Appendix II

Derivation of Bloch's Theorem

The wave function of an electron moving in a periodic potential is a solution of the Schrödinger equation, which is given by Eq. (8.41). Evaluating the Schrödinger equation at the coordinate point $\mathbf{r}+\mathbf{l}$, we obtain

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}+\mathbf{l})\right)\psi(\mathbf{r}+\mathbf{l}) = E\psi(\mathbf{r}+\mathbf{l}). \tag{II.1}$$

We may use Eq. (8.42) to replace the potential energy term in this equation with its value at the point $\mathbf{r}$ giving

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}+\mathbf{l}) = E\psi(\mathbf{r}+\mathbf{l}). \tag{II.2}$$

The functions $\psi(\mathbf{r})$ and $\psi(\mathbf{r}+\mathbf{l})$ are thus both solutions of the Schrödinger equation corresponding to the energy E. If the energy eigenvalue E is non-degenerate, the function $\psi(\mathbf{r}+\mathbf{l})$, which is obtained from $\psi(\mathbf{r})$ by a displacement by a lattice vector $\mathbf{l}$, must be proportional to $\psi(\mathbf{r})$. This is true for any $\mathbf{l}$. We consider first the function $\psi(\mathbf{r}+\mathbf{a_1})$ which corresponds to a single step in the direction $\mathbf{a}_1$. For this function, the appropriate relation of proportionality can be written

$$\psi(\mathbf{r}+\mathbf{a_1}) = \lambda_1\psi(\mathbf{r}). \tag{II.3}$$

Since the functions $\psi(\mathbf{r}+\mathbf{a}_1)$ and $\psi(\mathbf{r})$ are both normalized, we must have

$$|\lambda_1|^2 = 1. \tag{II.4}$$

We can thus write λ_1 in the form

$$\lambda_1 = e^{ik_1}, \tag{II.5}$$

where k_1 is a real number. Equation (II.3) then becomes

$$\psi(\mathbf{r}+\mathbf{a_1}) = e^{ik_1}(\mathbf{r}). \tag{II.6}$$

Similar equations can be derived for displacements in the $\mathbf{a}_2$ and $\mathbf{a}_3$ directions

$$\psi(\mathbf{r}+\mathbf{a_2}) = e^{ik_2}(\mathbf{r}), \psi(\mathbf{r}+\mathbf{a_3}) = e^{ik_3}(\mathbf{r}). \tag{II.7}$$

The effect of a general translation can be obtained by applying Eqs. (II.6) and (II.7) successively for translations in the $\mathbf{a}_1, \mathbf{a}_2$, and $\mathbf{a}_3$ directions

$$\begin{aligned}\psi(\mathbf{r}+1) &= \psi(\mathbf{r}+l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3)\\ &= e^{ik_1}\psi(\mathbf{r}+(l_1-1)\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3)\\ &= e^{ik_1l_1}\psi(\mathbf{r}+l_2\mathbf{a}_2+l_3\mathbf{a}_3)\\ &= e^{i(k_1l_1+k_2l_2+k_3l_3)}\psi(\mathbf{r}).\end{aligned} \tag{II.8}$$

To express this result in more general terms, we define a wave vector $\mathbf{k}$

$$\mathbf{k} = k_1\frac{\mathbf{b}_1}{2\pi} + k_2\frac{\mathbf{b}_2}{2\pi} + \frac{k_3\mathbf{b}_3}{2\pi}, \tag{II.9}$$

where $\mathbf{b}_1, \mathbf{b}_2$, and $\mathbf{b}_3$ are the reciprocal vectors corresponding to the unit vectors $\mathbf{a}_1, \mathbf{a}_2$, and $\mathbf{a}_3$. Using Eqs. (8.1) and (8.22), Eq. (II.8) can be written

$$\psi(\mathbf{r}+\mathbf{l}) = e^{i\mathbf{k}\cdot\mathbf{l}}\psi(\mathbf{r}), \tag{II.10}$$

which is a mathematical expression for the theorem. The proof of the theorem depends upon the potential energy being periodic.

A more general proof of Block's theorem including the case for which the energy E is degenerate can be found in the book by Ziman which is cited at the end of Chapter 8.