14

Bloch Waves

CHAPTER PREVIEW

This topic is rather mathematical, with long sequences of differential equations. The discussion of Bloch waves given here follows the treatment of Hirsch et al. which, in turn, was based on the original analysis of electron diffraction by Bethe (1928). The notation we will use closely follows that used by Bethe. Remember that **g** can be any reciprocal-lattice vector, although we will also use it to represent a specific vector.

This analysis leads directly to one of the most important concepts used to understand images of defects in thin foils: it explains the physical origin of the *extinction distance,* $\xi_{\mathbf{g}}$, and thus shows why it is so important. So again it is worth persevering. However, many successful microscopists have skipped this topic. We suggest you first skim through this chapter. Then, when you've recognized its importance and seen the key equations, go back to the beginning and work your way through.

We make certain assumptions about the materials we are considering and what voltages are used. You must keep these assumptions in mind when applying these concepts. The most important point is that, within the limits of our approximations, the analysis is rigorous and we can really understand the meaning of $\xi_{\mathbf{g}}$. If you've previously come across the idea of kinematical diffraction, this chapter will make it clear why this theory is, at best, only an approximation to reality.

We start by considering the property of a crystal which we know quite well, namely, the inner potential. You should remember that, strictly speaking, everything we are about to go through in this section applies only to perfect crystals; crystals with surfaces are not 'perfect.' The periodic nature of the crystal potential leads to the concepts of Bloch functions and Bloch waves.

We include a discussion of the two-beam case, since this can easily be solved analytically and can be related directly to the results discussed in Chapter 13 on diffracted beams. In Chapter 15 we will discuss a graphical representation of the equations we are deriving here. As with the Ewald sphere and reciprocal lattice, the diagrams make for an easier understanding and give a useful guide when you are actually using the TEM. We will consider absorption of Bloch waves here but when we use it in, e.g., Section 24.7, the physical significance will be more obvious.

14.1 WAVE EQUATION IN TEM

We are going to modify the Schrödinger equation for use in TEM to explain why the Bloch waves have the form they do. We are not going to try to be mathematically rigorous in deriving this modified equation; reference texts for this purpose are listed at the end of the chapter. Let's start with the time-independent Schrödinger equation

$$\left[-\frac{h^2}{8\pi^2 m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad (14.1)$$

The first term (in ∇^2) represents the kinetic energy and the second term, the potential energy; E represents the total energy. In TEM we usually talk in terms of the accelerating voltage and the crystal potential and, therefore, we rearrange this equation in terms of voltages. In doing so, we have to be careful about signs since the charge on the electron is negative and the applied electric field (associated with the accelerating voltage) points toward the gun! All that equation 14.1 says is that the electron has a kinetic energy due to the acceleration it is given in the gun. Initially, this is the total energy of the electron. When the electron passes through the crystal, it will have a potential energy due to the periodic potential associated with the atoms in the crystal.

THE SIGNS

- The charge on the electron, q, is a negative number, –e, where e is a positive number.
- The accelerating voltage, $-V$ (usually between 100 kV and 1 MV), is negative for a positive charge leaving the gun. This quantity, $-V$, is really the 'electric-field potential.'
- The initial energy given to the electron is a positive number, E (in eV); it is just the charge times the accelerating voltage. We can write this as eV where both e and V are positive numbers.
- The potential inside the crystal, $V(\mathbf{r})$, is a positive number reaching a local maximum at the nucleus of an atom; the nucleus is positive.
- The potential energy, V, of the electron outside the crystal is zero; it decreases when the electron is inside the crystal (V is q times $V(\mathbf{r})$, i.e., $-eV(\mathbf{r})$) and is therefore always a negative number.

Now we can rearrange equation 14.1 in terms of the accelerating voltage and the crystal potential

$$\nabla^2\psi(\mathbf{r}) + \frac{8\pi^2 me}{h^2}[V + V(\mathbf{r})]\psi(\mathbf{r}) = 0 \tag{14.2}$$

The task before us is obvious: we have to solve equation 14.2. In general, however, this is a difficult problem! What makes it possible for us is that $V(\mathbf{r})$ has special properties because we are only considering crystalline materials.

14.2 THE CRYSTAL

The basic property of a crystal is that its inner potential, $V(\mathbf{r})$, is *periodic*. We can therefore express this property as

$$V(\mathbf{r}) = V(\mathbf{r}+\mathbf{R}) \tag{14.3}$$

where $\mathbf{R}$ represents any lattice vector of the crystal and, as usual, $\mathbf{r}$ represents any real-space vector. Equation 14.3 is the fundamental definition of a perfect crystal: the environment at point $\mathbf{r}$ is identical to that at point $\mathbf{r} + \mathbf{R}$. We can draw this inner potential as shown in Figure 14.1 for the one-dimensional case and you can imagine it in 3D. The atomic nuclei are positively charged; the surrounding electrons gradually screen this charge and the atom appears neutral from the outside. In a crystal, a nucleus is never far away, so an electron which we 'shoot' through the crystal will always see a positive potential; hence $V(\mathbf{r})$ is always positive as noted in Section 14.1 and in Figure 3.1.

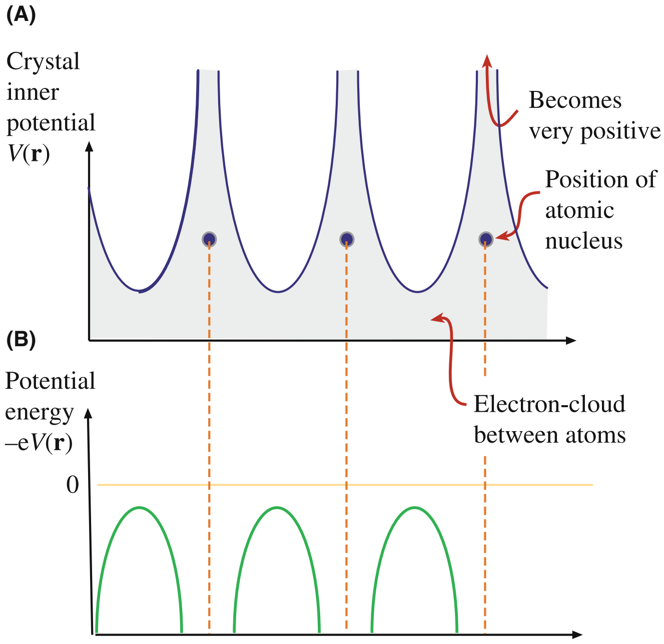

FIGURE 14.1. (A) The local charge sensed by the beam electron as it passes through a metal, represented as a row of 'ion' cores (black circles) in a sea of electrons. The local charge is very large and positive in the vicinity of the ion and becomes small, but not zero between the ions. The difference between the minimum charge and zero corresponds to the mean inner potential of the crystal, which is a few eV (positive). So the beam electron experiences a small positive attraction as it enters the crystal, hence its kinetic energy (velocity) increases. (B) $V(\mathbf{r})$ is the potential of the electrons, so their potential *energy* is negative and becomes more so, the closer they pass by the ions.

The electron beam can be described by its total wave function ψ^{tot} which must always be a solution of the Schrödinger equation; i.e., this equation describes how an electron behaves both inside and outside the crystal.

In the discussion which follows, we will use potentials so the units will be volts. You can always change to the energy formalism, but remember that the charge on the electron is a negative number.

We know that for any crystal the inner potential must be real, i.e., the potential energy must be real, so that $V(\mathbf{r})$ and its complex conjugate, which we denote as $V^*(\mathbf{r})$, are identical

$$V(\mathbf{r}) = V^*(\mathbf{r}) \tag{14.4a}$$

Now to make the treatment simple, we consider the case of crystals with a *center of symmetry*

$$V(\mathbf{r}) = V(-\mathbf{r}) \tag{14.4b}$$

The case of non-centrosymmetric crystals, such as GaAs, could be considered, but the equations would become much more complicated. Since $V(\mathbf{r})$ is periodic, we can express it as a Fourier series in which we sum over all the lattice points in reciprocal space

$$V(\mathbf{r}) = \sum_{\mathbf{g}} V_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}} \tag{14.5}$$

Here $V_{\mathbf{g}}$ is, by definition, the **g** component of V in the Fourier series. Now, in order to make future equations simpler we define a parameter $U_{\mathbf{g}}$ related to $V_{\mathbf{g}}$ by

$$V_{\mathbf{g}} = \frac{h^2}{2me} U_{\mathbf{g}} \tag{14.6}$$

In the Fourier series given in equation 14.5 and modified by equation 14.6, $V_{\mathbf{g}}$ and $U_{\mathbf{g}}$ are referred to as the Fourier coefficients. Equation 14.5 becomes

$$V(\mathbf{r}) = \frac{h^2}{2me} \sum_{\mathbf{g}} U_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}} \tag{14.7}$$

Now $V(\mathbf{r})$ has been expanded as a Fourier sum; all the conditions on $V_{\mathbf{g}}$ also apply to each $U_{\mathbf{g}}$ so that

$$U_{\mathbf{g}} = U^*_{\mathbf{g}} = U_{-\mathbf{g}} \tag{14.8}$$

You can check these relationships by just replacing **r** by –**r**, etc. Before continuing, however, you may find it useful to review the relative magnitudes of the energies which are summarized in Table 14.1.

Much of what we are now discussing is mathematically the same as you may have seen in condensed-matter physics. The big difference is that we are injecting electrons with kinetic energies which are 5–6 orders of magnitude greater than the band gap of Si. Notice that the mean inner potential energy is V in equation 14.1. The actual value of V is not as precise as it might sometimes appear. You should remember that it is the average background potential energy and is directly related to the characteristic length ξ_0 that we introduced in Chapter 13. More values of V are given in Table 14.2. One interesting feature of this table is that the magnitude of V only varies by a factor of 3 when the atomic number changes from 4 to 74.

TABLE 14.1 A Comparison of the Orders of Magnitudes of the Energies Being Discussed in This Chapter

Quantity	Energy (eV)
kT (room temp.: $T = 293$ K)	0.025
Band gap of Si	1.1
Mean inner potential energy for Si	~11
Energy of electrons in TEM	≥ 100,000

TABLE 14.2 Comparison of Mean Inner Potential Energies for Different Elements

Element	Inner Potential Energy (eV)
Be	7.8 ± 0.4
C	7.8 ± 0.6
Al	12.4 ± 1
Cu	23.5 ± 0.6
Ag	20.7 ± 2
Au	21.1 ± 2
Si	11.5
Ge	15.6 ± 0.8
W	23.4
ZnS	10.2 ± 1

14.3 BLOCH FUNCTIONS

Since the electron is in a periodic potential its wave function must have the symmetry of the crystal. The solutions to the Schrödinger equation which always have the required translation property are known as Bloch waves. Since these wave functions, $\psi^{(j)}(\mathbf{r})$, are special, we'll define them as

$$\psi^{(j)}(\mathbf{r}) = b\left(\mathbf{k}^{(j)}, \mathbf{r}\right) = b^{(j)}(\mathbf{r}) \tag{14.9}$$

The reason for the 'j' is that each Bloch wave has a single value of **k** (each Bloch wave is a plane wave) which we can denote as $\mathbf{k}^{(j)}$; in general, there will be more than one Bloch wave for a particular physical situation. The notation we will use is such that, whenever we have $\mathbf{k}^{(j)}$ in an expression, we will identify this by the superscript which implies that the function varies with $\mathbf{k}^{(j)}$. Bloch's theorem states that this wave function in a periodic potential can be written as

$$b^{(j)}(\mathbf{r}) = b\left(\mathbf{k}^{(j)}, \mathbf{r}\right) = \mu\left(\mathbf{k}^{(j)}, \mathbf{r}\right) e^{2\pi i \mathbf{k}^{(j)} \cdot \mathbf{r}} = \mu^{(j)}(\mathbf{r}) e^{2\pi i \mathbf{k}^{(j)} \cdot \mathbf{r}} \tag{14.10}$$

such that the *Bloch function*, $\mu^{(j)}(\mathbf{r})$, can itself be expressed as a Fourier series since $\mu(\mathbf{r})$ is also a periodic function of **r**

$$\mu^{(j)}(\mathbf{r}) = \sum_{\mathbf{g}} C^{(j)}_{\mathbf{g}}\left(\mathbf{k}^{(j)}\right) e^{2\pi i \mathbf{g} \cdot \mathbf{r}} \tag{14.11}$$

We'll call $C^{(j)}_{\mathbf{g}}$ the j-sub-g plane-wave amplitude and generally refer to the C values as the plane-wave amplitudes; they depend on which $\mathbf{k}^{(j)}$ we are considering, but not on **r**. We combine these definitions to give b which is itself dependent on j

$$b^{(j)}(\mathbf{r}) = \sum_{\mathbf{g}} C^{(j)}_{\mathbf{g}} e^{2\pi i (\mathbf{k}^{(j)} + \mathbf{g}) \cdot \mathbf{r}} \tag{14.12}$$

Using our notation, the superscript on C indicates that $C^{(j)}$ depends on j because it is associated with $\mathbf{k}^{(j)}$. We can now write the expanded expression for $b^{(j)}(\mathbf{r})$, which is a solution to the Schrödinger equation

$$b^{(j)}(\mathbf{r}) = C_{\mathbf{0}}^{(j)} e^{2\pi i \mathbf{k}^{(j)}\cdot\mathbf{r}} + C_{\mathbf{g}}^{(j)} e^{2\pi i(\mathbf{k}^{(j)}+\mathbf{g})\cdot\mathbf{r}} + \cdots \qquad (14.13)$$

The first term in this series is $C_{\mathbf{0}}$; the subscript is zero is because the length of this **g** vector is 0. Much of the following analysis is exactly the same as you may have encountered in studying semiconductor band-gap theory. The difference will be that we can make certain approximations which are only valid because the electrons used in TEM have much higher energies (100 keV to 1 MeV) than the inner potential of the crystal (~7–24 eV). It is always important to keep in mind the magnitude of the quantities we are considering and remember that the Bloch function has the periodicity of the lattice. When you are reading other texts, you'll see that physics textbooks will tend to omit the term 2π in such expressions so that $|\mathbf{k}|$ becomes $2\pi/\lambda$ instead of $1/\lambda$.

EACH BLOCH WAVE

The main point to remember is that each Bloch wave is associated with just one $\mathbf{k}^{(j)}$ but it is a continuously varying function of **r**. Each Bloch wave is a sum over all the points in reciprocal space. In other words, each Bloch wave depends on every **g**, and conversely, each **g** beam depends on every Bloch wave!

We haven't done anything yet, just restated the problem and remembered Bloch's theorem. The analysis we've just completed follows the original treatment of Bethe (1928). We can now express ψ^{tot} using equation 14.9 to give

$$\psi^{\text{tot}} = \sum_{j=1}^{n} \mathcal{A}^{(j)}\psi^{(j)} = \sum_{j=1}^{n} \mathcal{A}^{(j)} b\left(\mathbf{k}^{(j)}, \mathbf{r}\right) \qquad (14.14)$$

In this equation, $\mathcal{A}^{(j)}$ will be determined by the specimen type, the specimen orientation, etc., i.e., the boundary conditions. The $\mathcal{A}$s are known as the Bloch-wave excitation coefficients, since they tell us the relative contributions of each Bloch wave, i.e., how strongly each Bloch wave is excited.

14.4 SCHRÖDINGER'S EQUATION FOR BLOCH WAVES

What we are now going to do is to rewrite the Schrödinger equation to incorporate the properties of Bloch waves automatically. If you wish, you can skip this section and just accept the result given in equation 14.27. The way we include the periodicity is to express the inner potential in equation 14.2 as the Fourier series given in equation 14.7

$$\nabla^2\psi(\mathbf{r}) + \frac{8\pi^2 me}{h^2}\left(E + \frac{h^2}{2me}\sum_{\mathbf{g}} U_{\mathbf{g}} e^{2\pi i\mathbf{g}\cdot\mathbf{r}}\right)\psi(\mathbf{r}) = 0 \qquad (14.15)$$

Now we simplify the algebra to give

$$\nabla^2\psi(\mathbf{r}) + 4\pi^2\left(\frac{2me}{h^2}E + \sum_{\mathbf{g}} U_{\mathbf{g}} e^{2\pi i\mathbf{g}\cdot\mathbf{r}}\right)\psi(\mathbf{r}) = 0 \qquad (14.16)$$

and hence

$$\frac{1}{4\pi^2}\nabla^2\psi(\mathbf{r}) + \left(\frac{2me}{h^2}E + \sum_{\mathbf{g}} U_{\mathbf{g}} e^{2\pi i\mathbf{g}\cdot\mathbf{r}}\right)\psi(\mathbf{r}) = 0 \qquad (14.17)$$

Next, we can introduce a new quantity K which is defined by the equation

$$K^2 = \frac{2meE}{h^2} + U_{\mathbf{0}} = \chi^2 + U_{\mathbf{0}} \qquad (14.18)$$

With this definition we have removed the $U_{\mathbf{0}}$ term from the sum over all **g**, so that equation 14.15 is now

$$\frac{1}{4\pi^2}\nabla^2\psi(\mathbf{r}) + K^2\psi(\mathbf{r}) + \sum_{\mathbf{g}\neq 0} U_{\mathbf{g}} e^{2\pi i\mathbf{g}\cdot\mathbf{r}}\psi(\mathbf{r}) = 0 \qquad (14.19)$$

The reason for doing this is that we are going to be concerned with different diffraction vectors, **g**. The $U_{\mathbf{0}}$ term does not depend on **g**. We call $U_{\mathbf{0}}$ the (scaled) mean inner potential of the crystal; this potential is thus a 'background' or continuum property of the crystal; it does not directly depend on the crystal structure. (You may recognize this manipulation as the refractive-index idea reappearing.)

When $V(\mathbf{r})$ is 0, then $U_{\mathbf{0}}$ is 0 so that K^2 takes on a special value which we have already called χ^2

$$\chi^2 = \frac{2meE}{h^2} \qquad (14.20)$$

The mass, m, is actually the relativistic mass, not the rest mass; eE is the kinetic energy of the electron (in the vacuum between the gun and the specimen). We know that

$$\frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{p^2}{2m} = \frac{(hk)^2}{2m} \qquad (14.21)$$

where v is the velocity, **p** the momentum, and **k** a wave vector. Thus χ is the wave vector of the electron outside the crystal as we had in Chapter 13.

The meaning of K is now clear: **K** is the wave vector of the electron *inside* the specimen, i.e., after correcting for the refractive-index effect. Since $U_{\mathbf{0}}$ is a positive number, K is always larger than χ. Hence the kinetic energy of the electrons in the crystal is greater than in the vacuum. The potential energy inside the crystal is negative so, even though it may be counterintuitive, you now know that electrons travel faster in the crystal! The wavelength of the electrons in the crystal is therefore smaller than the wavelength outside (λ is the reciprocal of k).

ELECTRON SPEED IN A CRYSTAL

Electrons travel faster in the crystal. Light slows down in a crystal.

Remember that light is electromagnetic radiation. The refractive index for light is $n = c/v$ and is always ≥ 1; c is the velocity of light in a vacuum and v is the velocity in any other material. This is one of those cases where we have to be wary when applying ideas derived for light waves to electron waves.

DISPERSION

When discussing light, the word dispersion means *separation of electromagnetic radiation into constituents of different wavelength*. In electron optics, the meaning is exactly the same but we emphasize different **k** vectors or different energy.

Equations 14.18 and 14.20 are *dispersion relations*. Such equations relate the magnitude of the wave vector, K or χ, to the energy of the electron.

We want to simplify equation 14.19. We know that $\psi(\mathbf{r})$ is a Bloch wave (given by equation 14.12) so we can obtain an expression for $\nabla^2\psi(\mathbf{r})$ by differentiating $b^{(j)}(\mathbf{r})$. Remember that $C_{\mathbf{g}}^{(j)}$ does not depend on **r**

$$\nabla^2\psi(\mathbf{r}) = \sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)} \nabla^2 \left(e^{2\pi i\left(\mathbf{k}^{(j)} + \mathbf{g}\right) . \mathbf{r}} \right) \tag{14.22}$$

Thus we can write

$$\nabla^2\psi(\mathbf{r}) = -(2\pi)^2 \sum_{\mathbf{g}} \left|\mathbf{k}^{(j)} + \mathbf{g}\right|^2 C_{\mathbf{g}}^{(j)} e^{2\pi i\left(\mathbf{k}^{(j)} + \mathbf{g}\right) . \mathbf{r}} \tag{14.23}$$

Now we insert this expression in equation 14.19

$$\frac{1}{4\pi^2}\left(-4\pi^2 \sum_{\mathbf{g}} \left|\mathbf{k}^{(j)} + \mathbf{g}\right|^2 C_{\mathbf{g}}^{(j)} e^{2\pi i\left(\mathbf{k}^{(j)} + \mathbf{g}\right) . \mathbf{r}} \right) + K^2 \sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)} e^{2\pi i\left(\mathbf{k}^{(j)} + \mathbf{g}\right) . \mathbf{r}} + \sum_{\mathbf{h}\neq 0} U_{\mathbf{h}} e^{2\pi i \mathbf{h} . \mathbf{r}} \sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)} e^{2\pi i\left(\mathbf{k}^{(j)} + \mathbf{g}\right) . \mathbf{r}} = 0 \tag{14.24}$$

In doing so we replace the **g** in the summation in equation 14.19 by **h** just for clarity (!); both are called 'dummy' variables. If we sum over all the values of a variable we can 'center' the variable wherever we wish. We can further simplify the third term in equation 14.24 by combining the exponential terms and renaming **g**

$$\sum_{\mathbf{g}} \sum_{\mathbf{h}\neq 0} U_{\mathbf{h}} C_{\mathbf{g}}^{(j)} e^{2\pi i\left(\mathbf{k}^{(j)} + \mathbf{g} + \mathbf{h}\right) . \mathbf{r}} = \sum_{\mathbf{g}-\mathbf{h}} \sum_{\mathbf{h}\neq 0} U_{\mathbf{h}} C_{\mathbf{g}-\mathbf{h}}^{(j)} e^{2\pi i\left(\mathbf{k}^{(j)} + \mathbf{g}\right) . \mathbf{r}} \tag{14.25}$$

Now the sum over all **g–h** vectors is the same as the sum over all **g** vectors so we replace **g–h** by **g**. (Remember, all we are doing is renaming these dummy variables in a consistent way.) Then equation 14.24, and hence 14.19, becomes much simpler

$$\sum_{\mathbf{g}} \left(\left\{ -\left|\mathbf{k}^{(j)} + \mathbf{g}\right|^2 + K^2 \right\} C_{\mathbf{g}}^{(j)} + \sum_{\mathbf{h}\neq 0} U_{\mathbf{h}} C_{\mathbf{g}-\mathbf{h}}^{(j)} \right) e^{2\pi i(\mathbf{k}^{(j)} + \mathbf{g}) . \mathbf{r}} = 0 \tag{14.26}$$

We can obtain a useful relation by noting that the coefficients of each term in exp($2\pi i\mathbf{g}.\mathbf{r}$) must separately be equal to zero. The only way that equation 14.26 can be true is if the term inside the bracket is always zero. The result is a series of equations (one for each value of **g**)

$$\left\{ -\left|\mathbf{k}^{(j)} + \mathbf{g}\right|^2 + K^2 \right\} C_{\mathbf{g}}^{(j)} + \sum_{\mathbf{h}\neq 0} U_{\mathbf{h}} C_{\mathbf{g}-\mathbf{h}}^{(j)} = 0 \tag{14.27}$$

This is another really important set of equations; they restate the Bloch-wave expression of the Schrödinger equation.

Notice that we are not summing over **g** in equation 14.27. The reason for excluding $\mathbf{h} = 0$ from the sum is that we have already included it in the first term.

14.5 THE PLANE-WAVE AMPLITUDES

We can rewrite and reorder equation 14.27 by, yet again, renaming the variable **h** as **g–h**. When we do this, we must exclude $\mathbf{h} = \mathbf{g}$ in the sum

$$\left\{ K^2 - \left|\mathbf{k}^{(j)} + \mathbf{g}\right|^2 \right\} C_{\mathbf{g}}^{(j)} + \sum_{\mathbf{h}\neq \mathbf{g}} U_{\mathbf{g}-\mathbf{h}} C_{\mathbf{h}}^{(j)} = 0 \tag{14.28}$$

The reason for making this change is that it emphasizes that the 'U' terms are the features which couple together the 'C' terms. In other words, this equation tells us how the potential of the crystal, the U terms, mixes the different Bloch waves. The C terms are the Bloch-wave amplitudes. This is the *dynamical coupling* concept.

This equation represents a set of equations which are the fundamental equations of the dynamical theory. (They are called the secular equations in condensed-matter physics texts.) This equation also links the concepts of Bragg beams and Bloch waves.

$U_{\mathbf{g}-\mathbf{h}}$ is the component of the inner potential which couples the Bragg beams with reciprocal-lattice vectors **g** and **h** to one another.

Now we again simplify the situation by limiting the treatment to two beams, O and P; i.e., we consider the case where the only values of $C_{\mathbf{g}}$ which are *non-zero* are $C_0^{(j)}$ and $C_{\mathrm{P}}^{(j)}$ but U_{P} and $U_{-\mathrm{P}}$ are both allowed.

Remember that the superscript on C indicates that $\mathbf{k}^{(j)}$ is a variable. Note that P could be any diffracted beam. Letting $\mathbf{g} = \mathbf{0}$ in equation 14.27 gives

$$\left(K^2 - \left|\mathbf{k}^{(j)}\right|^2\right) C_{\mathbf{0}}^{(j)} + U_{-\mathbf{p}} C_{\mathbf{p}}^{(j)} = 0 \qquad (14.29)$$

In deriving this and the following equation, we consider all the possible values of **h** which would give us $C_{\mathbf{0}}^{(j)}$ or $C_{\mathbf{p}}^{(j)}$.

Next let $\mathbf{g} = \mathbf{p}$ in equation 14.28 and reverse the order of terms to emphasize that we have two equations in $C_{\mathbf{0}}$ and $C_{\mathbf{p}}$

$$U_{\mathbf{p}} C_{\mathbf{0}}^{(j)} + \left(K^2 - \left|\mathbf{k}^{(j)} + \mathbf{p}\right|^2\right) C_{\mathbf{p}}^{(j)} = 0 \qquad (14.30)$$

There are no other possible equations, so to solve these two equations we set the determinant of the coefficients equal to zero

$$\begin{vmatrix} K^2 - \left|\mathbf{k}^{(j)}\right|^2 & U_{-\mathbf{p}} \\ U_{\mathbf{p}} & K^2 - \left|\mathbf{k}^{(j)} + \mathbf{p}\right|^2 \end{vmatrix} = \left(K^2 - \left|\mathbf{k}^{(j)}\right|^2\right)\left(K^2 - \left|\mathbf{k}^{(j)} + \mathbf{p}\right|^2\right) - U_{\mathbf{p}} U_{-\mathbf{p}} = 0 \qquad (14.31)$$

The mean inner potential of the crystal is usually ≤20 V while the energy of the electrons is ≥100,000 eV. Because $|\mathbf{k}^{(j)} + \mathbf{p}|$ and $|\mathbf{k}^{(j)}|$ are both very close to K, it's the difference that is important. Since **P** could be any diffracted beam, we can rename it **G** to make it look more familiar!

$$\begin{vmatrix} K^2 - \left|\mathbf{k}^{(j)}\right|^2 & U_{-\mathbf{g}} \\ U_{\mathbf{g}} & K^2 - \left|\mathbf{k}^{(j)} + \mathbf{g}\right|^2 \end{vmatrix} = \left(K^2 - \left|\mathbf{k}^{(j)}\right|^2\right)\left(K^2 - \left|\mathbf{k}^{(j)} + \mathbf{g}\right|^2\right) - U_{\mathbf{g}} U_{-\mathbf{g}} = 0 \qquad (14.32)$$

Now we can use the simple algebraic relation

$$x^2 - y^2 = (x - y)(x + y) \qquad (14.33)$$

and make the high-energy approximation that $|\mathbf{k}^{(j)}|$, $|\mathbf{k}^{(j)} + \mathbf{g}|$, and K are all similar in magnitude. Then equation 14.32 becomes

$$\left(\left|\mathbf{k}^{(j)}\right| - K\right)\left(\left|\mathbf{k}^{(j)} + \mathbf{g}\right| - K\right) = \frac{U_{\mathbf{g}} U_{-\mathbf{g}}}{4K^2} = \frac{\left|U_{\mathbf{g}}\right|^2}{4K^2} \qquad (14.34)$$

It is important not to confuse $\mathbf{k}^{(j)}$ with $\mathbf{k}_{\mathrm{I}}$ or $\mathbf{k}_{\mathrm{D}}$ and to remember that $|\mathbf{K}|$ $(= |\mathbf{k}_{\mathrm{D}} - \mathbf{k}_{\mathrm{I}}|)$ is not K. Incidentally, it is not until we write this equation that we use the assumption that the crystal has a center of symmetry (see equation 14.4b).

Equation 14.34 is a more complex dispersion relation than equations 14.18 and 14.20. Since $\mathbf{k}^{(j)}$ can point in any direction, this dispersion relation defines a surface, known as the dispersion surface, which is just the locus of all allowed $\mathbf{k}^{(j)}$ vectors for a particular fixed energy. (See Chapter 15.) The simpler relations given in equations 14.18 and 14.20 each defined a sphere; the vectors K and χ can point in any direction.

From equation 14.29 (renaming **p** as **g**), we have

$$\frac{C_{\mathbf{g}}^{(j)}}{C_{\mathbf{0}}^{(j)}} = \frac{\left|\mathbf{k}^{(j)}\right|^2 - K^2}{U_{-\mathbf{g}}} \qquad (14.35)$$

which we can rewrite as

$$\frac{C_{\mathbf{g}}^{(j)}}{C_{\mathbf{0}}^{(j)}} = \frac{\left(\left|\mathbf{k}^{(j)}\right| - K\right)\left(\left|\mathbf{k}^{(j)}\right| + K\right)}{U_{-\mathbf{g}}} \approx \frac{2K\left(\left|\mathbf{k}^{(j)}\right| - K\right)}{U_{-\mathbf{g}}} \qquad (14.36)$$

Thus we can, in principle, say how $C_{\mathbf{0}}^{(j)}$ and $C_{\mathbf{g}}^{(j)}$ are related.

Now we could extend this analysis to show how all the values of C are related in a many-beam situation. If we did that we could write a new expression

$$\mathcal{A}^{(\mathrm{j})}\left\{\mathbf{C}_{\mathbf{g}}^{(\mathrm{j})}\right\} = \mathbf{0} \qquad (14.37)$$

where $\left\{C_{\mathbf{g}}^{(j)}\right\}$ now denotes a column vector with elements $C_{\mathbf{g}}^{(j)}$. $\mathcal{A}^{(j)}$ is a matrix defined by

$$a_{gg} = K^2 - \left|\mathbf{k}^{(j)} + \mathbf{g}\right|^2 \qquad (14.38)$$

with the off-diagonal elements given by the Fourier coefficients of the crystal potential

$$a_{gh} = U_{g-h} \qquad (14.39)$$

Here, g refers to rows and h to columns in the **A** matrix. Except in special cases, such as the two-beam case in equation 14.31, you'll only encounter this formalism in computer programs! A particularly clear case is given by Metherell and is adapted here for five beams, comprising **g**, **0**, **g**, 2**g**, and 3**g** beams. The 5 × 5 matrix can be written out (using g and h rather than **g** and **h**) as

$$\mathbf{A} = \begin{pmatrix} a_{-g-g} & U_{-g-0} & U_{-g-g} & U_{-g-2g} & U_{-g-3g} \\ U_{0-(-g)} & a_{00} & U_{0-g} & U_{0-2g} & U_{0-3g} \\ U_{g-(-g)} & U_{g-0} & a_{gg} & U_{g-2g} & U_{g-3g} \\ U_{2g-(-g)} & U_{2g-0} & U_{2g-g} & a_{2g2g} & U_{2g-3g} \\ U_{3g-(-g)} & U_{3g-0} & U_{3g-g} & U_{3g-2g} & a_{3g3g} \end{pmatrix} \qquad (14.40)$$

In the first column h is –g; in the second, h is zero, etc. In the first row 'g' is –g; in the second, 'g' is zero. So we can simplify this matrix as

$$\mathbf{A} = \begin{pmatrix} a_{-g} & U_{-g} & U_{-2g} & U_{-3g} & U_{-4g} \\ U_{g} & a_{0} & U_{-g} & U_{-2g} & U_{3g} \\ U_{2g} & U_{g} & a_{g} & U_{-g} & U_{-2g} \\ U_{3g} & U_{2g} & U_{g} & a_{2g} & U_{-g} \\ U_{4g} & U_{3g} & U_{2g} & U_{g} & a_{3g} \end{pmatrix} \qquad (14.41)$$

Some points to notice are

- The terms $U_\mathbf{g}$, $C_\mathbf{g}^{(j)}$, and a_g are related by a set of linear equations (the matrix in 14.37).
- We can't solve for actual values of the $C_\mathbf{g}^{(j)}$ terms, but we can find the ratios $C_\mathbf{g}^{(j)}/C_\mathbf{0}^{(j)}$.

We won't take this topic much further here but refer you again to the excellent article by Metherell who shows that equation 14.37 can be expressed as an eigenvalue equation where $\left\{C_\mathbf{g}^{(j)}\right\}$ appears as the eigenvectors and the wave vectors $\mathbf{k}^{(j)}$ appear as the eigenvalues. He expresses this equation as

$$M\left\{C_\mathbf{g}^{(j)}\right\} = \gamma^{(j)}\left\{C_\mathbf{g}^{(j)}\right\} \tag{14.42}$$

where the matrix $\mathbf{M}$ has diagonal elements m_{gg} and off-diagonal elements m_{gh}. The reason we mention this fact here is that the m_{gg} terms correspond to the excitation errors, s_g, and the m_{gh} terms correspond to the extinction distance $\xi_{\mathbf{g-h}}$. Remember that h is the column and notice that the subscript here is **g–h**; this extinction distance is related to the interference between the **g** beam and the **h** beam. Now if you're intrigued and your math is strong, see Metherell's article.

If you're familiar with this math approach, you'll recognize that eigenvectors must satisfy certain relations for normalization and orthogonality. If you look back to Chapter 13, you'll see that we normalized $C_\mathbf{g}^{(j)}$ in writing equation 13.30.

As you can see, the math is beginning to become tricky! In the next chapter, we will derive explicit expressions for $\xi_\mathbf{0}$ and $\xi_\mathbf{g}$ in the two-beam case, namely

$$\xi_\mathbf{0} = \frac{2K\cos\theta_\mathrm{B}}{U_\mathbf{0}} \tag{14.43}$$

and

$$\xi_\mathbf{0} = \frac{2K\cos\theta_\mathrm{B}}{U_\mathbf{g}} = \frac{1}{\Delta\mathbf{k}} \tag{14.44}$$

In our derivation we will use a graphical representation of the dispersion equations. This approach has much in common with the Ewald-sphere/reciprocal-lattice approach to understanding diffraction. It's particularly useful since it gives you, the microscopist, another picture, this time related to imaging.

14.6 ABSORPTION OF BLOCH WAVES

When we have just two beams excited, O and G, we showed in Section 13.9 that we can express the wave function ψ as

$$\psi(\mathbf{r}) = \mathcal{A}^{(1)}b^{(1)}(\mathbf{r}) + \mathcal{A}^{(2)}b^{(2)}(\mathbf{r}) \tag{14.45}$$

where

$$\mathcal{A}^{(1)} = \cos\frac{\beta}{2};\mathcal{A}^{(2)} = \sin\frac{\beta}{2} \tag{14.46}$$

We can plot these curves for $\mathcal{A}^{(1)}$ and $\mathcal{A}^{(2)}$ in relation to the positions of the atoms in a simple-cubic crystal where the electron beam is close to the [001] zone axis. Figure 14.2 shows that the intensity in Bloch wave 1 is centered on the column of atoms (Figure 14.2A) while that in Bloch wave 2 is centered between the atoms (Figure 14.2B). (If you read Hirsch et al., you should note that they have 1 and 2 reversed.) Therefore Bloch wave 1 interacts more strongly with the column of atoms and will be 'absorbed' preferentially. Conversely, Bloch wave 2 will be channeled through the specimen. The intensity in the **g** beam depends on the thickness of the specimen because of the interference between these two Bloch waves. This preferential absorption means that we may expect to 'lose' this thickness dependence even though we can still 'see' through the specimen. We'll return to this topic in Chapter 24.

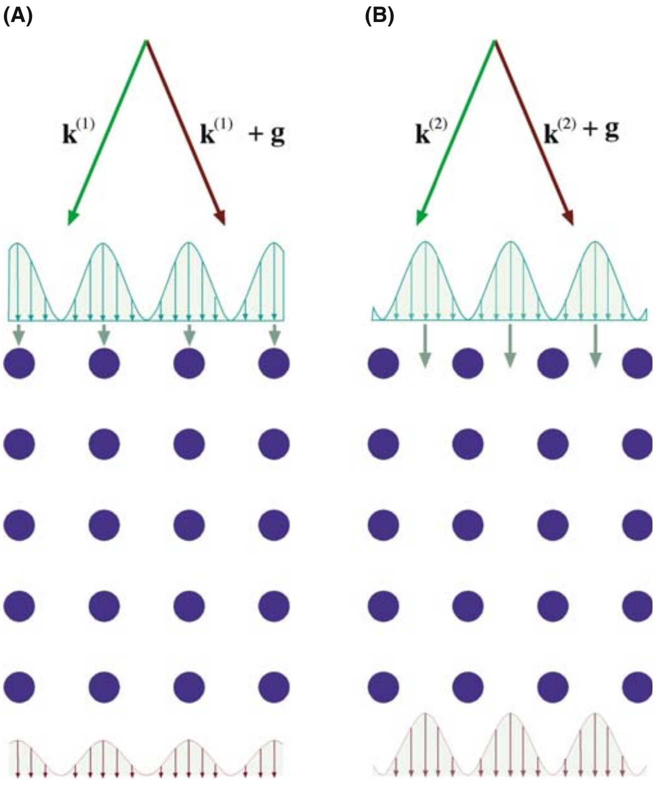

FIGURE 14.2. The two types of Bloch wave in the crystal aligned at the Bragg condition: (A) the maximum lies along the ion cores and Bloch wave 1 interacts strongly; (B) the maximum lies between the ions so that the interactions are weaker.

CHAPTER SUMMARY

We told you at the beginning of the chapter that this discussion would seem to be just theory or manipulating equations. There are, however, some really important ideas

- A basic property of a crystal is that its inner potential, $V(\mathbf{r})$, is periodic and positive.
- An electron in a crystal can be described by a sum of Bloch waves which themselves are solutions to the Schrödinger equation.
- The wave functions $\phi_\mathbf{0}$ and $\phi_\mathbf{g}$ are not solutions to this equation and therefore don't actually exist as waves in the crystal.
- All Bloch waves have the same total energy.

Therefore, if we really want to understand what goes on in the crystal, we must be able to understand the concept of Bloch waves. However, you can understand how to relate images to the structure of the specimen without considering Bloch waves. You just have to accept that the analysis using beams (hence $\phi_\mathbf{0}$ and $\phi_\mathbf{g}$) is phenomenological. Equations 14.27 and 14.28 give you the essential clue to what really happens: each set of equations tells us how the Bloch waves are coupled. When you've worked through this chapter, go through Sections 13.8 and 13.9 again.

There are many possible solutions to the Schrödinger equation, and each Bloch wave is a plane wave; that is, it can be associated with well-defined propagation vector $\mathbf{k}^{(j)}$ as shown in equation 14.9.

The Bloch waves are generally different because the $U_\mathbf{g}$ terms are different, i.e., they have different potential energies. Therefore, they have different kinetic energies and different wave vectors.

Finally, a word on relativity. We've kept our treatment as simple as possible, but you should remember that the equations should be relativistically corrected; most texts have ignored relativistic effects when discussing this topic.

REFERENCES

This chapter follows the treatment given by Hirsch et al. in Chapter 9 of their classic text; the details are provided by Metherell.

BLOCH WAVES

Ashcroft, NW and Mermin, ND 1976 *Solid State Physics* W.B. Saunders Co. Philadelphia PA. Chapter 8 ($2\pi/\lambda$ is used).

Bethe, HA 1928 *Theorie der Beugung von Elektronen an Kristallen* Ann. Phys. Lpz. **87** 55–129. Another classic reference (in German).

Howie, A 1971 in *Electron Microscopy in Materials Science* 275–305 Ed. U Valdré Academic Press New York.

Kittel, CJ 2004 *Solid-State Physics* 8th Ed. John Wiley & Sons New York. For the physicists.

Metherell, AJF 1975 in *Electron Microscopy in Materials Science* **II** 397–552 Eds. U Valdré and E Ruedl CEC, Brussels. This is perhaps the clearest and most comprehensive article available on this subject (over 150 pages long). It is strongly recommended reading if you've made it through this chapter and want to begin programming.

THE COMPANION TEXT

EMS can be used to simulate HRTEM images using the Bloch-wave approach.

SELF-ASSESSMENT QUESTIONS

Q14.1 Summarize the reasons for assigning the sign we do to the accelerating voltage, the sign of the energy of the electron, the sign of the potential, and the sign of the potential energy.

Q14.2 Even when the atomic number varies from 4 to 74, the inner potential energy only changes by a factor of ~3. Why?

Q14.3 You're told that the inner potential energy of W is 23.4. Comment on this value.

Q14.4 What is a Bloch wave?

Q14.5 What is a Bloch function?

Q14.6 What is the Bloch theorem?

Q14.7 Why are we talking about plane waves throughout this chapter?

Q14.8 Write down an equation relating K and χ.

Q14.9 Write down an expression relating K to E outside the crystal.

Q14.10 Write down the Bloch-wave expression for the Schrödinger equation. What does this equation tell you?

Q14.11 Explain in words the meaning of the term $U_{\mathbf{g-h}}$.

Q14.12 In a crystal, light slows down but electrons speed up. What is the fundamental difference between these two phenomena?

Q14.13 The terms $U_{\mathbf{g}}$, $C_{\mathbf{g}}^{(j)}$ and $a_{\mathbf{g}}$ are related by a set of linear equations through the matrix **A**. Write down the matrix **A** for the situation where only $\bar{\mathbf{g}}$, 0, **g**, 2**g**, and 3**g** are important.

Q14.14 In the two-beam diffraction situation, how many Bloch waves are important?

Q14.15 The 'U' terms are the features which couple together the 'C' terms. What does this mean?

Q14.16 $U_{\mathbf{g-h}}$ is the component of the inner potential which couples together the Bragg beams with reciprocal-lattice vectors **g** and **h**. We don't really have Bragg beams in a crystal. Explain this apparent inconsistency.

Q14.17 How is it possible for all Bloch waves to have the same energy?

Q14.18 In the TEM image, we lose thickness dependence even though we can still see through the specimen. How does Bloch wave theory explain this effect?

Q14.19 If your sample is YAG (bcc with $a = \sim 1$ nm) rather than a model, mono-atomic, simple-cubic crystal, how will your Bloch wave analysis be affected?

Q14.20 If you have a Si/SiO_2/Si sandwich of equally thick (20 nm) layers such that the beam passes through the layers in succession, how will this affect your discussion of Bloch waves?

TEXT-SPECIFIC QUESTIONS

T14.1 For discussion, compare how the velocity of electrons and light change when they enter a crystal. Consider (i) how this will be affected if the specimen is amorphous; (ii) if the accelerating voltage is increased from 100 kV to 1 MV; (iii) if the microscope were a TPM (p: positron) instead.

T14.2 Consider equation 14.44. Calculate a value for $\Delta\mathbf{k}$ when $s = 0$ for 100 kV, Cu 220. How does this value compare to **g** and λ^{-1} and why do we ask?

T14.3 Evaluate equation 14.20 for 100- kV electrons.

T14.4 How does Figure 14.1A differ for [001], [110], and [111] in Si and Cu?

T14.5 How would you modify Figure 14.1B to explain the values of Table 14.2 more clearly?

T14.6 Consider Figure 14.2. Imagine that the crystal is an extinction distance thick. Draw the intensity plots for the Bloch waves at depth $\xi/4$, $\xi/2$, $3\xi/4$, and ξ.

T14.7 Excluding the other III–V compounds which are closely related to GaAs, list five other crystal types that do not have a center of symmetry.

T14.8 Consider equations 14.1 and 14.2. Where does the relativistic correction enter?

T14.9 In equations 14.45 and 14.46, $\mathcal{A}^{(1)^2} + \mathcal{A}^{(2)^2}$ is 1. Why is this?

T14.10 The vectors **k** and $\boldsymbol{\chi}$ differ because of the refractive-index effect. How large is the refractive index and how does this quantity relate to (if it does) the refractive index for light?

T14.11 (Challenging) If the extinction distance depends on $U_{\mathbf{g}}$ for a crystal, can amorphous specimens show thickness fringes?

T14.12 (Challenging) Why does $\xi_{\mathbf{g}}$ decrease when both 220 and $2\bar{2}0$ are excited?