Consider a periodic solid with the unit cell, \((a, b, c)\).

The periodic potential, \(V(r)\), can be expanded as

\[
V(r) = \sum_{\mathbf{G}} V_{\mathbf{G}} \exp \left( i \mathbf{G} \cdot r \right)
\]

where

\[
V_{\mathbf{G}} = \frac{1}{\Omega} \int d\mathbf{r} V(r) \exp \left( -i \mathbf{G} \cdot \mathbf{r} \right)
\]

and the reciprocal vector is

\[
\mathbf{G} = \frac{2\pi}{\Omega} \left[ m_1 (b \times c) + m_2 (c \times a) + m_3 (a \times b) \right] \quad (m_1, m_2, m_3 \in \mathbb{Z})
\]

and \(\Omega = a \cdot (b \times c) = b \cdot (c \times a) = c \cdot (a \times b)\) is the unit-cell volume.
Bloch's Theorem

Assume that the unit cell is repeated \( M \times M \times M \) times, and we solved the Schrödinger equation,

\[
\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E \psi(\mathbf{r})
\]

in this "supercell".

We can expand the wave function as

\[
\psi(\mathbf{r}) = \sum_{\mathbf{k}} a_{\mathbf{k}} \exp \left( i\mathbf{k} \cdot \mathbf{r} \right)
\]

where

\[
a_{\mathbf{k}} = \frac{1}{M^2 \Omega} \int_{M^3 \Omega} d\mathbf{r} \psi(\mathbf{r}) \exp \left( -i \mathbf{k} \cdot \mathbf{r} \right)
\]

and

\[
\mathbf{k} = \frac{2\pi}{M^2 \Omega} \left[ m_1 \mathbf{M} (\mathbf{b} \times \mathbf{e}) + m_2 \mathbf{M} (\mathbf{c} \times \mathbf{a}) + m_3 \mathbf{M} (\mathbf{a} \times \mathbf{b}) \right]
\]

\[
= \frac{2\pi}{\Omega} \left[ \frac{m_1}{M} (\mathbf{b} \times \mathbf{e}) + \frac{m_2}{M} (\mathbf{c} \times \mathbf{a}) + \frac{m_3}{M} (\mathbf{a} \times \mathbf{b}) \right]
\]

Substituting Eq. (5) in (4),

\[
\sum_{\mathbf{k}} \frac{\hbar^2}{2m} a_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} + \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} \sum_{\mathbf{k}} a_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} = E \sum_{\mathbf{k}} a_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}}
\]

\[
= \sum_{\mathbf{k}} \sum_{\mathbf{G}} V_{\mathbf{G}} a_{\mathbf{k}-\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}
\]

\[\vdots\]

\[
\sum_{\mathbf{k}} \left[ \frac{\hbar^2}{2m} a_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} a_{\mathbf{k}-\mathbf{G}} - E a_{\mathbf{k}} \right] e^{i\mathbf{k} \cdot \mathbf{r}} = 0
\]
Therefore k\* components that are connected by the lattice reciprocal vectors, G, are coupled.

We can therefore label the eigenstates by \( k \) modulo \( G \), or \( k \) in the first Brillouin zone. An eigenstate can then be expressed as

\[
\psi_{k \mathbf{r}} = \sum_G a_G \exp\left[i(k + G) \cdot \mathbf{r}\right] \quad \text{for } k \text{ in 1st Brillouin zone} \tag{9}
\]

\[
= e^{ik \cdot \mathbf{r}} \sum_G a_G \exp(iG \cdot \mathbf{r}) \tag{10}
\]

\[
= e^{ik \cdot \mathbf{r}} u(\mathbf{r}) \tag{11}
\]

where \( u(\mathbf{r}) \) is periodic and \( k \) is in the 1st Brillouin zone.
Schrödinger Equation in Momentum Space

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_{kr}(r) = E \psi_{kr}(r) \tag{12}
\]

\[
\psi_{kr}(r) = \sum_{G} a_{kr+G} e^{i \cdot (k + G) \cdot r} \tag{13}
\]

Substituting Eq. (13) in (12),

\[
\sum_{G} \frac{\hbar^2}{2m} |k + G|^2 a_{kr+G} e^{i \cdot (k + G) \cdot r} + \sum_{G} V_{G'} e^{i \cdot G' \cdot r} a_{kr+G} e^{i \cdot (k + G) \cdot r} = E \sum_{G} a_{kr+G} e^{i \cdot (k + G) \cdot r}
\]

\[
\sum_{G} V_{G'} a_{kr+G} e^{i \cdot (k + G + G') \cdot r} = \sum_{G} V_{G} e^{i \cdot G' \cdot r} a_{kr+G} e^{i \cdot (k + G) \cdot r}
\]

\[
= \sum_{G} V_{G} a_{kr+G} e^{i \cdot (k + G) \cdot r}
\]

\[
= \sum_{G} V_{G} a_{kr+G} e^{i \cdot (k + G) \cdot r}
\]

\[
\therefore \frac{\hbar^2}{2m} |k + G|^2 a_{kr+G} + \sum_{G} V_{G} a_{kr+G} = E a_{kr+G} \tag{14}
\]