Appendix JJ

The Band Gap

To find the form of the wave function and the energy near the zone boundary, we consider the Schrödinger equation for the diffracted electron

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi_k = \varepsilon(k)\psi_k. \tag{JJ.1}$$

According to Eqs. (8.63) and (8.58), the wave function and the potential energy may be expressed in terms of plane waves as follows:

$$\psi_k(\mathbf{r}) = \sum_{g'} \alpha_{k-g'} e^{i(k-g')} \cdot \mathbf{r}, \tag{JJ.2}$$

and

$$V(\mathbf{r}) = \sum_{g''} V_{g''} e^{ig''\cdot\mathbf{r}}, \tag{JJ.3}$$

where the summations over g' and g'' extend over the vectors of the reciprocal lattice. Substituting these equations into Eq. (JJ.1) and using Eq. (8.63), we get

$$\sum_{g'} \varepsilon^0(k-g')\alpha_{k-g'} e^{i(k-g')\cdot\mathbf{r}} + \sum_{g',g''} V_{g''}\alpha_{k-g'} e^{(k-g'+g'')\cdot\mathbf{r}} = \varepsilon(\mathbf{k})\sum_{g'}\alpha_{k-g'} e^{i(k-g')\cdot\mathbf{r}}, \tag{JJ.4}$$

where $\varepsilon^0(\mathbf{k}-g')$ is the kinetic energy of a free electron with wave vector $\mathbf{k} - g'$. The term on the right-hand side of this last equation may be grouped together with the first term on the left-hand side giving

$$\sum_{g'}\left[\varepsilon^0(k-g') - \varepsilon(k)\right]\alpha_{k-g'} e^{i(k-g')\cdot\mathbf{r}} + \sum_{g',g''} V_{\mathbf{g}''}\alpha_{k-g'} e^{i(k-g'+g'')\cdot\mathbf{r}} = 0. \tag{JJ.5}$$

Multiplying Eq. (JJ.5) through from the left by $1/V^{1/2}$ and by the function,

$$\psi_k^*(\mathbf{r}) = \frac{1}{V^{1/2}} e^{-i\mathbf{k}\cdot\mathbf{r}}, \tag{JJ.6}$$

integrating over all space, and using Eq. (8.56), we obtain

$$\sum_{g'}[\varepsilon^0(\mathbf{k}-\mathbf{g}') - \varepsilon(\mathbf{k})]\alpha_{\mathbf{k}-\mathbf{g}'}\delta_{\mathbf{k},\mathbf{k}-\mathbf{g}'} + \sum_{g',g''} V_{g''}\alpha_{k-g'}\delta_{\mathbf{k},\mathbf{k}-\mathbf{g}'+\mathbf{g}''} = 0. \tag{JJ.7}$$

The Kronecker delta function $\delta_{k,k-g'}$ occurring in the first term is equal to one if $k = k - g'$, and, otherwise, is equal to zero. This Kronecker delta thus has the effect of reducing the first summation to a single term for which $g' = 0$. Similarly, the Kronecker delta in the second summation is one if $g' = g''$ being zero otherwise and reduces the double summation to a single summation. We have

$$[\varepsilon^0(\mathbf{k}) - \varepsilon(\mathbf{k})]\alpha_{\mathbf{k}} + \sum_{g'} V_{g'}\alpha_{k-g'} = 0. \tag{JJ.8}$$

As illustrated in Fig. 8.22, the crystal filed causes the wave function with wave vector $\mathbf{k}$ to interact with the state with wave vector $\mathbf{k} - \mathbf{g}$. For a particular reciprocal lattice vector $\mathbf{g}$, we thus ignore all coefficients except α_k and α_{k-g}. Equation (JJ.8) then becomes

$$[\varepsilon^0(\mathbf{k}) - \varepsilon(\mathbf{k})]\alpha_k + V_0\alpha_k + V_g\alpha_{k-g} = 0. \tag{JJ.9}$$

We note that the Fourier coefficient V_0 corresponds to a constant term in the potential energy $V(r)$ and may thus be taken to be zero. This eliminates the second term in the above equation, and we obtain

$$[\varepsilon^0(\mathbf{k}) - \varepsilon(\mathbf{k})]\alpha_k + V_g\alpha_{k-g} = 0. \tag{JJ.10}$$

A second equation for the coefficients, α_k and α_{k-g}, can be obtained by multiplying Eq. (JJ.5) through from the left by the function,

$$\psi^*_{k-g}(\mathbf{r}) = \frac{1}{V^{1/2}}e^{-i(k-g)\cdot\mathbf{r}}, \tag{JJ.11}$$

and integrating over all space as before. We get

$$[\varepsilon^0(\mathbf{k} - \mathbf{g}) - \varepsilon(\mathbf{k})]\alpha_{k-g} + \sum_{g'} V_{g'-g}\alpha_{k-g'} = 0. \tag{JJ.12}$$

Limiting ourselves again to the terms depending upon the coefficients, α_k and α_{k-g}, we note that the term in the sum for which $g' = g$ vanishes since we have supposed that the Fourier coefficient V_0 is equal to zero. Setting $g' = 0$ in the above summation leads to the equation

$$V_{-g}\alpha_k + [\varepsilon^0(k - g) - \varepsilon(\mathbf{k})]\alpha_{\mathbf{k}-\mathbf{g}} = 0. \tag{JJ.13}$$

The Fourier coefficient V_{-g} appearing in Eq. (JJ.13) is equal to the coefficient V^*_g which appears in the Fourier expansion of $V(\mathbf{r})^*$.

A trivial solution of Eqs. (JJ.10) and (JJ.13) can be obtained by taking the coefficients, α_k and $\alpha_{\mathbf{k}-\mathbf{g}}$, equal to zero. If the determinant of Eqs. (JJ.10) and (JJ.13) is not equal to zero, this is the only solution of the equations. In order to find a physically meaningful description of the diffracted electron, we thus set the determinant of the coefficients equal to zero. We have

$$\begin{bmatrix} [\varepsilon^0(\mathbf{k}) - \varepsilon(\mathbf{k})] & V_g \\ V^*_g & [\varepsilon^0(\mathbf{k} - \mathbf{g}) - \varepsilon(\mathbf{k})] \end{bmatrix} = 0. \tag{JJ.14}$$

The two free-electron states $e^{k\cdot r}$ and $e^{(k-g)\cdot r}$ have the same energy, $\varepsilon^0(\mathbf{k}) - \varepsilon(\mathbf{k} - \mathbf{g})$. If we denote this common value by ε^0, the quadratic equation resulting from Eq. (JJ.14) can be written

$$[\varepsilon(\mathbf{k}) - \varepsilon^0]^2 - |V_g|^2 = 0. \tag{JJ.15}$$

Equation (JJ.15) has two solutions

$$\varepsilon(\mathbf{k})^\pm = \varepsilon^0 \pm |V_g|. \tag{JJ.16}$$

The interaction of the two free-electron states with wave vectors $\mathbf{k}$ and $\mathbf{k} - \mathbf{g}$ thus cause a discontinuity in the energy at the zone boundary. The magnitude of the discontinuity depends upon the Fourier coefficients, V_g, which occur in the expansion of the potential energy.

An expression for the Fourier coefficients can be obtained by applying Eq. (8.26) to the periodic function $V(\mathbf{r})$, which gives

$$V_g = \frac{1}{v_{cell}} \int V(\mathbf{r})e^{-ig\cdot\mathbf{r}}\, dV. \tag{JJ.17}$$

We now divide Eq. (JJ.17) into real and imaginary parts by using Eurler's equation

$$V_g = \frac{1}{v_{cell}} \int V(\mathbf{r})\cos(g\cdot r)\, dV - \frac{i}{v_{cell}} \int V(\mathbf{r})\sin(g\cdot r)\, dV. \tag{JJ.18}$$

Most of the common three-dimensional lattices are symmetric with respect to inversion $\mathbf{r} \longrightarrow -\mathbf{r}$. The body- and face-centered cubic structures and the hexagonal close packed structures described in Chapter 8 are invariant with respect to

inversions provided that a suitable choice is made of the origin. If the potential $V(\mathbf{r})$ is symmetric with respect to inversion, the second integral in Eq. (JJ.18) vanishes, and the equation for the Fourier coefficients becomes

$$V_g = \frac{1}{v_{\text{cell}}} \int V(\mathbf{r}) \cos(g \cdot r) \, dV_r. \tag{JJ.19}$$

Since the electrons are attracted to the ion cores, the potential energy function $V(\mathbf{r})$ is negative in the neighborhood of each atom. It thus follows from Eq. (JJ.19) that the Fourier coefficient $V_{\mathbf{g}}$ are negative real numbers.

As discussed in Chapter 8, the crystal field mixes the two free-electron states $e^{k \cdot r}$ and $e^{(k-r) \cdot r}$ to produce states having energies ε^- and ε^+. We can derive a condition for the coefficients of the lower state by substituting the value of ε^- given by Eq. (JJ.16) into Eq. (JJ.10) to obtain

$$|V_g| \alpha_k + V_g \alpha_{k-g} = 0. \tag{JJ.20}$$

Since V_g is negative, $|V_g|$ is equal to $-V_g$. Using this result together with Eq. (JJ.20), one may readily show that the coefficients α_{k-g} is equal to the coefficient $\alpha_{\mathbf{k}}$. Similarly, we can derive a condition for the coefficients of the upper state by substituting the value of ε^+ given by Eq. (JJ.16) into Eq. (JJ.10) and using the relation $|V_g| = -V_g$ to obtain

$$V_g \alpha_k + V_g \alpha_{k-g} = 0. \tag{JJ.21}$$

This equation implies that for the upper state the mixing coefficient α_{k-g} is equal to $-\alpha_k$. The spatial form of the wave functions for the lower and upper states are discussed in the text.