

SOME THEORY ABOUT SURFACE STATES *

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The basic elements of the theory of surface states is reviewed. It is divided into its components as a problem of matching wave functions outside the surface to those inside the bulk crystal. The latter are evanescent waves, and it is shown how they are related to the ordinary Bloch bands of the crystal by extending these to complex k vectors. This allows one to relate to the problem of surface states some advances made in the theory of band structures.

One way of studying surface states has been to set up a model, or better a range of models, calculate numerically any surface states there may be, and then try to draw systematic conclusions. The difficulty is to decide which features are significant and which ones incidental to the model and then to discover in more basic terms why certain results emerge. There is, therefore, some value in proceeding another way, namely to dissect the problem and

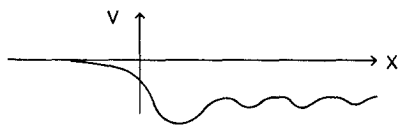


Fig. 1. Potential near a surface.

study its components. Basically we have a problem of matching: matching the wave function ψ_{Right} in the regular crystal to the wave function ψ_{Left} in the region outside the surface (fig. 1). The last atom at the surface may be of the same kind as the underlying crystal or it may be a different impurity atom. Let AA' represent the value of x where we affect the matching.

We start by restricting ourselves to the one-dimensional case, and consider first an energy E in the band. We can imagine that ψ_L is integrated inwards from $\psi_L = 0$ at $x = -\infty$ on the left, up to some definite value of ψ_L and $\psi'_L (\equiv d\psi/dx)$ at the matching point. On the right we put

$$\psi_R = \alpha\psi_k + \beta\psi_{-k} \quad (1)$$

where ψ_k and ψ_{-k} are the Bloch functions with energy E from the band. The point is that since we have two functions and two constants α and β in (1), we can always affect the matching for any energy in the band.

* Invited paper.

When, however, E lies in a band gap, there are still two solutions for ψ in the crystal – an ordinary second order differential equation must always have two solutions – but they are now evanescent waves as is well known, the one ψ_+ growing and the other ψ_- decaying on the average exponentially with x . To be precise, we have ¹⁾

$$\psi_{\pm}(x+a) = -\exp(\pm\mu a)\psi_{\pm}(x). \quad (2)$$

In this equation, we have a minus sign in front of the exponential if the band gap is at the zone boundary $k = \pi/a$ as assumed here, and a plus sign for a band gap at $k = 0$.

Where do these evanescent waves come from? Are they some spurious solutions unrelated to the familiar ideas of band structure? We shall now show how on the contrary they are very much part of the same scheme of things. We first note that (2) can be expressed in the usual form of the Bloch theorem

$$\psi_k(x+a) = \exp(ika)\psi_k(x) \quad (3)$$

if we take a complex value of k , namely

$$k = \pi/a \pm i\mu. \quad (4)$$

In fact it is not difficult to define E for an arbitrary complex k ²⁾. In general it is complex, but it is real along the real axis, and at values of k of the form (4) from $\mu = 0$ out to some μ_{\max} and then back again to $\mu = 0$ (fig. 2). The energy is increasing all the while along this route, so that we have passed



Fig. 2. Regions in complex k space where E is real.

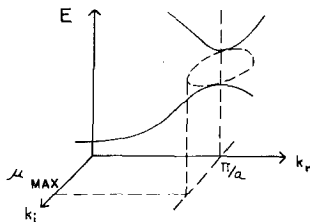


Fig. 3. Real lines in complex k space.

continuously from the lower to the upper band. In fig. 3 we plot E , where it is purely real, as a function of the real and imaginary parts k_r , k_i of k . We call these “real lines”. All pairs of bands are joined by such little loops of real line with complex k .

We see, therefore, that both the ordinary band states and the evanescent waves (2) are parts of a larger continuous whole, the complex band structure, namely the energy E considered as a complex function of the complex

variable k . This has important consequences. At the crudest level we can say that the wave function changes continuously along the loop, i.e., from $\cos \pi x/a$ to $\sin \pi x/a$ in the nearly free electron approximation, so that ψ'/ψ moves from zero to infinity. This result is independent of the nature of the periodic potential or the size of the band gap, something we shall use presently. At a more sophisticated level we can derive E and ψ for the complex k from what we know of the ordinary band states at real k . For instance, the " $k \cdot p$ method" for calculating band structures around some point k_0 works just as well for complex k as for real k . Thus we find that μ_{\max} is given by

$$\mu_{\max} \approx \frac{V_1}{(2\pi/a)} \quad (5)$$

where V_1 is half the band gap, which means ψ_{\pm} fall off over a distance greater than or equal to about V_1/E_F atomic spacings, typically 5 atoms. Incidentally, this slow fall-off applies whether or not there is an impurity atom on the surface with a strongly bound state but the amplitude of the tail in the substrate can vary. The slow fall-off also applies to metals just as much as to semiconductors, nor is there any reason why the coulomb electron-electron interaction should basically affect it (cf. the long range Friedel wiggles in the screening round an impurity). Finally, it is clear that the whole modern apparatus of orthogonalized plane waves and pseudo-potentials for calculating band structures can be applied just as well to determining the evanescent waves, and there is no reason why at least this part of the surface state problem should not be solved with as realistic potentials and accurate results as ordinary band structure calculations.

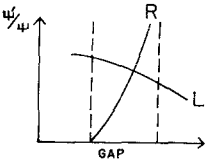


Fig. 4. Matching ψ'/ψ from Left and Right.

Having determined the evanescent waves in the periodic crystal, we return now to the problem of matching them to ψ_L . Instead of (1) we can use only a single function for ψ_R , namely, the decreasing exponential. We have only one constant to adjust, and cannot therefore make the match at an arbitrary given E . Instead we plot ψ'/ψ for ψ_L and ψ_R over a range of E , and if they cross that determines an allowed surface state (fig. 4). As already mentioned ψ'_R/ψ_R varies from 0 to ∞ over the gap, so that the existence or otherwise of a surface state is determined more or less only by the sign of ψ'_L/ψ_L .

Since ψ'_L/ψ_L is positive in the exponential region right outside the material, we conclude that the really crucial part of the whole calculation lies in the integration of ψ_L through the first layer of atoms. We expect the existence of surface states to be relatively insensitive to other features such as the exact bands in the substrate crystal and to be determined broadly speaking by some simple feature such as the sign of ψ'/ψ .

We turn now to the three-dimensional case, and assume that the surface is undistorted in the y and z directions parallel to the surface. The periodicity allows us to define k_y and k_z as good quantum numbers. The matching now has to be done over a whole plane, $x = 0$ say, or rather over a cell of this plane with k_y, k_z taking care of the rest. We need for this an infinite set of functions. The important ones are evanescent waves in the lower band gaps, the higher ones having a pure imaginary k_x given by

$$k_{x,mn} = -i[(k_y + m\pi/a)^2 + (k_z + n\pi/a)^2 - E]^{\frac{1}{2}}. \quad (6)$$

A section of a band structure with fixed k_y, k_z is shown in fig. 5. The bands are again joined by loops of real line in complex k . These can now occur not only at $k = 0$ (e.g., A'') and at the zone face (B), but also in the body of the zone such as at D, contrary to what Goodwin³) ostensibly proved. The states (6) lie on real lines leaving the bottom of the bands as at A' . Every maximum and minimum in the band structure has a pair of real lines leaving it running into the complex plane⁴).

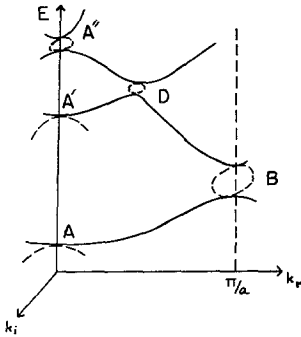


Fig. 5. Real lines in a section of a three-dimensional band structure.

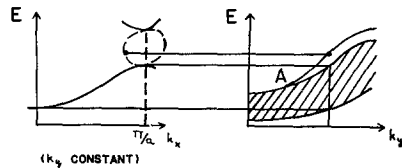


Fig. 6. Surface band plotted against k_y .

The matching conditions again determine a particular energy in the gap for the surface state if there is one, and the variation of this energy with k_y and k_z forms a surface band (fig. 6). Note that the surface state has to lie in a band gap of a section of the energy spectrum at a particular k_y, k_z , but this energy may or may not lie in the band at some different k_y, k_z . Note

also that the surface band may disappear beyond a certain k_y , k_z as shown at A (fig. 6).

Some practical points now arise, particularly relating to diamond, silicon and germanium, which may be worth mentioning. Firstly, a real source of difficulty in the past has been lack of precise knowledge about the absolute energy of the band structure relative to the vacuum level since this seriously affects ψ_L , but this can now be measured satisfactorily. Secondly, the surfaces of these materials are almost certainly somewhat distorted structures as mentioned by several abstracts for this conference which makes calculations very difficult. Some chemical model for the topmost surface layer of atoms will probably have to be used. However, chemical effects like dangling bonds and conjugated chains apart, when integrating ψ'_L/ψ_L inwards the result may depend much more on the density of atoms as a function of x normal to the face than on their disposition in y and z . Once E , k_y and k_z have been fixed, the wave function has relatively little freedom left to it as long as the atoms keep at a reasonable interatomic distance; at least this is so in the bulk structure of metals and alloys. Incidentally no one has so far determined exactly how the conduction and valence bands in the group IV semiconductors are joined to one another by loops of real line in complex k . There must be three pairs of real lines leaving the top of the valence band at $k = 0$ and it would help to know where they join the valence bands in order to write down possible wave functions for the surface states. It is interesting to note that in some sense band structures have less freedom about how they go than one might expect. Thus the bottom of the conduction band along ΓL in the zone has the shape shown in fig. 7a. The minimum is at the zone face at L. A slight change in potential cannot produce a dip with a minimum inside the zone because it would need topologically quite a different way of joining up the bands (fig. 7b).

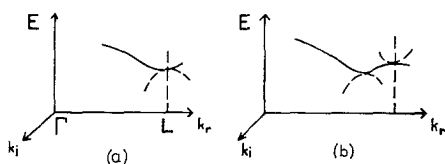


Fig. 7. Real line near zone face, (a) as in silicon and germanium, (b) if a minimum developed inside the zone face.

In recent years, there have been some developments in the ordinary theory of band structures which will probably affect surface state calculations in the future. Up to the present, the most realistic calculations have been done with methods based on LCAO (linear combination of atomic orbitals or

“tight binding”). In band structure calculations the trend has been exactly the reverse. All methods currently used for non-transition metals and semiconductors can be cast into the form of plane waves being scattered by some weak pseudo-potential of the atoms⁵⁾. In the LCAO method, one needs localized functions, and one can prove quite generally⁶⁾ that the most localized Wannier function that one can form from a band falls off as $\exp(-\mu_{\max}|x|)$ where μ_{\max} has the same value as in (5); i.e., the function cannot be localized better than 5 atomic spacings or more, and very high order overlap matrix elements have to be considered. It is not commonly realized that diamond is closer to being a free electron gas than copper is, in the sense that the band gap is smaller compared with the band width. Similarly the band structure of silicon can be fitted better with fewer parameters using a plane wave approach than with the LCAO Slater-Koster scheme⁷⁾. In particular the LCAO scheme cannot easily describe the sharp curvature of the bands near the maxima and minima, which is just where the evanescent waves in the band structure also lie.

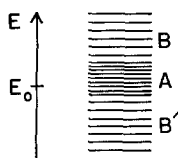


Fig. 8. Energy levels with a virtual bound state.

Finally, it remains to mention resonant or virtual bound states which come into some of the abstracts submitted for this conference. These are not true surface states in the sense discussed so far. Suppose some surface impurity atom has a well-defined state which is only slightly coupled to the atoms of the crystal, but whose energy E_0 falls in one of the bands of the crystal. The energy levels of the combined system are shown schematically in fig. 8. The energy levels at B and B' represent the ordinary quasi-continuum of band states. Then around E_0 there is a region (A) where the density of levels is abnormally high. The states in B, B' have $|\psi|^2$ large in the crystal and small on the impurity atom; the states in A are the reverse.

As discussed in detail in other abstracts for this conference, most of what has been said so far can be applied with very little modification to surface modes of vibration of a crystal, related to the ordinary phonon bands. Here one finds an interesting example of the difference between a genuinely local mode around an impurity surface atom, and virtual bound modes coupled to the phonon modes of the crystal. Suppose we give the atom a high energy. If there is a local mode, the energy can only decay out of it slowly via the anharmonic effects. If, however, there are only virtual bound modes, then

these have an amplitude both on the surface atom and in the crystal; the localization of the energy on the surface atom represents a phase coherence of the resonant modes and the energy will spread into the crystal as fast as they go out of phase, i.e., in a time \hbar/Δ where Δ is the width of the region A in fig. 8. This is determined by the strength of the coupling to the crystal, and not by higher anharmonic effects.

References

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