0.1 Electron-phonon coupling (V. M. Stojanović)

0.1.1 Derivation of the electron-phonon coupling Hamiltonian

Abandoning the adiabatic approximation, in the framework of which the band structure of solids is determined, we now discuss the non-adiabatic corrections to the electron motion – electron-phonon coupling (henceforth e-ph coupling). In what follows, we derive a general e-ph coupling Hamiltonian in second-quantization notation. For the sake of notational convenience, our derivation will assume *intraband* e-ph scattering (i.e., the initial and final electron states belong to the same Bloch band); the most general case, which also involves *interband* scattering, is completely analogous and only requires an additional, Bloch-band, index in all the expressions.

We start by noting that the total electron-lattice interaction potential can be written as a sum over all electron-ion pairs:

$$V_{\text{e-latt}} = \sum_{i,n} V_{\text{e-i}}(\mathbf{r}_i - \mathbf{R}_n) \ , \tag{1}$$

where $\mathbf{r}_i$ are the electronic and $\mathbf{R}_n$ the ionic positions. Upon expanding the right-hand side (hereafter RHS) of the last equation in terms of the atomic (ionic) displacements $\mathbf{u}_n$ from the equilibrium positions $\mathbf{R}_n^0$ (recall $\mathbf{R}_n = \mathbf{R}_n^0 + \mathbf{u}_n$), we obtain

$$V_{\text{e-latt}} = \sum_{i,n} V_{\text{e-i}}(\mathbf{r}_i - \mathbf{R}_n^0) - \sum_{i,n} \mathbf{u}_n \cdot \nabla_{\mathbf{R}_n} V_{\text{e-i}}(\mathbf{r}_i - \mathbf{R}_n)\big|_{\mathbf{R}_n=\mathbf{R}_n^0} + \dots \ , \tag{2}$$

where the ellipses stand for the terms of higher order in $\mathbf{u}_n$. The first term on the RHS is the static lattice-periodic potential, giving rise to the Bloch bands; the second term will yield the lowest-order (linear) e-ph interaction.

By making use of the standard procedure for switching between first and second quantizations (recall part I of the course !), we get the (linear) e-ph coupling Hamiltonian

$$H_{\text{e-ph}} = -\sum_{n} \mathbf{u}_n \cdot \sum_{\mathbf{k}\sigma,\mathbf{k}'\sigma'} \langle \mathbf{k}'\sigma' | \nabla_{\mathbf{R}_n} V_{\text{e-i}}(\mathbf{r} - \mathbf{R}_n)\big|_{\mathbf{R}_n=\mathbf{R}_n^0} | \mathbf{k}\sigma \rangle \, a^\dagger_{\mathbf{k}',\sigma'} a_{\mathbf{k},\sigma} \ , \tag{3}$$

where the operator $a^\dagger_{\mathbf{k},\sigma}$ ($a_{\mathbf{k},\sigma}$) creates (destroys) an electron with the quasimomentum $\mathbf{k}$ and spin σ. While the spin part of the last matrix element is easily seen to be equal to $\delta_{\sigma\sigma'}$, the coordinate part is given by

$$\langle \mathbf{k}' | \nabla_{\mathbf{R}_n} V_{\text{e-i}}(\mathbf{r} - \mathbf{R}_n)\big|_{\mathbf{R}_n=\mathbf{R}_n^0} | \mathbf{k} \rangle = \int d\mathbf{r} \, \Psi^*_{\mathbf{k}'}(\mathbf{r}) \nabla_{\mathbf{R}_n} V_{\text{e-i}}(\mathbf{r} - \mathbf{R}_n)\big|_{\mathbf{R}_n=\mathbf{R}_n^0} \Psi_{\mathbf{k}}(\mathbf{r}) \ , \tag{4}$$

with $\Psi_{\mathbf{k}}(\mathbf{r}) \equiv \langle \mathbf{r} | \mathbf{k} \rangle$ being the electron Bloch wave functions. By virtue of the Bloch theorem $\Psi_{\mathbf{k}}(\mathbf{r} + \mathbf{a}) = e^{i\mathbf{k}\cdot\mathbf{a}} \Psi_{\mathbf{k}}(\mathbf{r})$ and we further obtain

$$\langle \mathbf{k}' | \nabla_{\mathbf{R}_n} V_{\text{e-i}}(\mathbf{r} - \mathbf{R}_n)\big|_{\mathbf{R}_n=\mathbf{R}_n^0} | \mathbf{k} \rangle = e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}^0_\mathbf{n}} \mathbf{S}_{\mathbf{k},\mathbf{k}'} \ , \tag{5}$$

where

$$\mathbf{S}_{\mathbf{k},\mathbf{k}'} \equiv \int d(\mathbf{r} - \mathbf{R}_n^0) \Psi^*_{\mathbf{k}'}(\mathbf{r} - \mathbf{R}_n^0) \nabla_{\mathbf{R}_n} V_{\text{e-i}}(\mathbf{r} - \mathbf{R}_n)\big|_{\mathbf{R}_n=\mathbf{R}_n^0} \Psi_{\mathbf{k}}(\mathbf{r} - \mathbf{R}_n^0) \tag{6}$$

depends on $\mathbf{k}$ and $\mathbf{k}'$, but not on n. By combining Eqs. (3) and (5) we arrive at

$$H_{\text{e-ph}} = -\sum_{\mathbf{k},\mathbf{k}',\sigma} [\mathbf{S}_{\mathbf{k},\mathbf{k}'} \cdot \sum_n e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n^0} \mathbf{u}_n] a^\dagger_{\mathbf{k}',\sigma'} a_{\mathbf{k},\sigma} \, . \tag{7}$$

The displacement operators $\mathbf{u}_n$ can be expressed through the phonon creation and annihilation operators as

$$\mathbf{u}_n = \frac{1}{\sqrt{N}} \sum_{\mathbf{q},\lambda} \sqrt{\frac{\hbar}{2M\omega_\lambda(\mathbf{q})}} \, e^{i\mathbf{q}\cdot\mathbf{R}_n^0} (b^\dagger_{-\mathbf{q},\lambda} + b_{\mathbf{q},\lambda}) \mathbf{v}_\lambda \, , \tag{8}$$

where $\mathbf{q}$ are the phonon quasimomenta and the index λ runs over different phonon branches. We further notice that $e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{q})\cdot\mathbf{R}_n^0} = 1$ whenever $\mathbf{k}' - \mathbf{k} - \mathbf{q}$ is equal to a reciprocal lattice vector $\mathbf{K}$, i.e.,

$$\sum_n e^{i(\mathbf{k}-\mathbf{k}'+\mathbf{q})\cdot\mathbf{R}_n^0} = \sum_{\mathbf{K}} \delta_{\mathbf{k}'-\mathbf{k}-\mathbf{q},\mathbf{K}} \, . \tag{9}$$

Consequently, Eq. (7) can be recast as

$$H_{\text{e-ph}} = -\sum_{\mathbf{k},\mathbf{q},\mathbf{K},\lambda,\sigma} \sqrt{\frac{\hbar}{2MN\omega_\lambda(\mathbf{q})}} (b^\dagger_{-\mathbf{q},\lambda} + b_{\mathbf{q},\lambda}) \mathbf{v}_\lambda \cdot \mathbf{S}_{\mathbf{k},\mathbf{k}+\mathbf{K}+\mathbf{q}} \, a^\dagger_{\mathbf{k}+\mathbf{K}+\mathbf{q},\sigma} a_{\mathbf{k},\sigma} \, . \tag{10}$$

Upon introducing the abbreviation

$$G_\lambda(\mathbf{k},\mathbf{q},\mathbf{K}) \equiv -\sqrt{\frac{\hbar}{2M\omega_\lambda(\mathbf{q})}} \, \mathbf{v}_\lambda \cdot \mathbf{S}_{\mathbf{k},\mathbf{k}+\mathbf{K}+\mathbf{q}} \tag{11}$$

we can rewrite the Hamiltonian of Eq. (10) in a more succinct form:

$$H_{\text{e-ph}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k},\mathbf{q},\mathbf{K},\lambda,\sigma} G_\lambda(\mathbf{k},\mathbf{q},\mathbf{K}) a^\dagger_{\mathbf{k}+\mathbf{K}+\mathbf{q},\sigma} a_{\mathbf{k},\sigma} (b^\dagger_{-\mathbf{q},\lambda} + b_{\mathbf{q},\lambda}) \, . \tag{12}$$

The last equation should be interpreted as follows: an electron, originaly in the state $(\mathbf{k},\sigma)$, can be scattered into the final state $(\mathbf{k}+\mathbf{q}+\mathbf{K},\sigma)$ [note that such scattering processes – taking place in the periodic, static lattice potential – conserve momentum only up to an arbitrary reciprocal lattice vector] either by absorbing the phonon $(\mathbf{q},\lambda)$ or by emitting the phonon $(-\mathbf{q},\lambda)$. The normal-scattering processes ($\mathbf{K} = 0$) usually dominate over the Umklapp-scattering ($\mathbf{K} \neq 0$) ones; by completely neglecting the Umklapp scattering in the last equation and introducing $\gamma_\lambda(\mathbf{k},\mathbf{q}) \equiv G_\lambda(\mathbf{k},\mathbf{q},\mathbf{K}=0)$, we finally obtain

$$H_{\text{e-ph}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k},\mathbf{q},\lambda,\sigma} \gamma_\lambda(\mathbf{k},\mathbf{q}) a^\dagger_{\mathbf{k}+\mathbf{q},\sigma} a_{\mathbf{k},\sigma} (b^\dagger_{-\mathbf{q},\lambda} + b_{\mathbf{q},\lambda}) \, . \tag{13}$$

The functions $\gamma_\lambda(\mathbf{k},\mathbf{q})$ are usually referred to as the e-ph vertex functions.

The total Hamiltonian of a coupled e-ph system is given by

$$H = H_{\text{e}} + H_{\text{e-ph}} + H_{\text{ph}} \, , \tag{14}$$

where $H_{\rm e}$ is the bare-electron and $H_{\rm ph}$ the phonon part. Regardless of the form of the vertex functions $\gamma_\lambda(\mathbf{k},\mathbf{q})$, the last Hamiltonian commutes with the total crystal-momentum operator

$$\mathbf{K}\equiv\sum_{\mathbf{k},\sigma}\mathbf{k}\,a^\dagger_{\mathbf{k},\sigma}a_{\mathbf{k},\sigma}+\sum_{\lambda,\mathbf{q}}\mathbf{q}\,b^\dagger_{\mathbf{q},\lambda}b_{\mathbf{q},\lambda}\,. \tag{15}$$

The joint eigenstates of H and $\mathbf{K}$ are the Bloch states of the coupled e-ph system.

0.1.2 Derivation of the electron-phonon (inelastic) scattering rates

The momentum-space form of the most general (multi-band) e-ph-coupling Hamiltonian reads

$$\hat{H}_{\text{e-ph}}=\frac{1}{\sqrt{N}}\sum_{nn',\mathbf{k},\mathbf{q},\lambda}\gamma^\lambda_{n'n}(\mathbf{k},\mathbf{q})\,\hat{a}^\dagger_{n',\mathbf{k}+\mathbf{q}}\hat{a}_{n,\mathbf{k}}(\hat{b}^\dagger_{-\mathbf{q},\lambda}+\hat{b}_{\mathbf{q},\lambda})\,, \tag{16}$$

where $\hat{a}_{n,\mathbf{k}}$ destroys an electron with quasimomentum $\mathbf{k}$ in the n-th Bloch band, $\hat{b}_{\mathbf{q},\lambda}$ a phonon of branch λ with quasimomentum $\mathbf{q}$ (frequency $\omega_{\lambda,\mathbf{q}}$), and $\gamma^\lambda_{n'n}(\mathbf{k},\mathbf{q})$ stand for the (bare) e-ph interaction vertex functions.

We now derive inelastic scattering rates (inverse scattering time) using the Fermi Golden rule expression

$$W_{f,i}=\frac{2\pi}{\hbar}|M_{f,i}|^2\delta(\epsilon_f-\epsilon_i)\,, \tag{17}$$

where $M_{f,i}$ in our case will be the matrix element of the Hamiltonian in Eq. (16) between the final and initial states:

$$M_{f,i}\equiv\langle f|\hat{H}_{\text{e-ph}}|i\rangle\,. \tag{18}$$

The total inelastic scattering rate for an electron out of the state with quasimomentum $\mathbf{k}$ in n-th Bloch band is given by

$$\left(\frac{1}{\tau}\right)_{n,\mathbf{k}}=\sum_{n',\mathbf{q},\lambda}W^{\mathbf{q},\lambda}_{n'n}\,, \tag{19}$$

where $W^{\mathbf{q},\lambda}_{n'n}$ is the scattering rate corresponding to the case where the phonon mode $(\mathbf{q},\lambda)$ is involved in the scattering process and the final electron belongs to the n'-th Bloch band.

For the scattering process involving an emission of the phonon $(-\mathbf{q},\lambda)$ and an electron scattered from $(n,\mathbf{k})$ to $(n',\mathbf{k}'=\mathbf{k}+\mathbf{q})$ this matrix element is given by

$$M_{f,i}=\langle n_{\lambda,\mathbf{q}}+1;\,(n',\mathbf{k}+\mathbf{q})|\frac{1}{\sqrt{N}}\gamma^\lambda_{n'n}(\mathbf{k},\mathbf{q})\hat{a}^\dagger_{n',\mathbf{k}+\mathbf{q}}\hat{a}_{n,\mathbf{k}}\hat{b}^\dagger_{-\mathbf{q},\lambda}|(n,\mathbf{k});\,n_{\lambda,\mathbf{q}}\rangle\,, \tag{20}$$

that is,

$$M_{f,i}=\frac{\gamma^\lambda_{n'n}(\mathbf{k},\mathbf{q})}{\sqrt{N}}\sqrt{n_{\lambda,\mathbf{q}}+1}\,, \tag{21}$$

while the argument of the delta function in Eq. (17) is

$$\epsilon_f - \epsilon_i = \epsilon_{n',\mathbf{k}+\mathbf{q}} + \hbar\omega_{\lambda,-\mathbf{q}} - \epsilon_{n,\mathbf{k}} \ . \tag{22}$$

In like manner, for the process involving an absorption of the phonon $(\mathbf{q},\lambda)$ and an electron scattered from $(n,\mathbf{k})$ to $(n',\mathbf{k}'=\mathbf{k}+\mathbf{q})$ we have

$$M_{f,i} = \langle n_{\lambda,\mathbf{q}} - 1;\ (n',\mathbf{k}+\mathbf{q})| \frac{1}{\sqrt{N}} \gamma^{\lambda}_{n'n}(\mathbf{k},\mathbf{q}) \hat{a}^{\dagger}_{n',\mathbf{k}+\mathbf{q}} \hat{a}_{n,\mathbf{k}} \hat{b}_{\mathbf{q},\lambda} |(n,\mathbf{k});\ n_{\lambda,\mathbf{q}}\rangle \ , \tag{23}$$

that is,

$$M_{f,i} = \frac{\gamma^{\lambda}_{n'n}(\mathbf{k},\mathbf{q})}{\sqrt{N}} \sqrt{n_{\lambda,\mathbf{q}}} \ , \tag{24}$$

and

$$\epsilon_f - \epsilon_i = \epsilon_{n',\mathbf{k}+\mathbf{q}} - \hbar\omega_{\lambda,\mathbf{q}} - \epsilon_{n,\mathbf{k}} \ . \tag{25}$$

In deriving Eqs. (21) and (24) we have just made use of the standard bosonic relations $b|n\rangle = \sqrt{n}|n-1\rangle$ and $b^{\dagger}|n\rangle = \sqrt{n+1}|n+1\rangle$.

Now using the Fermi Golden rule expression we obtain

$$\begin{aligned} W^{\mathbf{q},\lambda}_{n'n} = \frac{2\pi}{\hbar} \Big\{ & \frac{1}{N} |\gamma^{\lambda}_{n'n}(\mathbf{k},\mathbf{q})|^2 n_{\lambda,\mathbf{q}}\, \delta(\epsilon_{n',\mathbf{k}+\mathbf{q}} - \hbar\omega_{\lambda,\mathbf{q}} - \epsilon_{n,\mathbf{k}}) \\ & + \frac{1}{N} |\gamma^{\lambda}_{n'n}(\mathbf{k},\mathbf{q})|^2 (n_{\lambda,\mathbf{q}}+1)\, \delta(\epsilon_{n',\mathbf{k}+\mathbf{q}} + \hbar\omega_{\lambda,-\mathbf{q}} - \epsilon_{n,\mathbf{k}}) \Big\} \ , \end{aligned} \tag{26}$$

i.e., the total scattering rate is given by

$$\begin{aligned} \left(\frac{1}{\tau}\right)_{n,\mathbf{k}} = \frac{1}{N} \sum_{n',\mathbf{q},\lambda} \frac{2\pi}{\hbar} |\gamma^{\lambda}_{n'n}(\mathbf{k},\mathbf{q})|^2 \Big\{ & n_{\lambda,\mathbf{q}}\, \delta(\epsilon_{n',\mathbf{k}+\mathbf{q}} - \hbar\omega_{\lambda,\mathbf{q}} - \epsilon_{n,\mathbf{k}}) \\ & + (n_{\lambda,\mathbf{q}}+1)\, \delta(\epsilon_{n',\mathbf{k}+\mathbf{q}} + \hbar\omega_{\lambda,-\mathbf{q}} - \epsilon_{n,\mathbf{k}}) \Big\} \ . \end{aligned} \tag{27}$$

Note that the last expression can be recast more succinctly as

$$\left(\frac{1}{\tau}\right)_{n,\mathbf{k}} = \frac{2\pi}{N\hbar} \sum_{n',\mathbf{q},\lambda} |\gamma^{\lambda}_{n'n}(\mathbf{k},\mathbf{q})|^2 [\Delta^{\lambda;-}_{n'n}(\mathbf{k},\mathbf{q}) + \Delta^{\lambda;+}_{n'n}(\mathbf{k},\mathbf{q})] \ , \tag{28}$$

where

$$\Delta^{\lambda;\pm}_{n'n}(\mathbf{k},\mathbf{q}) \equiv (n_{\lambda,\mathbf{q}} + 1/2 \pm 1/2) \delta(\epsilon_{n',\mathbf{k}+\mathbf{q}} - \epsilon_{n,\mathbf{k}} \pm \hbar\omega_{\lambda,\mathbf{q}}) \tag{29}$$

and we made use of the fact that $\omega_{\lambda,-\mathbf{q}} = \omega_{\lambda,\mathbf{q}}$. Here $\Delta^{\lambda;+}_{n'n}(\mathbf{k},\mathbf{q})$ $[\Delta^{\lambda;-}_{n'n}(\mathbf{k},\mathbf{q})]$ corresponds to the emission (absorption) of a phonon $(\mathbf{q},\lambda)$ and

$$n_{\lambda,\mathbf{q}} \equiv [\exp(\beta\hbar\omega_{\lambda,\mathbf{q}}) - 1]^{-1} \tag{30}$$

are the phonon occupation numbers at temperature T $[\beta \equiv (k_B T)^{-1}]$.