

Chemisorbtion — the basic concepts and models

Bedřich Velický

VII.

NEVF 514 Surface Physics

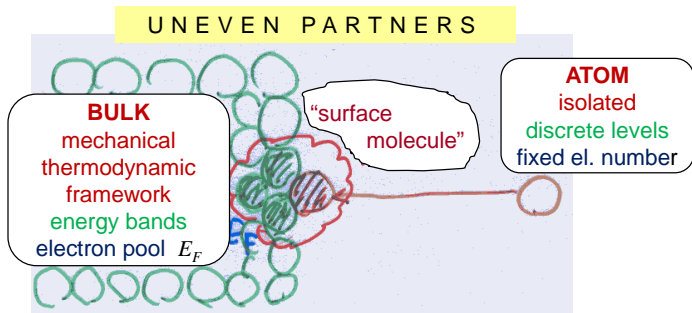
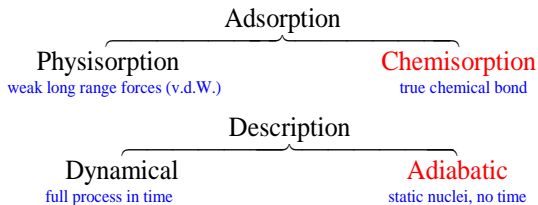
Winter Term 2013 - 2014

Troja, 15th November 2013

This class ...

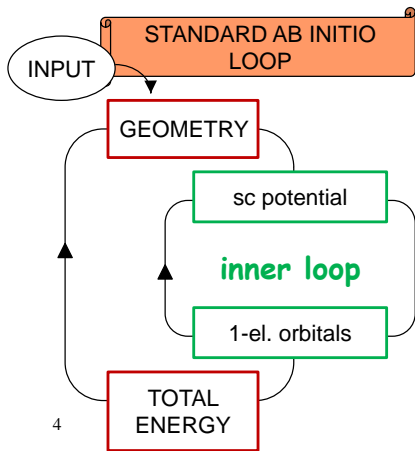
- ... is an introduction into the
microscopic physics of adsorption
- two model treatments of chemisorption of atoms
- a sequence of simple models of electronic states
culminating with the Anderson-Grimley-Newns m.
- semi-infinite jellium with adsorbates as a model
treated in LDA ... an ab initio approach

Adsorption of atoms



Questions the adiabatic theory may answer

Trustworthy answers are given by a fully *ab initio* theory at the cost of an extensive computational effort; models provide illustrative partial results of a limited reliability achieved in a “cheap” manner



QUESTIONS AT TWO LEVELS

□ adsorption energy

$$E_{\text{ADS}} = E(\text{clean}) + E(\text{atom}) - E_{\text{TOT}} \geq 0$$

□ adsorption site

□ adsorption geometry

□ vibrational properties

□ □ □

□ chemical bond + electron structure

□ electronic properties

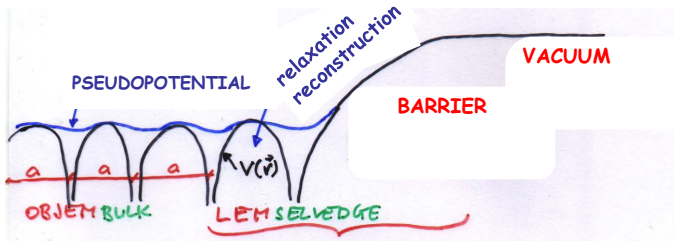
□ □ □

Model one-electron Hamiltonians

to study in a non- selfconsistent way the
orbital structure of electrons near a
surface with adsorbates
(instead of the inner "green" loop)

One-electron potential at a clean surface

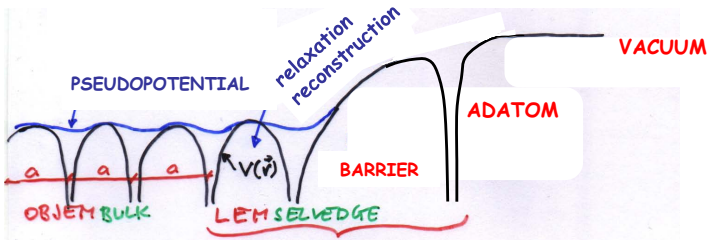
- atomic around each site
- periodic in the bulk
- the zero fixed by the barrier with respect to infinity in the vacuum
- the potential inside may be smoothed using the pseudopotential concept



**MODELS I. AND II.
of Lecture 3.**

One-electron potential with an adatom

- atomic around each site
- periodic in the bulk
- the zero fixed by the barrier with respect to infinity in the vacuum
- the potential inside may be smoothed using the pseudopotential concept
- the adatom creates a local disturbance just above the surface



MODELS: A. Sommerfeld
B. tight binding (LCAO)
C. AGN

What we are going to do

(I.) solve the one-electron Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V(\mathbf{r})\right)\psi_\alpha(\mathbf{r}) = E_\alpha \psi_\alpha(\mathbf{r})$$

(II.) Many-electron state \equiv sequence of occup. numbers $\{n_{\alpha\sigma}\}$

- add spin $\sigma = \uparrow, \downarrow$
- Pauli principle $0 \leq n_{\alpha\sigma} \leq 1$
- Aufbau principle fill from the bottom up

(III.) Charge balance $\sum n_{\alpha\sigma} = N_\uparrow^{(e)} + N_\downarrow^{(e)} = N^{(e)} = \sum Z_J$

$T=0$

... Fermi energy

$$n_{\alpha\sigma} = \mathcal{G}(E_F - E_\alpha)$$

... HOMO highest occupied

... LUMO lowest unoccupied

(IV.) Observables

$$\text{local particle density } n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r})$$

$$\text{local spin density } m(\mathbf{r}) = n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})$$

$$n_\sigma(\mathbf{r}) = \langle \hat{n}_\sigma(\mathbf{r}) \rangle = \sum n_{\alpha\sigma} |\psi_{\alpha\sigma}(\mathbf{r})|^2 \quad \text{orbital interpretation}$$

double average

Three of the ways to solve the Schrödinger eq.

one-electron Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_e}\Delta + V(\mathbf{r})\right)\psi_\alpha(\mathbf{r}) = E_\alpha \psi_\alpha(\mathbf{r})$$

in real space

on-shell at E_α
matching of the wave function
(boundary conditions)
textbook approach
MODEL A. choose simple $V(\mathbf{r})$

orbital representation

Schrödinger eq. → matrix
problem $\psi = \sum_\lambda c_\lambda \varphi_\lambda$
$$\sum_\mu (\langle \lambda | \hat{H} | \mu \rangle - E \langle \lambda | \mu \rangle) c_\mu = 0$$

$$H_{\lambda\mu} - E S_{\lambda\mu}$$

tight binding

on-shell at E_α
basis of atomic-like orbitals
sparse matrix techniques
today a recognized approach
MODEL B. fitted matrix elem.

orbital representation

Schrödinger eq. → matrix eq.
basis of fragment eigenstates
Green's function technique
elementary use of universal method
MODEL C. AGN

Outline

Schrödinger 1D model

Tight binding model

Anderson-Grimley-Newns model

Jellium model

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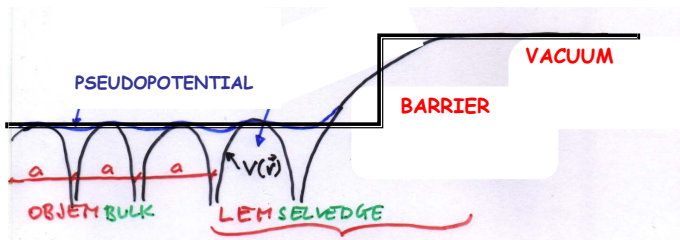
textbook approach

MODEL A. choose simple $V(\mathbf{r})$

On the way to the Sommerfeld type model **A**.

CLEAN SURFACE

- The smooth pseudopotential bottom is modeled by a completely flat Sommerfeld plateau
- The barrier is modeled by a step-like abrupt rise from the plateau to the vacuum zero

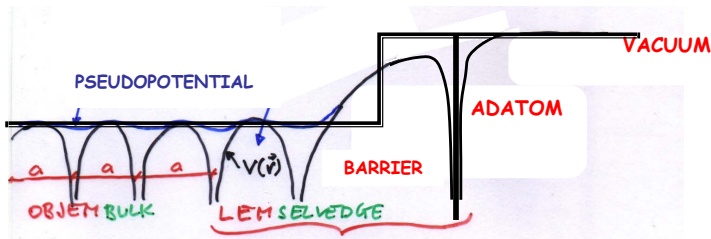


MODELS I. Lecture 3

On the way to the Sommerfeld type model **A**.

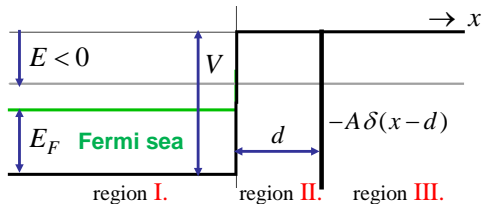
SURFACE DECORATED BY AN ADATOM

- The smooth pseudopotential bottom is modeled by a completely flat Sommerfeld plateau
- The barrier is modeled by a step-like abrupt rise from the plateau to the vacuum zero
- The atomic potential is modeled by an attractive δ -well
- Unrealistic model soluble by hand and giving very good insight



MODEL A.

MODEL A. 1D Sommerfeld, step barrier, δ -atom 1



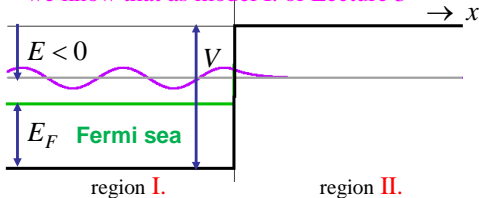
Three parameters V, A, d

Three matching regions

MODEL A. 1D Sommerfeld, step barrier, δ -atom 2

SUBSTRATE ALONE

we know that as model I. of Lecture 3



RESULT

- standing wave in region I.
- exponential leaking into region II.
- energy dependent phase shift needed for smooth matching

Solution of the Schrödinger equation by matching **A. SEMI-INFINITE SAMPLE**

bound states $\left\{ \begin{array}{ll} \text{I. } \psi = \alpha e^{ikx} + \beta e^{-ikx} & \frac{\hbar^2}{2m} k^2 = E + V \\ -V < E < 0 & k^2 + \kappa^2 = \frac{2m}{\hbar^2} V \equiv k_0^2 \\ \text{II. } \psi = \gamma e^{-\kappa x} & \frac{\hbar^2}{2m} \kappa^2 = -E \end{array} \right.$

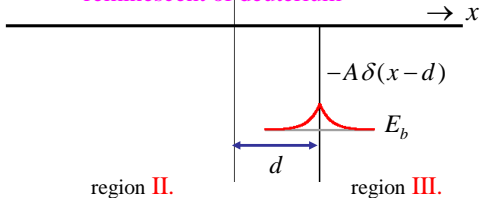
$$\begin{aligned} \alpha &= |\alpha| e^{i\Delta} & \tan \Delta &= \frac{\kappa}{k} \\ \beta &= |\alpha| e^{-i\Delta} & \sin \Delta &= \frac{\kappa}{k_0} \\ \gamma &= 2|\alpha| \cos \Delta & \cos \Delta &= \frac{k}{k_0} \end{aligned}$$

$$\begin{aligned} \psi(x) &= 2A \cos(kx + \Delta) & x < 0 \\ &= 2A \cos \Delta \cdot e^{-\kappa x} & x > 0 \end{aligned}$$

MODEL A. 1D Sommerfeld, step barrier, δ -atom 3

THE δ -ATOM ALONE

reminescent of deuterium



$$\kappa_b = \frac{2m}{\hbar^2} \cdot \frac{A}{2}$$

$$E_b = -\frac{\hbar^2}{2m} \cdot \frac{A^2}{4}$$

select A so that

$$-V < E_b < 0$$

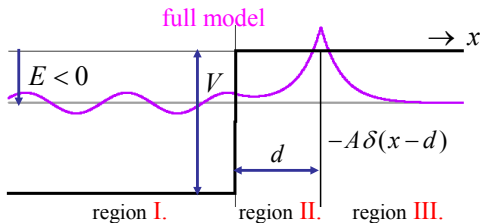
$$\psi = \varepsilon e^{-\kappa_b |x-d|}$$

$$-\frac{\hbar^2}{2m} \psi'' - A \delta(x-d) \psi = E \psi \quad \left| \int_{d-\omega}^{d+\omega} dx \right.$$

$$-\frac{\hbar^2}{2m} (\psi'(d+\omega) - \psi'(d-\omega)) - A \psi(d) = O(\omega)$$

MODEL A. 1D Sommerfeld, step barrier, δ -atom 4

SUBSTRATE + THE δ -ATOM



$$\begin{aligned} \text{I.} \quad & \psi = \alpha e^{ikx} + \beta e^{-ikx} \\ \text{II.} \quad & \psi = \gamma e^{\kappa x} + \delta e^{-\kappa x} \\ \text{III.} \quad & \psi = \varepsilon e^{-\kappa(x-d)} \end{aligned}$$

$$\alpha = |\alpha| e^{i\Delta}, \beta = |\alpha| e^{-i\Delta}$$

$$\tan \Delta = \frac{\kappa}{k} \cdot \frac{\frac{\kappa}{\kappa_b} - 1 - e^{-2\kappa d}}{\frac{\kappa}{\kappa_b} - 1 + e^{-2\kappa d}}$$

$$y = \frac{\kappa^2}{k^2} = \frac{|E|}{V - |E|}$$

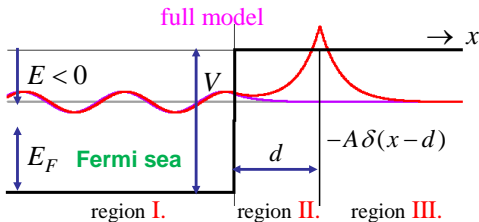
$$\frac{\varepsilon^2}{|\alpha|^2} = \frac{2e^{-2\kappa d} \left(\frac{\kappa}{\kappa_b} \right)^2}{(1+y) \left(\frac{\kappa}{\kappa_b} - \left[1 - e^{-2\kappa d} \frac{1-y}{1+y} \right] \right)^2 + (2e^{-2\kappa d})^2}$$

resonance shifted exponential broadening

For the adsorbate, the atomic bound state dissolves into a resonance in the bulk band
The coupling and the resonance width depends on $e^{-2\kappa d}$

MODEL A. 1D Sommerfeld, step barrier, δ -atom 5

SUBSTRATE + THE δ -ATOM



GLOBAL AND LOCAL EFFECTS

- locally, the band states are strongly affected
- global effect of a single atom is small (change in the phase shift)

- | | | |
|----------------------|--|------------------------------|
| 1. quantization | $k = \frac{\pi}{L} \cdot n + \frac{2A}{L}$ | } unchanged by the adsorbate |
| 2. normalization | $\int dx \psi ^2 = 2 \alpha ^2 L + o(L)$ | |
| 3. density of states | $g(E) = \frac{L\sqrt{2m}}{h} \frac{1}{\sqrt{V-E}}$ | |

Refresher

Band filling without spin

$$\mathcal{N}^{(e)} \equiv \mathcal{N}(E_F) = \sum_{E_k \leq E_F} 1 = \sum_k \mathcal{G}(E_F - E_k) \quad \text{general definition}$$

$$E_k = \frac{\hbar^2}{2m} k^2 \quad k = \frac{\pi}{L} \cdot n + \frac{2\Delta}{L} \quad n = \begin{cases} 2p \\ 2p+1 \end{cases}$$

$$n(E) \approx \frac{1}{\pi\hbar} \sqrt{2mE} \cdot L \quad \text{for } L \gg a \quad \text{suitable for smoothing}$$

$$\mathcal{N}(E) = \frac{1}{\pi\hbar} \sqrt{2mE} \cdot L, \quad \text{in particular} \quad \boxed{\mathcal{N}^{(e)} = \frac{1}{\pi\hbar} \sqrt{2mE_F} \cdot L}$$

DOS density of states *hustota stavů*

$$\mathcal{N}(E) \equiv \int_{-\infty}^E d\eta \underset{\text{DOS}}{g(\eta)} \quad \underset{\text{IDOS}}{g(E)} = \frac{d\mathcal{N}}{dE} \quad \text{general definition}$$

$$\frac{d}{dE} \mathcal{G}(E) = \delta(E) \quad g(E) = \sum_k \delta(E - E_k) \quad \text{basic form}$$

$$g(E) = \frac{\sqrt{2m}}{h} \cdot \frac{1}{\sqrt{E}} \cdot L \quad \text{our model}$$

Refresher

LDOS local density of states

$$n(x) = \sum_k |\psi_k(x)|^2 \int_{-\infty}^{E_F} d\eta \delta(\eta - E_k) \equiv \int_{-\infty}^{E_F} d\eta \overset{\text{LDOS}}{g(x, \eta)} \quad \text{SUM RULE I.}$$

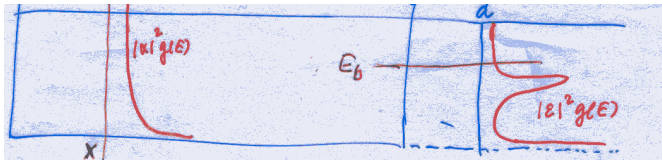
$$g(x, E) = \sum_k |\psi_k(x)|^2 \delta(E - E_k)$$

$$\int dx g(x, E) = \sum_k \underbrace{\int dx |\psi_k(x)|^2}_1 \delta(E - E_k) = g(E) \quad \text{SUM RULE II.}$$

LDOS for our model

$$g(x, E) = |\psi_{k(E)}(x)|^2 \sum_k \delta(E - E_k) = |\psi_{k(E)}(x)|^2 g(E)$$

$$g(d, E) = |\varepsilon|^2 g(E)$$



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orbital representation

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problem $\psi = \sum_{\lambda} c_{\lambda} \varphi_{\lambda}$

$$\sum_{\mu} (\underbrace{\langle \lambda | \hat{H} | \mu \rangle}_{H_{\lambda\mu}} - E \underbrace{\langle \lambda | \mu \rangle}_{S_{\lambda\mu}}) c_{\mu} = 0$$

tight binding

on-shell at E_{α}

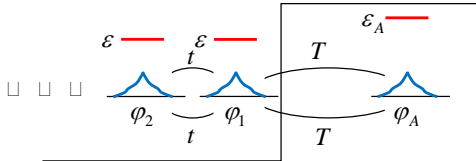
basis of atomic-like orbitals

sparse matrix techniques

today a recognized approach

MODEL B. fitted matrix elem.

Tight binding method



orbital representation

Schrödinger eq. \rightarrow matrix problem

$$\psi = \sum_{\lambda} c_{\lambda} \varphi_{\lambda}$$

$$\sum_{\mu} (\underbrace{\langle \lambda | \hat{H} | \mu \rangle}_{H_{\lambda\mu}} - E \underbrace{\langle \lambda | \mu \rangle}_{S_{\lambda\mu}}) c_{\mu} = 0$$

1D s-band with nearest neighbor hopping

write $\psi = c_0 \varphi_A + c_1 \varphi_1 + c_2 \varphi_2 + c_3 \varphi_3 + \dots$

Schrödinger equation becomes a difference equation for the coefficients c_n

$$(\varepsilon_A - E)a_0 + Ta_1 = 0 \quad \text{termination of the chain of equations}$$

$$Ta_0 + (\varepsilon - E)a_1 + ta_2 = 0$$

$$ta_1 + (\varepsilon - E)a_2 + ta_3 = 0$$

...

$$ta_n + (\varepsilon - E)a_{n+1} + ta_{n+2} = 0$$

(to infinity)

The states form a band, $\varepsilon - 2t \leq E \leq \varepsilon + 2t$

In a chain of N substrate atoms, there are $N+1$ states
(N of the substrate+one dissolved adatom state)

Projected density of states (PDOS)

Again, distinguish the global and the local properties

Orbital occupancy

Probability amplitude = $\int d^3\mathbf{r} \psi_{\alpha}^*(\mathbf{r}) \varphi(\mathbf{r}) = \langle \alpha | \varphi \rangle$

$$n_{\varphi} = \sum_{\alpha} n_{\alpha} |\langle \alpha | \varphi \rangle|^2 = \int dE \underbrace{f_{\text{FD}}(E) \sum_{\alpha} \delta(E - E_{\alpha}) |\langle \alpha | \varphi \rangle|^2}_{\text{PDOS } g_{\varphi}(E)}$$

SUM RULE $\int dE g_{\varphi}(E) = 1$

In words, the orbital is spread over all eigenenergies with the total weight equal to 1.

PDOS for the adatom in our model

$$g_A(E) = \sum_{\alpha} \delta(E - E_{\alpha}) |\langle \alpha | A \rangle|^2 = \sum_{\alpha} \delta(E - E_{\alpha}) |c_0(E_{\alpha})|^2$$

$$g_A(E) = |c_0(E)|^2 \sum_{\alpha} \delta(E - E_{\alpha}) = |c_0(E)|^2 \cdot g(E)$$

- resonant behavior
 - width $\propto |T|^2$
- } just like in the previous model

Schrödinger 1D model

Tight binding model

Anderson-Grimley-Newns model

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Schrödinger eq. → matrix eq.

basis of fragment eigenstates

Green's function technique

elementary use of universal method

MODEL C. AGN

Anderson - Grimley - Newns model

1

Widely used

Conceptually crucial also today

- System = substrate + adsorbate + coupling

$$\hat{H} = \hat{H}_S + \hat{H}_A + \hat{V}$$

- While we may visualize these parts in space,
their description is abstract

$$\hat{H} = \underbrace{\sum_b |b\rangle E_b \langle b| + |A\rangle E_A \langle A|}_{\text{unperturbed } \hat{H}_0} + \underbrace{\sum_b |b\rangle V_{bA} \langle A| + h.c.}_{\text{perturbation } \hat{V}}$$

- Somewhat like "tunneling Hamiltonians"
- P.W. Anderson thought about a d-level impurity in bulk
- Not 1D, it may cover any 3D situation, if the bands and the couplings are properly chosen

Anderson - Grimley - Newns model

2



Schrödinger eq.

$$(E - \hat{H}) |\psi\rangle = 0 \quad |\psi\rangle = \alpha |A\rangle + \sum \beta_b |b\rangle$$

$$\begin{cases} (E - E_A)\alpha + \sum V_{Ab}\beta_b = 0 \\ (E - E_b)\beta_b + \sum V_{bA}\alpha = 0 \end{cases}$$

E_A bound state

$$E = E_A + \sum \frac{|V_{bA}|^2}{E - E_b}$$

secular equation
for the bound state energy

provided it does not fall into the band

Inside the band, the adsorbate level becomes unstable

Golden rule decay rate (for weak coupling)

$$w = \frac{2\pi}{\hbar} \sum |V_{bA}|^2 \delta(E - E_b)$$

Self-consistent exact equation for

the complex energy of the resonant state

$$E = E_A + \sum \frac{|V_{bA}|^2}{E + i0 - E_b}$$

this gives the
resonant energy
its imaginary part

Anderson - Grimley - Newns model

3

Dirac identity

$$\frac{1}{E - E_b + i0} = \frac{1}{E - E_b} - i\pi\delta(E - E_b)$$

Making sense of the equation for the complex energy of the resonance

$$E = E_A + \sum \frac{|V_{bA}|^2}{E + i0 - E_b} \quad (*)$$

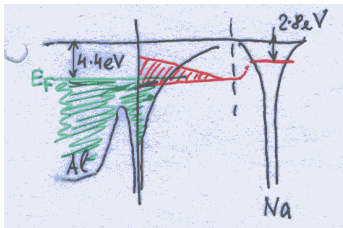
adsorption function $\Sigma(E + i0) = \sum \frac{|V_{bA}|^2}{E - E_b} - i\pi \sum |V_{bA}|^2 \delta(E - E_b)$

(self-energy)

$$= \Lambda(E) - i\Delta(E)$$

First iteration of (*) yields

$$E = E_A + \Lambda(E_A) - i\Delta(E_A) \text{ agrees with Golden Rule}$$



EXAMPLE Na on Al

(synopsis of ab initio calculations)

- the level goes down
- broadens
- the Fermi energy fixed
- partial occupancy results
- Al is more electronegative than Na
- back effect of occupancy on the level

A gentle introduction into the kingdom of Green's functions

PDOS $g_A(E) = \sum \delta(E - E_\zeta) |\langle A | \zeta \rangle|^2$

transformation $g_A(E) = -\pi^{-1} \text{Im} \sum \langle A | \zeta \rangle \frac{1}{E + i0 - E_\zeta} \langle \zeta | A \rangle$

Green's function $\hat{G}(E + i0) = \sum |\zeta \rangle \frac{1}{E + i0 - E_\zeta} \langle \zeta |$

Schrödinger eq. $(z - \hat{H})\hat{G}(z) = \hat{I} = \sum |\zeta \rangle \langle \zeta |$

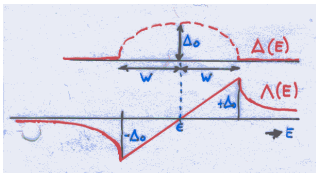
projected GF $\langle A | \hat{G}(z) | A \rangle = \frac{1}{z - E_A - \Sigma(z)}; \Sigma(z) = \sum \frac{|V_{bA}|^2}{z - E_b}$

PDOS again $g_A(E) = -\pi^{-1} \text{Im} \langle A | \hat{G}(E + i0) | A \rangle$
 $= \frac{\pi^{-1} \Delta(E)}{(E - E_A - \Lambda(E))^2 + \Delta^2(E)}$

nearly Lorentzian, except for the energy dependence of Λ and Δ

Anderson - Grimley - Newns model

5



Grimley semi-elliptic model
of the chemisorption function

$$\Delta(E) = A_0 \left(1 - \left(\frac{E - \epsilon}{w}\right)^2\right)^{1/2}$$

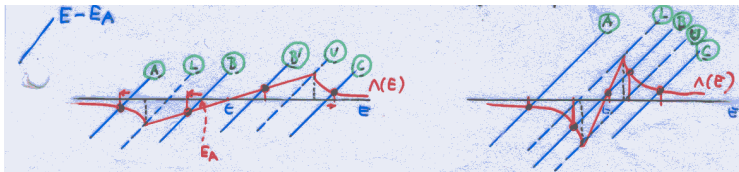
$\Lambda(E)$ by Kramers-Kronig

A_0 coupling strength, w half-band width

Zeros of eq. $E - E_A - \Lambda(E) = 0$ adsorbate induced $\left\{ \begin{array}{l} \text{bound states} \\ \text{resonances} \end{array} \right.$

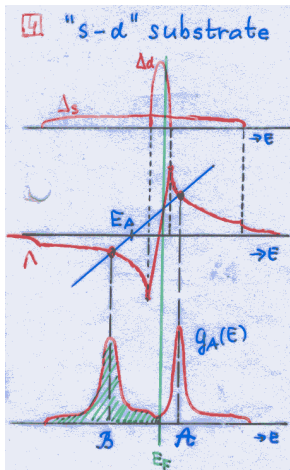
Two basic situations

- 1 $\frac{A_0}{w} < 1$ weak coupling 2 $\frac{A_0}{w} > 1$ strong coupling



Anderson - Grimley - Newns model

6



- wide s band } overlap
narrow d band }
- $\Delta(E) = \Delta_s(E) + \Delta_d(E)$
- $\Lambda(E) = \Lambda_s(E) + \Lambda_d(E)$
- adsorbate coupled to both
- forms a "surface molecule" with the substrate: **two levels**
- interference with the s band **virtual (resonant) levels**
- total weight of both limited by the sum rule to ≈ 1
- in a d metal, the lower (bonding) resonance is occupied
the upper (antibonding) resonance is empty

Schrödinger 1D model

Tight binding model

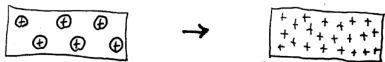
Anderson-Grimley-Newns model

Jellium model

Recapitulation of bulk jellium

1

Definition neutral crystal \rightarrow ionic charge evenly spread



$$n^+ = \sum Z_J \delta(\mathbf{r} - \mathbf{R}_J) \rightarrow n^J = \frac{1}{\Omega} \int_{\Omega} d^3\mathbf{r} n^+(\mathbf{r})$$

- single parameter $n = n^+$
determines all equilibrium properties

- WIGNER RADIUS volume per electron

$$\frac{1}{n} = \frac{4\pi}{3} (a_0 r_s)^3$$

Bohr radius □ □ dimensionless parameter

$$\frac{n}{\text{m}^3} = 1.612 \times 10^{30} r_s^{-3}$$

simple metals $r_s = 2 \dots 6$

Recapitulation of bulk jellium

2

TOTAL ENERGY/ELECTRON atomic units

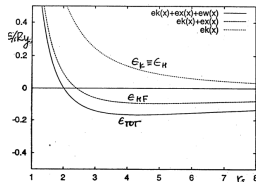
$$\begin{aligned}\epsilon_{\text{TOT}} &= \epsilon_H + \epsilon_X + \epsilon_C \\ &= \frac{2.21}{r_s^2} - \frac{0.916}{r_s} - \frac{0.88}{r_s + 8.7}\end{aligned}$$

WIGNER FORMULA

Jellium is stabilized by exchange
and further by the correlations

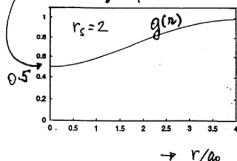
XC hole

$$g(r) \equiv \frac{n_2(r)}{n^2}$$



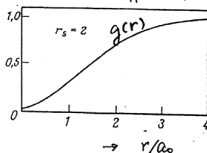
EXCHANGE HOLE

- only kinematic (Pauli) correlation
- ... opposite spins only at $r \rightarrow \infty$
- ... analytic formula



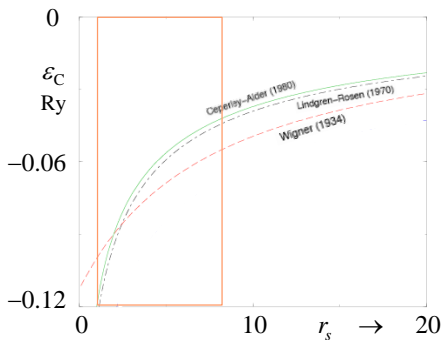
FULL XC HOLE

- additional Coulomb repulsion
- ... both spins affected
- ... numerical result (not difficult)




Recapitulation of bulk jellium

3



Correlation energy in jellium

- Wigner ... historical, approx.
- compared with QMC numerical, heavy computation
- in practice -- Perdew-Zunger fit by analytic expressions
-  range of previous slide

Recapitulation of DFT-LDA

1

Write Euler-Lagrange equations

$e'^2 = 0$ non-interacting el 's

$e'^2 \neq 0$ Kohn-Sham theory

$$\mathcal{E}_0[n] = \mathcal{T}_s[n] + \int d\mathbf{r}^3 v_0(\mathbf{r})n(\mathbf{r})$$

$$\mathcal{E}[n] = \mathcal{T}_s[n] + \mathcal{G}[n] + \int d\mathbf{r}^3 v(\mathbf{r})n(\mathbf{r})$$

$$\delta\mathcal{E}_0 - \mu\delta\mathcal{N}^{(e)} = 0$$

$$\delta\mathcal{E} - \mu\delta\mathcal{N}^{(e)} = 0 \quad \mu \text{ Lagrange multiplier}$$

$$\frac{\delta\mathcal{T}_s}{\delta n(\mathbf{r})} + v_0(\mathbf{r}) = \mu$$

$$\frac{\delta\mathcal{T}_s}{\delta n(\mathbf{r})} + \underbrace{\frac{\delta\mathcal{G}}{\delta n(\mathbf{r})}}_{v_{\text{eff}}(\mathbf{r})} + v(\mathbf{r}) = \mu$$

Here, the solution is known

Use the eff. potential as a real one

$$\left(-\frac{\hbar^2}{2m_e}\Delta + v_0(\mathbf{r})\right)\psi_\alpha = E_\alpha \psi_\alpha$$

$$\left(-\frac{\hbar^2}{2m_e}\Delta + v_{\text{eff}}(\mathbf{r})\right)\psi_\alpha = E_\alpha \psi_\alpha$$

$$n(\mathbf{r}) = \sum |\psi_\alpha(\mathbf{r})|^2$$

$$n(\mathbf{r}) = \sum |\psi_\alpha(\mathbf{r})|^2$$

$$\mathcal{E}_0 = \sum E_\alpha = \mathcal{T}_s + \int d\mathbf{r}^3 v_0 n$$

$$\mathcal{E} = \mathcal{T}_s + \mathcal{G} + \int d\mathbf{r}^3 v n$$

$$\mathcal{E} = \sum E_\alpha - \int d\mathbf{r}^3 (v_{\text{eff}} - v)n + \mathcal{G}$$

$$\mu = \frac{\delta\mathcal{E}}{\delta\mathcal{N}^{(e)}}$$

This is the complete set of equations of the Kohn-Sham theory

Recapitulation of DFT-LDA

2

Exact decomposition

$$\mathcal{G}[n] = \frac{1}{2} \int d^3\mathbf{r} n(\mathbf{r}) \int d^3\mathbf{r}' \frac{e'^2}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r}') + \frac{1}{2} \int d^3\mathbf{r} n(\mathbf{r}) \int d^3\mathbf{r}' \frac{e'^2}{|\mathbf{r}-\mathbf{r}'|} h_{xc}^{\text{KS}}(\mathbf{r}, \mathbf{r}')$$

$\equiv \mathcal{U}_{\text{H}} + \mathcal{E}_{\text{XC}}$ defines KS XC energy

KS XC hole different from the true one, but similar properties

sum rule $\int d^3\mathbf{r}' h_{xc}^{\text{KS}}(\mathbf{r}, \mathbf{r}') = -1$

XC energy per particle $\mathcal{E}_{\text{XC}}^{\text{KS}}(\mathbf{r}, n) = \frac{1}{2} \int d^3\mathbf{r}' \frac{e'^2}{|\mathbf{r}-\mathbf{r}'|} h_{xc}^{\text{KS}}(\mathbf{r}, \mathbf{r}')$

Effective potential

$$\mathcal{V}_{\text{eff}}(\mathbf{r}) = \mathcal{V}(\mathbf{r}) + \frac{\delta \mathcal{G}}{\delta n(\mathbf{r})} = \mathcal{V}(\mathbf{r}) + \mathcal{V}_{\text{H}}(\mathbf{r}) + \frac{\delta \mathcal{E}_{\text{XC}}}{\delta n(\mathbf{r})}$$

Final expression for the total energy

$$\mathcal{E} = \sum E_{\alpha} - \mathcal{U}_{\text{H}} - \int d\mathbf{r}^3 \mathcal{V}_{\text{xc}} n + \mathcal{E}_{\text{XC}}$$

Recapitulation of DFT-LDA

3

For jellium, KS theory is exact

$$\varepsilon_{\text{XC}}^{\text{KS}}(\mathbf{r}, n) = \varepsilon_{\text{XC}}^{\text{J}}(n)$$

LDA Ansatz

$$\varepsilon_{\text{XC}}^{\text{KS}}(\mathbf{r}, [n]) = \varepsilon_{\text{XC}}^{\text{J}}(n(\mathbf{r})) \quad \text{defines the LDA XC energy}$$

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta \mathcal{E}_{\text{XC}}}{\delta n(\mathbf{r})} \rightarrow \frac{\partial}{\partial n}(n \varepsilon_{\text{XC}})$$

LDA KS equations

$$\left(-\frac{\hbar^2}{2m_e} \Delta + v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}^{\text{J}}(\mathbf{r})\right) \psi_{\alpha} = E_{\alpha} \psi_{\alpha}$$

- (1) As easy to solve as Hartree or Slater equations
- (2) Of course, by iteration in a self-consistent cycle

Clean semi-infinite jellium

- semi-infinite jellium far more realistic than truncated Sommerfeld
- simplest theory of surface ever -- a single parameter n^+ or r_s
- treated in DFT-LDA means fully ab initio, no additional fudging with parameters etc.
- the calculation permitted to find also total energies, in particular the surface energy
- here, we inspect only a few figures of surface charge distribution and related quantities (N.D. Lang and W. Kohn, PRB 1(1970), 4555)

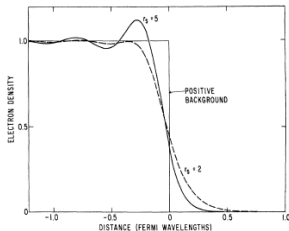


FIG. 2. Self-consistent charge density near metal surface for $r_s = 2$ and $r_s = 5$ (uniform positive background model).

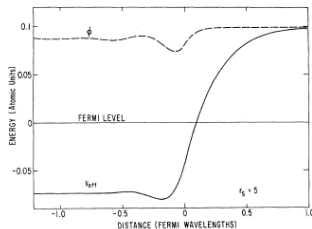
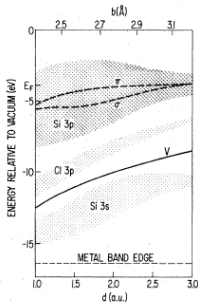


FIG. 3. Effective one-electron potential v_{eff} , with electrostatic part ϕ , near metal surface (positive background model; $r_s = 5$).

Semi-infinite jellium as a substrate 1

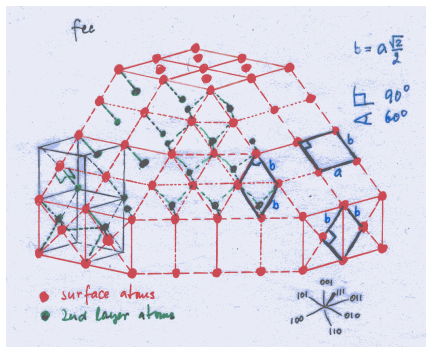
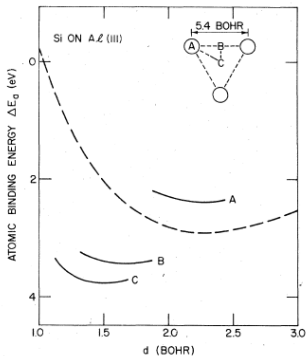
- semi-infinite jellium (parameter r_s) is approached by a point charge Z
- treated in DFT-LDA means fully ab initio
- the calculation permitted to find also total energies and the equilibrium distances of the adsorbed atoms
- here, we inspect only a few figures
(N.D. Lang and A.R. Williams, PRB 18(1978), 616)



Semi-infinite jellium as a substrate

2

Adatom	d_{eq} (bohrs)	ΔE_a (eV)
H	1.1	1.5
Li	2.5	1.3
O	1.1	5.4
Na	3.1	0.9
Si	2.3	3.0
Cl	2.6	3.6



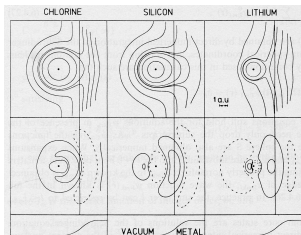
Atomic chemisorption on jellium surface

Model: Semiinfinite jellium + an adatom at a distance d from the edge of the positive background.

Solving the Schrödinger equation at the surface

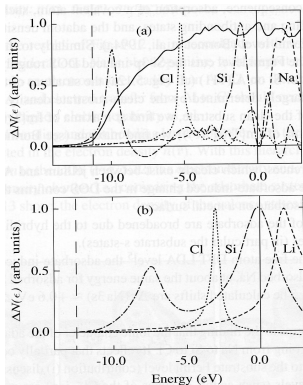
$$\begin{aligned} \text{density} &\Longleftrightarrow \text{potential} & E &= E[\rho^-(\vec{r})] \\ &[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(\rho^-, \vec{r}_{||}, z)]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \\ E &= \sum_{i \text{ occ}} \epsilon_i ; & \rho^-(\vec{r}) &= \sum_{i \text{ occ}} |\psi_i(\vec{r})|^2 \end{aligned}$$

- the perturbing potential ($V_{\text{eff}} - V_{\text{eff}}^0$) is short-ranged due to metallic screening.



Contours of constant charge density for Cl, Si, and Li atoms on a jellium substrate ($r_s = 2$ a.u.) Upper row: total charge density. Center row: variation of charge density. Solid (dashed) curves denote a surfeit (depletion) of electron. Bottom row: bare metal electron density profile. [From Wilke and Scheffler, 1996.](#)

Adsorption of isolated adatoms



a) Adsorbate-induced change of the density of states for three different adatoms on the Al(111) substrate and b) on jellium with an electron density corresponding to Al. The dashed line indicates the bottom of the band of the substrate. From Bormet, 1994 (top) and Lang and Williams, 1978 (bottom).

- Na, Cl - excellent agreement with the induced DOS on jellium
- Si - interaction with substrate splits the Si 3p induced resonance into occupied bonding and empty antibonding states

The end