

1 From Tight-Binding Wannier Hamiltonian to Dipole Elements

Starting from the Tight-Binding hamiltonian in the Wannier basis set

$$H_{ij}(\mathbf{R}\sigma) = \langle w_{i\sigma} | \hat{H} | w_{j\sigma} \mathbf{R} \rangle \quad (1)$$

where $|w_{i\sigma} \mathbf{R}\rangle$ is the wannier function i of the σ spin channel in the unitary cell \mathbf{R} . A Fourier transform of the hamiltonian allows us to consider only the wannier functions in the unitary cell 0; in the collinear case, the hamiltonians in the two spin channels are considered separately:

$$H_{ij}(\mathbf{k}\sigma) = \sum_{\mathbf{R}} H_{ij}(\mathbf{R}\sigma) e^{i\mathbf{k}\cdot\mathbf{R}} \quad (2)$$

At this point, the hamiltonian is diagonalized in order to obtain Bloch states

$$H_{ij}(\mathbf{k}\sigma) |n\sigma\mathbf{k}\rangle = \epsilon_{n\sigma}(\mathbf{k}) |n\sigma\mathbf{k}\rangle = \sum_j H_{ij}(\mathbf{k}\sigma) C_{j\sigma}^{n\mathbf{k}} |w_{j\sigma} \mathbf{0}\rangle = \epsilon_{n\sigma}(\mathbf{k}) C_{i\sigma}^{n\mathbf{k}} |w_{i\sigma} \mathbf{0}\rangle \quad (3)$$

where $|n\sigma\mathbf{k}\rangle$ is the Bloch state n of the spin channel σ at the \mathbf{k} point of the Brillouin zone, and $C_{j\sigma}^{n\mathbf{k}}$ is its projection over the j wannier function of the basis set. From the Bloch states in the two spin channel a spinor is built

$$|n\mathbf{k}\rangle = |n\uparrow\mathbf{k}\rangle |n\downarrow\mathbf{k}\rangle = \sum_{i\sigma} C_{i\sigma}^{n\mathbf{k}} |w_{i\sigma} \mathbf{0}\rangle \quad (4)$$

At this point, the Bloch states allow to define a generalized dipole element

$$\rho_{\sigma(n1,\mathbf{k}1)(n2,\mathbf{k}2)}(\mathbf{G}; \mathbf{r}1, \mathbf{r}2, \mathbf{q}) = \langle n1\mathbf{k}1 - \mathbf{r}1 | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | n2\mathbf{k}2 - \mathbf{r}2 \rangle = \sum_j (C_{j\sigma}^{n1\mathbf{k}1-\mathbf{r}1})^* e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}_j} C_{j\sigma}^{n2\mathbf{k}2-\mathbf{r}2} \quad (5)$$

where $n1, n2, \mathbf{k}1, \mathbf{k}2, \mathbf{G}$ are considered as variables, while $\mathbf{q}, \mathbf{r}1, \mathbf{r}2, c$ are considered as parameters (obviously the two states $n1$ and $n2$ have spin σ). The following notation for ρ will be used:

$$\rho_{\sigma(n1,\mathbf{k}1-\mathbf{r}1)(n2,\mathbf{k}2-\mathbf{r}2)}(\mathbf{G}, \mathbf{q}) \equiv \rho_{\sigma(n1,\mathbf{k}1)(n2,\mathbf{k}2)}(\mathbf{G}; \mathbf{r}1, \mathbf{r}2, \mathbf{q}) \quad (6)$$

2 From Dipole Elements to BSE Hamiltonian

Before building the BSE hamiltonian, we need to construct our screening potential

$$\epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}\omega) = \delta_{\mathbf{G}\mathbf{G}'} + v_{\mathbf{G}}(\mathbf{q}) \chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q}\omega) \quad (7)$$

where $v(\mathbf{q})$ ($v(\mathbf{q}) = -4\pi e^2/|\mathbf{q}|^2$) is the Coulomb potential (in case of 2D systems a cutoff has been considered along the non-periodic direction) and χ is the

response function, which at the RPA order can be obtained solving the Dyson equation

$$\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q}\omega) = \sum_{\mathbf{G}_1} \left[\delta_{\mathbf{G}\mathbf{G}_1} - v_{\mathbf{G}}(\mathbf{q}) \chi_{\mathbf{G}_1\mathbf{G}}^0(\mathbf{q}\omega) \right]^{-1} \chi_{\mathbf{G}_1\mathbf{G}'}^0(\mathbf{q}\omega) \quad (8)$$

where (where Ω is the crystal volume)

$$\begin{aligned} \chi_{\mathbf{G}\mathbf{G}'}^0(\mathbf{q}\omega) &= \sum_{\sigma c v \mathbf{k}} (\rho_{\sigma(c\mathbf{k})(v\mathbf{k}-\mathbf{q})}(\mathbf{G}, \mathbf{q}))^* \rho_{\sigma(c\mathbf{k})(v\mathbf{k}-\mathbf{q})}(\mathbf{G}', \mathbf{q}) S_{cv\mathbf{k}\mathbf{q}\omega\sigma} \\ S_{cv\mathbf{k}\mathbf{q}\omega\sigma} &= \left[\frac{1}{\omega + \epsilon_{v\sigma}(\mathbf{k} - \mathbf{q}) - \epsilon_{c\sigma}(\mathbf{k}) + i\eta} - \frac{1}{\omega + \epsilon_{c\sigma}(\mathbf{k}) - \epsilon_{v\sigma}(\mathbf{k} - \mathbf{q}) - i\eta} \right] \end{aligned} \quad (9)$$

The BSE hamiltonian projected on a basis of electron-hole transitions $t : (n1\mathbf{k}1) \rightarrow (n2\mathbf{k}2)$ can be written as

$$\langle t | H_{BSE} | t' \rangle = E_t \delta_{tt'} + \langle t | (v - W) | t' \rangle \quad (10)$$

where W is the screened potential. The screened potential W can be written in reciprocal space as:

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}) v(\mathbf{q} + \mathbf{G}') \quad (11)$$

where the invariance under translation of ϵ and a symmetrization in the pair $(\mathbf{G}, \mathbf{G}')$ have been considered. Distinguishing between resonant transitions $r : (v\mathbf{k} - \mathbf{q}) \rightarrow (c\mathbf{k})$ and anti-resonant transitions $a : (c\mathbf{k}) \rightarrow (v\mathbf{k} + \mathbf{q})$, the BSE hamiltonian can be written in the following block form (in the long-wavelength limit $\mathbf{q} \rightarrow 0$)

$$H_{BSE} = \begin{pmatrix} H_{rr} & H_{ra} \\ -(H_{ra})^* & -(H_{rr})^* \end{pmatrix} \quad (12)$$

Writing the two main elements of the BSE hamiltonian in terms of the generalized dipole elements, we have for the resonant part $r = (\sigma_c c \sigma_v v \mathbf{k})$:

$$\begin{aligned} H_{rr'} &= E_r \delta_{rr'} + (\delta_M v_{rr'} - W_{rr'}) \\ v_{rr'} &= \frac{1}{N} \sum_{\mathbf{G} \neq 0} v(\mathbf{q} + \mathbf{G}) (\rho_{\sigma_{c'}}(\mathbf{c}'\mathbf{k}')(\mathbf{v}'\mathbf{k}' - \mathbf{q})(\mathbf{G}, \mathbf{q}))^* \rho_{\sigma_c(c\mathbf{k})(v\mathbf{k}-\mathbf{q})}(\mathbf{G}, \mathbf{q}) \delta_{\sigma_{c'}\sigma_v} \delta_{\sigma_c\sigma_v} \\ W_{rr'} &= \frac{1}{N} \sum_{\mathbf{G}\mathbf{G}'} W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) (\rho_{\sigma_{c'}}(\mathbf{c}'\mathbf{k}')(\mathbf{c}\mathbf{k})(\mathbf{G}, \mathbf{q}))^* \rho_{\sigma_{v'}(\mathbf{v}'\mathbf{k}' - \mathbf{q})(v\mathbf{k}-\mathbf{q})}(\mathbf{G}', \mathbf{q})^* \delta_{\sigma_{c'}\sigma_c} \delta_{\sigma_{v'}\sigma_v} \end{aligned} \quad (13)$$

while for the coupling part, considering $a = (\sigma_v v \sigma_c c \mathbf{k})$:

$$\begin{aligned}
H_{ra'} &= (\delta_M v_{ra'} - W_{ra'}) \\
v_{ra'} &= \frac{1}{N} \sum_{\mathbf{G} \neq \mathbf{0}} v(\mathbf{q} + \mathbf{G}) (\rho_{\sigma_{v'}}(v' \mathbf{k}' + \mathbf{q}') (c' \mathbf{k}') (\mathbf{G}, \mathbf{q}))^* \rho_{\sigma_c}(c \mathbf{k}) (v \mathbf{k} - \mathbf{q}) (\mathbf{G}, \mathbf{q}) \delta_{\sigma_{v'} \sigma_{c'}} \delta_{\sigma_c \sigma_v} \\
W_{ra'} &= \frac{1}{N} \sum_{\mathbf{G} \mathbf{G}'} W_{\mathbf{G} \mathbf{G}'}(\mathbf{q}) (\rho_{\sigma_{v'}}(v' \mathbf{k}' + \mathbf{q}) (c \mathbf{k}) (\mathbf{G}', \mathbf{q}))^* \rho_{\sigma_{c'}}(c' \mathbf{k}') (v \mathbf{k} - \mathbf{q}) (\mathbf{G}, \mathbf{q}) \delta_{\sigma_{c'} \sigma_v} \delta_{\sigma_c \sigma_{v'}}
\end{aligned} \tag{14}$$

Note that N is equal to the number of \mathbf{k} vectors considered in the FBZ, while δ_M is equal to 2 in the case of non-magnetic calculations and to 1 in the case of magnetic calculations.

3 From BSE Hamiltonian to Optical Spectra

At this point, the BSE hamiltonian can be diagonalized, we have followed the usual procedure and a procedure passing through a Cholesky factorization (Structure preserving parallel algorithms for solving the Bethe–Salpeter eigenvalue problem Meiyue Shao, Felipe H. da Jornada, Chao Yang, Jack Deslippe, Steven G. Louie). From the excitonic eigenvalue E_λ and eigenvector A^λ (orthonormalized), we can build the oscillator force of the excitonic state λ :

$$f_\alpha^\lambda = \sum_{\sigma c v \mathbf{k}} \rho_{\sigma(c \mathbf{k})}(v \mathbf{k} - \mathbf{q}_\alpha) (\mathbf{0}, \mathbf{q}_\alpha) (A_{\sigma c v \mathbf{k}}^\lambda)^* \tag{15}$$

This allow us to express the macroscopic dielectric function as:

$$(\epsilon_M)_\alpha(\omega) = 1 - \lim_{q_\alpha \rightarrow 0} \frac{8\pi}{|\mathbf{q}_\alpha|^2} \sum_\lambda \frac{f_\alpha^\lambda (f_\alpha^\lambda)^*}{\omega - E_\lambda} \tag{16}$$

where Ω is the primitive cell volume and α the direction of the electric field.