Let us look for all solutions to the Schrödinger equation (8.2) that have the Bloch form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r}), \tag{8.47}$$

where $\mathbf{k}$ is fixed and u has the periodicity of the Bravais lattice. Substituting this into the Schrödinger equation, we find that u is determined by the eigenvalue problem

$$\begin{aligned} H_{\mathbf{k}}u_{\mathbf{k}}(\mathbf{r}) &= \left(\frac{\hbar^2}{2m}\left(\frac{1}{i}\nabla + \mathbf{k}\right)^2 + U(\mathbf{r})\right)u_{\mathbf{k}}(\mathbf{r}) \\ &= \mathcal{E}_{\mathbf{k}}u_{\mathbf{k}}(\mathbf{r}) \end{aligned} \tag{8.48}$$

with boundary condition

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}). \tag{8.49}$$

Appendix E

The Velocity and Effective Mass of Bloch Electrons

One may evaluate the derivatives $\partial\mathcal{E}_n/\partial k_i$ and $\partial^2\mathcal{E}_n/\partial k_i\partial k_j$ by noting that they are the coefficients of the linear and quadratic terms in $\mathbf{q}$, in the expansion

$$\mathcal{E}_n(\mathbf{k}+\mathbf{q}) = \mathcal{E}_n(\mathbf{k}) + \sum_i \frac{\partial\mathcal{E}_n}{\partial k_i} q_i + \frac{1}{2}\sum_{ij} \frac{\partial^2\mathcal{E}_n}{\partial k_i\,\partial k_j} q_i q_j + O(q^3). \tag{E.1}$$

Since, however, $\mathcal{E}_n(\mathbf{k}+\mathbf{q})$ is the eigenvalue of $H_{\mathbf{k}+\mathbf{q}}$ (Eq. (8.48)), we can calculate the required terms from the fact that

$$H_{\mathbf{k}+\mathbf{q}} = H_{\mathbf{k}} + \frac{\hbar^2}{m}\mathbf{q}\cdot\left(\frac{1}{i}\nabla + \mathbf{k}\right) + \frac{\hbar^2}{2m}q^2, \tag{E.2}$$

as an exercise in perturbation theory.

Perturbation theory asserts that if $H = H_0 + V$ and the normalized eigenvectors and eigenvalues of H_0 are

$$H_0\psi_n = E_n^0\psi_n, \tag{E.3}$$

then to second order in V, the corresponding eigenvalues of H are

$$E_n = E_n^0 + \int d\mathbf{r}\,\psi_n^* V\psi_n + \sum_{n'\neq n} \frac{\left|\int d\mathbf{r}\,\psi_n^* V\psi_{n'}\right|^2}{(E_n^0 - E_{n'}^0)} + \cdots. \tag{E.4}$$

To calculate to linear order in $\mathbf{q}$ we need only keep the term linear in $\mathbf{q}$ in (E.2) and insert it into the first-order term in (E.4). In this way, we find that

$$\sum_i \frac{\partial\mathcal{E}_n}{\partial k_i} q_i = \sum_i \int d\mathbf{r}\, u_{n\mathbf{k}}^* \frac{\hbar^2}{m}\left(\frac{1}{i}\nabla + \mathbf{k}\right)_i q_i u_{n\mathbf{k}}, \tag{E.5}$$

(where the integrations are either over a primitive cell or over the entire crystal, depending on whether the normalization integral $\int d\mathbf{r}\,|u_{n\mathbf{k}}|^2$ has been taken equal to unity over a primitive cell or over the entire crystal). Therefore

$$\frac{\partial\mathcal{E}_n}{\partial\mathbf{k}} = \frac{\hbar^2}{m}\int d\mathbf{r}\, u_{n\mathbf{k}}^*\left(\frac{1}{i}\nabla + \mathbf{k}\right)u_{n\mathbf{k}}. \tag{E.6}$$

If we express this in terms of the Bloch functions $\psi_{n\mathbf{k}}$ via (8.3), it can be written as

$$\boxed{\frac{\partial\mathcal{E}_n}{\partial\mathbf{k}} = \frac{\hbar^2}{m}\int d\mathbf{r}\,\psi_{n\mathbf{k}}^*\frac{1}{i}\nabla\psi_{n\mathbf{k}}.} \tag{E.7}$$

Since $(1/m)(\hbar/i)\nabla$ is the velocity operator,[1] this establishes that $(1/\hbar)(\partial\mathcal{E}_n(\mathbf{k})/\partial\mathbf{k})$ is the mean velocity of an electron in the Bloch level given by n, $\mathbf{k}$.

---

[1] The velocity operator is $\mathbf{v} = d\mathbf{r}/dt = (1/i\hbar)[\mathbf{r}, \mathbf{H}] = \mathbf{p}/m = \hbar\nabla/mi$.