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## SPRING COLLEGE IN CONDENSED MATTER
## ON
## "THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
## (25 April - 17 June 1988)

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# METAL SURFACE ELECTRONIC STRUCTURE

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# SURFACE PHYSICS

## METAL ELECTRONIC STRUCTURE

Books : Electronic properties of surfaces, ed. M. Prutton
(Adam Hilger 1984)

Modern techniques of surface science,
D.P. Woodruff and T.A. Delchar (Cambridge 1988)

### Potential felt by electrons at surface

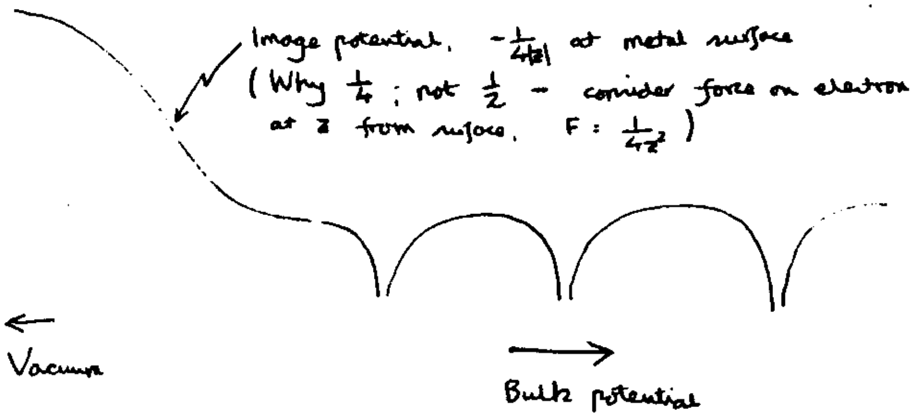


Image potential, $-\frac{1}{4|z|}$ at metal surface
(Why $\frac{1}{4}$; not $\frac{1}{2}$ – consider force on electron at $z$ from surface, $F = \frac{1}{4z^2}$)

Surface destroys 3D periodicity of bulk crystal, but still has 2D periodicity parallel to surface.

### 2D Bloch property

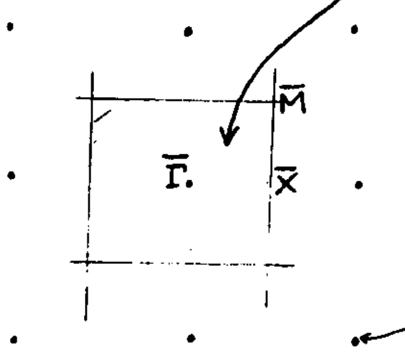
Wavefunctions can be labelled with 2D Bloch wavevector $\underset{\sim}{K}$, such that:

$$\psi_{\underset{\sim}{K}}(\underset{\sim}{R}+\underset{\sim}{R}_I, z) = e^{i\underset{\sim}{K}\cdot\underset{\sim}{R}_I}\,\psi_{\underset{\sim}{K}}(\underset{\sim}{R}, z)$$

— $\underset{\sim}{R}_I$ is a vector of the surface mesh.

As in 3D, Bloch wavevector not defined to within a reciprocal lattice vector: here we can add a surface reciprocal vector $\underset{\sim}{G}$ to $\underset{\sim}{K}$. This is because $\underset{\sim}{G}\cdot\underset{\sim}{R}_I = 2\pi r$

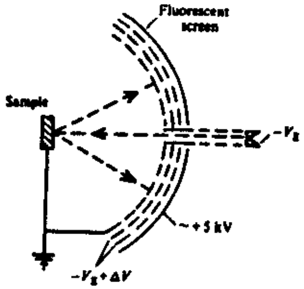
$\underset{\sim}{K}$ can be chosen to lie in first surface Brillouin zone: e.g. for fcc (001) surface:



Conventional labelling

reciprocal lattice points

Example of scattering through $\underset{\sim}{G}$ by surface: Low Energy Electron Diffraction (LEED)



(Energy of LEED electrons incident on sample ~ 20 - 300 eV)

Wavefunction in LEED has the form:

incident wave

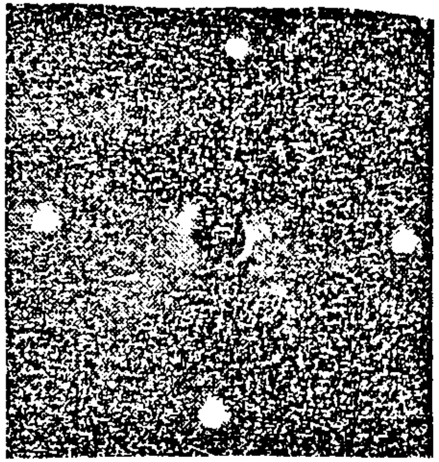
$$\psi = e^{i\underset{\sim}{K}\cdot\underset{\sim}{\rho}}\, e^{ikz} + \sum_{\underset{\sim}{g}} A_{\underset{\sim}{g}}\, e^{i(\underset{\sim}{K}+\underset{\sim}{g})\cdot\underset{\sim}{\rho}}\, e^{-ik_{\underset{\sim}{g}} z},$$

$\underset{\sim}{r}$ in vacuum.

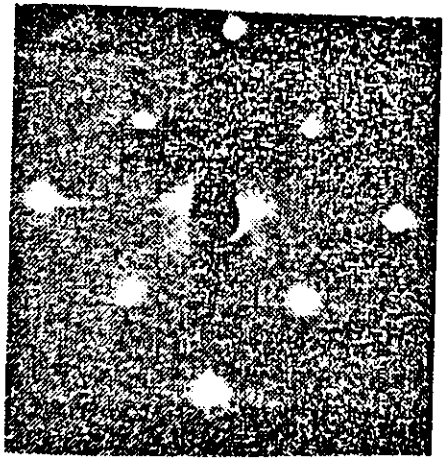
reflected waves, scattered by $\underset{\sim}{g}$

So, studying diffracted beams gives reciprocal mesh. The amplitudes $A_{\underset{\sim}{g}}$ contain information about detailed structure.

Example of LEED: W(001)

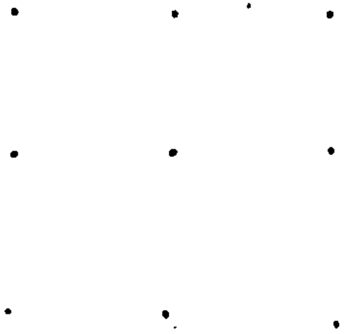


High T

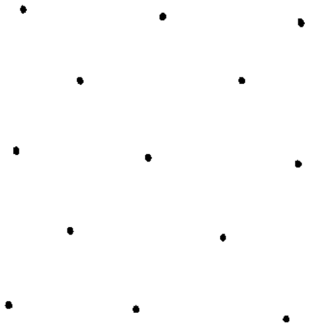


Low T
with extra diffraction spots

Reciprocal meshes are:

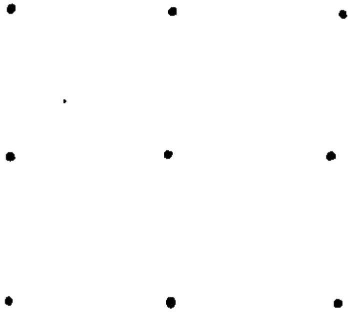


High T

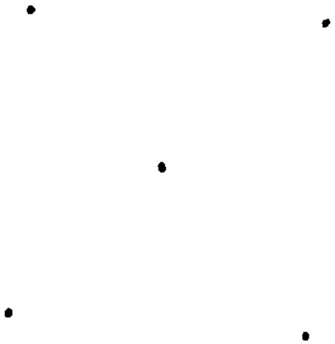


Low T

Real space meshes:



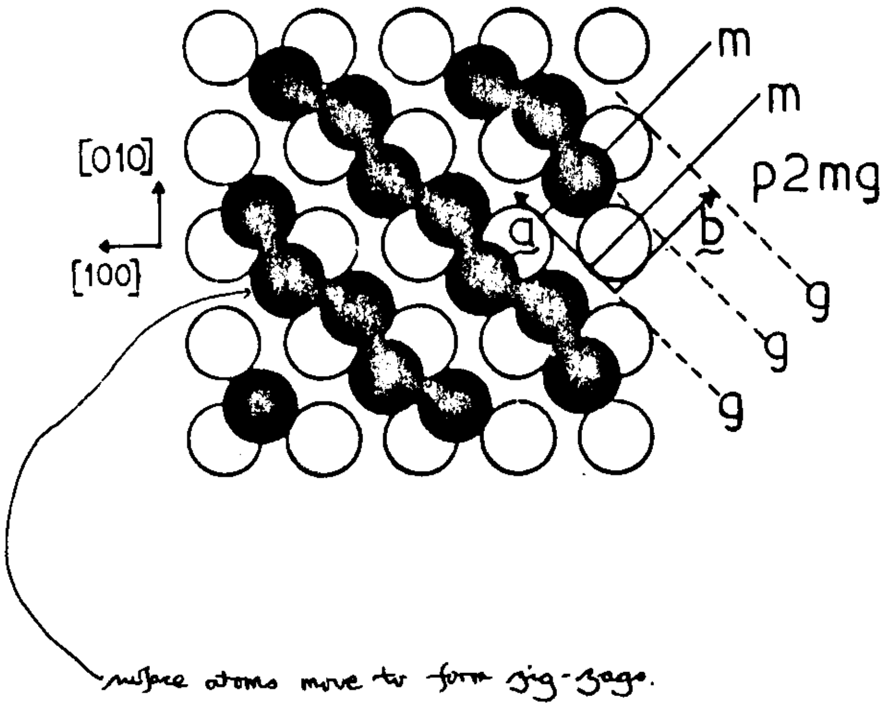
Ideal surface



$\sqrt{2} \times \sqrt{2}$ R 45°
reconstruction

N.B. Notation: unit cell has sides each $\sqrt{2}$ × original unit cell, rotated by 45°.

Actual structure in reconstruction is:



surface atoms move to form zig-zags.

## Wavefunctions in a semi-infinite solid, with a surface

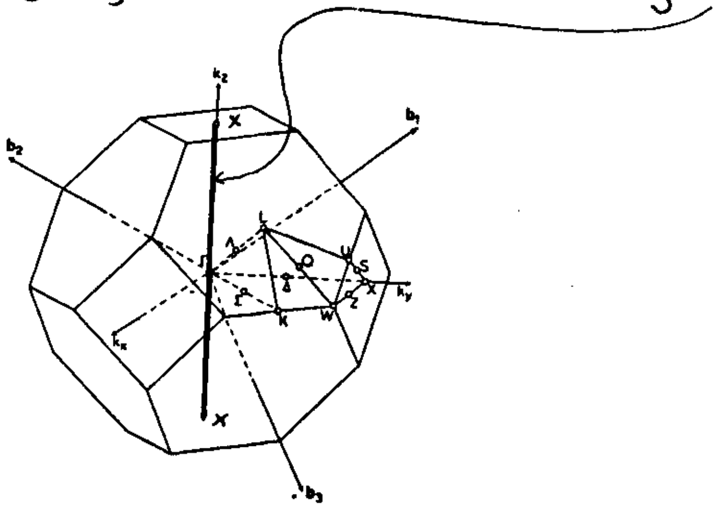
There are 2 classes of wavefunction, with energy below the vacuum level:

i Bulk states hitting surface, and reflected

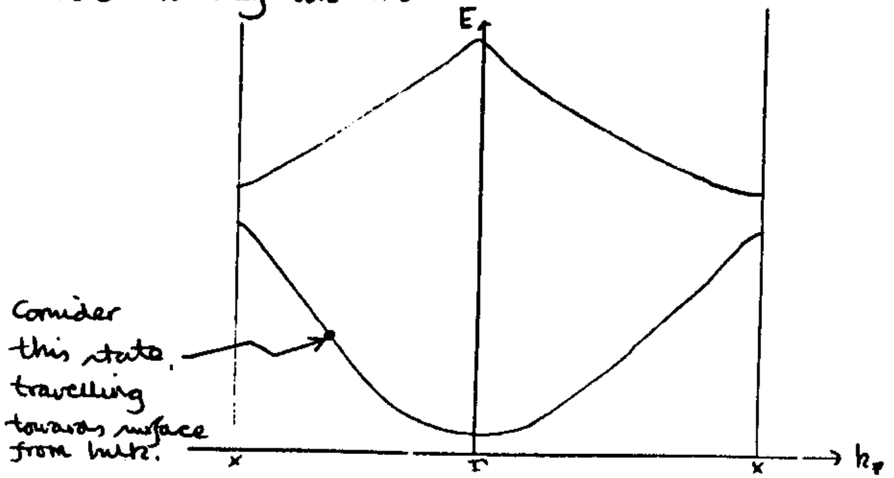
ii Localised surface states

## Bulk states at the surface

Fixing wavevector $\underset{\sim}{K}$ parallel to surface, consider bulk bandstructure as a function of $k_z$, wavevector component perpendicular to the surface. If for example we are working at $\underset{\sim}{K} = 0$ ($\bar{\Gamma}$) on fcc (001), bulk bands projecting on to this wavevector lie along $X\Gamma X$



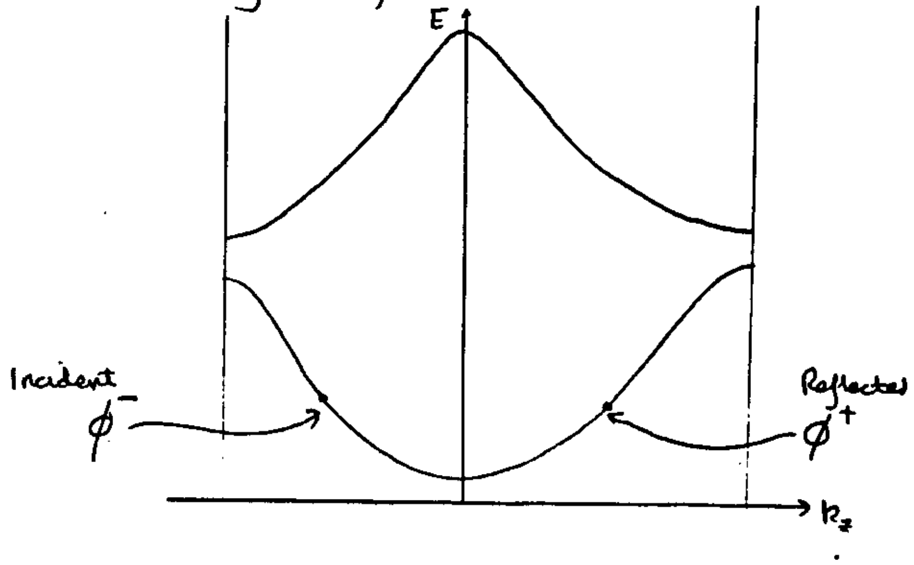
These bands may look like:



Consider this state, travelling towards surface from bulk.

This will be scattered by the surface into reflected waves travelling back into solid with same $\underline{K}$ $(+\underline{G})$ and energy E

Consider first a one-dimensional case (with no potential variation parallel to surface). With a one dimensional potential there is only one reflected wave :



and wavefunction in solid has the form :

$$\psi = \phi^- + r\,\phi^+ .$$

For simplicity assume step potential,

then vacuum solution has the form $\psi = t\,e^{\gamma' z}$.

$\psi$, $\psi'$ must match across surface

$$\Longrightarrow r, t$$

In full three-dimensional case there may be more than one reflected wave, but there are also evanescent waves of the form :

$$\phi^+_{\underline{K},\underline{G};E} \approx e^{i(\underline{K}+\underline{G}).\underline{\rho}}\, e^{-\gamma_{\underline{G}} z}$$

where $|\underline{K}+\underline{G}|^2 - \gamma^2 = 2E$

— these evanescent waves are not allowed in $\infty$ crystal, but only in semi-infinite case.

There is a 1:1 relationship between reflected + evanescent waves, and surface reciprocal lattice vectors $\underline{G}$, so we label these waves with $\underline{G}$. Wavefunction in solid then has form :

$$\psi = \phi^- + \sum_{\underline{G}} r_{\underline{G}}\, \phi^+_{\underline{K},\underline{G};E} .$$

In vacuum, solution has the form:

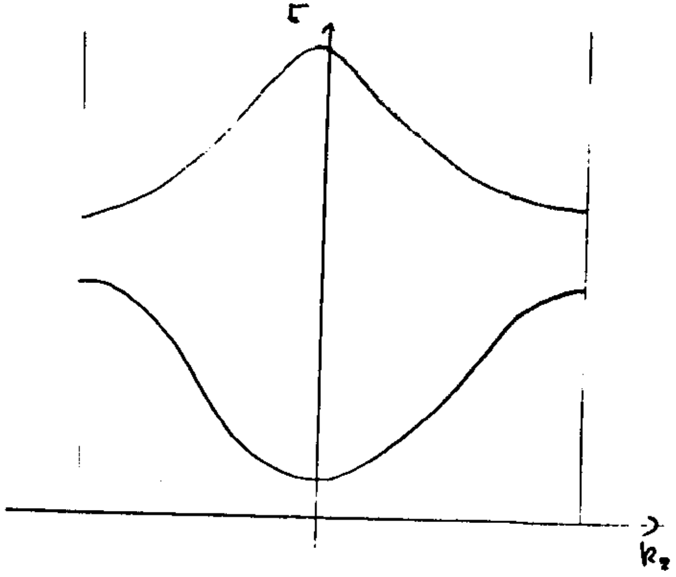
$$\psi = \sum_{\underline{G}} t_{\underline{G}}\, e^{i(\underline{K}+\underline{G}).\underline{R}}\, e^{\gamma'_{\underline{G}} z}$$

waves decaying away into vacuum.

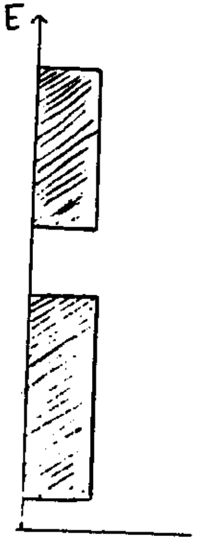
To match $\psi$, $\psi'$ we expand these expressions in 2D Fourier series made up of plane waves $e^{i(\underline{K}+\underline{G}).\underline{R}}$.

If $N$ = number of $\underline{G}$'s in Fourier series, this gives $2N$ matching conditions from which we can find $N$ $\gamma_{\underline{G}}$'s, and $N$ $t_{\underline{G}}$'s, i.e. wavefunction everywhere.

So bulk bands give continua of states, with energy gaps, at fixed $\underline{K}$:

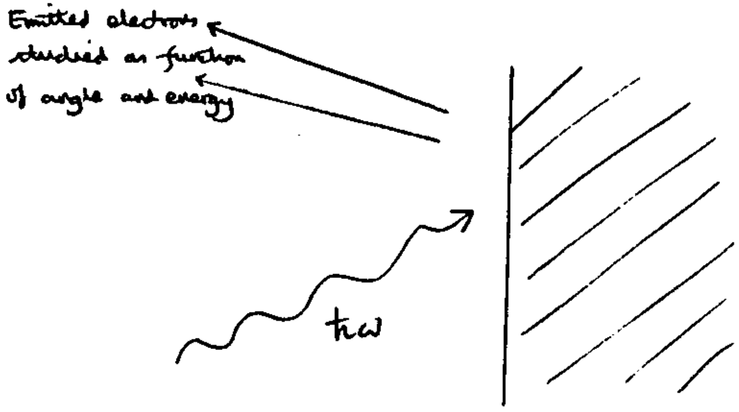


Bulk

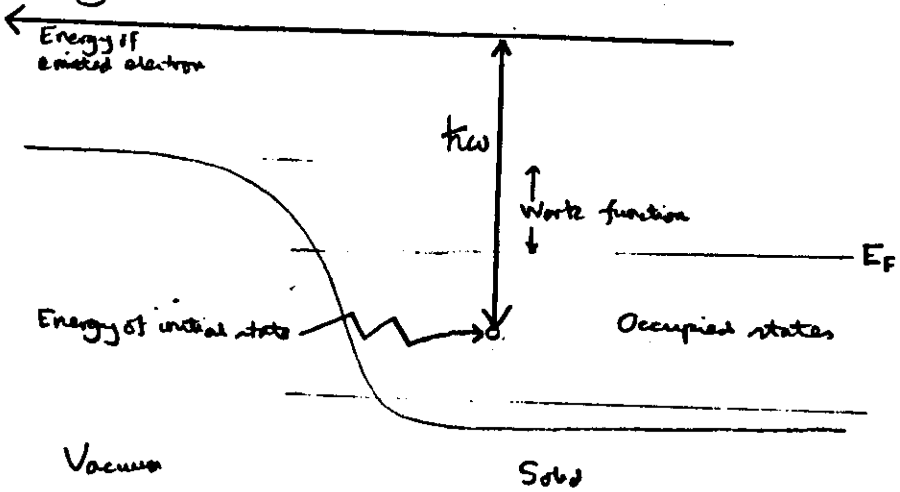


Surface

These states can be detected using Angle Resolved Photoemission



Energy conservation ⟹

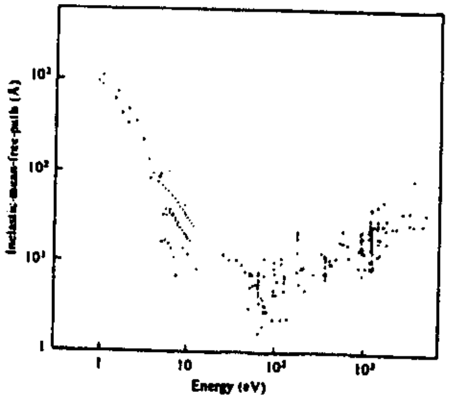


$\underline{K}$ conservation ⟹

From angle and energy of emitted electron we can find $\underline{K}$. Conservation of $\underline{K}$ across surface, to within $\underline{G}$, means that we know wavevector $\underline{K}$ of initial state

As mean free path of photoemitted electrons is quite short,

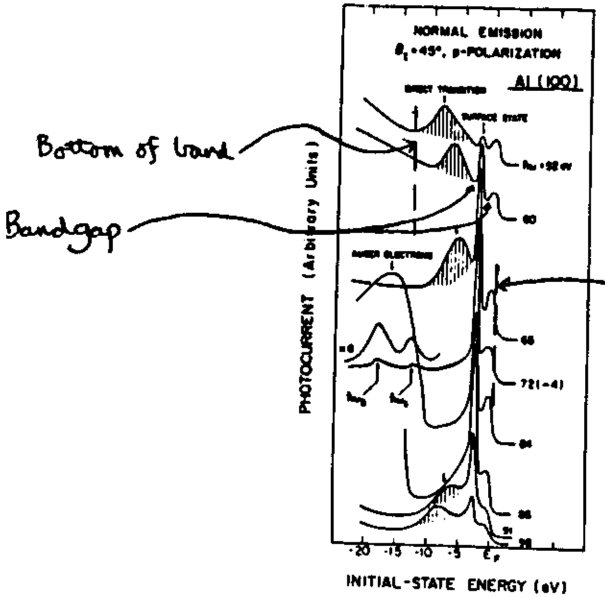
Collection of experimental determinations of inelastic scattering electron mean-free-paths as a function of energy above the Fermi level for many different materials (after Seah & Dench, 1979).



photoemission is detecting states at the surface.

Example for Al (001):

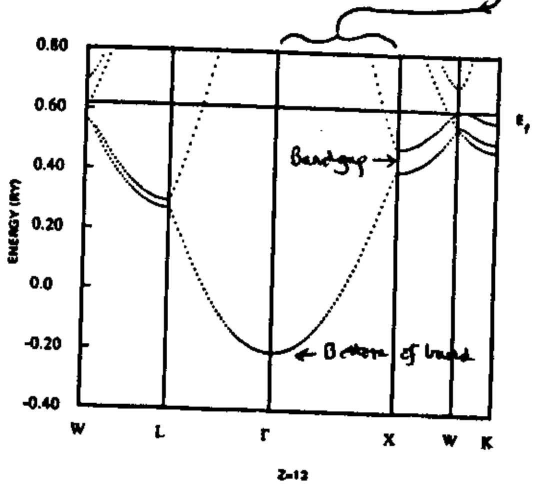
Normal emission
$\Longrightarrow \underset{\sim}{k} = 0$ states



Normal-emission photoelectron spectra plotted as a function of binding energy with respect to the Fermi energy.

(different curves come from different photon energies)

Compare with Al bandstructure for $\underset{\sim}{k} = 0$:



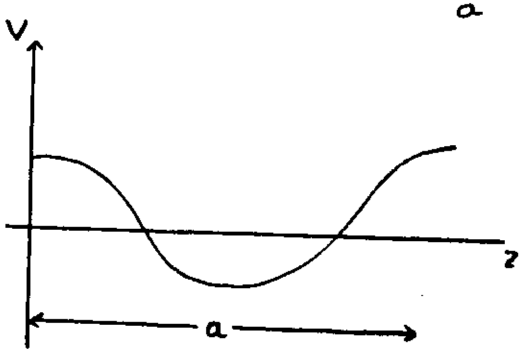
Photoemission shows very large feature with an energy in the bandgap. This is a localised surface state.

Shockley surface states

A surface state is a wavefunction with an energy in a bulk energy gap; in the energy gap the solutions of the bulk Schrödinger equation decay exponentially into the solid; as the energy is below the vacuum zero the wavefunction also decays exponentially into the vacuum, giving a state localised at the surface.

Consider the bandgap of a nearly-free-electron material (like Al) with a one-dimensional potential varying like:

$$V(z) = 2V \cos \frac{2\pi z}{a}$$



This potential opens up an energy gap in the bandstructure at $k_z = \pm \pi/a$, and around $k_z = \pi/a$ the solutions of the bulk Schrödinger equation have the form:

$$\phi = a e^{i k_z z} + b e^{i(k_z - g_z) z} \qquad \left(g_z = \frac{2\pi}{a}\right)$$

Substituting this into the Schrödinger equation $a$ and $b$ are given by matrix equation:

$$\begin{pmatrix} \frac{k_z^2}{2} - E & V \\ V & (k_z - g_z)^2/2 - E \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = 0.$$

This has a solution when

$$E = \frac{1}{4}\left\{ [k_z^2 + (k_z - g_z)^2] \pm \sqrt{[k_z^2 - (k_z - g_z)^2]^2 + 16V^2} \right.$$

In infinite crystal, $k_z$ is real, and this gives an energy gap of $2|V|$ at $k_z = \pi/a = g/2$.

Energies <u>in</u> the gap correspond to complex $k_z = \kappa + i\gamma$

$$E = \frac{1}{4}\left\{ \kappa^2 + 2i\kappa\gamma - \gamma^2 + \kappa'^2 + 2i\kappa'\gamma - \gamma^2 \right.$$
$$\left. \pm \sqrt{(\kappa^2 + 2i\kappa\gamma - \gamma^2 - \kappa'^2 - 2i\kappa'\gamma + \gamma^2)^2 + 16V^2} \right\}$$

$(\kappa' = \kappa - g_z)$. We can satisfy imaginary part of this equation by putting $\kappa = \frac{\pi}{a}$.

$$\therefore E = \frac{1}{4}\left\{ 2(\kappa^2 - \gamma^2) \pm \sqrt{16V^2 - 16\kappa^2\gamma^2} \right\}$$

$$\therefore E = \frac{\kappa^2 - \gamma^2}{2} \pm \sqrt{V^2 - \kappa^2\gamma^2}.$$

Rewriting this we obtain:

$$\gamma^2 = -2E - \kappa^2 + 2\sqrt{V^2 + 2E\kappa^2}.$$

$\Rightarrow$ At bottom of gap, $E = \frac{\kappa^2}{2} - |V|$, $\gamma = 0$

top of gap, $E = \frac{\kappa^2}{2} + |V|$, $\gamma = 0$

<u>and in the middle of gap, $\gamma \approx |V|/(\pi/a)$.</u>

Corresponding wavefunction is:

$$\phi = \left(a e^{i\kappa z} + b e^{-i\kappa z}\right) e^{-\gamma z},$$

with

$$\frac{a}{b} = \frac{-V}{\frac{1}{2}(\kappa^2-\gamma^2) - E + i\kappa\gamma} = \frac{\frac{1}{2}(\kappa^2-\gamma^2) - E - i\kappa\gamma}{-V}$$

Clearly

$$\left(\frac{a}{b}\right)^2 = \frac{\frac{1}{2}(\kappa^2-\gamma^2) - E - i\kappa\gamma}{\frac{1}{2}(\kappa^2-\gamma^2) - E + i\kappa\gamma}$$

= complex number of modulus 1

So we can write wavefunction as.

$$\underline{\phi = \cos(\kappa z + \chi)\, e^{-\gamma z}}.$$

$V$ positive $\Longrightarrow$ $\chi$ varies between $\frac{\pi}{2}$ at bottom of gap, and 0 at top.

$V$ negative $\Longrightarrow$ $\chi$ varies between 0 at bottom of gap, and $-\frac{\pi}{2}$ at top.

This wavefunction is not allowed in infinite crystal, but it is allowed in semi-infinite crystal - if it can be matched on to vacuum solution,

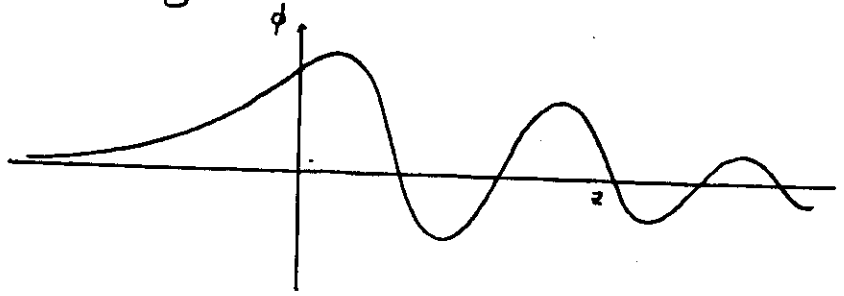
$$\underline{\phi = b e^{\gamma' z} \qquad z < 0}.$$

Logarithmic derivative of r.h. solution at $z = 0$

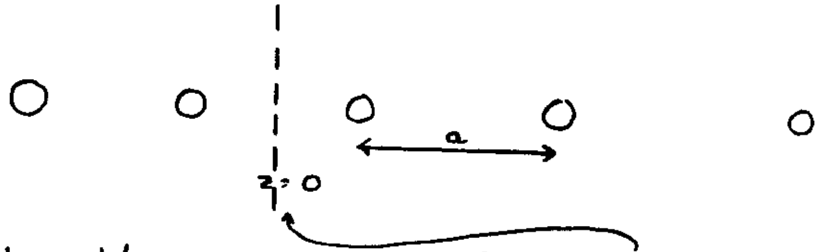
$$= -\gamma - \kappa \tan\chi.$$

This varies between $-\infty$ and 0 if $V$ is positive or between 0 and $+\infty$ if $V$ is negative.

On vacuum side, log. derivative is positive. So it is possible to match the wavefunction at some energy in gap if $V$ is negative:



– this is a Shockley surface state.

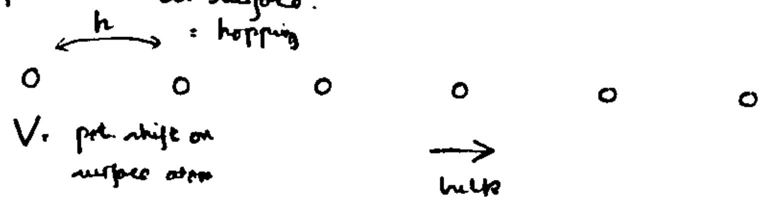


Now $V$ −ve with respect to origin at surface ≡ +ve $V$ with respect to an origin on the atom. With such an origin the pseudopotential for Al has a positive component so we would expect to see a Shockley surface state.

Shockley surface states are characteristic of narrow bandgaps.

## Tamm surface states

These states occur in tight-binding systems with a shift in potential at surface.



Write $$\psi = \underbrace{a_0 \phi_0}_{\text{surface atom}} + \underbrace{a_1 \phi_1}_{\text{subsurface atom}} + a_2 \phi_2 \ldots \quad \ldots$$

where a's satisfy equation:

$$\begin{pmatrix} V & h & & \\ h & 0 & h & \\ & h & 0 & h \\ & & h & \ddots \end{pmatrix} \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ \vdots \end{pmatrix} = E \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ \vdots \end{pmatrix}$$

Let us now look for a solution of this matrix equation in which there is a simple factor relating coefficients on adjacent atoms:

$$a_1 = \alpha a_0$$

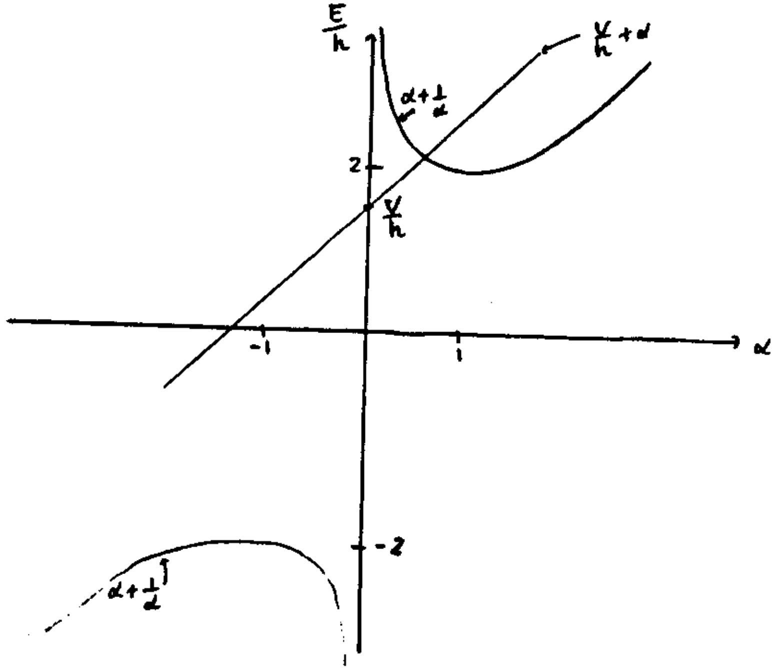
$$a_2 = \alpha a_1 \qquad \text{etc.}$$

Equation corresponding to second and subsequent rows of matrix

$$\Rightarrow \quad \frac{E}{h} = \alpha + \frac{1}{\alpha}.$$

Equation corresponding to first row is:

$$\frac{E}{h} = \alpha + \frac{V}{h}.$$



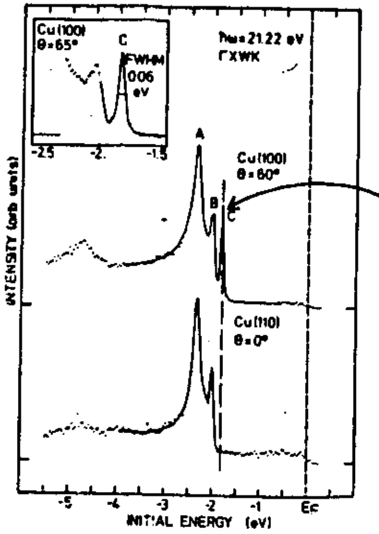
For a localised state we require $|\alpha| < 1$. Such a solution exists for $\frac{V}{h} > 1$, with energy $E > 2h$ (as shown) and for $\frac{V}{h} < -1$, with energy $E < -2h$.

So a shift $V$ with magnitude greater than $h$ pulls off a surface state either from the top or bottom of the bulk band. The bulk band itself has energies:

$$-2h \leqslant E \leqslant +2h.$$

This is a Tamm surface state.

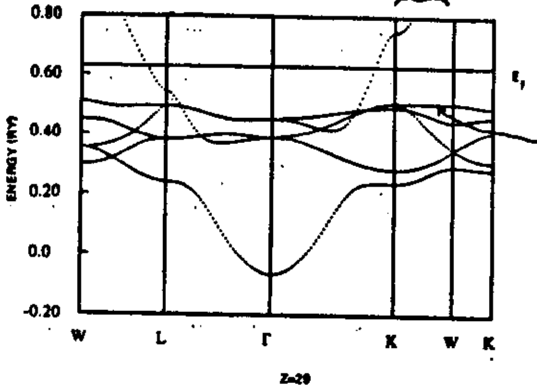
Example: photoemission from $\overline{M}$ on Cu(001):



Tamm surface state

ARPEDC's from Cu(100) and Cu(110). The photoelectrons are collected in the (001) mirror plane. The polar angle θ is referred to the surface normal.

XW projects onto $\overline{M}$ in fcc (001), and in this direction Cu bandstructure shows a very flat band:



This is made up of $d_{xy}$ orbitals, with little overlap in z-direction $\Longrightarrow$ flat band.

Little overlap means that a small shift in surface potential can pull off Tamm state, as observed.

Importance of surface states on metals:

- show up strongly in photoemission, hence good test of theory
- contribute to surface density of states, possible importance in surface reconstruction, surface magnetism, adsorption.

## Image states:

P.M. Echenique and J.B. Pendry, J. Phys. C 11 p. 2065
N V. Smith, Phys. Rev. 32 p 3549

Electrons can be trapped by the image potential, if their energy coincides with a bulk bandgap, so that they cannot propagate inside the solid. These are the image potential surface states, or Rydberg states, which have most of their charge density outside the solid, and are normally unoccupied.

Suppose the electron feels $V(z) = -\frac{1}{4z}$, $z > 0$ (vacuum)

and at $z = 0$ we require the wavefunction to be zero.

Then for $z > 0$, which we take as the vacuum half-space here,

$$\psi(\underset{\sim}{r}) = e^{i\underset{\sim}{K}\cdot\underset{\sim}{R}}\,\phi(z).$$

where:

$$-\frac{1}{2}\frac{d^2\phi}{dz^2} - \frac{\phi}{4z} = \left(E - \frac{K^2}{2}\right)\phi.$$

C.f. $l = 0$ radial equation for hydrogen atom:

$$-\frac{1}{2}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{ZR}{r} = \epsilon R.$$

Putting $R = \frac{u}{r}$ this becomes:

$$-\frac{1}{2}\frac{d^2u}{dr^2} - \frac{Zu}{r} = \epsilon u,$$

— the same as our surface equation, with $Z = \frac{1}{4}$, $\epsilon = E - \frac{K}{2}$

Now eigenvalues of hydrogenic equation are

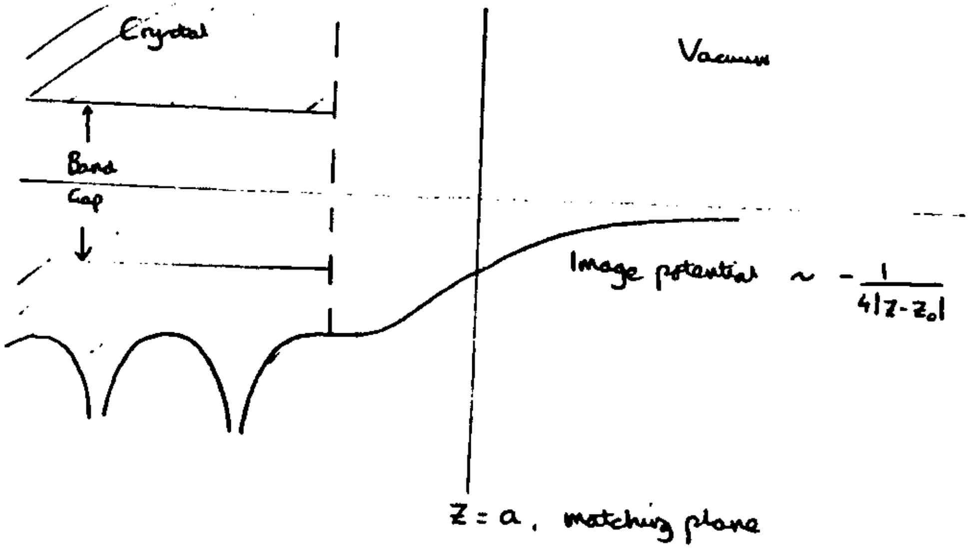
$$\epsilon = -Z^2/2n^2,$$ giving finite $R(r)$ as $r \to 0$

— hence giving $u(r) \to 0$ as $r \to 0$.

This is the behaviour we require in the surface model, so the eigenvalues of the Rydberg surface states are:

$$\underline{\underline{E = -\frac{1}{32n^2} + \frac{K^2}{2}}}$$

Full treatment:

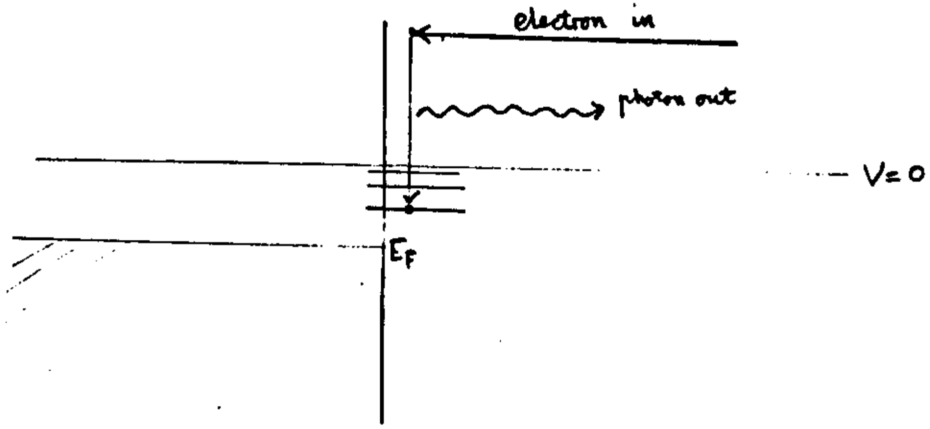


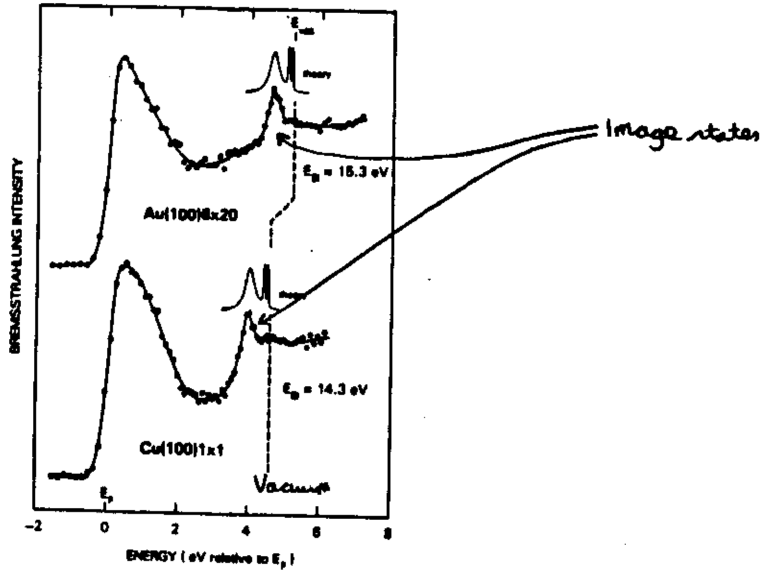
For $z > a$, solutions of the Schrödinger equation with $V = -\frac{1}{4|z-z_0|}$ are Whittaker functions.

For $z < a$, can find solutions for the semi-infinite crystal + potential barrier.

Match $\phi$, $d\phi/dz$ at $z = 0$, $\Longrightarrow$ eigenstates.

These unoccupied states can be measured using inverse photoemission :





(D. Straub and F. J. Himpsel
Phys Rev. Letts. 52 p. 1922 (1984)).

## Calculating the properties of surfaces

To find the surface electronic structure, hence surface properties (charge density, work function, surface density of states, surface energy, stable structure ---) use density functional theory (P. Hohenberg & W. Kohn, Phys. Rev. 136 B864, (1964); W. Kohn & L. J. Sham, Phys Rev 140 A1133 (1965); N. D. Lang, in Solid State Physics 28 p 225 (1973)) to reduce the interacting electron problem to 1-electron form:

$$\left(-\tfrac{1}{2}\nabla^2 + V_{ion}(\underline{r}) + V_H(\underline{r}) + V_{xc}(\underline{r})\right)\psi_i(\underline{r}) = \epsilon_i\,\psi_i(\underline{r})$$

$V_{ion}$: potential due to ions

$V_H$: Hartree potential (electrostatic) due to electron charge density

$V_{xc}$: Exchange-correlation potential to allow for exchange interaction and correlated motion of electrons

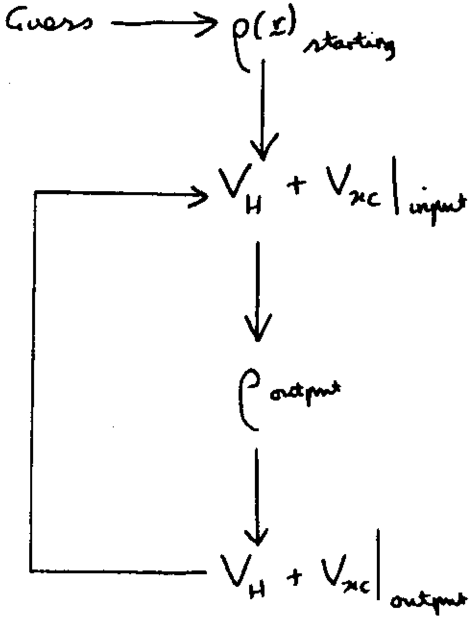
$V_H$ and $V_{xc}$ depend on electronic charge density:

$$V_H(\underline{r}) = \int d\underline{r}'\ \rho(\underline{r}')/|\underline{r}-\underline{r}'|$$

$V_{xc}(\underline{r})$ in local density approxn. (LDA) $= V_{xc}(\rho(\underline{r}))$

where $\rho(\underline{r}) = \sum_{i<E_F} |\psi_i(\underline{r})|^2$.

So the potential felt by the electrons depends on their charge density, which must be found self-consistently



Iterate until input and output potentials are the same.

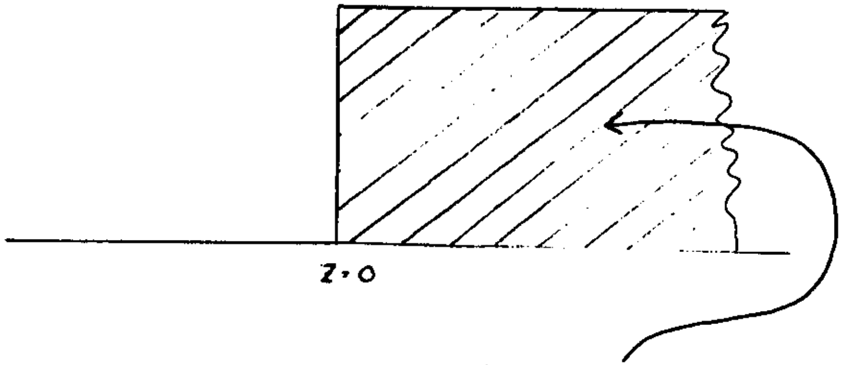
Lack of periodicity perpendicular to surface makes it difficult to solve the Schrödinger equation at the surface.

Jellium model of s-p bonded metals

(N. D. Lang and W. Kohn, Phys. Rev. B1 4555 (1970); N. D Lang in Solid State Physics 28 p 225 (1973)).

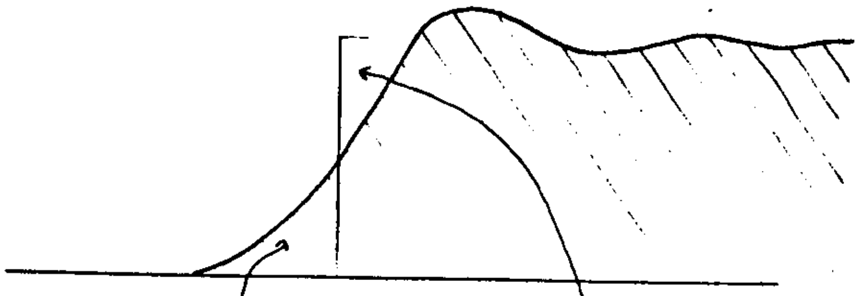
Weak pseudopotentials in s-p bonded metals like Na, Mg and Al ⟹ nearly-free-electron picture.

Zeroth approximation :

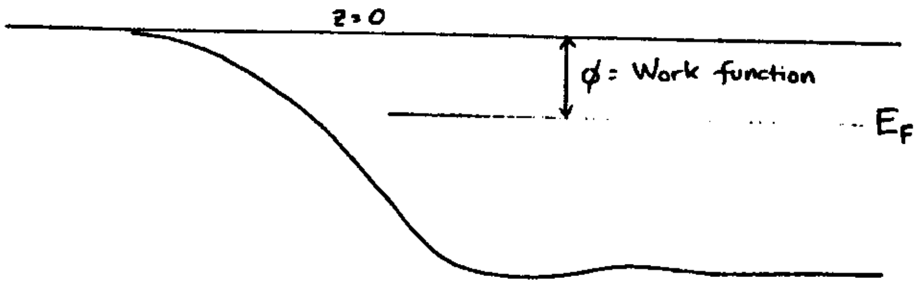


Ions smeared out into a uniform positive background, chopped off at Z = 0.

Electron density is roughly :



Excess negative charge + excessive positive charge ⟹ surface dipole, so that $V_{ion}+V_H+V_{xc}$ is :



Solution of Schrödinger equation with this potential is:

$$\psi_i(\underline{r}) \sim e^{i\underline{K}\cdot\underline{R}} \sin(k_z z - \gamma(k_z)),$$

$$E = \tfrac{1}{2}(K^2 + k_z^2)$$

In the surface region, the Schrödinger equation must be integrated numerically, and by matching amplitude and derivative in the asymptotic region, $\gamma$ can be found.

From the wavefunctions below $E_F$ $\rho(\underline{r})$ can then be found, hence $V_H + V_{xc}$.

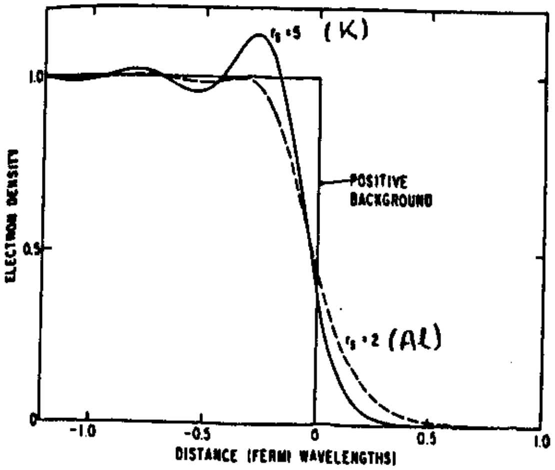
Self-consistency in $V$ is difficult to achieve at surface, because charge overflowing ⇒ surface dipole and shifts in whole potential. Standard procedure to cope with self-consistency

$$V^{(n)}_{input} = (1-\alpha)\,V^{(n-1)}_{input} + \alpha\,V^{(n-1)}_{output},$$

with <u>small</u> (~ 1 - 10%) mixing parameter.

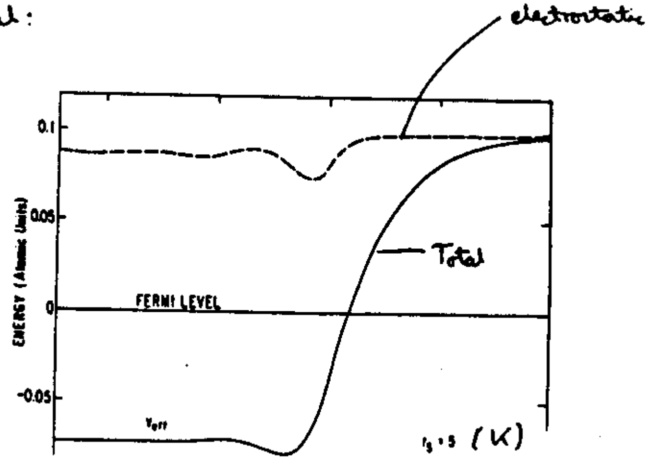
Lang and Kohn's results –

Charge density at surface:



Note overflow of charge at surface, and Friedel oscillations extending into bulk (decaying as $1/z^2$)

Potential:



## Work functions:

Effects of pseudopotential included via perturbation theory. A subtle problem because the pseudopotential affects two contributions to work function:

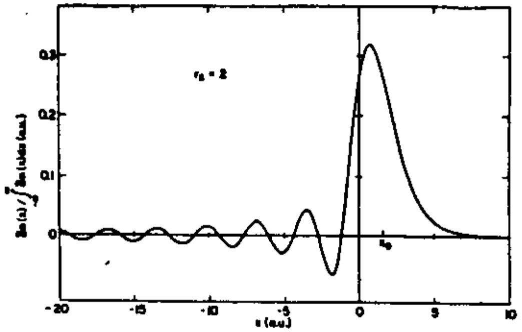
(i) mean potential inside solid

(ii) surface charge distribution.

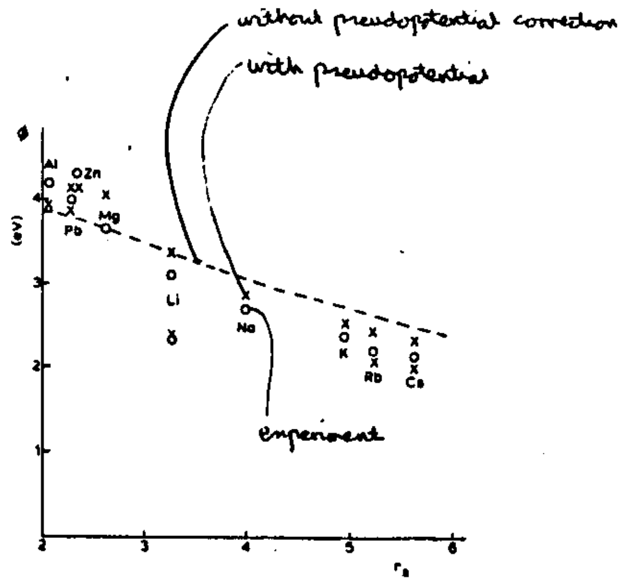
But $\phi$ : energy needed to remove e to $\infty$, so first-order perturbation theory gives effect of pseudopotential:

$$\delta\phi = \int d\underline{r}\ \ \delta V(\underline{r}) \left[ \underbrace{\rho_{N-1}(\underline{r}) - \rho_N(\underline{r})} \right]$$

charge deficit sits on surface of a metal, giving rise to an external field. So $[\rho_{N-1} - \rho_N]$ can be found from self-consistent calculations with and without field:



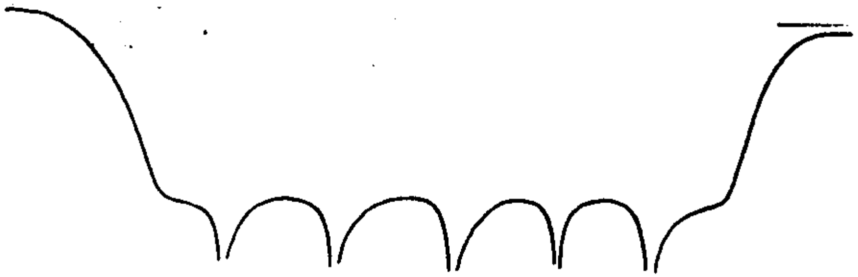
results -



note that work function tends to increase with electron density, but nevertheless remarkably uniform, between 2 - 4 eV: this is because in high electron density metals $E_F$ is big, but surface dipole is also big, and these effects tend to cancel.

## Slab calculations

To avoid difficulties of handling a semi-infinite system, slab geometry is often used, with slabs typically 5-7 layers thick:



System is now finite in z-direction, and standard basis set methods of solving Schrödinger equation can be used, e.g. LAPWs (H. Krakauer, M. Posternak and A.J. Freeman, 1979, Phys Rev. B <u>19</u> p 1706)

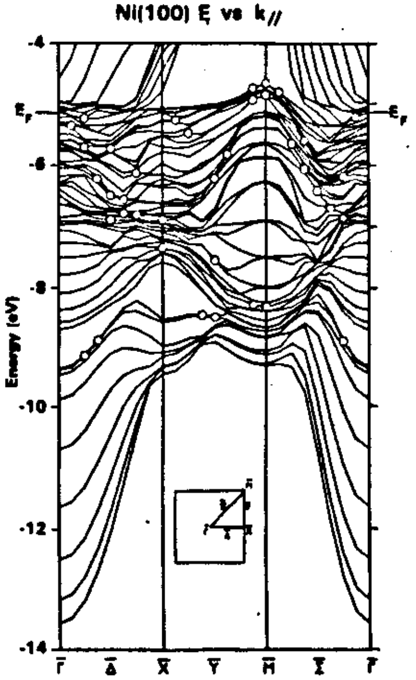
Gaussians (P.J. Feibelman, Phys. Rev. Letts. <u>54</u>, 2627 (1985))

Plane waves with pseudopotentials (S.G. Louie, K.M. Ho, J.R. Chelikowsky and M.L. Cohen, Phys. Rev. B <u>15</u>, 5627 (1977)).

Finite thickness $\Longrightarrow$ discrete states, at fixed $\underset{\sim}{k}$, and no <u>real</u> distinction between surface states, and bulk states at the surface. However, density of states adequate for most comparison with photoemission.

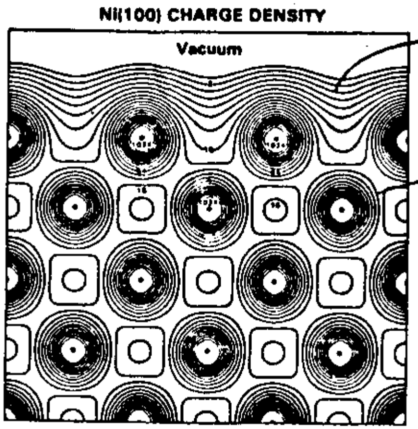
Example of slab calculation: Ni (001), 9-layer slab.

Two-dimensional energy bands as function of $\underline{k}$:



Ni(100) E vs k//

Charge density:



Ni(100) CHARGE DENSITY

note ρ decaying exponentially into vacuum

second-layer ρ is essentially bulk-like

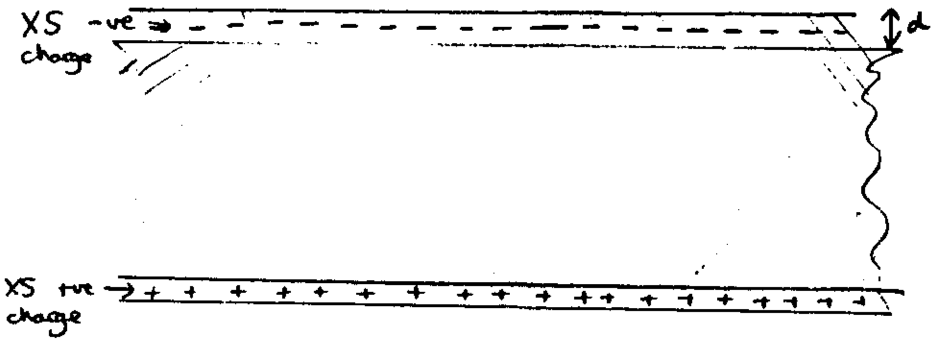
$\phi$ = 5.1 eV from calcn., c.f. expt'l 5.0 – 5.2 eV
(F.J. Arlinghaus, J.G. Gay & J.R. Smith PR <u>B21</u> p 20!,

## Many-body effects at surfaces

Electron-electron interaction ⇒ plasma oscillations

Bulk plasmons: (Kittel: Introduction to Solid St. Phys.)

Consider a slab of positive jellium with electron gas displaced by $d$:



Surface charge density on each side of slab $= \pm ned$ where $n =$ bulk electron density

$$\therefore \text{ Electric field in slab} = 4\pi ned$$

$$\therefore \text{ Force on electron} = 4\pi ne^2 d$$

$$\therefore \quad m\omega^2 d = 4\pi ne^2 d$$

$$\therefore \quad \omega^2 = 4\pi ne^2/m, \quad \text{(cgs)}$$

where $\omega =$ frequency with which electron gas oscillates – the bulk plasma frequency.

$$\therefore \quad \underline{\underline{\omega_p = \sqrt{4\pi ne^2/m}}}$$

Alternatively, equation of motion of classical electrons in an oscillating electric field is:

$$m\frac{d^2x}{dt^2} = eE, \quad \text{so with } x = x_0 e^{i\omega t}, \; E = E_0 e^{i\omega t},$$

$$x_0 = -\frac{eE_0}{m\omega^2}$$

$$\therefore \text{ Polarization } P = -\frac{ne^2}{m\omega^2}E$$

$$\therefore \quad D = \left(1 - \frac{4\pi ne^2}{m\omega^2}\right)E$$

$$\& \quad \epsilon(\omega) = 1 - \frac{4\pi ne^2}{m\omega^2}.$$

Clearly, finite $E$ and zero $D$ (self-sustaining oscillations) occur when

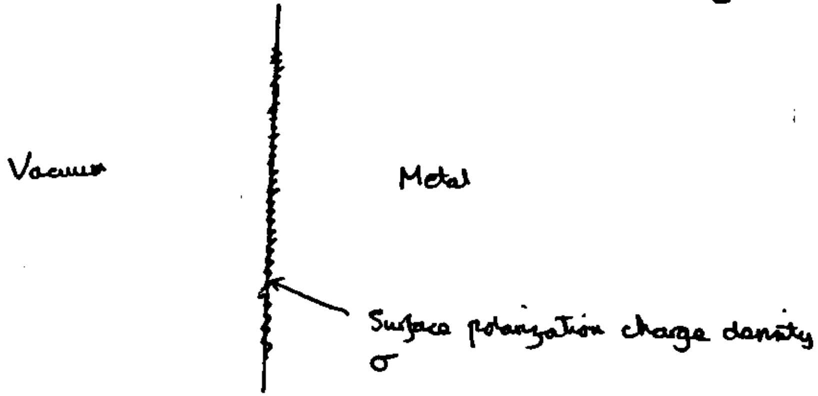
$$\epsilon(\omega) = 0$$

$$\therefore \quad \omega^2 = 4\pi ne^2/m\omega^2, \quad \text{as before.}$$

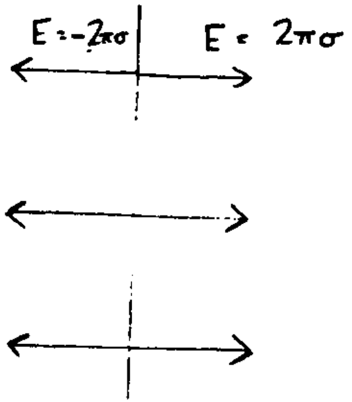
Microscopic study shows that $\epsilon$ is a function of wavevector as well as $\omega$; classical result corresponds to $q \to 0$ limit (D. Pines, Elementary Excitations in Solids, Benjamin 1963)

Surface plasmons:

Self-sustaining, oscillating, surface polarization charge –



Electric field produced by this is:



So $D_{vacuum} = -2\pi\sigma$, $D_{metal} = 2\pi\sigma\epsilon$.

But $D_\perp$ is continuous, ∴ $\epsilon(\omega) = -1$.

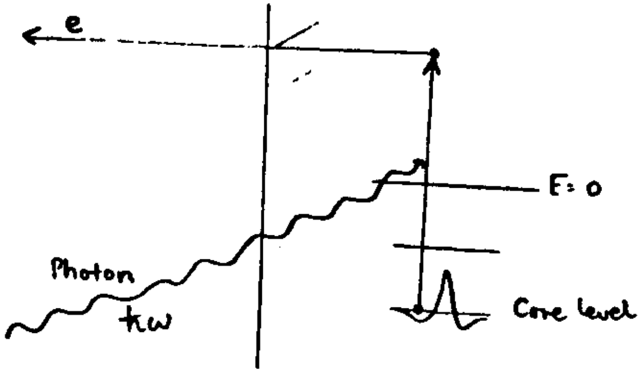
So surface plasmon occurs when $\epsilon(\omega) = -1$

$$\therefore \quad \underline{\omega_s = \omega_p/\sqrt{2}}.$$

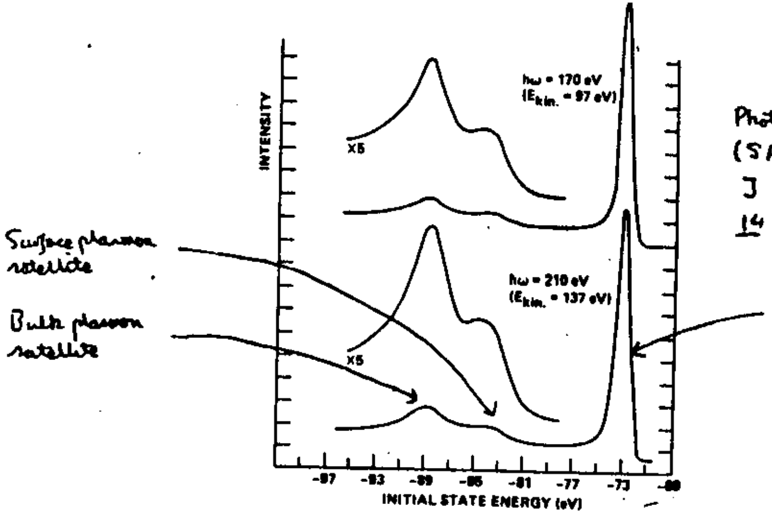
(R.H. Ritchie, Phys Rev. 106, 874 (1957))

The plasma oscillations are quantized, with energy $\hbar\omega_p$, $\hbar\omega_s$. For Al, $\hbar\omega_p \simeq 15$ eV, $\hbar\omega_s \simeq 10$ eV.

Plasmons show up in energy-loss experiments in electron scattering, e.g. as satellites in core-level photoemission:

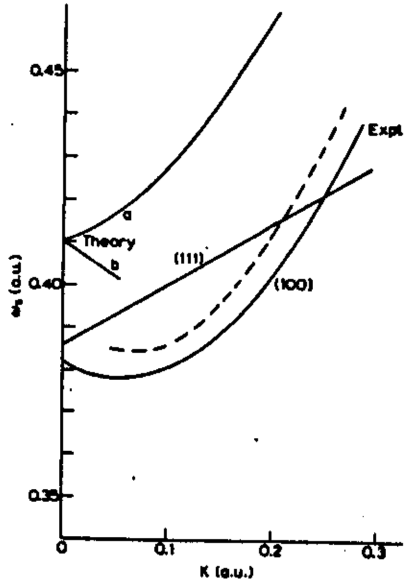


Photon absorbed, excites core electron into a state which can leave the solid. Outgoing e + core hole can excite surface and bulk plasmons:



Photoemission from Al 2p (SA Flodström et al J Vac. Sci. Technol. 14 p303 (1977))

Surface plasmons have well-defined wavevector $\underline{K}$ parallel to surface, and microscopic theory gives dispersion:



Al surface plasmon dispersion

a } Theory with different surface charge density profiles
b } (J.E. Inglesfield and E. Wikborg, Solid St. Commun. <u>14</u> (1974) p 661,
P.J. Feibelman, Phys Rev. <u>B9</u> (1974) p 7077)

Expt - Inelastic LEED (C.B Duke et al. Phys Rev. <u>B12</u> (1974) p.4050)

Surface plasmons important, because external charges interact with them. Van der Waal's forces, for example, can be treated as the shift in zero-point energy of surface plasmons.