Surface States
Low dimensional systems and nanostructures
Maider Ormaza Saezmiera
Motivation

- Understand of heterogeneous catalysis.
- Semiconductor Industry and Nanotechnology.
- Study of two dimensional systems.
Basic Theory
To describe electrons in a crystal ($10^{23}$ e$^-$) we have to use

- **Adiabatic Approximation.**

- **One electron approximation**, where each e$^-$ moves under the influence of a periodic potential.

Now, to obtain the band structure, we have to solve...

$$\nabla^2 \psi + V(\vec{r})\psi = E\psi$$

Bloch’s Theorem tells that the solution...

$$\psi_{k}(\vec{r}) = u_{k}(\vec{r})e^{ik\vec{r}}$$
Kronig-Penney model

Direct matching procedure

\[
\frac{(mV_0 bc)}{h^2 k_1 c} \sin(k_1 c) + \cos(k_1 c) = \cos(kc) \leq 1
\]
Electrons at surfaces

Igor Tamm showed first the existence of surface states in 1932.

What happens if our crystal is finite?

\[ \psi_k(r) = u_k(r)e^{ikr} \]

We could have real and complex \( k \)!
One-dim. Schrödinger equation: 
\[ \left[ -\frac{d^2}{dz^2} + V(z) \right] \psi = E \psi \]

Periodic Potential: 
\[ V(z) = -V_0 + 2V_g \cos g z \]

We try this solution: 
\[ \psi_k(z) = A e^{ikz} + B e^{i(k-G)z} \]
We get this secular equation:

\[
\begin{bmatrix}
  k^2 - V_0 - E & V_g \\
  V_g & (k - g)^2 - V_0 - E
\end{bmatrix}
\begin{bmatrix}
  A \\
  B
\end{bmatrix} = 0
\]

The eigenvalues are

\[E = -V_0 + \left(\frac{1}{2}g\right)^2 + \left(\kappa^2 \pm (g^2\kappa^2 + V_g^2)^{\frac{1}{2}}\right)
\]

The eigenvectors are

\[\psi_k = e^{i\kappa z} \cos\left(\frac{1}{2}g z + \delta\right) \quad \text{where} \quad e^{2i\delta} = \frac{E - k^2}{V_g}\]
The wave function monotonically damped in the direction of vacuum and damped in an oscillatory way in the direction of the crystal.
The energy levels that are in the gaps, are known as \textit{surface states}. 
Shockley state exists, if:

1. $V_g > 0$
2. matching conditions are fulfilled for $\psi$, $\frac{d\psi}{dz}$

Tamm States
This surface states are obtained using the tight-binding model.
DFT
density functional theory

\[ E(\rho(\vec{r})) = T + U + E_{xc} \]

- Kinetik energy
- Coulomb term
- Exchange-correlation term

\[ U = U_{ec} + U_{ee} + U_{cc} \]

Hohenberg-kohn Theorem states that the total energy of a system is a unique functional of the electron density.
The energy of the ground state is found by looking for the density which minimizes the energy functional.

To obtain this density…\textit{Kohn-Sham equation}

\[-\frac{\hbar^2}{2m} \nabla^2 \psi_i(r) + v_{\text{eff}}(r) \psi_i(r) = \epsilon_i \psi_i\]

Effective potential for one e⁻

The density is given by…

\[\rho(r) = \sum |\psi_i(r)|^2\]

Self-consistent solution!
Jellium Model + DFT

Positive fixed background

Density

$$n_+(\mathbf{r}) = \hat{n} \rightarrow z \leq 0$$
$$0 \rightarrow z > 0$$

It can be also written

$$\frac{1}{\hat{n}} = \frac{4}{3\pi} r_s^3$$

Volume of an $e^-$

e$^-$ spill out!
Experimental Techniques
Surface science

We need ultra high vacuum

\[ p < 10^{-9} \text{ mbar} \]

Vacuum pumps

Bake out
Scanning Tunneling microscope (STM)

- Sharp tip very close to the surface
- Measure the current between the tip and the surface.
- Quantum tunnelling

\[ I \approx e^{-ikz} \]
STM modes
If we change the applied voltage...

STM image of Ag rows on vicinal Si(111).

a) Empty states ($U_{\text{tip}} = -1 \text{V}$),
b) Filled States ($U_{\text{tip}} = 1.5 \text{V}$)

STM measures the electronic topology of a surface

$$I \approx e^{-ikz} d(r, \epsilon)$$
Low Energy Electron diffraction (LEED)

The mean free path of low energy $e^-$ is small → Surface sensitive

When $\lambda \approx d$

Diffraction

Formation of diffraction pattern

Qualitative information about the surface symmetries and periodicities.
Electrons interact strongly with matter. 

Multiple scattering

Dynamic theory

Diamond-type (1 1 1) surface
ARPES

Based on the photoelectric effect

$E_{\text{kin}}, \theta, \varphi$

$E_{\text{kin}} = h\omega - \Phi - |E_B|$
We obtain directly the band structure
References

• Solid State Physics, Aschcroft & Mermin
• Physics at surfaces, A.Zangwill
• Basic Theory of Surface States, Sydney G. Davison & Maria Steslicka.
• Lecture Notes on Surface Science, P.Hofmann (2005)
• Electronic Structure of low-dimensional systems analized by ARPES}, Aitor Mugarza (Doctoral thesis)
• Introduction to nanotechnology, Henrik Bruus
• www.physinet.uni-hamburg.de
• www.nanoed.org
• Estructura electrónica de superficies: estados de superficie}, H.Herrera & C.Mora.
• Surface Science, K.Oura & Co.
• http://newton.ex.ac.uk/research/qsystems/people/jenkins/mbody.html
• www.unc.edu/shubin/dft.html
Thank you for your attention!!!