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BASIC STRUCTURAL AND ELECTRONIC PROPERTIES OF SEMICONDUCTOR SURFACES
(Lectures I & II)

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These are preliminary lecture notes, intended only for distribution to participants.

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BASIC STRUCTURAL AND ELECTRONIC PROPERTIES OF SEMICONDUCTOR SURFACES.

a

1.1 - One dimensional chain of atoms.

A simple model like one-dimensional (1D) linear chain, with a termination, can provide an introductory point of view on the formation of electronic surface states. Let us consider the infinite chain of *Fig. 1a*. The simplest way to describe an electron in this 1D crystal is to consider a periodic potential of cosine-type

$$V(z) = V_0 + V_g(e^{igz} + e^{-igz}) \tag{1.1}$$

where only a component of the periodic potential is retained. Here $g = 2\pi/a$, a being the lattice parameter of the linear chain. Near the boundary of the Brillouin Zone (BZ), *i.e.* for $k \simeq g/2$, the Bloch-type eigenfunctions ca be approximated by the sum of two terms:

$$\psi(z) = c_1 e^{ikz} + c_2 e^{i(g-k)z} \tag{1.2}$$

The energy eigenvalues can be obtained by the secular system of equations

$$\begin{pmatrix} k^2 - E & V_g \\ V_g & (k-g)^2 - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{1.3}$$

where Rydbergs have been used as energy units. Two bands $E = E_k^{\pm}$, separated by a gap, are obtained

$$E_k^{\pm} = \frac{1}{2}\{k^2 + (k-g)^2 \pm \sqrt{[k^2 - (k-g)^2]^2 - 4|V_g|^2}\} \tag{1.4}$$

$$\psi_k^{\pm}(z) = e^{ikz} \pm \frac{E_k^{\pm} - k^2}{V_g} e^{i(k-g)z} \tag{1.5}$$

The minimum gap is obtained at the border of the 1D BZ (see *Fig. 1b*), where

$$E_{g/2}^{\pm} = \frac{g^2}{4} \pm |V_g| \tag{1.6}$$

$$\psi_{g/2}^{\pm}(z) = e^{igz/2} \pm \frac{|V_g|}{V_g} e^{-igz/2} \tag{1.5}$$

so that for $V_g < 0$ one has
$\psi_{g/2}^{+}(z) = 2i\, sin(gz/2)$ and $\psi_{g/2}^{-}(z) = 2\, cos(gz/2)$
and for $V_g > 0$ one gets
$\psi_{g/2}^{+}(z) = 2\, cos(gz/2)$ and $\psi_{g/2}^{-}(z) = 2i\, sin(gz/2)$.
The charge distribution of the lower-energy state has a maximum in the midway between the two atoms if $V_g < 0$, as the potential is attractive in the region of the bond. If $V_g > 0$ the lower energy state is mainly localized at the atomic sites.

The approximate wavefunctions considered here are Bloch states wich verify the conditions

$$\psi_k(z+a) = e^{ika}\psi_k(z) \tag{1.8}$$

$$|\psi_k(z+a)|^2 = |\psi_k(z)|^2. \tag{1.9}$$

They can be written as

$$\psi_k(z) = e^{ikz}u_k(z) \tag{1.10}$$

with $u_k(z+a) = u(z)$.

1.2 - Evanescent wavefunctions, truncated chain and surface states

Before considering the case of a terminated lattice, we can extend the class of functions (1.5) to complex values of k but with real values of energy in eq. (1.4). The condition (1.9) is not satisfied. If we write $k = g/2 - i\chi$ with $\chi > 0$, we find

$$E^{\pm}_{g/2-i\chi} = \frac{g^2}{4} - \chi^2 \pm \sqrt{|V_g|^2 - g^2\chi^2} \tag{2.1}$$

The values of the energy are real, if $\chi < |V_g|/g$, and they are found in the region of the forbidden gap. (See *Fig. 1c*). The corresponding wavefunctions are still eigenstates of the chain hamiltonian and of the lattice translation operator. They are Bloch states, satisfying eq. (1.8), but, with complex k, they are of evanescent type. The phase factor in eq. (1.10) becomes $e^{igz/2}e^{\chi z}$, vanishing when $z \to -\infty$ and diverging when $z \to \infty$. The wavefunctions with energy *in the gap* can be written as

$$\psi_{g/2-i\chi}(z) = e^{\chi z}(e^{igz/2} + e^{2i\delta}e^{-igz/2})$$
$$= e^{\chi z}e^{i\delta}cos(gz/2 - \delta) \tag{2.2}$$

where δ is a phase, depending on the energy, which moves from 0 to $\pi/2$ when the energy goes from the lower to the upper edge of the gap, when it is $V_g < 0$. If $V_g > 0$, δ goes from $-\pi/2$ to 0, when ones passes from the lower to the upper edge of the gap. The two types of evanescent states are drawn in *Fig. 1d*.

Then we assume that the chain is terminated at the midpoint of two neighbouring atoms at $z = 0$, so that the crystal is located in $z < 0$; the potential in the external region $z > 0$ is approximated by a constant term V_{out}, greater than the value of the energy at the upper edge of the gap. The Bloch functions must be matched at $z = 0$ with the external solution

in the semiaxis $z > 0$, having the form e^{-qz}, with $q = \sqrt{V_{out} - E}$, at each energy E where the matching is possible.
In the region of allowed bulk bands the extenal solution is matched to a combination of $\psi_k(z)$ and $\psi_{-k}(z)$ at every E_k with real k. In the region of the gap, the matching condition is obtained by equating the logaritmic derivative of the evanescent solution and the external decaying function:

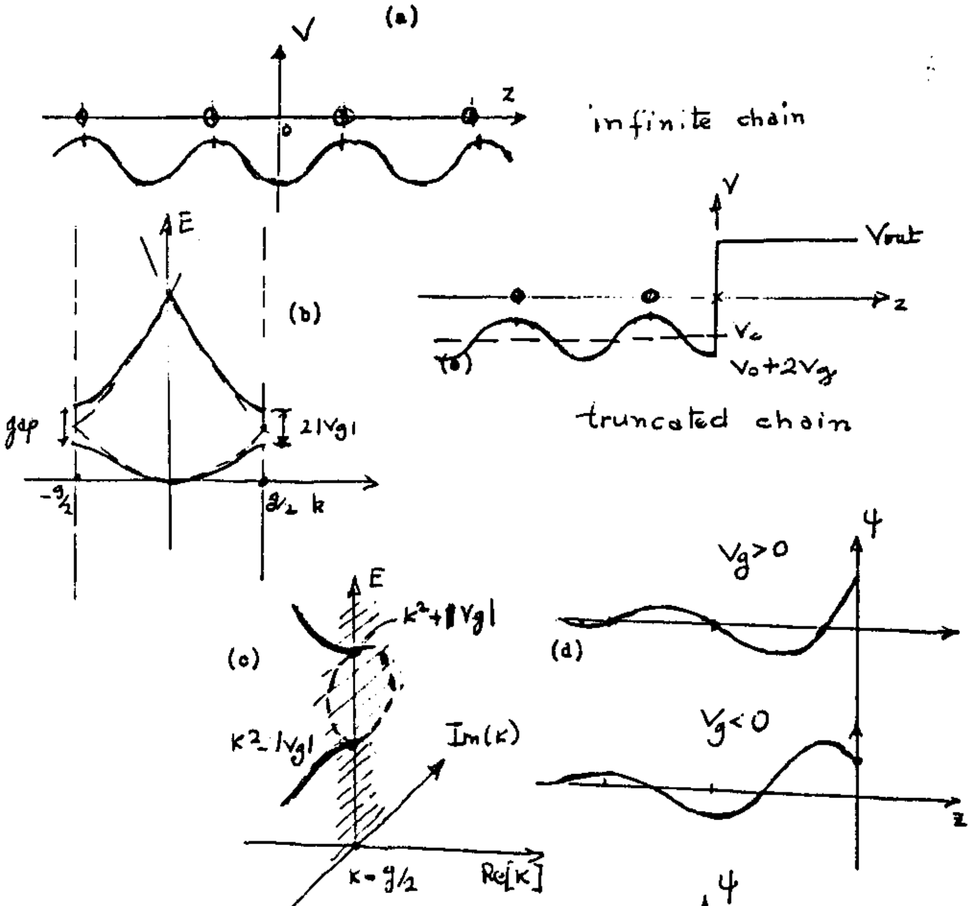
$$-q = \chi - tg(\delta). \tag{2.3}$$

χ and q are positive and depend on energy. This equation has a solution only in the case when δ is positive, *i.e.* when $V_g < 0$. V_g is negative, we know, when the lower-edge state $\psi^-_{g/2}$ has a maximum of the charge density distribution at the midpoint of the interatomic distance, which is the truncation point. The matching condition fixes the energy of a new state, obtained by matching an external exponentially decaying function and an internal evanescent wave with a decay length $1/\chi$. This state is a *surface state*, being *localised in the surface region* and its energy eigenvalue lies *in the bulk energy gap*.

1.3 - k-complex energy dispersion and matching conditions

In our simple model we found a single surface state if $V_g < 0$. This condition is a particular formulation of the Shockley theorem[1].
In more general cases it is possible to follow the same procedure solving the band structure - also in a three-dimensional (3D) crystal - obtaining evanescent solutions by removing the reqirement of real **k** values, allowing complex values of k_z, the component of **k** normal to the surface.
These solutions must be found at every energy and a linear combination of them must be matched, with its derivative, with the external decaying function and its derivative. If the energy is in a forbidden gap the existence of a solution of the mathching problem originates a surface state.
In the region of the energy values of bulk state continuum, the *travelling* bulk states with components k_z and $-k_z$ are mixed, to be matched to the external solution. In this way a propagating wave is completely reflected by the surface.
For the empty bands, with energy higher than the vacuum level ($E > V_{out}$), the travelling internal solutions can be combined and matched to an external travelling state. They correspond, in the 3D case, to to the so called LEED states.
Moreover forbidden gaps can exist also in the empty states above the vacuum level. In these region of *forbidden* energy for travelling waves, evanescent solutions match a combination of external propagating waves. These kind of states can play an important role, when they are used as

final states for the excitation of an electron, in surface sensitive spectroscopies.



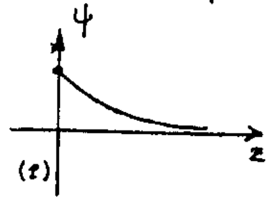


Fig.1 a)infinte chain potential
b)band structure (real k)
c)band structure (complex k)
d)evanescent waves
e)truncated chain potential
f) outer solution

1.4 - Thight-binding model for the linear chain.

To have a further example on the origin of the surface states, let us consider the linear chain in the tight-binding scheme. We choose a chain with one atom per unit cell and describe the wavefunctions in terms of a linear combination of atomic-like orbitals. At each site l we have the set of functions $\{\phi_\alpha(z - la)\}$. We combine them to obtain Bloch function for the infinite chain:

$$\psi_k^{(\alpha)}(z) = \frac{1}{\sqrt{N}} \sum_l e^{ikla} \phi_\alpha(z - la)$$

$$\psi_k(z) = \sum_\alpha c_k(\alpha) \psi_k^{(\alpha)}(z) = \frac{1}{\sqrt{N}} \sum_\alpha \sum_l c_k(\alpha) e^{ikla} \phi_\alpha(z - la) \qquad (4.1)$$

From $H\psi_k(z) = E\psi_k(z)$ one has the secular system:

$$\sum_\alpha \{H_{\beta\alpha}(k) - E_k S_{\beta\alpha}(k)\} c_k(z) = 0 \qquad (4.2)$$

where

$$S_{\beta\alpha}(k) = \sum_l e^{ikla} \int \phi_\beta^*(z) \phi_\alpha(z - la) dz = \sum_l e^{ikla} S_{\beta\alpha}(0, l) \qquad (4.3)$$

$$H_{\beta\alpha}(k) = \sum_l e^{ikla} \int \phi_\beta^*(z) H \phi_\alpha(z - la) dz = \sum_l e^{ikla} E_{\beta\alpha}(0, l) \qquad (4.4)$$

If the crystal periodicity is lost because of the presence os some defects or to the trmination of the chain, we cannot use longer Eq. (4.1) with, the phase factors containing the wavevector k, and we must replace $e^{ikla} c_k(\alpha)$ by $A_{l\alpha}$. Then we write:

$$\psi(z) = \sum_\alpha A_{l\alpha} \phi_\alpha(z - la) \qquad (4.1')$$

The secular equations are then given by:

$$\sum_{l'} \sum_\alpha \{H_{\beta\alpha}(l; l') - E S_{\beta\alpha}(l; l')\} A_{l'\alpha} = 0 \qquad (4.2')$$

Let us oversimplify the problem, solving the *bulk* case with a set of two orbitals (α label can indicate s or p = orbitals as shown in *Fig. 2* and assuming $S_{\beta\alpha}(l; l') = \delta_{\beta\alpha} \delta_{ll'}$. Orbital functions on different sites are orthogonal, as in the *Slater-Koster* model[2]. The integrals $E_{\beta\alpha}(l; l')$ are assumed to be different from zero only for $l = l'$ or $l' = l \pm 1$, so that only *nearest-neighbour* interactions are included:

$E_{ss}(l;l) = E_s \qquad E_{pp}(l;l) = E_p \qquad E_{sp}(l;l) = E_{ps}(l;l) = 0$

$E_{ss}(l;l\pm 1) = -\gamma_{ss} \qquad E_{pp}(l;l\pm 1) = \gamma_{pp}$

$E_{sp}(l;l\pm 1) = -E_{ps}(l;l\pm 1) = \pm\gamma_{sp}$

where all the γ's are positive. The Eq. (4.2) for the infinite chain becomes

$$\begin{cases} (H_{ss} - E_k)c_k(s) + H_{sp}c_k(p) = 0 \\ H_{ps}c_k(s) + (H_{pp} - E_k)c_k(p) = 0 \end{cases} \qquad (4.5)$$

with

$H_{ss} = E_s - 2\gamma_{ss}cos(ka)$

$H_{pp} = E_p + 2\gamma_{pp}cos(ka)$

$H_{sp} = -H_{ps} = 2i\gamma_{sp}sin(ka)$

Let us semplify the model furtherly by putting $\gamma = \gamma_{ss} = \gamma_{pp} = \gamma_{sp}$ and choosing the origin of the energy scale to have $(E_p + E_s)/2 = 0$. We write $\Delta = (E_p - E_s)/2 > 0$, where $\Delta > 0$.

We obtain:

$$E_k^{\pm} = \pm\sqrt{\Delta^2 + 4\gamma^2 + 4\gamma\Delta cos(ka)} \qquad (4.6)$$

with

$$\begin{cases} (E_k^{\pm} - \Delta - 2\gamma cos(ka)c_k(s) \; + \; 2i\gamma sin(ka)c_k(p) = 0 \\ -2i\gamma sin(ka)c_k(s) \; + \; (E_k^{\pm} + \Delta + 2\gamma cos(ka)c_k(p) = 0 \end{cases} \qquad (4.7)$$

At the center of the BZ, $k = 0$ (the Γ point), we have:

$$E_\Gamma^- = -(\Delta + 2\gamma) \qquad E_\Gamma^+ = +(\Delta + 2\gamma) \qquad (4.8)$$

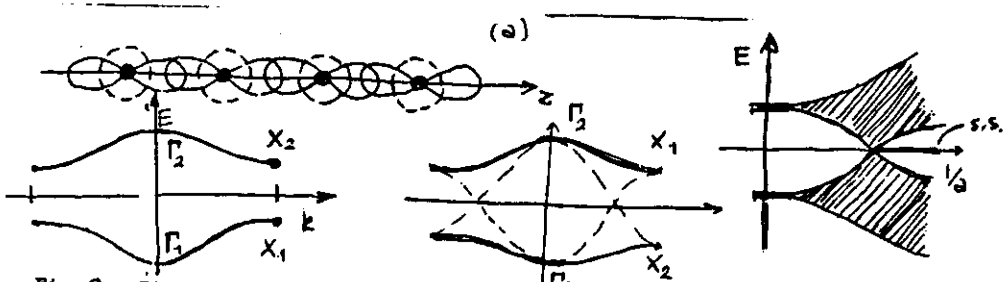


Fig. 2 - Tight-binding basis(a). Crossed or uncrossed bands (b). Surface and bulk levels as a function of lattice spacing in terminated chain

The first eigenvalue corresponds to a state composed of pure s orbitals, the second of pure p orbitals, as it follows from Eq. (4.5).

At the BZ border, $k = \pi/a$ (the X point), one has:

$$E_X^{\pm} = \pm|\Delta - 2\gamma| \qquad (4.9)$$

As $sin(ka)$ also vanishes at X, also the two states at the zone boundary are pure s or p. If $2\gamma < \Delta$ the lower state is s-type and the upper is p-type. If $2\gamma > \Delta$ the two states have energies in opposite order. The effect of large γ values is to create an *hybridisation* gap. In the case of $2\gamma > \Delta$ each band changes its orbital composition on going from Γ to X. (See *Fig. 2*).

Let us consider the case of a terminated chain. We must use the more general secular equation (4.2') and see if there are solution at each energy or not. We put the last atom of the chain at $l = 0$ and the first missing atom at $l = 1$. To build up the function of the type (4.1') we can use at each energy the solutions of equations ((4.3), writing:

$$A_{l\alpha} = \sum_j c(\alpha; k_j)e^{ik_jla}a_j \qquad (4.10)$$

where $k_j = k_j(E)$ are the solutions of the secular equations, as a function of E, obtained at any energy. They can be real values if E is inside one of the two bands (4.6) and in this case two values k and $-k$ are found. If E is not in these regions one obtaines complex solutions for k (*evanescent states*) which can give rise to localized states. One has also to include appropriate boundary conditions to represent the missing terms in the Hamiltonian (4.2') and to ensure the appropriate behaviour (no divergence) well inside the bulk.

In our simple case real values of E in the gap are obtained with $k_{1,2} = \pi/a \mp i\chi$ with $\chi > 0$. We must accept only $k_{1,2} = \pi/a - i\chi$, to avoid divergences in the phase factors in eq. (4.10), being the atomic positions of the semi-infinite row in $l < 0$ sites. Then there is only one term in the j-sum (4.10).

The other boundary condition to take into account in solving (4.2') is the surface termination. In our case, where only nearest neughbour interation are included, it is simply equivalent to

$$\sum_\alpha E_{\beta\alpha}(0;1)A_{1\alpha} = 0 \qquad (4.11)$$

From (4.10) we obtain:

$$\sum_\alpha E_{\beta\alpha}(0;1)c_{k_1}(\alpha)e^{ik_1a} = 0 \qquad (4.12)$$

In our model we have $E_{ss}(0;1) = -\gamma$ and $E_{sp}(0;1) = \gamma$, so that it is $c_{k_1}(s) = c_{k_1}(p)$. From (4.5) it follows that the only acceptable solution is $E = 0$, the centre of the gap.
In this way we find a state mainly localised at the surface and decaying inside the crystal with decay length $1/\chi$. Its orbital composition is given by a symmetric combination of $\psi_s(z)$ and $\psi_p(z)$, *i.e.* it is an *hybrid* orbital pointing in the positive direction of z (out of the surface).
We can note that it is possible to transform the basis of s and p orbitals in a basis of *hybrid sp* orbitals, by symmetric and antisymmetric combination of them. The two orbitals have directional lobes pointing respetively towards $z > 0$ and $z < 0$. The *surface state*, if it exists, is made of orbitals of the first type, with a major contribution coming from the surface atom at $l = 0$ *dangling bond*.
The condition of existence is $c(s) = c(p) \neq 0$; in order to satisfy with this solution Eqs. (4.7) it is necessary to have not only $E = 0$ but also:

$$\Delta + 2\gamma cos(k_1 a) - 2i\gamma sin(k_1 a) = 0 \qquad (4.13)$$

Because one has $2cos(k_1 a) = e^{\chi a} + e^{-\chi a}$ and $-2isin(k_1 a) = -e^{\chi a} + e^{-\chi a}$, the condition is:

$$\Delta = 2\gamma e^{-\chi a} \qquad (4.14)$$

which can be satisfied only for $2\gamma > \Delta$, *i.e.* in the case of a gap of hybridization type. In this case the lower bulk energy state at X point is made by a combination of p orbitals with a large value of the charge density at the middle of the bond. If we create the surface at this point and if the lower edge of the gap corresponds to a bonding state, a surface state of the *dangling bond* type appears in the gap. We obtain a result consistent with the one obtained in Paragraph 2, using plane waves.
The energy of this state is 0, in our scale $1/2(E_p + E_s)$, the mean energy values calculated for the hybrid orbital. From eq. (4.14) it is clear that this state decays rapidly inside the chain if 2γ is much larger than Δ.
A choice of a less symmetrical model with $\gamma_{ss} \neq \gamma_{pp} \neq \gamma_{sp}$ would give less simple formulas, but essentially the same physical picture.

1.5 *Classification of surface states.*

Using two complementary approaches, we have seen that states localized at the terminating region of the linear chain with an exponential decay inside the bulk can arise in particular conditions. In both models the crystal is terminated abruptly and, roughly speaking, the condition of existence of surface states in the gap is linked to the possibility of accommodating electronic charge density in the region of the broken bond. In both models the potential seen by the electron repeats periodically up to the termination and there is a sudden discontinuity at the surface. The

reality should present a smoother profile. The potential at last atomic sites is not necessarily the continuation of the perfect bulk potential and in the external region it should continuously reach the vacuum level. Additionally the equilibrium position of the last atoms in the chain can change with a local relaxation of the interatomic distance.
These effects can be introduced in the tight-binding model by changing the values of the intra-atomic parameters and of the hopping integrals in the last atoms of the chain. These changes can give rise to states localized at the surface and located in energy near the edges of band gap and inside it, also in absence of Shockley states. These surface states are commonly classified as Tamm sTATES[3].
Similar states which come out from the border of band, mainly arising from the orbital of the same type, are encountred in the study of ionic crystal. The 1D ionic crystal is a sequence of different atoms carrying different orbitals with $\Delta > \gamma$. The two bands are separated by a wide gap, not of hybritization type. Bands are *uncrossed*, but the last atom of the chain has a different environment respect to the atoms of the same type inside the bulk.
We can consider an *sp*-chain like the one considered in §1.4, but with different sites for s and p orbital. Δ is reduced in the last two planes and the possible consequence is the presence of a state immediately above the valence band (1st band), if the termination is at an anion site, or immediately below the conduction (2nd band), if the terminating atomic is the cation[4]. Both kinds of states can be found in a real surface where both atomic species are present. Their presence reduces the gap at the surface. Also in the case of partially ionic semiconductors the states originating from the hybridisation gap can have different energy location as a function of the atom at the surface which mainly contribute to the state.
A review of one dimensional models for the study of surface states is given in Ref. 5.

1.5 - The three-dimensional case.

The previous description can be generalised to a realistic description (3D) for a semi-infinite crystal. The $z = 0$ plane divides the region ($z < 0$) where the bulk potential is imperturbed, from a *selvage* region containing the outer atomic planes ($z > 0$), where the potential can vary respect to the bulk and continuously change to reach the vacuum value. The infinite crystal one-electron problem is considered as completely solved: $E_n(\mathbf{k})$ and $\psi_{n\mathbf{k}}(\mathbf{r})$ are known across the whole 3D BZ, including the extension to complex values of k_z.
One has to match at every value of energy E, the external ($z > 0$) solution with the internal one ($z < 0$). The 3D $\mathbf{k}$ vector is not a good

label for the state but only $\mathbf{k}_{\parallel} = (k_x, k_y)$ and one has to mix all the solutions with the same energy E corresponding to different k_z including also the decaying solutions of the type $k_z = \kappa - i\chi$. Thus one has to extend the bulk calculation to the complex values of k_z in order to include all bands of evanescent states, which branches out of maxima and minima of the real-k band structure. *Fig. 3* indicates schematically a possible mixture of different (periodic and evanescent) states.
At a given $\mathbf{k}_{\parallel}$ one has:

$$\psi_{in}(\mathbf{r}, \mathbf{k}_{\parallel}, E) = \sum_i A_i \psi(\mathbf{r}, \mathbf{k}_{\parallel}, k_z^i(E)) \qquad z < 0 \qquad (6.1)$$

and

$$\psi_{out}(\mathbf{r}, \mathbf{k}_{\parallel}, E) = \sum_n B_n \chi_n(\mathbf{r}, \mathbf{k}_{\parallel}, E) \qquad z > 0 \qquad (6.2)$$

A solution exists only if the matching of the two functions and their derivatives respect to z is possible at every point of the plane $z = 0$. If, at given $\mathbf{k}_{\parallel}$ and E, bulk periodic states exist one finds how the surface modifies the bulk wave functions.
If the extended bulk states are mixed with evanescent states in the matching procedure, one gets a state which is a combination of the two types (travelling and localized) of functions. These states are called *surface resonances*.
If no bulk state exists at E, one has to match only decaying states on both sides (for $E < V_{out}$). If the matching condition is satisfied a true *surface state* arises.

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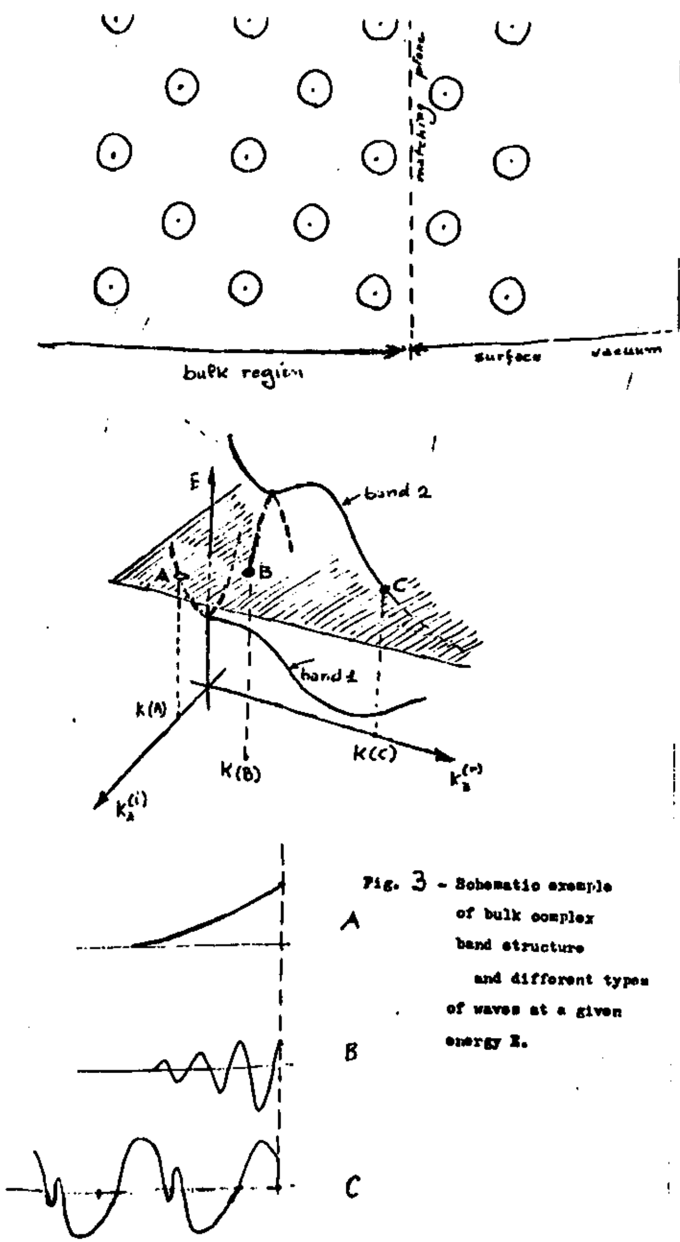


Fig. 3 - Schematic example of bulk complex band structure and different types of waves at a given energy E.

2. Surfaces in 3D: Ideal Surfaces.

2.1 – Ideal surfaces and surfaces periodicity.

If the surface terminating a 3D crystal retains, up to the outermost plane of atoms, the atomic geometrical arrangement of the corresponding bulk planes, the surface is call <u>ideal</u>. The surface plane has the periodicity in 2D of the bulk plane having the same crystal indexes and the locations of the atoms in the 2D unit cell are not changed respect the ones of a bulk plane.

If this is not the case, there are different degrees of deviation from ideality:

a) a <u>uniform desplacement</u> of the the atoms on an outer plane inwards or outwords respect to each layer equilibrium position in the bulk. This <u>relaxation</u> does not change the surface periodicity or the symmetry of the terminated crystal respect to the <u>ideal</u> configuration.

b) <u>in-plane</u> shift of the equilibrium atomic positions at the last planes and/or <u>different</u> <u>normal</u> <u>displacements</u> of atoms inside the unit cell. Periodicity of the ideal surface is not lost, but symmetry is changed.

c) Different shifts in the positions of atoms in neighbouring cells or ordered sequencies of defect or vacancies, with a periodi arrangement, creating a new larger unit cell, i.e. a <u>reconstruction</u>.

d) geometrical disorder of the surface planes, with loose of 2D-periodicity

The presence of relaxation or reconstruction is a common feature in most semiconductor surfaces, and we will treat this subject in the following paragraphs.
We now consider the types of 2D Bravais lattices: they are five in number and in Fig. 3 direct and reciprocal lattices are shown, with in evidence the basis vectors of the direct and reciprocal mesh. They are:

$$\vec{a}_1 = (a_{1x}, a_{1y}) \qquad \vec{a}_2 = (a_{2x}, a_{2y})$$

$$\vec{b}_1 = \frac{2\pi\,(a_{2y}, -a_{2x})}{a_{1x}a_{2y} - a_{2x}a_{1y}} \qquad \vec{b}_2 = \frac{2\pi\,(-a_{1y}, a_{1x})}{a_{1x}a_{2y} - a_{2x}a_{1y}}$$

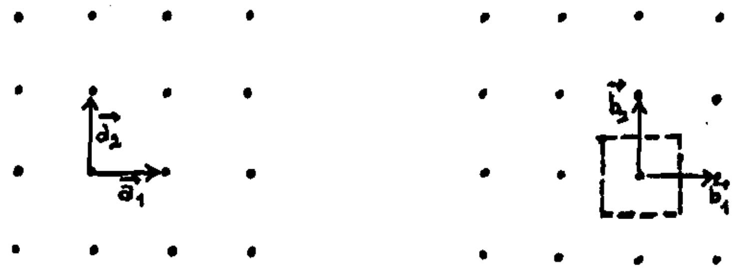
Also the 2D-Brillouin zones are shown.

2.2 – Remapping of bulk states – Projected bulk band structure.

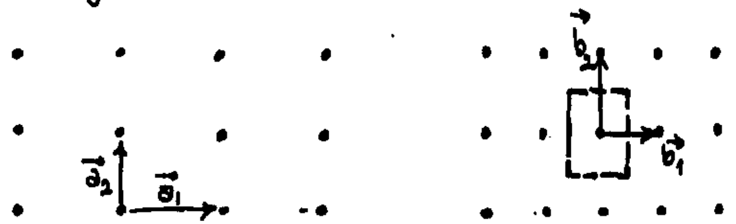
To identify where true surface states can exist, we must consider the values of $\vec{k}_{\parallel}$ where the gaps in the bulk states distribution are present, $\vec{k}_{\parallel} = (k_x, k_y)$ being a vector of the 2D BZ. To identify the gaps one has to remap the 3D BZ in a prismatic shape, with the 2D BZ as its basis where $k_{\parallel} = (k_x, k_y)$ is limited, and $-\pi/d \le k_z < \pi/d$ where d is an interplanar distance.

This construction can be done for the surfaces (001), (110) and (111) of a diamond or zinc-blend structure. In Fig 5 the 3DBZ for the F.C.C. (face center cubic) lattice is drawn together with its prismatic rearrangement for the case of (001) surface. The 2DBZ is shown with high symmetry points and directions. The sequence of plane for this surface is a sequence of AA'BB'AA'.... planes with atoms distributed on a

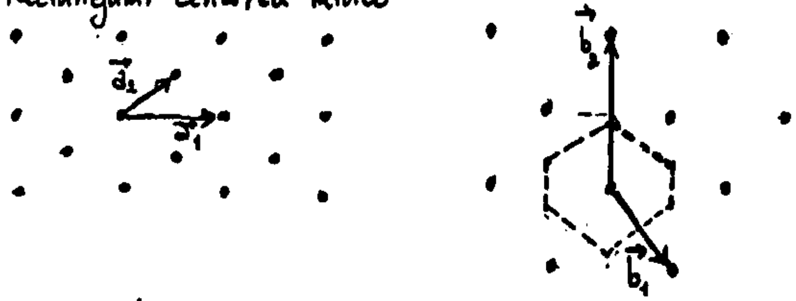
1) Square lattice $a_1 = a_2$ $\alpha = 90°$



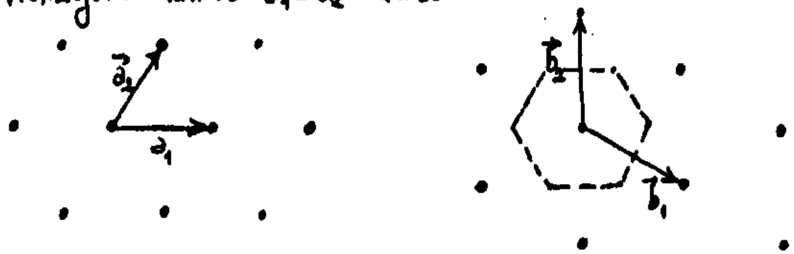
2) Rettangular lattice $a_1 \neq a_2$ $\alpha = 90°$



3) Rectangular centered lattice



4) Hexagonal lattice $a_1 = a_2$ $\alpha = 60°$



5) Oblique lattice

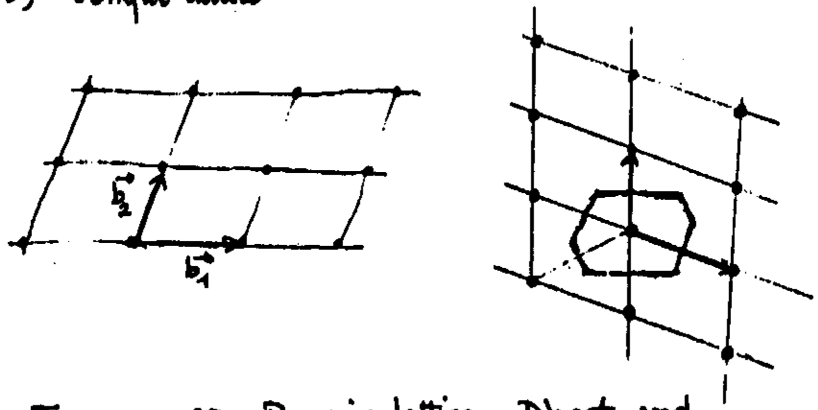


Fig = 2D - Bravais lattice _ Direct and Reciprocal spaces _ Brillouin zones _

FCC

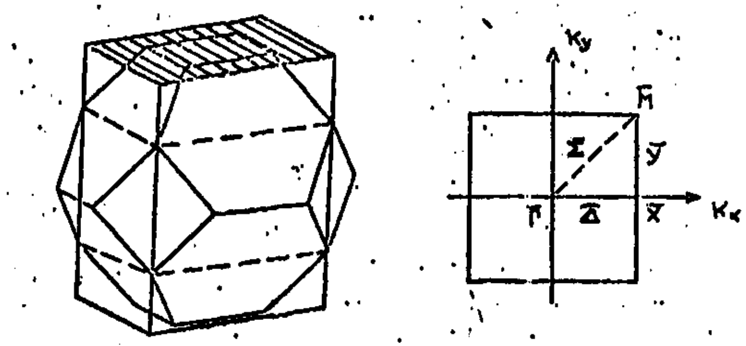


Fig - the 3DBZ for FCC crystals is folded into a prismatic shape. The basis is the 2D BZ for (001) surface. High symmetry points and directions in the 2DBZ are also indicated.

square lattice. Two neighbouring planes contains atoms of two different sublattices.

The (110) surface [which is the cleavage surface for ionic zinc-blende structure semiconductors] contains two atoms of different sublattices on the same plane. (See Fig 6). The Bravais lattice is rectangular The 2DBZ is indicated in the Figure. We note that the plane normal to [$\bar{1}$10] direction passing through an atom is a reflection plane for the crystal.

Let us consider the (111) ideal surface. Each atom at the surface is bonded to tree atoms at the second plane belonging to a different sublattice. The sequence is AA'BB'CC'AA'.....

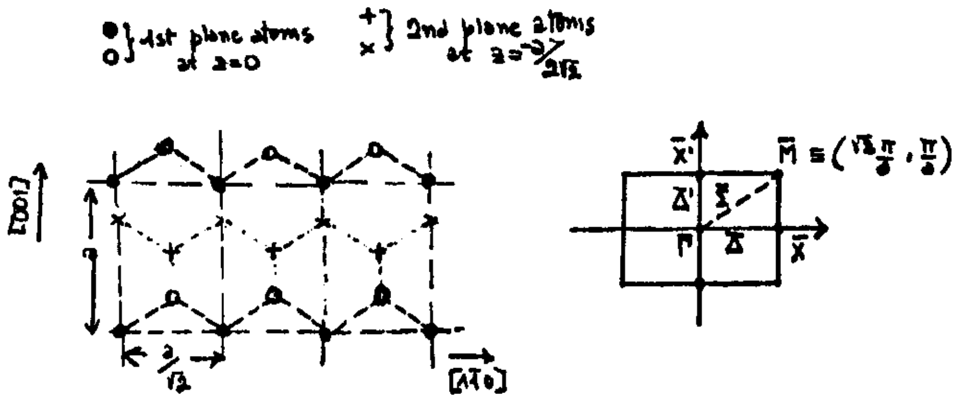


Fig 6a – Direct lattice and 2DBZ for (110) surface of diamond and zinc blende structure

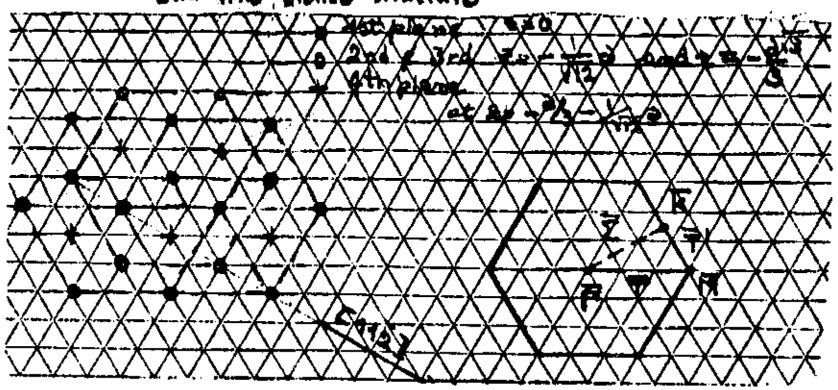


Fig 6b – Direct lattice and 2D BZ for (111) ideal surface of diamond and zinc blende structure.

At every $\vec{K}_{\|}$ point of the 2DBZ we have to plot the energy bands as a function of k_z and find the Energy segments of existing bulk states. In symmetry directions where eigenstates belong to different representations of the group of the $\vec{K}_{\|}$ vector, we must separate energy intervals belonging to different representation of the group. We obtain in this way the "projected bulk band structure" (PBBS) associated to that ideal surface. It contains continua of bulk states separated by gaps, which do not necessarily extends to the whole 2DBZ. For istance for the (110) surface of zinc-blende structure compounds one obtaines three kind of gaps: 1) the gap between the conduction and valence band which has different width at different $\vec{K}_{\|}$. 2) the gap between the lower band (mainly anion-derived s band) and the other valence band. It extends from ~-10eV to ~-6÷7eV from valence band maximum E_v. this gap closes at $\bar{\Gamma}$ in diamond structure. 3) A lens extending on the external part of the 2DBZ at a few eV below E_v. All this gaps can accomodate surface states which will present a dispersion as a function of $\vec{K}_{\|}$ inside them. Usually when a dispersion curve crosses the border of the gap or of the empty lens, it continues inside the bulk state region as a surface resonance.

A surface state can also arise in a gap of state of a given symmetry, being degenerate with the continuum of state of other symmetry. This can occurr only in high symmetry direction of the 2DBZ; when $\vec{K}_{\|}$ moves away from it, the state become again a surface resonance.

We will present in Fig 7-9 examples of dispersion of surface states compared with the continua of bulk states along high symmetry directions of 2DBZ of surface of semiconductors. These examples are output of theoretical calculations, where, usually, one does not solve the problem of the semiinfinite crystals, but describe a system composed of a finite number of atomic planes. The "slab" must be sufficiently thick to reproduce both bulk continua (represented as a set of discrete levels) and the surface bands.[10] The comparison with bulk projected bands (considerably easier to calculate than the surface problems) is a tool to check the outcome of the calculation.

2.3 - The local density of states.

To have a comparison between the electronic structure of a solid and the electronic structure at the surface, we an introduce the local density of states. It can be asily evaluated in calculation of electronic structure where we replace the semiinfinite crystal with a finite r periodically repeated slab (where a stack of atomic lanes plus a vacuum region are present). In this case discrete set of eigenvalue is obtained $\psi^{(j)}_{\vec{k}_\parallel}(\vec{r})$ having nergies E_j. The local density of states is defined as

$$n(E,\vec{r}) = \sum_j \sum_{\vec{k}_\parallel} \psi^{(j)}_{\vec{k}_\parallel}(\vec{r})\, \delta(E-E_j) \qquad (3.1)$$

integral on the whole space give the total density states. If we integrate on a plane normal to z in the it cell A_0 we have

$$n(E,z) = \sum_j \sum_k \int_{A_0} d\vec{x}_\parallel\, \psi^{(j)}_{\vec{k}_\parallel}(\vec{x}_\parallel, z)\, \delta(E-E_j) \qquad (3.2)$$

ing the contribution to the density of state at different distance the surface. If we consider the contribution of a plane of s considering the region from $(z_m+z_{m-1})/2$ to $(z_m+z_{m+1})/2$ e define, for instance

$$n(E,m) = \int_{(z_m+z_{m-1})/2}^{(z_m+z_{m+1})/2} dz\; n(E,z) \qquad (3.3)$$

and see how the density of states changes on passing from the outer plane to other planes and then to the bulk. It is possible point out the general feature of the LDOS at the first atomic planes:

a) reduction of the average with of the bands, due to the reduced atomic coordination at the surface

b) a change near the band edges. 2D critical points presenting step-like or logaritmic edges in the DOS, the presence of the surface (also not strictly a 2D system) can introduce sharper edges.

c) the presence of strong new peaks and structures due to surface bands or resonances, including states localized also the second plane (back bonds)

d) presence of depleted region in bulk due to orthogonalization of states in the continuum to surface resonances (anti-surface states)

The behaviour of the LDOS at the outer planes is particularly crucial in defining the surface properties of semiconductors

2.4 - States in the gap: band bending, Fermi level pinning and related phenomena.