g., in electrolyte).

Point charges move exactly in that position where it is needs to be, as required by the electrostatics.



Screening by moving charges results in exponential decay of the concentration of mobile charges, $n(r) \sim \exp(-Kr)/r$.

The charge perturbation may be a point charge but also a **surface**.

Screening in quantum mechanics: Friedel oscillations

Quantum physics: **screening** of the charge is **oscillatory**.

$E_F = \hbar^2 k_F^2 / (2m)$, d is the dimensionality ($d=1, 2, 3$).

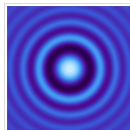
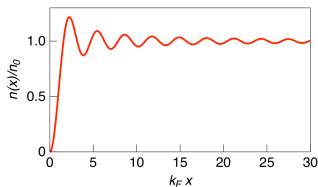
$$n(r) \sim \frac{\sin(2k_F r)}{r^d}$$

Formally:

Friedel oscillations result from the abrupt cut-off of the states at E_F .

Intuitive hand-waving argument:

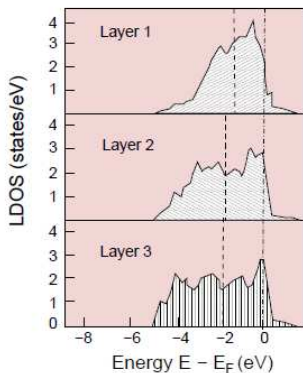
Electrons participating in the screening are not point charges but waves. Due to the finite dimensions of the screening chunks, some screening charge is “misplaced”, which requires compensation by opposite charges.



Charge at surfaces relaxes in an oscillatory way.

Band narrowing (1)

Rule of thumb: the **width of the band** is roughly proportional to the square root of the **number of neighbouring atoms** (coordination number).



Local DOS in respective layer.

surface

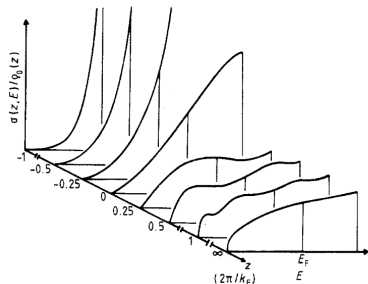
sub-surface

sub-sub-surface (bulk)

Reduction of the coordination number at the surface leads to less hybridization, which means more atomic-like character of electron states, which means **narrowing of bands** at the surface.

Band narrowing (2)

When going from bulk to the surface to the vacuum above it, the electronic structure gradually changes.



Werner *et al.* 1975

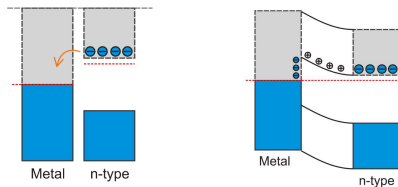
Local density of states in the bulk, at the surface and above the surface calculated for a selfconsistent model jellium potential.

Results for jellium model:

DOS for free electrons at the surface reflects its localized nature.

DOS for free electrons in the three dimensions goes like \sqrt{E} .

Band bending (1): semiconductor and metal



Doped semiconductor: chemical potential is close to the bottom of the conduction band.

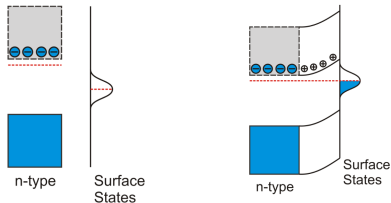
Mark Greiner

Electrons flow from doped n-levels of the semiconductor to the metal until the chemical potentials equilibrate and a barrier forms.

To move an electron from the semiconductor to the metal hence requires additional energy to overcome this barrier.

Corresponding energy levels in the metal are higher than in the semiconductor: the bands are bent “upwards” to higher energies when approaching the metal.

Band bending (2): semiconductor and surface state



Suppose that a **surface state** exists in the middle of the gap. Its local chemical potential is lower than the chemical potential of the doped semiconductor.

Mark Greiner

Electrons flow from doped n-levels of semiconductor to the surface state until chemical potentials equilibrate and a barrier forms.

The energy of the surface state increases with respect to what it would be for an undoped semiconductor.

The energy bands of an **n-doped** semiconductor are **bent upwards** to higher energies when approaching the surface.

For a **p-doped semiconductor**, they are **bent downwards**.

This occurs only for **doped** semiconductors.

Outline

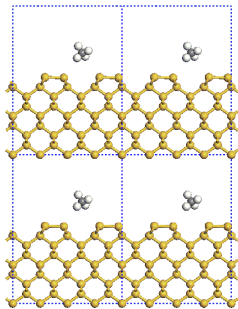
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Dealing with surfaces: Supercell calculations



<http://www.tcm.phy.cam.ac.uk/castep>

simulating an adsorbate
on the surface
by repeating the supercell

Create a surface “artificially”, by **forcing a periodicity** to the non-periodic system.

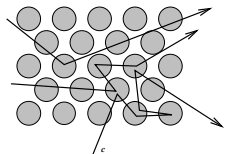
Advantage: Using all the polished tools for bulk calculations.

Sometimes, the artificial periodicity leads to issues.

Other techniques dealing with a truly semi-infinite system can be used (e.g., Green function methods).

Dealing with surfaces: Green's function method

Korringa-Kohn-Rostoker a.k.a. multiple-scattering method.



Reformulated version as
KKR-Green's function method.

- ▶ Relatively slow and somewhat cumbersome.
- ▶ Efficient when treating surfaces, adsorbates, disorder.

Crash course on Green's functions: mathematics

Linear differential operator L_x (e.g., $-\frac{d^2}{dx^2} - V(x)$), equation

$$L_x u(x) = f(x) . \quad (1)$$

If we define Green function $G(x, x')$ as a solution of

$$L_x G(x, x') = \delta(x - x') , \quad (2)$$

then solution of Eq. (1) can be obtained as

$$u(x) = \int G(x, x') f(x') dx'$$

because

$$\begin{aligned} L_x \left(\int G(x, x') f(x') dx' \right) &= \int L_x G(x, x') f(x') dx' = \\ &= \int \delta(x - x') f(x') dx' = f(x) \end{aligned}$$

Solution to Eq. (2) is not unique.

Particular Green's function is determined by boundary conditions.

Crash course on Green's functions: quantum theory (1)

Hamiltonian of **unperturbed** (here: free electron) **system**:

$$H_0(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2$$

$$H_0(\mathbf{r})\psi_0(\mathbf{r}) = E \psi_0(\mathbf{r})$$

Homogeneous linear differential equation:

$$(E - H_0(\mathbf{r})) \psi_0(\mathbf{r}) = 0 .$$

Corresponding Green's function G_0 is determined by

$$(E - H_0(\mathbf{r})) G_0(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$$

$$G_0(\mathbf{r}, \mathbf{r}') = \frac{1}{E - H_0(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}')$$

A kind of “ $\pm i\epsilon$ ” term is typically added to the denominator. It specifies the type of Green's function via boundary conditions (retarded, advanced, lesser, greater, god-knows-which, ...).

Crash course on Green's functions: quantum theory (2)

Consider a system “perturbed” by the potential $V(\mathbf{r})$.

In practice, $V(\mathbf{r})$ may represent a surface, an adsorbate, an impurity, or many-body effects.

$$(H_0(\mathbf{r}) + V(\mathbf{r})) \psi(\mathbf{r}) = E \psi(\mathbf{r})$$

Inhomogeneous differential equation:

$$(E - H_0(\mathbf{r})) \psi(\mathbf{r}) = V(\mathbf{r}) \psi(\mathbf{r})$$

Schrödinger equation can be transformed to an integral form by employing the Green's function $G_0(\mathbf{r}, \mathbf{r}')$ of the unperturbed system,

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int d\mathbf{r}' G_0(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi(\mathbf{r}') .$$

Crash course on Green's functions: quantum theory (3)

Hamiltonian $H(\mathbf{r}) = H_0(\mathbf{r}) + V(\mathbf{r})$, corresponding Green's function $G(\mathbf{r}, \mathbf{r}')$:

$$(E - H_0(\mathbf{r}) - V(\mathbf{r})) G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') ,$$

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{E - H_0(\mathbf{r}) - V(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}') .$$

Green's function of the **perturbed system** $G(\mathbf{r}, \mathbf{r}')$ can be expressed in terms of Green's function of the **unperturbed system** $G_0(\mathbf{r}, \mathbf{r}')$ via the **Dyson equation**:

$$G(\mathbf{r}, \mathbf{r}') = G_0(\mathbf{r}, \mathbf{r}') + \int d\mathbf{r}'' G(\mathbf{r}, \mathbf{r}'') V(\mathbf{r}'') G_0(\mathbf{r}'', \mathbf{r}') .$$

Knowing $G(\mathbf{r}, \mathbf{r}')$, we can write the wave function $\psi(\mathbf{r})$ as

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi_0(\mathbf{r}') .$$

Why Green's functions?

Working with Green's functions does not bring anything really new.

Nominally, it is just another formal complication to please the mathematical gods.

However, working with Green's functions is (often) **practical**: various **approximations** can be more easily introduced and step-by-step improved in the Green's functions formalism.

Green's function relates to **response function**: it describes how $\psi_0(\mathbf{r})$ respond to perturbation $V(\mathbf{r})$ to change into $\psi(\mathbf{r})$.
Natural framework for transport, spectroscopy and so on.

Spectral function $A(\varepsilon)$ is related to retarded Green function:

$$A_{mm'}(\varepsilon) := -\frac{1}{\pi} \text{Im} G_{mm'}^{(+)}(\varepsilon)$$

Surfaces via Green's function methods

Proper **semi-infinite system**, no supercell.

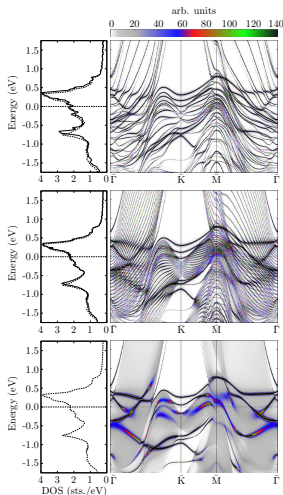
Bloch spectral function: generalization of the band-structure for non-periodic systems

Surface of a 14-layers slab.

Surface of a 38-layers slab.

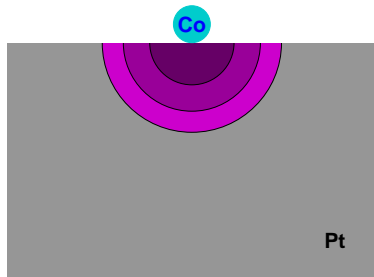
Surface of a semi-infinite layer.

Only true surface states and resonances remain, **no spurious bands**.



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Adsorbates and impurities



Green's function formalism:

Embedded cluster in an infinite host.

For small impurities such as adatoms, supercell techniques can be used without creating any “issues”.

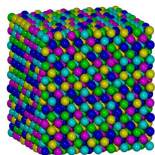
However, when dealing with clusters of hundreds of atoms, Green's function formalism is more suitable.

Disorder: Dealing with substitutional alloys

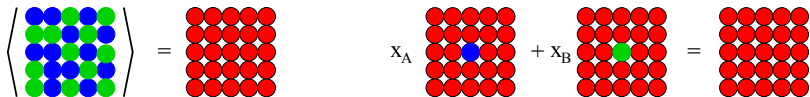
1. Simulating random occupation of sites via supercells:

Exact if the supercell is large enough.

Computationally cumbersome.



2. Coherent potential approximation (CPA):



Mean-field approach: define a suitable effective medium so that the scattering properties of its artificial atom reproduce scattering properties of the original atoms in this medium.

Formulated in terms of Green's function. Computationally efficient.

Find the timetable and slides on the web

<http://crysa.fzu.cz/ondra/teor-surf-phys>

