1 From Tight-Binding Wannier Hamiltonian to Dipole Elements

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

$$H_{ij}(\boldsymbol{R}\sigma) = \langle w_{i\sigma}\boldsymbol{0}|\,\hat{H}\,|w_{j\sigma}\boldsymbol{R}\rangle \tag{1}$$

wher $|w_{i\sigma}\boldsymbol{R}\rangle$ is the wannier function i of the σ spin channel in the unitary cell $\boldsymbol{R}$. 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:

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

This is equivalent to Fourier transform its wannier basis set

$$|w_{j\sigma}\boldsymbol{k}\rangle = \sum_{\boldsymbol{R}} |w_{j\sigma}\boldsymbol{R}\rangle\, e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \tag{3}$$

At this point, the hamiltonian is diagonalized in order to obtain Bloch states in the basis of the Fourier-transformed wannier functions

$$H_{ij}(\boldsymbol{k}\sigma)\,|n\sigma\boldsymbol{k}\rangle = \epsilon_{n\sigma}(\boldsymbol{k})\,|n\sigma\boldsymbol{k}\rangle \tag{4}$$

$$\sum_j H_{ij}(\boldsymbol{k}\sigma)C^{n\boldsymbol{k}}_{j\sigma}\,|w_{j\sigma}\boldsymbol{k}\rangle = \epsilon_{n\sigma}(\boldsymbol{k})C^{n\boldsymbol{k}}_{i\sigma}\,|w_{i\sigma}\boldsymbol{k}\rangle \tag{5}$$

where $|n\sigma\boldsymbol{k}\rangle$ is the Bloch state n of the spin channel σ at the $\boldsymbol{k}$ point of the Brillouin zone, and $C^{n\boldsymbol{k}}_{j\sigma}$ is its projection over the j Fourier-transformed wannier function of the Fourier-transformed basis set

$$|n\sigma\boldsymbol{k}\rangle = \sum_j C^{n\boldsymbol{k}}_{j\sigma}\,|w_{j\sigma}\boldsymbol{k}\rangle \tag{6}$$

$$= \sum_j C^{n\boldsymbol{k}}_{j\sigma} \sum_{\boldsymbol{R}} |w_{j\sigma}\boldsymbol{R}\rangle\, e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \tag{7}$$

From the Bloch states in the two spin channels a spinor is built

$$|n\boldsymbol{k}\rangle = |n\uparrow\boldsymbol{k}\rangle \otimes |n\downarrow\boldsymbol{k}\rangle = \sum_{i\uparrow} C^{n\boldsymbol{k}}_{i\uparrow}\,|w_{i\uparrow}\boldsymbol{k}\rangle \otimes \sum_{i\downarrow} C^{n\boldsymbol{k}}_{i\downarrow}\,|w_{i\downarrow}\boldsymbol{k}\rangle \tag{8}$$

Before proceeding it is necessary to decompose each wannier function in a set of atomic orbitals functions (here the projection on spatial eigenstates is considered to facilitate the decomposition)

$$\langle\boldsymbol{r}|w_{j\sigma}\boldsymbol{R}\rangle = \sum_m D^m_{j\sigma}\,\langle\boldsymbol{r}-\boldsymbol{R}|\phi_{m\sigma}\rangle \tag{9}$$

$$= \sum_m D^m_{j\sigma}R(|\boldsymbol{r}-\boldsymbol{R}|)_{m\sigma}Y_{m\sigma}(\theta,\phi) \tag{10}$$

where the radial and angular parts of the atomic orbtials functions have been separated.

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

$$\begin{aligned}\rho_{\sigma(n1,\boldsymbol{k1})(n2,\boldsymbol{k2})}(\boldsymbol{G};\boldsymbol{p1},\boldsymbol{p2},\boldsymbol{q})\\ = \langle n1\boldsymbol{k1}-\boldsymbol{p1}|\, e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\hat{\boldsymbol{r}}}\,|n2\boldsymbol{k2}-\boldsymbol{p2}\rangle\\ = \sum_j\sum_l (C^{n1\boldsymbol{k1}-\boldsymbol{p1}}_{j\sigma})^* C^{n2\boldsymbol{k2}-\boldsymbol{p2}}_{l\sigma}\sum_{\boldsymbol{R}}\sum_{\boldsymbol{R'}} e^{-i(\boldsymbol{k1}-\boldsymbol{p1})\cdot\boldsymbol{R}} e^{i(\boldsymbol{k2}-\boldsymbol{p2})\cdot\boldsymbol{R'}}\,\langle w_{j\sigma}\boldsymbol{R}|e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\hat{\boldsymbol{r}}}|w_{l\sigma}\boldsymbol{R'}\rangle\end{aligned}$$

where

$$\begin{aligned}\langle w_{j\sigma}\boldsymbol{R}|e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\hat{\boldsymbol{r}}}|w_{l\sigma}\boldsymbol{R'}\rangle\\ = \sum_s\sum_t (D^s_{j\sigma})^* D^t_{l\sigma}\int d\boldsymbol{r}\,\langle\phi_{s\sigma}|\boldsymbol{r}-\boldsymbol{r_j}-\boldsymbol{R}\rangle\, e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}\,\langle\boldsymbol{r}-\boldsymbol{r_l}-\boldsymbol{R'}|\phi_{t\sigma}\rangle\end{aligned} \tag{11}$$

As a simplifying approximation, the wannier functions can be described as delta functions, in order to simplify our generalized dipole element formula

$$|w_{\boldsymbol{r_j}j\sigma}\boldsymbol{R}\rangle = |(\boldsymbol{r_j}+\boldsymbol{R})j\sigma\rangle \tag{12}$$

then

$$\langle w_{j\sigma}\boldsymbol{R}|e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\hat{\boldsymbol{r}}}|w_{l\sigma}\boldsymbol{R'}\rangle = \delta_{jl}\delta_{\boldsymbol{RR'}}e^{(\boldsymbol{q}+\boldsymbol{G})\cdot(\boldsymbol{r_j}+\boldsymbol{R})} \tag{13}$$

where the orthonormality between the wannier functions have been used. At this point the generalized dipole element formula becomes

$$\begin{aligned}\rho_{\sigma(n1,\boldsymbol{k1})(n2,\boldsymbol{k2})}(\boldsymbol{G};\boldsymbol{p1},\boldsymbol{p2},\boldsymbol{q})\\ = \sum_j (C^{n_1\boldsymbol{k1}-\boldsymbol{p1}}_{j})^* C^{n2\boldsymbol{k2}-\boldsymbol{p2}}_{j} e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r_j}}\end{aligned} \tag{14}$$

where the fact that $\boldsymbol{G}$ is a vector of the reciprocal lattice has been used, and the conservation law $\boldsymbol{k1}-\boldsymbol{p1}=\boldsymbol{k2}-\boldsymbol{p2}-\boldsymbol{q}$ is implied.

The following notation for ρ will be used:

$$\rho_{\sigma(n1,\boldsymbol{k1}-\boldsymbol{r1})(n2,\boldsymbol{k2}-\boldsymbol{r2})}(\boldsymbol{G},\boldsymbol{q}) \equiv \rho_{\sigma(n1,\boldsymbol{k1})(n2,\boldsymbol{k2})}(\boldsymbol{G};\boldsymbol{r1},\boldsymbol{r2},\boldsymbol{q}) \tag{15}$$

where $n1, n2, \boldsymbol{k1}, \boldsymbol{k2}, \boldsymbol{G}$ are considered as variables, while $\boldsymbol{q}, \boldsymbol{r1}, \boldsymbol{r2}$,$c$ are considered as parameters (obviously the two states $n1$ and $n2$ have spin σ)(N_w is the number of wannier functions).

2 From Dipole Elements to BSE Hamiltonian

2.1 Dielectric Function

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

$$\epsilon^{-1}_{\boldsymbol{GG'}}(\boldsymbol{q}\omega) = \delta_{\boldsymbol{GG'}} + v_{\boldsymbol{G}}(\boldsymbol{q})\chi_{\boldsymbol{GG'}}(\boldsymbol{q}\omega) \tag{16}$$

where $v(\boldsymbol{q})$ ($v(\boldsymbol{q}) = \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\boldsymbol{q}|^2}$ with $[v] = eVAng^3$) 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

$$\sum_{\boldsymbol{G_1}} \left[\delta_{\boldsymbol{G}\boldsymbol{G_1}} - \chi^0_{\boldsymbol{G}\boldsymbol{G_1}}(\boldsymbol{q}\omega) v_{\boldsymbol{G_1}}(\boldsymbol{q})\right] \chi_{\boldsymbol{G_1}\boldsymbol{G'}}(\boldsymbol{q}\omega) = \chi^0_{\boldsymbol{G}\boldsymbol{G'}}(\boldsymbol{q}\omega) \tag{17}$$

where (where Ω is the crystal volume)

$$\chi^0_{\boldsymbol{G}\boldsymbol{G'}}(\boldsymbol{q}\omega) = \frac{1}{\Omega}\sum_{\sigma c v \boldsymbol{k}} (\rho_{\sigma(c\boldsymbol{k})(v\boldsymbol{k}-\boldsymbol{q})}(\boldsymbol{G},\boldsymbol{q}))^* \rho_{\sigma(c\boldsymbol{k})(v\boldsymbol{k}-\boldsymbol{q})}(\boldsymbol{G'},\boldsymbol{q}) S_{cv\boldsymbol{k}\boldsymbol{q}\omega\sigma}$$
$$S_{cv\boldsymbol{k}\boldsymbol{q}\omega\sigma} = \left[\frac{1}{\omega + \epsilon_{v\sigma}(\boldsymbol{k}-\boldsymbol{q}) - \epsilon_{c\sigma}(\boldsymbol{k}) + i\eta} - \frac{1}{\omega + \epsilon_{c\sigma}(\boldsymbol{k}) - \epsilon_{v\sigma}(\boldsymbol{k}-\boldsymbol{q}) - i\eta}\right] \tag{18}$$

2.2 From the dipole elements to the BSE hamiltonian (in the $\boldsymbol{q} \to 0$ limit)

The BSE hamiltonian projected on a basis of electron-hole transitions $t : (n1\boldsymbol{k1}) \to (n2\boldsymbol{k2})$ can be written as

$$\langle t| H_{BSE} |t'\rangle = E_t \delta_{tt'} + \langle t| (v - W) |t'\rangle \tag{19}$$

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

$$W_{\boldsymbol{G}\boldsymbol{G'}}(\boldsymbol{q}) = \epsilon^{-1}_{\boldsymbol{G}\boldsymbol{G'}}(\boldsymbol{q}) v(\boldsymbol{q}+\boldsymbol{G'}) \tag{20}$$

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

$$H_{BSE} = \begin{pmatrix} H_{rr} & H_{ra} \\ -(H_{ra})^* & -(H_{rr})^* \end{pmatrix} \tag{21}$$

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

$$H_{rr'} = E_r \delta_{rr'} + (\delta_M v_{rr'} - W_{rr'})$$
$$v_{rr'} = \frac{1}{\Omega}\sum_{\boldsymbol{G}\neq\boldsymbol{0}} v(\boldsymbol{q}+\boldsymbol{G}) (\rho_{\sigma_{c'}(c'\boldsymbol{k'})(v'\boldsymbol{k'}-\boldsymbol{q})}(\boldsymbol{G},\boldsymbol{q}))^* \rho_{\sigma_c(c\boldsymbol{k})(v\boldsymbol{k}-\boldsymbol{q})}(\boldsymbol{G},\boldsymbol{q}) \delta_{\sigma_{c'}\sigma_{v'}} \delta_{\sigma_c\sigma_v}$$
$$W_{rr'} = \frac{1}{\Omega}\sum_{\boldsymbol{G}\boldsymbol{G'}} W_{\boldsymbol{G}\boldsymbol{G'}}(\boldsymbol{k}-\boldsymbol{k'}) (\rho_{\sigma_{c'}(c'\boldsymbol{k'})(c\boldsymbol{k})}(\boldsymbol{G},\boldsymbol{k}-\boldsymbol{k'}))^* \rho_{\sigma_{v'}(v'\boldsymbol{k'}-\boldsymbol{q})(v\boldsymbol{k}-\boldsymbol{q})}(\boldsymbol{G'},\boldsymbol{k}-\boldsymbol{k'}))^* \delta_{\sigma_{c'}\sigma_c} \delta_{\sigma_{v'}\sigma_v}$$

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

$$H_{ra'} = (\delta_M v_{ra'} - W_{ra'})$$

$$v_{ra'} = \frac{1}{\Omega}\sum_{\boldsymbol{G}\neq\boldsymbol{0}} v(\boldsymbol{q}+\boldsymbol{G})(\rho_{\sigma_{v'}(v'\boldsymbol{k'}+\boldsymbol{q'})(c'\boldsymbol{k'})}(\boldsymbol{G},\boldsymbol{q}))^*\rho_{\sigma_c(c\boldsymbol{k})(v\boldsymbol{k}-\boldsymbol{q})}(\boldsymbol{G},\boldsymbol{q})\delta_{\sigma_{v'}\sigma_{c'}}\delta_{\sigma_c\sigma_v}$$

$$W_{ra'} = \frac{1}{\Omega}\sum_{\boldsymbol{GG'}} W_{\boldsymbol{GG'}}(\boldsymbol{k}-\boldsymbol{k'})(\rho_{\sigma_{v'}(v'\boldsymbol{k'}+\boldsymbol{q})(c\boldsymbol{k})}(\boldsymbol{G'},\boldsymbol{k'}+\boldsymbol{q}-\boldsymbol{k}))^*\rho_{\sigma_{c'}(c'\boldsymbol{k'})(v\boldsymbol{k}-\boldsymbol{q})}(\boldsymbol{G},\boldsymbol{k'}-\boldsymbol{k}-\boldsymbol{q})\delta_{\sigma_{c'}\sigma_v}\delta_{\sigma_c\sigma_{v'}}$$

Note that $\Omega = N * V_{primitivecell}$ where N is equal to the number of $\boldsymbol{k}$ 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).

3.1 Absorption Spectra in the Tamn-Dancoff approximation

From the excitonic eigenvalue E_λ and eigenvector A^λ (orthonormalized), we can build the oscilator force of the excitonic state λ:

$$f_\alpha^\lambda = \sum_{\sigma cv\boldsymbol{k}} \rho_{\sigma(c\boldsymbol{k})(v\boldsymbol{k}-\boldsymbol{q}_\alpha)}(\boldsymbol{0},\boldsymbol{q}_\alpha)(A^\lambda_{\sigma cv\boldsymbol{k}})^* \tag{22}$$

This allow us to express the macroscopic dielectric function as:

$$(\epsilon_M)_\alpha(\omega) = 1 - \lim_{q_\alpha\to 0}\frac{e^2}{\epsilon_0|\boldsymbol{q}_\alpha|^2}\frac{1}{\Omega}\sum_\lambda \frac{f_\alpha^\lambda (f_\alpha^\lambda)^*}{\omega - E_\lambda} \tag{23}$$

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

4 From RPA dielectric function to Optical Spectra

The inversion of the dielectric function should be sufficient to obtain the absorption spectra; however, due to the instability of this procedure, another approach will be used

$$\epsilon_M(\omega) = 1 - lim_{\boldsymbol{q}\to 0} v_{\boldsymbol{G}=\boldsymbol{0}}\bar{\chi}_{\boldsymbol{G}=\boldsymbol{0}\boldsymbol{G'}=\boldsymbol{0}} \tag{24}$$

where

$$\bar{\chi}_{\boldsymbol{GG'}} = \chi^0_{\boldsymbol{GG'}} + \chi^0_{\boldsymbol{GG_1}} T_{\boldsymbol{G_1G_2}} \bar{v}_{\boldsymbol{G_2}} \chi^0_{\boldsymbol{G_2G'}} \tag{25}$$

$$T_{\boldsymbol{G_1G_2}} = [\delta_{\boldsymbol{G_1G_2}} - \bar{v}_{\boldsymbol{G_1}} \chi^0_{\boldsymbol{G_1G_2}}]^{-1} \tag{26}$$

$$\bar{v}_{\boldsymbol{G_1}} = [0 \;\; if \; |\boldsymbol{G_1}| = 0 \;\; and \; v_{\boldsymbol{G_1}} \;\; if \; |\boldsymbol{G_1}| \neq 0] \tag{27}$$