## 3. Electronic Structure of Surfaces ; 3.1 Work function of metals

The detailed electronic structure of the surface is relevant, when ever an electron is removed from the solid, even if the electron originates from deep in the bulk. The distortions of the electronic charge distribution of surface atoms (and atoms near the surface) contribute significantly to the work necessary to remove an electron from the solid. These distortions make the „extraction work" dependent on surface orientation and on the species adsorbed to the surface. These effects are crucial for contact potentials, for thermionic emission and for photo emission.

Let us first consider an infinite crystal. We may describe the potential $V^{inf}(\vec{r})$ of an electron in an infinite crystal (the potential that appears in the corresponding one electron Schrödinger equation) as a sum of contributions from primitive cells around each lattice point:

$$V^{inf}(\vec{r}) = \sum_{\vec{R}} v(\vec{r} - \vec{R})$$

with $\qquad v(\vec{r}) \qquad -e \frac{1}{4\pi\varepsilon_0} \int_{cell} \rho(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} d\vec{r}'$
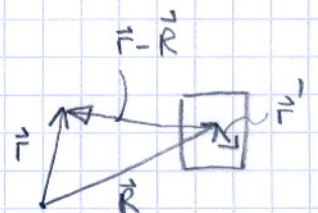
In distances large compared to the dimension of the cell we may use the multipol expansion of electrostatics:

$$\frac{1}{|\vec{r} - \vec{r}'|} = \frac{1}{r} - (\vec{r}' \cdot \nabla) \cdot \frac{1}{r} + \frac{1}{2} (\vec{r}' \cdot \nabla)^2 \cdot \frac{1}{r^2} -$$

$$= \frac{1}{r} + \frac{\vec{r}' \cdot \vec{e}_r}{r^2} + \frac{3(\vec{r}' \cdot \vec{e}_r)^2 - \vec{r}'^2}{r^3} + \frac{1}{r} O\left(\frac{\vec{r}'}{r}\right)^3$$

Thus $\qquad v(\vec{r}) = -e \frac{1}{4\pi\varepsilon_0} \left(\frac{Q}{r} + \frac{\vec{P} \cdot \vec{e}_r}{r^2} + O\left(\frac{1}{r^3}\right) \right)$

with $\qquad Q = \int_{cell} d\vec{r}' \cdot \rho(\vec{r}') \qquad\qquad \vec{P} = \int_{cell} d\vec{r}' \cdot \vec{r}' \cdot \rho(\vec{r}')$

$\qquad\qquad$ „charge" $\qquad\qquad\qquad\qquad\qquad$ „dipole moment"

Since the crystal is electrically neutral and since $\rho(\vec{r})$ has the periodicity of the lattice, each primitive cell must be neutral: $Q = 0$

In a crystal with inversion symmetry, there is no dipole moment from a Wigner-Seitz cell. In a cubic crystal, which we assume for simplicity, the coefficient for $\frac{1}{r^3}$ vanishes and inversion symmetry again requires a vanishing coefficient of the $\frac{1}{r^4}$ term. Thus $V(\vec{r})$ decreases as $\frac{1}{r^5}$, very rapidly at large distances from the cell. Thus $V^{int}(\vec{r})$ is well approximated by contributions from cells within a distance of a few lattice spacings from $\vec{r}$.

Consider now a finite crystal, by assuming that only in some volume the lattice cells are occupied. Assume further that the charge density of each cell is completely unaffected by this finiteness, even if a cell is close or at the surface. Then

$$V^{fin}(\vec{r}) = \sum_{\vec{R} \text{ in Vol}} V(\vec{r} - \vec{R})$$

Inside the crystal, a few lattice spacings away from the surface, we have $V^{fin}(\vec{r}) = V^{int}(\vec{r})$. Outside the crystal, a few lattice spacings away from the surface $V^{fin}(\vec{r}) = 0$, because of the rapidly decaying contributions of the cells to $V^{fin}(\vec{r})$ with increasing distance. Consequently ε_F (or more generally μ) would remain unchanged compared to the infinite crystal. Thus, in the absence of charge distortions at the surface we would have

$$W_A = V^{fin}_{out} - \varepsilon_F = -\varepsilon_F \qquad (*) \qquad \text{see Fig. 3.1}$$

with W_A being the work needed to extract an electron.

<u>Equation $(*)$ is wrong</u>. The reasons are: (i) Reconstruction and Relaxation move the nuclei from their lattice positions affecting the charge distribution; (ii) The charge distribution of the surface atoms

themselves are likely to be different from the bulk due to a changed bonding. This work depends thus on the details of the surface: steps, orientation, roughness, adsorbates etc.

Let us consider first a situation, in which the distortion of the unit cell does not involve a surface charge, i.e. $Q = 0$. This may realized, if all crystal faces are equivalent (see below). At macroscopic distances away from such a surface there will still no $\vec{E}$-fields present. Due to symmetry no net dipole moment may involve $\parallel$ to the surface, but only $\perp$ to the surface. A dipole moment $\perp$ to the surface has in macroscopic distances no $\vec{E}$-field (consider a plate capacitator). However within the dipole layer there are substantial electric fields $\vec{E}$ $\perp$ to the surface. Moving an electron through this dipole layer requires work $W_S = e \int \vec{E} \, d\vec{l}$. The correct work function is thus

$$W_A = -\mathcal{E}_{\mp} + W_S \qquad \text{(compare Fig. 3.2)}$$

Calculated example:
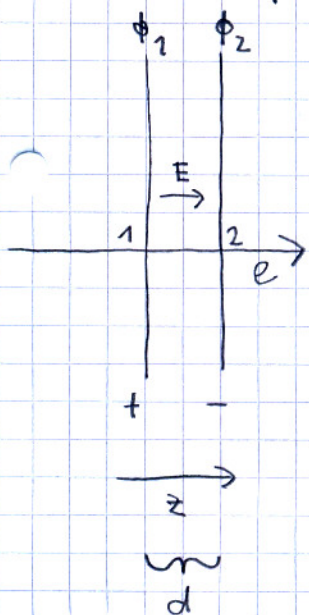
$\vec{E} = 0$ outside dipole layer

$\vec{E} = \dfrac{\sigma}{\varepsilon_o} \vec{e}_z$ inside dipole layer

Change in pot. energy from $1 \to 2$ is work done

$W_S = -\int \vec{\mp} \, d\vec{l} = -\int q\vec{E} \, d\vec{l} \overset{q=-e}{=} e\int \vec{E} \, d\vec{l} = e \, \dfrac{\sigma \cdot d}{\varepsilon_o}$

$W_S = q(\phi_2 - \phi_1) = -e(\phi_2 - \phi_1)$ ϕ = electrostatic potential

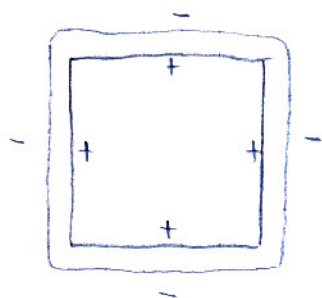Assumptions: atomic surface density $\approx 1.2 \cdot 10^{19} / m^2$
one elementary charge per atomic unit $\sigma = 2C/m^2$
displaced by $\approx 0.1 \, \text{Å}$

$\Rightarrow W_S = e \cdot \dfrac{2C/m^2 \cdot 10^{-11} m \; Vm}{8.9 \cdot 10^{-12} \, As} \approx 2.2 \, eV$

our result is of the proper magnitude.
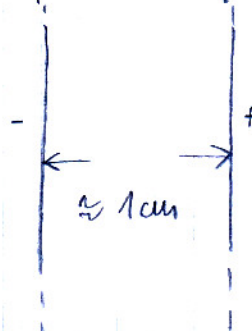
Warning: Do not confuse work function with polar surfaces

work function   polar surface

W_A independent of
crystal size

$W_A \approx eV$

$$U = |\phi_2 - \phi_1| = \frac{2C/m^2 \cdot 10^{-2} m \; Vm}{8.9 \cdot 10^{-12} As} \approx 2.2 \cdot 10^{9} V$$

Voltage increases with size.
enormous contribution to ions
potential energy.

Note that in Fig. 3.2 we made a specific choice for the zero of the potential energy consistent with the usual definition in electrostatics (see page 37) Other choices are useful and possible.

Consider now the situation sketched in Fig. 3.3. A crystal with faces F and F' has work functions W_A and W_A' which are in general not identical. Following the circular process indicated in Fig. 3.3 a perpetuum mobile would result. We take out the e^- by paying the lower work function $W_A < W_A'$ and obtain the work $W_A' > W_A$ back by reintroducing the e^-. Consequently there must be a compensating $\vec{E}$-field which causes work to be done by changing from F to F'.
The two faces are thus at different electrostatic potentials satisfying

$$- e(\phi - \phi') = W_A - W_A'$$

Since a double layer does not create a macroscopic electric field outside the metal, this field arises from a net surface charge. The exterior fields are extremely small compared to the field in the double layer

The difference of the two integrals $\int \vec{E} \, d\vec{e}$ and $\int \vec{E}' \, d\vec{e}'$ through the two double layers must be compensated by the $\vec{E}$-field along the long path from face F to F'. In order to have a definition of work function of a crystal face, that does not depend on the presence of other faces, the work to be done against external fields is not included in this concept.

[Definition: The work function of a surface is defined as the minimum work necessary to move an electron from the crystal interior through that surface to a point in a microscopic distance ($\approx 1 \mu m$) above the surface.

Up to now we neglected that the removed electron interacts with the solid by the interaction of the removed e^- with its positive image charge in the metal. By choosing in our definition a distance $\approx 1 \mu m$ the image charge effects have become negligible
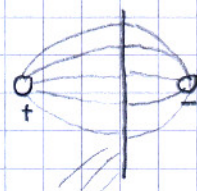
Next consider two metals with different work functions W_A and W_A' that are brought into contact through a metal wire (compare Fig 3.4). Electrons will flow between them till their chemical potentials align. This flow results from a flow of charge between the surfaces, such that the potential in the interior shifts all bulk levels and the chemical potential. The charge transfer causes the surfaces of the two metals to be at different electrostatic potential ϕ and ϕ' such that $-e(\phi - \phi') = W_A - W_A'$. The difference in potential is known as _contact potential_ and it is accompanied by the formation of an $\vec{E}$-field between the metals.

The first method we discuss to measure work function is based on measuring a contact potential. We bring a probe plate of known work function $W_{A,P}$ into close contact to a crystal face of unknown work function $W_{A,C}$. The probe together with the crystal face forms a capacitance C.

Due to the difference in work function $W_{A,P} - W_{A,C} = -e(\phi_P - \phi_C) = -e\,\Delta\phi$ a potential difference $\Delta\phi$ between the two plates exists. The capicator thus carries a charge $Q = C \cdot \Delta\phi$.

We may vibrate the probe plate giving rise to a time dependent capacitance with a non vanishing derivative $C = \tilde{C} + C_0 \sin\omega t \rightarrow \frac{dC}{dt} = C_0 \cos\omega t$. If we add an additional voltage U_{comp} and connect the two capacitator plates through an Ampmeter we will measure a current

$$I = \frac{dC}{dt} \cdot (\Delta\phi + U_{comp}).$$

Only if $\Delta\phi = -U_{comp}$ the current vanishes and from $\Delta\phi$ we obtain the unknown $W_{A,C}$. See Figs. 3.5 + 3.6

Now we will consider in more detail, what the nature of the surface dipole is and how it depends on surface structure. To this end we will consider the jellium model, a solid with a surface in which the ion cores are replaced by a uniform positive charge distribution (the jellium). If we apply density functional theory to this simple model, we still get a reasonable description for simple metals like Na, Mg or Al [Density functional theory (DFT) is a highly efficient computational scheme, which allows to obtain precise results for the ground state of many body systems by minimizing the system energy as a functional of the electron density]. Fig 3.7 displays the results of such calculations. The charge density of the electrons (as well as the one of the positive back-ground) is expressed by the dimensionless parameter r_s where $r_s \cdot a_0$ is the radius of a sphere containing one e^- (a_0 is the Bohr radius).

Two features are obvious from Fig. 3.7

(i) The electron density does not follow abruptly the positive background, but approaches the bulk values from the surface in an oscillatory way, with an oscillation period of $\frac{\lambda_F}{2} = \frac{\pi}{K_F}$. Such electron density oscillations due to

a potential step are named Friedel oscillations. We will encounter them later on in a number of situations.

(ii) The charge spills out into the vacuum beyond the positive background, causing a positive surface charge at slightly negative z-values (still inside the jellium) and negative surface charge at slightly positive z-values (just outside the jellium). In effect a double layer or dipole layer results with the dipole moment $\vec{p}$ directed into the solid. It is this double layer which gives enhances the work function above the value that would arise from a solid with undistorted charge distribution up to the surface. The origin of the charge spill-out may be traced back to a lowering of the electron kinetic energy. The expectation value of the kinetic energy $\langle T \rangle = -\frac{\hbar^2}{2m} \langle \Psi | \Delta | \Psi \rangle$ decreases, if the curvature of the wave function diminishes, i.e. if the electron density varies only smoothly. Fig. 3.8 displays a number of work functions calculated with the jellium model and compares them to experiment.

Let us now investigate how the work function depends on the crystal orientation. Besides the double layer due to charge spill out increasing the work function, there is an opposite effect of smoothening of the charge distribution on corrugated surfaces. Again, to lower the kinetic energy large curvatures in the electron wave function and thus the charge density are avoided. For a simple cubic surface as depicted in Fig. 3.9 The charge smoothening thus will add electronic charge to depressions and remove charge from protrusions. In consequence a smoothening dipole layer contribution results, which is opposite to the spill out dipole layer.

Thus, the more open, corrugated a surface, the lower its work function. This is consistent with the order of W_A values for a number

of low index surfaces as presented in the table of Fig. 3.10. The same smoothening effect will take place also at single steps on low index surfaces. Indeed, careful work function measurements show, that W_A decreases linearly with the step concentration as shown in Fig 3.11. This allows one to attribute a step dipole moment per unit length to steps. The charge deficit at the upper edge of steps due to the charge smoothening (also named Smoluchowski effect) makes these locations most susceptible to adsorption and reaction. At the upper step edge atoms and molecules like H_2O, Xe, O, CO bind with considerable preference; examples gives Fig 3.12. Finally adsorption itself will change the strength of double layer. While Cl adsorption extracts charge from the metal to the adsorbate, Cs adsorption donates e^- to the metal :

$$\underline{\begin{array}{ccc} Cl^- & Cl^- & Cl^- \\ + & + & + \\ \end{array}} \qquad \underline{\begin{array}{ccc} Cs^+ & Cs^+ & Cs^+ \\ & & \\ \end{array}}$$

Consequently in the first case the work function increases with coverage and in the second it decreases with it; as shown in Fig 3.13.

The work is of decisive importance for thermionic electron emission from metals. To prepare free e^- beams usually a tip-shaped piece of metal is heated. Electrons with sufficient energy to overcome the work function barrier W_A leave the crystal with the proper direction of momentum and are removed by a mild $\vec{E}$-field to suppress space charge built up.
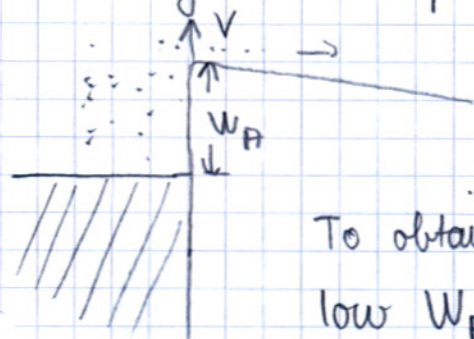
$$j = - \frac{em}{2\pi^2 \hbar^3} (k_B \cdot T)^2 \cdot e^{-W_A/k_B T}$$

To obtain high currents with low heating powers low W_A emitters are needed :

LaB_6, Th coated Ir, Cs coated W