
Appendix: Effective Mass Theorem

For solving a Schrödinger equation with a slowly varying perturbation $\delta V(\mathbf{r})$ in a crystal,

$$[H_0 + \delta V(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (\text{A.1})$$

with $H_0 = \frac{p^2}{2m_0} + V(\mathbf{r})$ the unperturbed Hamiltonian, we may expand the new eigenstates as the linear superposition of the perfect bulk eigenstates $\psi_{j\mathbf{k}}(\mathbf{r})$, thus we look for a solution in the form of

$$\psi(\mathbf{r}) = \sum_j \int f_j(\mathbf{k}) \psi_{j\mathbf{k}}(\mathbf{r}) d\mathbf{k}, \quad (\text{A.2})$$

where

$$f_j(\mathbf{k}) = \int_{\Omega} \psi_{j\mathbf{k}}^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} \quad (\text{A.3})$$

is the projection of $\psi(\mathbf{r})$ on the bulk eigenstates $\psi_{j\mathbf{k}}(\mathbf{r})$. We integrate over k because that with the breaking of the translational symmetry, now the eigenstates are the mixture from the original eigenstates over the whole Brillouin zone. The summation is over the band we include in our calculation. Sometimes one band is not very bad, such as for the donor states for GaAs, which are generally on the magnitude of meV below the conduction band edge. On the other occasions such as for the acceptor states or the valence subband structures in a quantum well, we need to include the HH, LH, and split-off hole states based on the Luttinger Hamiltonian, and sometimes we shall also put the conduction band into consideration in addition.

Before proceeding, we first consider the integral

$$I = \int_{\Omega} F(\mathbf{r}) u(\mathbf{r}) d\mathbf{r}, \quad (\text{A.4})$$

where Ω is the volume of the crystal, $F(\mathbf{r})$ is a slowly varying function at the scale of the primitive cell, and $u(\mathbf{r})$ is a periodic function with the periodicity

of the lattice. Varying “slowly” here means that in the scale of a primitive cell, the quantities it refers to can be assumed unchanged. There are typically two length scales in our considered systems. One is a relatively macroscopic scale such as the quantum well width, on which the perturbation and the envelope function vary. The other is the scale of the crystal primitive cell, or about the lattice constant, on which the periodic part of the Bloch function varies. Using these spatial properties of the functions, we can factorize an integral over the whole crystal into a product of two integrals as in the following,

$$\begin{aligned}
 I &= \int_{\Omega} F(\mathbf{r})u(\mathbf{r})d\mathbf{r} = \sum_{\mathbf{R}_n} \int_{\Omega_0} F(\mathbf{r} - \mathbf{R}_n)u(\mathbf{r} - \mathbf{R}_n)d\mathbf{r} \\
 &= \sum_{\mathbf{R}_n} F(\mathbf{r} - \mathbf{R}_n) \int_{\Omega_0} u(\mathbf{r} - \mathbf{R}_n)d\mathbf{r} \\
 &= \frac{1}{\Omega} \int_{\Omega} F(\mathbf{r})d\mathbf{r} \int_{\Omega_0} u(\mathbf{r})d\mathbf{r},
 \end{aligned} \tag{A.5}$$

where Ω_0 is the volume of the primitive cell. In the above derivation, the periodicity of $u(\mathbf{r})$ is used.

According to the discussions in the last chapter, the bulk eigenstates $\psi_{j\mathbf{k}}(\mathbf{r})$ are Bloch functions with the periodic part being superpositions of the band edge function u_{i0} , i.e.,

$$\psi_{j\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_i c_{ji}(\mathbf{k})u_{i0}(\mathbf{r}). \tag{A.6}$$

Inserting the above equation into (A.2), we obtain

$$\begin{aligned}
 \psi(\mathbf{r}) &= \sum_{i,j} \int e^{i\mathbf{k}\cdot\mathbf{r}} c_{ji}(\mathbf{k})f_j(\mathbf{k})u_{i0}(\mathbf{r})d\mathbf{k} \\
 &= \sum_i \left(\int e^{i\mathbf{k}\cdot\mathbf{r}} F_{i\mathbf{k}}d\mathbf{k} \right) u_{i0}(\mathbf{r}) \\
 &= \sum_i F_i(\mathbf{r})u_{i0}(\mathbf{r}),
 \end{aligned} \tag{A.7}$$

where we define

$$F_{i\mathbf{k}} = \sum_j c_{ji}(\mathbf{k})f_j(\mathbf{k}) \tag{A.8}$$

and

$$F_i(\mathbf{r}) = \int e^{i\mathbf{k}\cdot\mathbf{r}} F_{i\mathbf{k}}d\mathbf{k}. \tag{A.9}$$

So eventually we expressed the eigenstates of the perturbed system as a sum of modulated periodic band edge functions. The $F_i(\mathbf{r})$ s are the envelope functions.

Inserting (A.7) into (A.1), then multiplying $e^{-i\mathbf{k}'\cdot\mathbf{r}}u_{i0}^*(\mathbf{r})$, and then integrating over the volume of the crystal, we obtain

$$\sum_j \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} \int d\mathbf{k} F_{j\mathbf{k}} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} u_{i0}^*(\mathbf{r}) \times \left[\frac{\hbar^2 k^2}{2m_0} + E_j - E + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p} + \delta V(\mathbf{r}) \right] u_{j0}(\mathbf{r}) = 0. \quad (\text{A.10})$$

Here we can use (A.5) to greatly reduce the complexity of the above equation. Following the same procedure, we have

$$\frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} u_{i0}^*(\mathbf{r}) \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p} u_{j0}(\mathbf{r}) = \delta_{\mathbf{k},\mathbf{k}'} \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p}_{ij}, \quad (\text{A.11})$$

where the identity

$$\frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} = \delta_{\mathbf{k},\mathbf{k}'} \quad (\text{A.12})$$

is used, and \mathbf{p}_{ij} is the momentum matrix element between states $u_{i0}(\mathbf{r})$ and $u_{j0}(\mathbf{r})$. Similarly,

$$\frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} u_{i0}^*(\mathbf{r}) \delta V(\mathbf{r}) u_{j0}(\mathbf{r}) = \delta V_{\mathbf{k}-\mathbf{k}'} \delta_{i,j}, \quad (\text{A.13})$$

where

$$\delta V_{\mathbf{k}-\mathbf{k}'} = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} \delta V(\mathbf{r}) \quad (\text{A.14})$$

is actually the Fourier transformation of $\Delta V(\mathbf{r})$, and we used the property that periodic Bloch states are orthonormal in a primitive cell, i.e.,

$$\frac{1}{\Omega} \int_{\Omega} u_{j0}^* u_{i0} d\mathbf{r} = \frac{1}{\Omega_0} \int_{\Omega_0} u_{j0}^* u_{i0} d\mathbf{r} = \delta_{ij}. \quad (\text{A.15})$$

Using these results, (A.10) finally becomes

$$\left(\frac{\hbar^2 k^2}{2m_0} + E_i \right) F_{i\mathbf{k}} + \frac{\hbar}{m_0} \sum_j \mathbf{k} \cdot \mathbf{p}_{ij} F_{j\mathbf{k}} + \int d\mathbf{k}' \delta V_{\mathbf{k}-\mathbf{k}'}(\mathbf{r}) F_{i\mathbf{k}'} = E F_{i\mathbf{k}}. \quad (\text{A.16})$$

This equation clearly shows that δV mixes the states with different k , but does not couple one state with the other. Next, we deal with the coupling from the other bands using perturbation theory. One approximation is to neglect the effects of the perturbative potential to the other bands. Then if we consider a singly degenerate band i , and assume that one band j only couples with band i , then for all the other bands, (A.16) becomes

$$\left(\frac{\hbar^2 k^2}{2m_0} + E_j\right) F_{j\mathbf{k}} + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p}_{ij} F_{i\mathbf{k}} = E F_{j\mathbf{k}}. \quad (\text{A.17})$$

By approximating $E \simeq E_i + \frac{\hbar^2 k^2}{2m_0}$, we have

$$F_{j\mathbf{k}} = \frac{\hbar}{m_0} \frac{\mathbf{k} \cdot \mathbf{p}_{ij}}{E_i - E_j} F_{i\mathbf{k}}. \quad (\text{A.18})$$

Inserting the above equation into (A.16), we obtain the equation for band i ,

$$\left(\frac{\hbar^2 k^2}{2m_0} + E_i + \frac{\hbar^2}{m_0^2} \sum_{j \neq i} \frac{|\mathbf{k} \cdot \mathbf{p}_{ij}|^2}{E_i - E_j}\right) F_{i\mathbf{k}} + \int d\mathbf{k}' \delta V_{\mathbf{k}-\mathbf{k}'}(\mathbf{r}) F_{i\mathbf{k}'} = E F_{i\mathbf{k}}. \quad (\text{A.19})$$

Comparing with (4.116), we can write the above equation as

$$\left(\frac{\hbar^2 k^2}{2m^*} + E_i\right) F_{i\mathbf{k}} + \int d\mathbf{k}' \delta V_{\mathbf{k}-\mathbf{k}'}(\mathbf{r}) F_{i\mathbf{k}'} = E F_{i\mathbf{k}}, \quad (\text{A.20})$$

where m^* is exactly the effective mass for band i in the perfect crystal. Taking a Fourier transform of the above equation from the reciprocal space to the real space, the above equation becomes

$$\left[-\frac{\hbar^2 \nabla^2}{2m^*} + \delta V(\mathbf{r})\right] F_i(\mathbf{r}) = E F_i(\mathbf{r}), \quad (\text{A.21})$$

which is an equation for the envelope function $F_i(\mathbf{r})$. Following the same procedure, a coupled second-order differential equation set can be obtained for the envelope functions for a degenerate set, written in a matrix form as $(H + \delta V)F = EF$, where F is the envelope function in a form of $1 \times n$ vector, if the band considered is n -fold degenerate, and H is in the same form as for a perfect crystal with k_i replaced by $-i \frac{\partial}{\partial x_i}$, where $x_i = x, y, z$.

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