

Physics of surfaces and interfaces

1. Surface electronic states: Tamm, Shockley and image-potential states. Quasiparticle interference and quantum corrals

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International summer school at Beijing Institute of Technology, 16th – 26th July 2023

Outline of mini-course and requirements

God made solids, but surfaces were the work of the Devil.
W. Pauli

Outline: preliminary

- * Lecture 1: Surface electronic states: Tamm, Schockley and image-potential states. Quasiparticle interference and quantum corrals (July, 17)
- * Lecture 2: Scanning tunneling microscopy and spectroscopy. Quantum-well states and tunneling interferometry (July, 18)
- * Lecture 3: Surface, edge and domain-wall superconductivity in nanostructured hybrid samples (July, 19)
- * Lecture 4: Thermodynamic aspects of physics of surfaces and interfaces (July, 20)

Requirements:

- * Differential and integral calculus, including calculus of variations
- * Basics of quantum mechanics, solid-state physics, thermodynamics, and electrodynamics

Outline of current lecture

- * Introduction
- * Band spectrum and surface states in the tight-binding approximation
- * Band spectrum and surface states in the nearly-free-electron approximation
- * Quasiparticle interference and quantum corrals
- * Image potential. Image-potential states as modified surface states
- * Stark-shifted image-potential states in linearly increasing potential

Introduction

Band spectrum of crystals: general consideration (1)

We consider an electron in a crystal with periodic arrangement of positively charged ions.



It is well known that the solutions of the stationary Schrödinger equation

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

for electron in an arbitrary periodic potential $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{a})$ have a form of so-called Bloch states – modulated plane waves of constant amplitudes

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

where n is integer index, $u_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{a})$ is an arbitrary periodic function, and \mathbf{k} is the wave vector (quasi-momentum).

Band spectrum of crystals: general consideration (2)

The energy of the Bloch electronic waves $\psi_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$ should generally depend on the number of quantum state n and the wave vector $\mathbf{k} = \mathbf{p}/\hbar$

$$E_{n,\mathbf{k}} = E_{n,\mathbf{k}+\mathbf{K}},$$

where \mathbf{K} is the reciprocal lattice vector

$$\mathbf{K} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3,$$

which can be presented as a linear combination of the primitive translation vectors in the inverse k -space

$$\mathbf{b}_1 = 2\pi \frac{[\mathbf{a}_2 \times \mathbf{a}_3]}{(\mathbf{a}_1 \cdot [\mathbf{a}_2 \times \mathbf{a}_3])}, \quad \mathbf{b}_2 = 2\pi \frac{[\mathbf{a}_3 \times \mathbf{a}_1]}{(\mathbf{a}_1 \cdot [\mathbf{a}_2 \times \mathbf{a}_3])}, \quad \mathbf{b}_3 = 2\pi \frac{[\mathbf{a}_1 \times \mathbf{a}_2]}{(\mathbf{a}_1 \cdot [\mathbf{a}_2 \times \mathbf{a}_3])}.$$

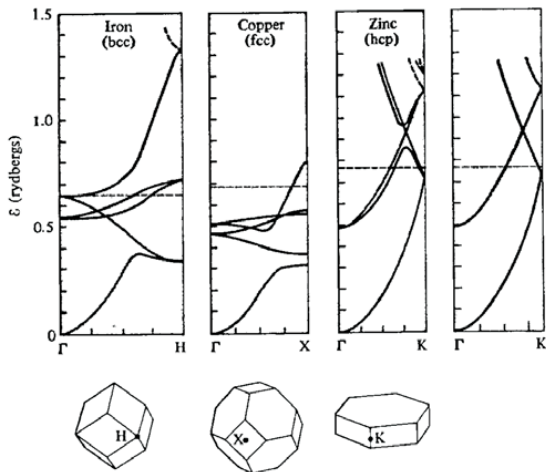
Set of all electronic levels $E_{n,\mathbf{k}}$ for given n is called n -th allowed energy band. Set of $E_{n,\mathbf{k}}$ for all n determines the resulting energy structure of crystal.

It should be stressed that all these relationships are strict mathematical consequences of translational symmetry and they are valid for any crystals of arbitrary dimension.

Presence of surfaces and internal defects immediately destroy N -dimensional periodicity of crystal, what leads to a drastic modification of both energy spectrum and wave functions.

Band spectrum of crystals: general consideration (3)

Figure was taken from Ashcroft and Mermin, Solid-state physics (1970).



In 1D crystals energy allowed energy bands never overlap – below we focus on this case.

In 2D and 3D crystals allowed energy bands may overlap.

Terminology

1. Tight-binding approximation

In the approach, the electronic wave functions are usually considered as a linear combination of localized atomic orbitals (LCAO).

Surface states described in the framework of a tight-binding model are often referred to as **Tamm** states (1932).

2. Approximation of nearly-free electrons

In the approach, the electronic wave functions are usually considered as plane delocalized electronic waves.

Surface states described in the framework of a nearly-free-electron model are often referred to as **Shockley** states (1939).

Thus, there is no strict physical distinction between Tamm and Shockley states, but the mathematical approaches used in describing them are completely different.

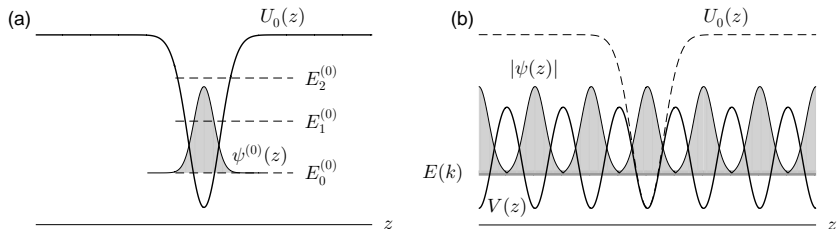
I prefer to use generalized terms 'surface electronic states' or 'Tamm-Shockley states'.

Part I

Band spectrum and wave functions in the tight-binding approximation

Band spectrum and wave functions (1)

Let $U_0(z)$ be non-perturbed potential energy of an electron around an isolated ion:



The eigenfunctions $\psi_n^{(0)}(z)$ and eigenenergies $E_n^{(0)}$, describing an electron in this single-well potential, should meet the stationary Schrödinger equation

$$\hat{H}_0 \psi_n^{(0)}(z) = E_n^{(0)} \psi_n^{(0)}(z),$$

where $\hat{H}_0 = -(\hbar^2/2m^*) d^2/dz^2 + U_0(z)$ is the Hamiltonian, n is integer index. A potential, corresponding to the sum of the isolated potential wells

$$V(z) = \sum_m U_0(z + ma),$$

should be the periodic function with the period a , where a is the lattice constant.

Band spectrum and wave functions (2)

Wave functions $\psi(z)$ of electron in the periodic potential $V(z)$ of arbitrary shape should be the solutions of the stationary Schrödinger equation

$$\hat{H} \psi(z) = E \psi(z),$$

where the Hamiltonian has the following form

$$\begin{aligned} \hat{H} &= - \left(\frac{\hbar^2}{2m^*} \right) \frac{d^2}{dz^2} + V(z) \pm U_0(z) = \left\{ - \left(\frac{\hbar^2}{2m^*} \right) \frac{d^2}{dz^2} + U_0(z) \right\} + V(z) - U_0(z) = \\ &= \hat{H}_0 + V(z) - U_0(z). \end{aligned}$$

We note that the perturbation $V(z) - U_0(z)$ is negative (see figure at page 10).

For simplicity we consider the formation of the s -band, corresponding to $n = 0$. If overlapping of the wave functions localized at neighbour sites are negligibly small, then we can find the solution in the form of the superposition of non-perturbed wave functions $\psi^{(0)}(z + ma)$, localized near m -th ion

$$\psi(z) = \sum_m b_m \psi^{(0)}(z + ma).$$

In order to find the coefficients b_m we apply the variational principle of quantum mechanics.

Variational principle of quantum mechanics

One can multiply both left-hand side and right-hand side of the Schrödinger equation $\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$ by $\psi^*(\mathbf{r})$ and get the relationship

$$\psi^*(\mathbf{r}) \hat{H}\psi(\mathbf{r}) = E\psi^*(\mathbf{r})\psi(\mathbf{r}).$$

After integration we come to the exact relationship

$$E = \frac{\int \psi^*(\mathbf{r}) \hat{H}\psi(\mathbf{r}) dV}{\int \psi^*(\mathbf{r})\psi(\mathbf{r}) dV}.$$

Replacing the exact solution $\psi(\mathbf{r})$ by a trial function $\psi_{app}(\mathbf{r})$, we can estimate the eigenenergy

$$E_{app} = \frac{\int \psi_{app}^*(\mathbf{r}) \hat{H}\psi_{app}(\mathbf{r}) dV}{\int \psi_{app}^*(\mathbf{r})\psi_{app}(\mathbf{r}) dV}.$$

Intermediate conclusion: the closer the approximate solution $\psi_{app}(\mathbf{r})$ to the true wave function $\psi(\mathbf{r})$, the lower the estimate of the energy E_{app} is

$$E = \min E_{app} = \min \frac{\int \psi_{app}^*(\mathbf{r}) \hat{H}\psi_{app}(\mathbf{r}) dV}{\int \psi_{app}^*(\mathbf{r})\psi_{app}(\mathbf{r}) dV}.$$

Alternative: seeking minimal zero value of an auxiliary functional

$$F \equiv \int \psi_{app}^*(\mathbf{r})(\hat{H} - E_{app})\psi_{app}(\mathbf{r}) dV \rightarrow \min.$$

System of equations for the coefficients b_m (1)

Let us compose an approximate trial solution (aka ansatz) in the form of the linear combination of the non-perturbed shifted wave functions $\psi^{(0)}(z)$

$$\psi_{app}(z) = \sum_m b_m \psi^{(0)}(z + ma) = \sum_m b_m \psi_m(z),$$

where

$$\psi_n(z) = \psi^{(0)}(z + na)$$

is the ground-state wave function localized at the n -th ion.

After substitution $\psi_{app}(z)$ into the auxiliary functional F , we get the following problem for searching its minimal value

$$\begin{aligned} F &= \int_{-\infty}^{\infty} \psi_{app}^*(z) (\hat{H} - E_{app}) \psi_{app}(z) dz = \\ &= \sum_{m'} \sum_m b_{m'}^* b_m \int_{-\infty}^{\infty} \psi_{m'}^*(z) \left((\hat{H}_0 - E_{app}) + (V(z) - U_0(z)) \right) \psi_m(z) dz. \end{aligned}$$

System of equations for the coefficients b_m (2)

Taking into account that $\hat{H} = \hat{H}_0 + V(z) - U_0(z)$ and $\hat{H}_0 \psi_n^{(0)}(z) = E_n^{(0)} \psi_n^{(0)}(z)$, we get

$$\begin{aligned} F &= \sum_{m'} \sum_m b_{m'}^* b_m \int \psi_{m'}^*(z) \left((\hat{H}^{(0)} - E) + (V(z) - U_0(z)) \right) \psi_m(z) dz = \\ &= \sum_{m'} \sum_m b_{m'}^* b_m \int \psi_{m'}^*(z) \left((E^{(0)} - E) + (V(z) - U_0(z)) \right) \psi_m(z) dz = \\ &= \sum_{m'} \sum_m b_{m'}^* b_m \left[(E^{(0)} - E) S_{m',m} - P_{m',m} \right], \end{aligned}$$

where

$$S_{m',m} = \int \psi_{m'}^*(z) \psi_m(z) dz > 0 \quad \text{and} \quad P_{m',m} = \int \psi_{m'}^*(z) (V(z) - U_0(z)) \psi_m(z) dz < 0$$

are the overlap integrals for the wave functions, localized at the atoms with different indexes.

From the conditions $dF/db_{m'}^* = 0$ corresponding to the extrema of the functional with respect to all b_m independently, one can get an infinite system of linear algebraic equation for determination of the expansion coefficients b_m

$$\sum_m b_m \left[(E^{(0)} - E) S_{m',m} + P_{m',m} \right] = 0 \quad (*).$$

Energy spectrum for 1D periodic crystal (1)

Provided that the wave functions of electrons, localized at neighbour atoms, are practically not overlapped and the probability of hopping of electron from one atom to next atom is extremely small, one can consider the following simple expressions

$$S_{m',m} = \int \psi_{m'}^*(z) \psi_m(z) dz \quad \Longrightarrow \quad S_{m',m} = \delta_{m',m},$$

$$P_{m',m} = \int \psi_{m'}^*(z) (V(z) - U_0(z)) \psi_m(z) dz \quad \Longrightarrow \quad P_{m',m} = \alpha \delta_{m',m}, \quad \alpha < 0,$$

where $\delta_{m',m}$ is the Kronecker delta function. The system of equations (*) takes the form

$$\sum_m b_m \left[(E^{(0)} - E) \delta_{m',m} + \alpha \delta_{m',m} \right] = 0 \quad \Longrightarrow \quad b_m \left[(E^{(0)} - E) + \alpha \right] = 0$$

for all m .

It gives us the energy spectrum of electron in a periodic array of non-interacting potential wells

$$E = E^{(0)} + \alpha.$$

In the other words, the parameter $\alpha < 0$ describes the shift of energy of electron in the periodic potential as compared with the non-perturbed energy of electron in a single potential well.

Energy spectrum for 1D periodic crystal (2)

In order to take into account non-zero probability of hopping of electron from one atom to next, we have to consider the following expressions

$$S_{m',m} = \int \psi_{m'}^*(z) \psi_m(z) dz \implies S_{m',m} = \delta_{m',m},$$

$$P_{m',m} = \int \psi_{m'}^*(z) (V(z) - U_0(z)) \psi_m(z) dz \implies$$

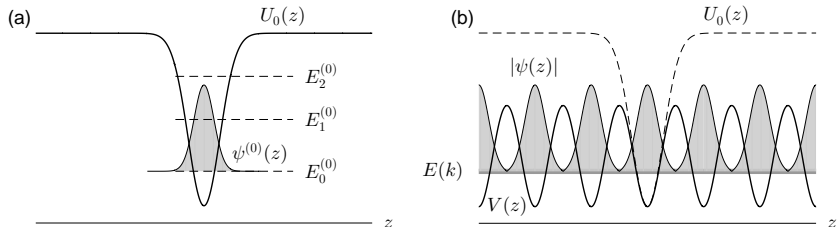
$$P_{m',m} = \alpha \delta_{m',m} + \beta (\delta_{m',m-1} + \delta_{m',m+1}), \quad \alpha < 0, \quad \beta < 0$$

where the parameter $\alpha < 0$ accounts the lowering of the mean potential energy and the parameter $\beta < 0$ describes the amplitude of probability for tunneling $m \rightarrow m - 1$ and $m \rightarrow m + 1$.

After substituting $S_{m',m}$ and $P_{m',m}$ into the system of equations (*), one can get a three-diagonal matrix equation

$$b_m (E^{(0)} - E) + b_m \alpha + \beta (b_{m-1} + b_{m+1}) = 0.$$

Energy spectrum for 1D periodic crystal (3)



The system of equations for electron in one-dimensional periodic potential is the following

$$b_m (E^{(0)} - E + \alpha) + \beta (b_{m-1} + b_{m+1}) = 0.$$

We look for the solution in the form of a plane electronic wave of constant amplitude $b_m = B e^{ikam}$, where B is a constant independent on m ; k is a real-valued wave vector.

After substituting of b_m into the master equation, we get

$$e^{ikam} (E^{(0)} - E + \alpha) + \beta (e^{ika(m-1)} + e^{ika(m+1)}) = 0.$$

After rearranging one can get a band spectrum in the following form

$$E(k) = E^{(0)} + \alpha + 2\beta \cos ka = E^{(0)} - |\alpha| - 2|\beta| \cos ka.$$

Energy spectrum for 1D periodic crystal (4)

It is easy to see that the ground-state discrete energy level for electron in a single potential well generates an allowed s -band of the finite width $4|\beta|$ for electron in periodic potential:

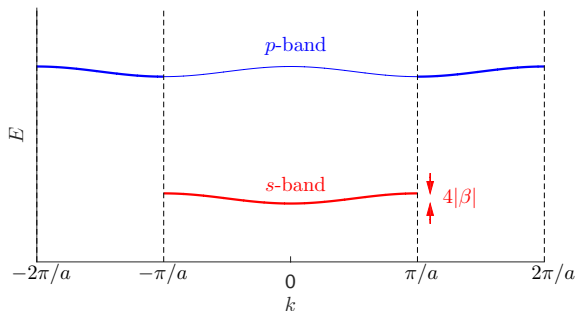
$$E(k) = E^{(0)} - |\alpha| - 2|\beta| \cos ka.$$

Extremal values:

$$E_{min} = E^{(0)} - |\alpha| - 2|\beta| \quad \text{at} \quad k = 0$$

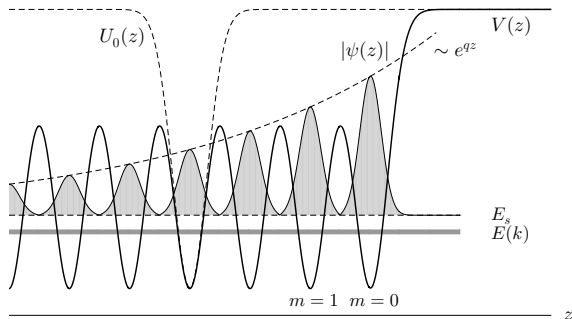
$$E_{max} = E^{(0)} - |\alpha| + 2|\beta| \quad \text{at} \quad k = \pm \frac{\pi}{a}$$

Reminder: $\pm\pi/a$ are the boundaries of the first Brillouin zone for 1D lattice.



Band spectrum for 1D semi-infinite crystal (1)

It should be repeated that any boundaries and defects break periodicity and leads to non-applicability of the Bloch theorem. Let the index $m = 0$ corresponds to the potential well at the edge. It is reasonable to introduce a modified parameter α_0 for the last potential well, what meets the criterion $\alpha < \alpha_0 < 0$.



New system of equations accounting the difference in α

$$b_0 (E^{(0)} - E + \alpha_0) + \beta (0 + b_1) = 0 \quad \text{for } m = 0$$

$$b_m (E^{(0)} - E + \alpha) + \beta (b_{m-1} + b_{m+1}) = 0 \quad \text{for } m \neq 0.$$

Band spectrum for 1D semi-infinite crystal (2)

As before, we look for the solution in the form $b_m = C e^{ikam}$, then the eigenenergy E_s should meet the equations

$$(E^{(0)} - E_s + \alpha_0) + \beta e^{ika} = 0 \quad \text{and} \quad (E_0^{(0)} - E_s + \alpha) + \beta (e^{ika} + e^{-ika}) = 0.$$

We subtract the first equation from the second equation and find, that the allowed values of k vector should satisfy the relationship

$$e^{ika} = \frac{\beta}{\alpha_0 - \alpha} < 0.$$

Apparently, this equation has no real-valued solution.

A complex-valued solution has the form $k = k_0 - iq$, where

$$e^{ik_0 a} = -1 \quad \text{or} \quad k_0 = \pm \frac{\pi}{a}$$

and

$$e^{qa} = \frac{|\beta|}{\alpha_0 - \alpha} > 0.$$

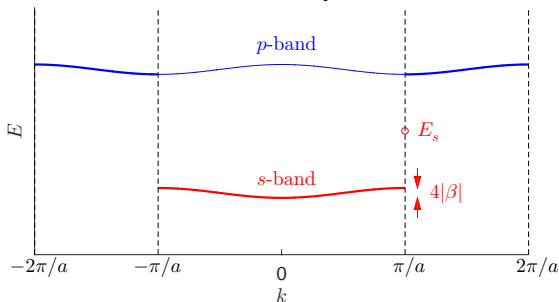
Band spectrum for 1D semi-infinite crystal (3)

After substituting $e^{ika} = \beta/(\alpha_0 - \alpha)$ into the equation $(E^{(0)} - E_s + \alpha_0) + \beta e^{ika} = 0$, one can find the energy of the surface state

$$E_s = E^{(0)} + \alpha_0 + \frac{\beta^2}{\alpha_0 - \alpha}.$$

It is easy to see that this energy is larger than the top of the allowed s -band

$$\begin{aligned} E_s - E_{max} &= E^{(0)} + \alpha_0 + \frac{|\beta|^2}{(\alpha_0 - \alpha)} - (E_0 + \alpha + 2|\beta|) = \\ &= \frac{1}{(\alpha_0 - \alpha)} (|\beta| - (\alpha_0 - \alpha))^2 > 0 \quad \text{q.e.d.} \end{aligned}$$

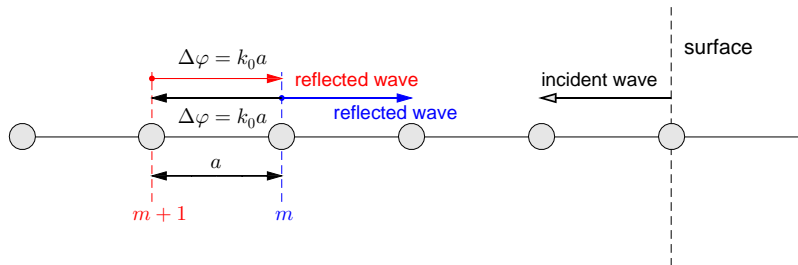


Surface states and Wulff–Bragg–von Laue resonance

The condition $k_0 = \pi/a$ corresponds to the Bragg resonance on the periodic structure.

The criterion of the coherent back-scattering of electronic waves by neighbor atoms with indexes m and $m + 1$

$$\Delta\varphi_{total} = 2 \cdot k_0 a = 2\pi n \quad \text{or} \quad k_0 = \frac{\pi n}{a}.$$



Important conclusion: if the real part of the wave vector k_0 of the incident electronic wave meets the Bragg condition of resonant back-scattering ($k_0 = \pi n/a$), such wave cannot pass through the periodic structure.

As a result, crystal acts like ideal mirror fully reflecting the incident wave with $k_0 = \pi n/a$.

Part II

Band spectrum and surface states in the nearly-free-electron approximation

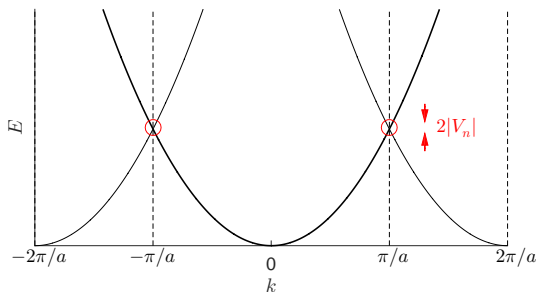
Energy spectrum of free electron in 1D

Electron in free space

$$E_k = \frac{\hbar^2 k^2}{2m^*}$$

Electron in a periodic potential of infinitely small amplitude

$$E_k = \frac{\hbar^2 (k + K)^2}{2m^*} \quad \text{for arbitrary } K = \frac{2\pi n}{a}.$$



It is well known that splitting of energy levels near the boundaries of the n -th Brillouin zone at $k = nK/2 = \pi n/a$ (points of degeneracy) is controlled by the amplitude of the n -th Fourier component of periodic potential.

Energy spectrum of electron in semi-infinite 1D potential (1)

Let us consider one-dimensional crystal terminated at $z = 0$

$$V(z) = \begin{cases} 0 & \text{at } z > 0, \\ V(z+a) & \text{at } z < 0, \end{cases}$$

where a is the period. We assume that potential energy of electron can be written in the following form

$$V(z) = V_0 + 2V_n \cos\left(\frac{2\pi n}{a} z\right) = V_0 + V_n e^{i2\pi n z/a} + V_n e^{-i2\pi n z/a},$$

where V_0 is the mean value, $2V_n$ is the amplitude of the n -th Fourier component of the potential, $k_{Br} = K/2 = \pi n/a$ is the boundary of the n -th Brillouin zone, $K = 2\pi n/a$ is the reciprocal lattice vector.

We seek solutions of the Schrödinger equation

$$-\frac{\hbar^2}{2m^*} \frac{d^2}{dz^2} \psi(z) + V(z) \psi(z) = E \psi(z),$$

inside the crystal in the form of combination of two non-uniform electronic waves

$$\psi(z) = A e^{ik_0 z + qz} + B e^{ik_0 z - i2\pi n z/a + qz},$$

where $q > 0$ is the decrement. Such the presentation looks reasonable provided that the the vector k_0 is close to the boundary of the Brillouin zone: $k_0 \simeq K/2 = \pi n/a$.

Energy spectrum of electron in semi-infinite 1D potential (2)

After substituting of the ansatz into the Schrödinger equation and rearranging, we get

$$\begin{aligned} & -\frac{\hbar^2}{2m^*} (ik_0 + q)^2 A e^{(ik_0+q)z} - \frac{\hbar^2}{2m^*} \left(ik_0 - \frac{i2\pi n}{a} + q \right)^2 B e^{(ik_0 - i2\pi n/a + q)z} + \\ & + \left(V_0 + V_n e^{i2\pi n z/a} + V_n e^{-i2\pi n z/a} \right) \left(A e^{(ik_0+q)z} + B e^{(ik_0 - i2\pi n/a + q)z} \right) = \\ & = E \left(A e^{(ik_0+q)z} + B e^{(ik_0 - i2\pi n/a + q)z} \right) \quad (*). \end{aligned}$$

Since travelling electronic waves e^{ikz} and $e^{ik'z}$ with different wave vectors are linearly-independent solutions, the equality (*) should be fulfilled for the components proportional e^{ikz} and $e^{ik'z}$ independently. It gives us the system of equations for the determination of parameters A и B (so-called secular equations)

$$\begin{aligned} A \left(V_0 - \frac{\hbar^2}{2m^*} (ik_0 + q)^2 - E \right) + B V_n &= 0, \\ A V_n + B \left(V_0 - \frac{\hbar^2}{2m^*} \left(ik_0 - i \frac{2\pi n}{a} + q \right)^2 - E \right) &= 0. \end{aligned}$$

Nonzero solutions of uniform linear system of equation with zero right-hand parts exist if a determinant of the corresponding matrix \hat{M} is equal to zero

$$\det \hat{M} = \left(V_0 - \frac{\hbar^2}{2m^*} (ik_0 + q)^2 - E \right) \left(V_0 - \frac{\hbar^2}{2m^*} \left(ik_0 - i \frac{2\pi n}{a} + q \right)^2 - E \right) - V_n^2 = 0.$$

Energy spectrum of electron in semi-infinite 1D potential (3)

After solving this quadratic equation with respect to E , we get the energy spectrum

$$E = V_0 + \frac{1}{2} \frac{\hbar^2}{2m^*} \left\{ k_0^2 + \left(k_0 - \frac{2\pi n}{a} \right)^2 - 2q^2 - 2iq \left(2k_0 - \frac{2\pi n}{a} \right) \right\} \pm \frac{1}{2} \sqrt{\left(\frac{\hbar^2}{2m^*} \right)^2 \left\{ k_0^2 - \left(k_0 - \frac{2\pi n}{a} \right)^2 - 2iq \frac{2\pi n}{a} \right\}^2 + 4V_n^2}.$$

Generally speaking, the dependence of E on k_0 and q is a **complex-valued** function.

It means that non-uniform electronic plane waves with arbitrary parameters k_0 и q cannot be stationary solution of the Schrödinger equation.

Indeed, the state with $Im E \neq 0$ is a decaying state

$$\Psi(x, t) = A \exp(ikx - i\omega t) \quad \text{and} \quad \omega = \frac{E}{\hbar} \quad \text{and} \quad E = Re E - i Im E \quad \implies$$
$$\Psi(x, t) = A \exp\left(ikx - i \frac{Re E \cdot t}{\hbar}\right) \cdot \exp\left(-\frac{Im E \cdot t}{\hbar}\right).$$

There are two peculiar cases corresponding to $Im E = 0$ and possible stationary solutions.

Energy spectrum of electron in 1D periodic potential

The general expression is

$$E = V_0 + \frac{1}{2} \frac{\hbar^2}{2m^*} \left\{ k_0^2 + \left(k_0 - \frac{2\pi n}{a} \right)^2 - 2q^2 - 2i q \left(2k_0 - \frac{2\pi n}{a} \right) \right\} \pm \frac{1}{2} \sqrt{\left(\frac{\hbar^2}{2m^*} \right)^2 \left\{ k_0^2 - \left(k_0 - \frac{2\pi n}{a} \right)^2 - 2i q \frac{2\pi n}{a} \right\}^2 + 4V_n^2}.$$

The eigen-energy E becomes real-valued function at $q = 0$ and arbitrary k_0 :

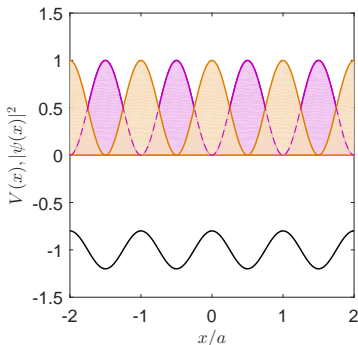
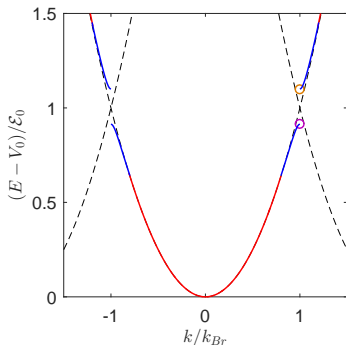
$$E(k_0) = V_0 + \frac{\hbar^2}{4m^*} \left\{ k_0^2 + \left(k_0 - \frac{2\pi n}{a} \right)^2 \right\} \pm \frac{1}{2} \sqrt{\left(\frac{\hbar^2}{2m^*} \right)^2 \left\{ k_0^2 - \left(k_0 - \frac{2\pi n}{a} \right)^2 \right\}^2 + 4V_n^2}$$

It means that plane electronic waves of constant amplitude are the stationary solutions of the Schrödinger equation within the first Brillouin zone of bulk crystal.

Standing electronic waves in 1D periodic potential

Constructive interference of two travelling plane waves of equal amplitudes results in a formation of standing wave with zero group velocity

$$\psi(z) = A e^{i\pi z/a} + B e^{i\pi z/a - i2\pi z/a} = |A| \left(e^{i\delta} e^{i\pi z/a} + e^{-i\delta} e^{-i\pi z/a} \right) = \frac{|A|}{2} \cos\left(\frac{\pi z}{a} + \delta\right)$$



The boundaries of the n -th forbidden energy band at $k_0 = \pi n/a$

$$V_0 + \hbar^2 k_0^2 / 2m^* - |V_n| < E < V_0 + \hbar^2 k_0^2 / 2m^* + |V_n|$$

The width of n -th forbidden energy band is equal to $2|V_n|$.

Energy spectrum of electron in semi-infinite 1D periodic potential (1)

The general expression is

$$E = V_0 + \frac{1}{2} \frac{\hbar^2}{2m^*} \left\{ k_0^2 + \left(k_0 - \frac{2\pi n}{a} \right)^2 - 2q^2 - 2iq \left(2k_0 - \frac{2\pi n}{a} \right) \right\} \pm \frac{1}{2} \sqrt{\left(\frac{\hbar^2}{2m^*} \right)^2 \left\{ k_0^2 - \left(k_0 - \frac{2\pi n}{a} \right)^2 - 2iq \frac{2\pi n}{a} \right\}^2 + 4V_n^2}.$$

The eigenenergy E becomes real-valued function at $k_0 = \pi n/a$ and arbitrary q . It gives us the energy of the electronic state localized near the edge

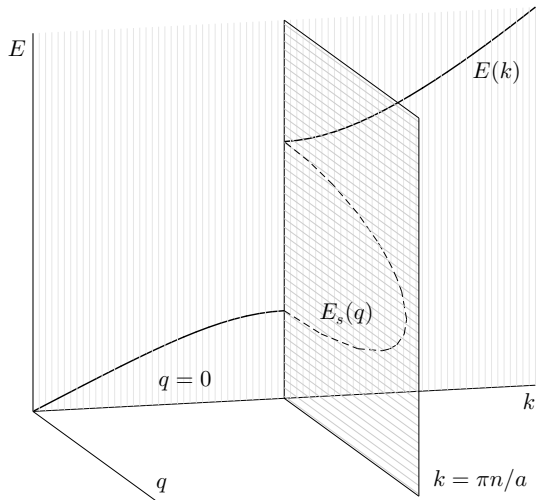
$$E_s(q) = V_0 + \frac{\hbar^2}{2m^*} (k_0^2 - q^2) \pm \sqrt{|V_n|^2 - q^2 \left(\frac{\hbar^2}{2m^*} \right)^2 \left(\frac{2\pi n}{a} \right)^2}.$$

Comparing E_s with the boundaries of the forbidden band

$$V_0 + \hbar^2 k_0^2 / 2m^* - |V_n| < E < V_0 + \hbar^2 k_0^2 / 2m^* + |V_n|,$$

we conclude that the surface state belongs to the forbidden band.

Energy spectrum of electron in semi-infinite 1D periodic potential (2)



Analytical solution of the full problem (1)

In order to determine the energy of the surface electronic state and other relevant parameters, one should match the non-uniform electronic wave function inside the crystal

$$\psi_{in}(z) = A e^{i\pi n z/a + qz} + B e^{-i\pi n z/a + qz} \quad \text{at } z < 0$$

with the exponentially-decaying wave function outside the crystal

$$\psi_{out}(z) = C e^{-pz} \quad \text{at } z > 0$$

together with their first derivatives $d\psi/dz$ at $z = 0$

Here $q > 0$ and $p > 0$ are the coefficients, which characterizes the rate of decaying of the wave functions inside and outside the crystal, correspondingly.

Solution: surface state exists only at $V_0 < 0$ and $V_n < 0$ provided $V = 0$ at vacuum side.

see Goodwin, Proc. Camb. Phil. Soc. (1939)

$$A = e^{i\delta} \quad \text{and} \quad B = e^{-i\delta}, \quad \text{where} \quad \cos^2 \delta = \frac{\hbar^2}{2m^*} \cdot \left(\frac{\pi n}{a}\right)^2 \cdot \frac{1}{(-V_0 - V_n)}$$

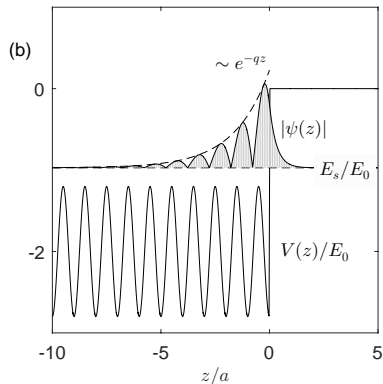
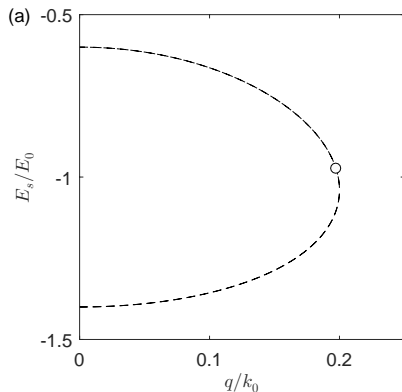
$$q = -\frac{1}{2} \cdot \frac{\pi n}{a} \cdot \frac{V_n}{\mathcal{E}_0} \sin 2\delta \quad \text{and} \quad p + q = \frac{\pi n}{a} \tan \delta$$

$$E_s = -\frac{\hbar^2 p^2}{2m^*} = V_0 + \frac{(-V_0)^2}{(-V_0 - V_n)^2} \frac{\hbar^2}{2m^*} \left(\frac{\pi n}{a}\right)^2 + \frac{(-V_0)(-V_n)}{(-V_0 - V_n)}$$

Analytical solution of the full problem (2)

$$\psi_{in}(z) = A e^{i\pi n z/a + qz} + B e^{-i\pi n z/a + qz} \quad \text{at } z < 0$$

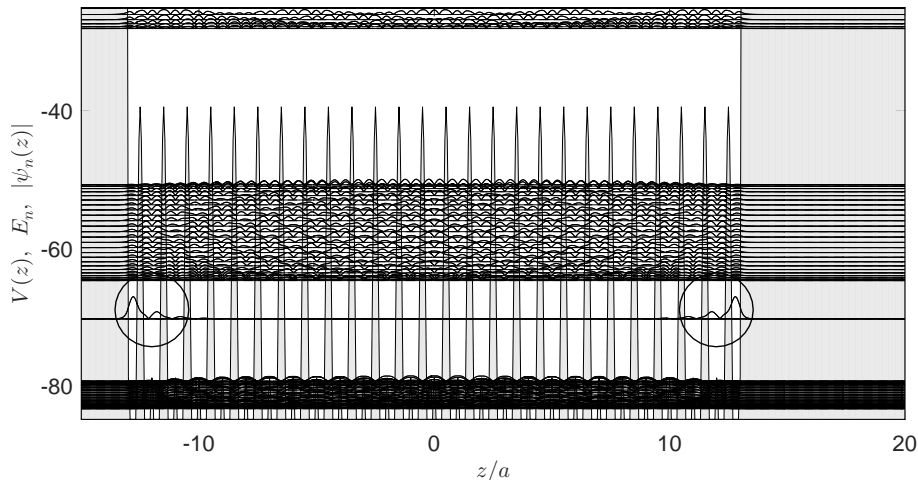
$$\psi_{out}(z) = C e^{-pz} \quad \text{at } z > 0$$



Surface electronic states: numerical simulation

Considered model profile of potential energy ($V_1 < 0$ and $V_2 > 0$)

$$V(z) = V_0 + 2V_1 \cos\left(\frac{2\pi z}{a}\right) + 2V_2 \cos\left(\frac{4\pi z}{a}\right)$$



Generalization for three-dimensional case

Localized one-dimensional solutions $\psi_n(z)$, considered above, can be generalized for three-dimensional crystals. For nearly-free electron gas the wave function can be written in the following form

$$\psi(\mathbf{r}) = A \cdot e^{ik_x x + ik_y y} \cdot \psi_n(z)$$

and it corresponds to nearly-free 2D electrons. Here x and y are the lateral coordinates, k_x and k_y are the components of the wave vector along the surface.

The energy of nearly-free 2D electrons is

$$E_{n, k_{\parallel}} = \frac{\hbar^2 k_x^2}{2m^*} + \frac{\hbar^2 k_y^2}{2m^*} + E_n,$$

provided that $|k_x| \ll k_{SB}$ и $|k_y| \ll k_{SB}$, where k_{SB} is the boundary value for the surface Brillouin zone.

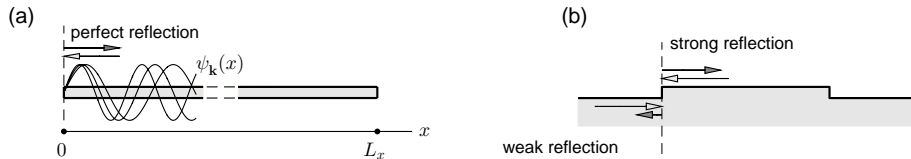
Thus, each surface state generates a subband of surface states in 3D bulk crystals. The density of surface states is about 10^{15} cm^{-2} , i. e. it is of the order of the number of atoms at surface per 1 cm^2 .

Part III

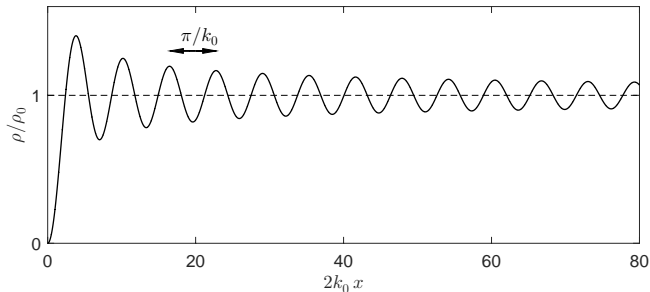
Quasiparticle interference and quantum corrals

Quasiparticle interference (QPI) near defects at surface

Elastic scattering of surface waves at defects leads to peculiar interference patterns

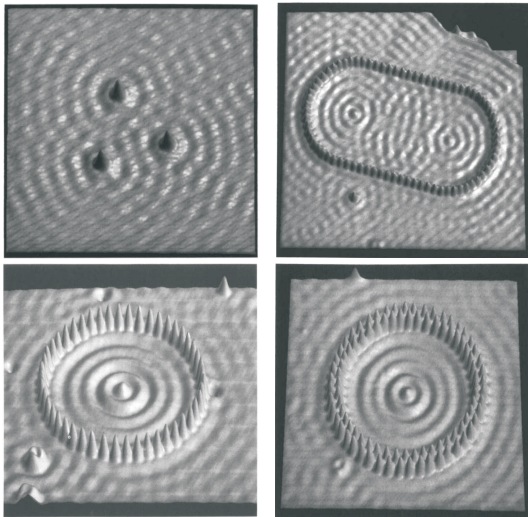


Nonuniform local density of states (see a detailed explanation at the next lecture)



Quasiparticle interference and quantum corrals

Adatoms Fe on atomically flat Cu(111) surface



Crommie, Lutz, Eigler, Heller, Surf. Rev. Lett., vol. 2, 127-137 (1995)

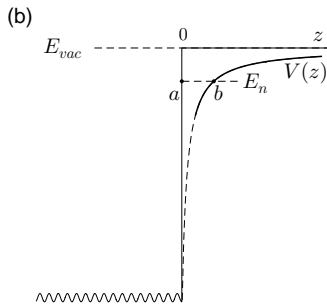
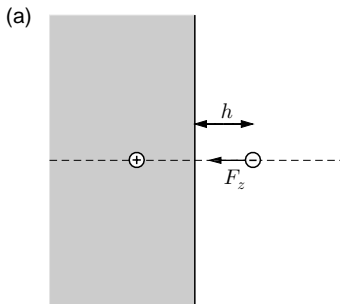
Part IV

Image-potential states. Stark-shifted image-potential states

Image potential in electrostatics

It is known that a probe charge located outside a conductive sample generate a charge at the surface of the opposite sign. The interaction of the probe charge with the charged flat surface of bulk sample can be viewed as the electrostatic interaction of the probe charge and the mirror (image) charge. A Coulomb force acting between point charges e and $-e$ at a distance $2h$ as well as corresponding potential are equal

$$F_z(h) = -\frac{1}{\epsilon} \frac{e^2}{(2h)^2} \quad \text{and} \quad U(z) = E_{vac} - \int_z^{+\infty} F_z(h') dh' = E_{vac} - \frac{1}{\epsilon} \frac{e^2}{4z}.$$



Surface electronic states in the image potential (1)

Electrons can be potentially localized in the effective potential well formed by the Coulomb image potential from one side and the surface of the crystal from the other side.

If the energy of the image-potential states is in the forbidden band of bulk crystal, such states can be quasi-stationary and slowly decaying, affecting optical and transport properties of nanostructured samples.

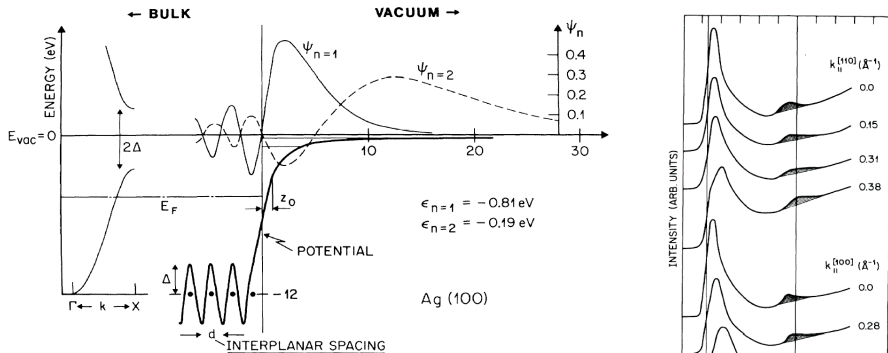


FIG. 2. Energy and spatial scales characterizing image states on metal surfaces. Shown are the fundamental ($n=1$) image state, with no nodes in the vacuum region, and the first excited ($n=2$) image state, with one node. Also shown are the effective one-electron potential and the bulk energy-band structure that produce these image states. The quantity z_0 (taken to be $\sim 1 \text{ \AA}$) specifies the distance from the surface beyond which the potential is purely Coulombic (imagelike). The parameters Δ , width of the gap, its position, and the Fermi energy E_F have been taken from self-consistent band-structure calculations (Ref. 12). The image plane corresponds to $z=0$.

Surface electronic states in the image potential (2)

Let us assume that (i) $E_{vac} = 0$ and (ii) the energy of the localized states belongs to the forbidden band of bulk crystal. The effective potential for non-transparent wall at $z = 0$ can be written in the form

$$U(z) = \begin{cases} \infty & \text{at } z < 0, \\ -e^2/4z & \text{at } z > 0, \end{cases}$$

where z is the distance measured from the surface, $a = 0$ and $b = e^2/4|E_n|$ are classical turning points for a particle with energy $E_n = -|E_n|$.

Within quasi-classical Wentzel-Kramers-Brillouin (WKB) approximation, one can estimate the change of the phase of the electronic wave function for the round trip ($a \rightarrow b \rightarrow a$)

$$\frac{1}{\hbar} \int_a^b p(z) dz + \varphi_b + \frac{1}{\hbar} \int_b^a (-p(z)) dz + \varphi_a = 2\pi n,$$

where φ_a and φ_b are the phase shifts for reflected waves at points a and b , correspondingly; $n = 0, 1 \dots$ is the number of quantum-well state.

After rearranging, we come to the Bohr-Sommerfeld quantization rule

$$\frac{1}{2\pi\hbar} \oint p(z) dz = n + \gamma, \quad \text{where } \gamma = -\frac{\varphi_a}{2\pi} - \frac{\varphi_b}{2\pi} \simeq \frac{3}{4}.$$

Surface electronic states in the image potential (3)

After substituting $p(z) = \sqrt{2m_0(E - U(z))}$ into the Bohr-Sommerfeld quantization rule, we get

$$\frac{1}{2\pi\hbar} \oint p(z) dz = \frac{1}{\pi\hbar} \int_0^b \sqrt{2m_0(E_n - U(z))} dz = \frac{e^2}{\pi\hbar} \sqrt{\frac{2m_0}{|E_n|}} \frac{\pi}{8} = n + \gamma.$$

As a result, the spectrum of the localized electronic states in the image-potential with non-penetrable well is given by a simple relationship

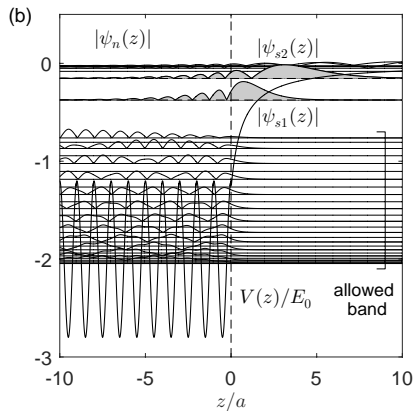
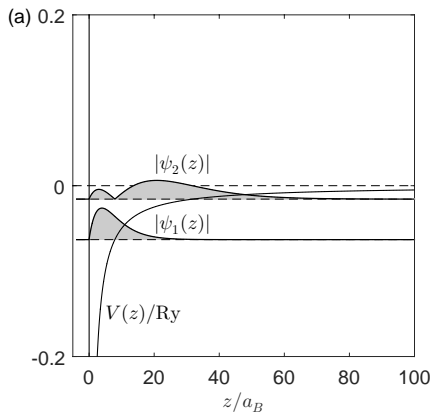
$$E_n = -\frac{m_0 e^4}{32\hbar^2} \cdot \frac{1}{(n + \gamma)^2} = -\frac{1}{16} \frac{\text{Ry}}{(n + \gamma)^2},$$

где Ry (rydberg) $\equiv me^4/(2\hbar^2) = 13.6$ eV is the ionization energy for hydrogen atom in the ground state.

The factor 1/16 reflects the fact that the distance is measured from the surface, which is twice as small as the distance between the centers of the probe and image charges.

Flat surface of bulk conducting crystal can be considered as two-dimensional analog of hydrogen atom.

Surface electronic states in the image potential: numerical simulation



Stark-shifted image-potential states (1)

The shift of the quantum-well states in an uniform electrical field (i. e. in a linearly increasing potential) is analogue of the Stark effect for hydrogen-like atom in electric field.

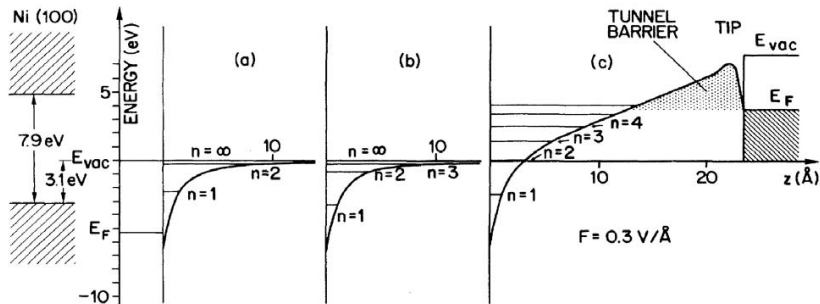


FIG. 1. Energy diagram for the electrostatic potential (including image) at a metal surface. On the left, the projected bulk band structure of the Ni(100) surface is shown shaded. Note the 7.1-eV band gap straddling the vacuum level $E_{vac}=0$. (a) For simplicity, only the $n=1$ and $n=2$ hydrogenic (quantum defect) energy levels are shown. (b) The surface corrugation affects the electronic x,y movement pulling the levels down, as seen by inverse photoemission. (c) Expansion and shift of the image-state spectrum by an applied field, F . The heavy solid line is the crystal potential plus the field potential.

Binnig, Frank, Fuchs, Garcia, Reihl, Rohrer, Salvan,... Phys. Rev. Lett., vol. 55, 991-994 (1985)

Stark-shifted image-potential states (2)

We can neglect the contribution of the image potential and assume that the potential energy near the flat metallic surface has the following linear shape

$$V(z) = \begin{cases} \infty & \text{при } z < 0, \\ U^* + F^* \cdot z & \text{при } z \geq 0; \end{cases}$$

with the non-penetrable wall at $z = 0$. Here U is the bias voltage, $U^* = E_F + W_s - |e|U$ is the energy of the bottom of the triangular potential well, and F^* is the effective electrical field near the surface.

The Bohr-Sommerfeld quantization rule is

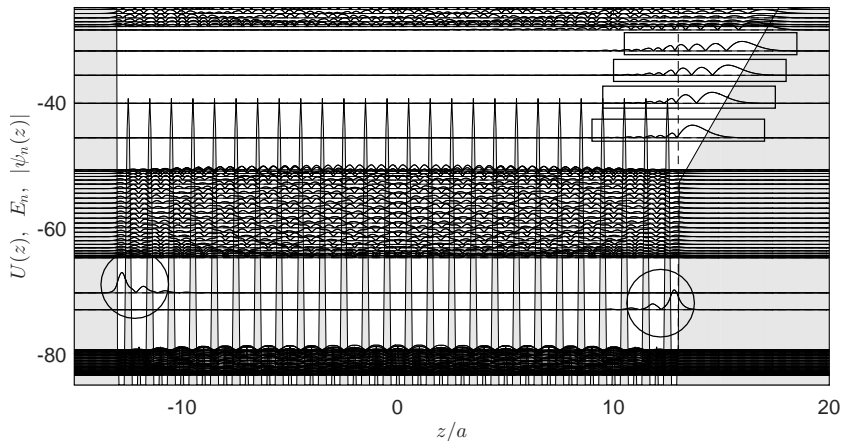
$$\frac{1}{\pi\hbar} \int_a^b p(z) dz = n - 1 + \gamma, \quad n = 1, 2, \dots$$

where $a = 0$ and $b = (E - U^*)/F^*$ are classical turning points, m_0 is mass of electron in vacuum, n is integer index, $\gamma \simeq 3/4$.

After substituting $p(z) = \sqrt{2m_0(E_n - V(z))}$ and integration, we arrive at the spectrum of the quantum-well states in the triangular potential well

$$E_n = E_F + W_s - |e|U + \left\{ \frac{3}{2} \frac{\pi\hbar}{\sqrt{2m_0}} F_n^* \cdot \left(n - \frac{1}{4} \right) \right\}^{2/3}.$$

Stark-shifted image-potential states in a linearly increasing potential: numerical simulation



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