

2. Electron Surface Levels for a Weak Periodic Potential¹⁰

The method of Chapter 9 can be used to investigate electronic surface levels. Consider a semi-infinite crystal with a plane surface, perpendicular to a reciprocal lattice vector \mathbf{K} (crystal surfaces are parallel to lattice planes). Taking the x -axis to lie along \mathbf{K} and the origin to be a Bravais lattice point, to a rough approximation we can represent the potential of the semi-infinite crystal by $V(x) = U(x)$, $x < a$; $V(x) = 0$, $x > a$. Here $U(x)$ is the periodic potential of the infinite crystal. The distance a lies between zero and the interplanar distance in the family of planes parallel to the surface, and should be chosen in any particular problem to give that $U(x)$ which most resembles the actual potential at the surface.

¹⁰ See E. T. Goodwin, *Proc. Camb. Phil. Soc.* **35**, 205 (1935).

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We continue to assume that the Fourier components $U_{\mathbf{k}}$ are real. However, if we wish the lowest level outside of the crystal to have energy 0, we can no longer neglect the zeroth Fourier component U_0 within the crystal, as we did in Chapter 9. The result of retaining U_0 is simply to shift the formulas of Chapter 9 for the levels within the crystal by that amount. Note that U_0 need not be small for the method of Chapter 9 to work, in contrast to the Fourier components $U_{\mathbf{k}}$, with $\mathbf{k} \neq 0$.

We examine a Bloch level for the infinite crystal with a wave vector \mathbf{k} that is near the Bragg plane determined by \mathbf{K} , but near no other Bragg plane, so that in a weak periodic potential the wave function of the level is a linear combination of plane waves with wave vectors \mathbf{k} and $\mathbf{k} - \mathbf{K}$. In Chapter 9 we required \mathbf{k} to be real, to satisfy the Born-von Karman boundary condition. In a semi-infinite crystal, however, the component of \mathbf{k} normal to the crystal surface need not be real, provided that it yields a decaying wave in the negative x -direction (into the metal). Outside of the metal, the Bloch function must be joined onto a solution of the free-space Schrödinger equation that decays in the positive x -direction (away from the metal). Thus, outside the metal we take

$$\psi(x) = e^{-\epsilon x + i k_{\parallel} x}, \quad x > a, \quad (18.33)$$

and inside,

$$\psi(x) = e^{i\epsilon_0 x + i k_{\parallel} x} \{c_{\mathbf{k}} + c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}x}\}, \quad x < a, \quad (18.34)$$

where k_{\parallel} is the part of \mathbf{k} parallel to the surface, and the coefficients in (18.34) are determined by the secular equation (9.24) (with the energy ϵ shifted by the constant U_0):

$$\begin{aligned} (\epsilon - \epsilon_{\mathbf{k}}^0 - U_0)c_{\mathbf{k}} - U_{\mathbf{K}}c_{\mathbf{k}-\mathbf{K}} &= 0, \\ -U_{\mathbf{K}}c_{\mathbf{k}} + (\epsilon - \epsilon_{\mathbf{k}-\mathbf{K}}^0 - U_0)c_{\mathbf{k}-\mathbf{K}} &= 0. \end{aligned} \quad (18.35)$$

- (a) Verify that for (18.35) to yield real energies for $q \neq 0$ it is necessary that $\epsilon_0 = K/2$.
 (b) Show that when $k_{\parallel} = K/2$, the resulting energies are

$$\epsilon = \frac{\hbar^2}{2m} \left(k_{\parallel}^2 + \frac{1}{4} K^2 - q^2 \right) + U_0 \pm \sqrt{U_{\mathbf{K}}^2 - \left(\frac{\hbar^2}{2m} qK \right)^2}. \quad (18.36)$$

- (c) Show that continuity of ψ and $V\psi$ at the surface leads to the condition

$$p + q = \frac{1}{2} K \tan \left(\frac{K}{2} a + \delta \right), \quad (18.37)$$

where

$$\frac{c_{\mathbf{k}}}{c_{\mathbf{k}-\mathbf{K}}} = e^{2i\delta}. \quad (18.38)$$

- (d) Taking the case $a = 0$, and using the fact that outside of the metal

$$\epsilon = \frac{\hbar^2}{2m} (k_{\parallel}^2 - p^2), \quad (18.39)$$

show that (18.35) to (18.39) have a solution:

$$q = -\frac{1}{4} K \frac{U_{\mathbf{K}}}{\epsilon_0} \sin 2\delta,$$

where

$$\sec^2 \delta = -\frac{(U_0 + U_{\mathbf{K}})}{\epsilon_0}, \quad \epsilon_0 = \frac{\hbar^2}{2m} \left(\frac{K}{2} \right)^2. \quad (18.41)$$

(Note that this solution exists only when U_0 and $U_{\mathbf{K}}$ are negative, and $|U_0| + |U_{\mathbf{K}}| > \epsilon_0$.)

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