Solving the optical spectra starting from a Tight-Binding model

February 12, 2024

1 The BSE equation approach

Starting from the tight-binding hamiltonian in a localized basis set

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

where $|w_{i\sigma}\mathbf{0}\rangle$ is the Wannier function i of the σ spin channel in the unitary cell $\mathbf{0}$. In the collinear case, the hamiltonians in the two spin channels are considered separately:

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

$$H_{ij}(\boldsymbol{k}\sigma)\,|n\sigma\boldsymbol{k}\rangle = \epsilon_{n\sigma}(\boldsymbol{k})\,|n\sigma\boldsymbol{k}\rangle \tag{3}$$

$$\sum H_{ij}(\boldsymbol{k}\sigma)C^{n\boldsymbol{k}}_{j\sigma}\,|w_{j\sigma}\mathbf{0}\rangle = \epsilon_{n\sigma}(\boldsymbol{k})C^{n\boldsymbol{k}}_{i\sigma}\,|w_{i\sigma}\mathbf{0}\rangle \tag{4}$$

where $|n\sigma k\rangle$ is the Bloch function n of the σ spin channel at the k point of the Brillouin zone and C its expansion in the localized basis set. From the Bloch functions of the two spin channels the respective spinor is built

$$|n\boldsymbol{k}\rangle = |n\uparrow\boldsymbol{k}\rangle\,|n\downarrow\boldsymbol{k}\rangle = \sum_{i\sigma} C^{nk}_{i\sigma}\,|w_{i\sigma}\mathbf{0}\rangle \tag{5}$$

At this point, from the Bloch functions dipole elements are built

$$\rho_{nm}(\boldsymbol{kqG}) = \langle n\boldsymbol{k}|\,e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}\,|m\boldsymbol{k}-\boldsymbol{q}\rangle \tag{6}$$

$$= \sum_{i\sigma}(C^{n\boldsymbol{k}}_{i\sigma})^{*}e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}_{i}}C^{m\boldsymbol{k}-\boldsymbol{q}}_{i\sigma} \tag{7}$$

These dipole elemnts allow us to calculate the IPA response function easily (at temperature $0K$)

$$\chi^{0}_{\boldsymbol{GG'}}(\boldsymbol{q}\omega) = \sum_{cv\sigma}\int_{BZ}\frac{d\boldsymbol{k}}{(2\pi)^3}(\rho_{cv\boldsymbol{k}\sigma}(\boldsymbol{qG}))^{*}\rho_{cv\boldsymbol{k}\sigma}(\boldsymbol{qG'})\times$$
$$\left[\frac{1}{\omega+\epsilon_{v\sigma}(\boldsymbol{k}-\boldsymbol{q})-\epsilon_{c\sigma}(\boldsymbol{k})+i\eta} - \frac{1}{\omega+\epsilon_{c\sigma}(\boldsymbol{k})-\epsilon_{v\sigma}(\boldsymbol{k}-\boldsymbol{q})-i\eta}\right]$$

From the IPA response function the dielectric function can be obtained as

$$(\epsilon^{(0)})^{-1}_{\boldsymbol{GG'}}(\boldsymbol{q}\omega) = \delta_{\boldsymbol{GG'}} + v_{\boldsymbol{G}}(\boldsymbol{q})\chi^{0}_{\boldsymbol{GG'}}(\boldsymbol{q}\omega)$$

The successive perturbative orders can be easily obtained (future implementation).

From these quantities we can build the BSE hamiltonian.

1.1 Usual procedure

Considering first the electron-hole exchange

$$V_{ij} = \frac{1}{\Omega}\sum_{\boldsymbol{G}\neq\boldsymbol{0}} v(G)\rho_{cv\sigma_c}(\boldsymbol{k0G})(\rho_{c'v'\sigma_{c'}}(\boldsymbol{k'0G}))^*\delta_{\sigma_c\sigma_v}\delta_{\sigma_{c'}\sigma_{v'}}$$
$$with\ i = (\sigma_c\sigma_v cv\boldsymbol{k})and\ j = (\sigma_{c'}\sigma_{v'}c'v'\boldsymbol{k'})$$

then the electron-hole attraction (from screened exchange potential: static screening at the IPA level)

$$W_{ij} = \frac{1}{\Omega}\sum_{\boldsymbol{GG'}} v(\boldsymbol{q}+\boldsymbol{G})(\epsilon^{(0)})^{-1}_{\boldsymbol{GG'}}(\boldsymbol{q}0)\rho_{cc'\sigma_c}(\boldsymbol{kqG})(\rho_{vv'\sigma_{v'}}(\boldsymbol{kqG'}))^*\delta_{\sigma_c\sigma_{c'}}\delta_{\sigma_v\sigma_{v'}}$$
$$with\ i = (\sigma_c\sigma_v cv\boldsymbol{k})and\ j = (\sigma_{c'}\sigma_{v'}c'v'\boldsymbol{k'})$$

and combining them

$$H_{ij} = (\epsilon_{c\boldsymbol{k}} - \epsilon_{v\boldsymbol{k}})\delta_{cc'}\delta_{vv'}\delta_{\boldsymbol{kk'}}\delta_{\sigma_v\sigma_{v'}}\delta_{\sigma_c\sigma_{c'}} - (2V - W)_{ij} \tag{8}$$

1.2 Cholesky procedure

The BSE hamiltonian can be built directly considering the resonant part

$$H^{(rr)}_{ij} = \frac{1}{\Omega}\sum_{\boldsymbol{G}}\Bigg[\ v(\boldsymbol{q}+\boldsymbol{G})\rho_{c'v'\sigma_{c'}}(\boldsymbol{k'qG})(\rho_{cv\sigma_c}(\boldsymbol{kqG}))^*$$
$$-\sum_{\boldsymbol{G'}} v(\boldsymbol{q}+\boldsymbol{G})(\epsilon^{(0)})^{-1}_{\boldsymbol{GG'}}(\boldsymbol{q}0)\rho_{c'v'\sigma_{c'}}(\boldsymbol{kqG})(\rho_{cv\sigma_c}(\boldsymbol{k'qG'}))^*\Bigg]\ \delta_{\sigma_{c'}\sigma_{v'}}\delta_{\sigma_c\sigma_v}$$
$$with\ i = (\sigma_c\sigma_v cv\boldsymbol{k})and\ j = (\sigma_{c'}\sigma_{v'}c'v'\boldsymbol{k'})$$

and the resonant-antiresonant coupling part

$$H^{(ra)}_{ij} = \frac{1}{\Omega}\sum_{\boldsymbol{G}}\Bigg[\ v(\boldsymbol{q}+\boldsymbol{G})\rho_{v'c'\sigma_{v'}}(\boldsymbol{k'qG})(\rho_{cv\sigma_c}(\boldsymbol{kqG}))^*$$
$$-\sum_{\boldsymbol{G'}} v(\boldsymbol{q}+\boldsymbol{G})(\epsilon^{(0)})^{-1}_{\boldsymbol{GG'}}(\boldsymbol{q}0)\rho_{v'c'\sigma_{v'}}(\boldsymbol{k'qG})(\rho_{cv\sigma_c}(\boldsymbol{kqG'}))^*\Bigg]\ \delta_{\sigma_{c'}\sigma_{v'}}\delta_{\sigma_c\sigma_v}$$
$$with\ i = (\sigma_c\sigma_v cv\boldsymbol{k})and\ j = (\sigma_{c'}\sigma_{v'}c'v'\boldsymbol{k'})$$

In this way, it has a form which allows to diagonalize it following a more efficient algorithm

$$H_{ij} = \begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \tag{9}$$

where

$$A_{ij} = H^{(rr)}_{ij} - (P_0^{-1}(0))_{ij} = H^{(rr)}_{ij} - (\epsilon_c(\boldsymbol{k}) - \epsilon_v(\boldsymbol{k'}))\delta_{cc'}\delta_{vv'}\delta_{\sigma_c\sigma_{c'}}\delta_{\sigma_v\sigma_{v'}}\delta_{\boldsymbol{kk'}}$$
$$B_{ij} = H^{(ra)}_{ij}$$

The Cholesky procedure is:
1) Construct M

$$M = \begin{pmatrix} Re\{A+B\} & Im\{A-B\} \\ -Im\{A+B\} & Re\{A-B\} \end{pmatrix} \tag{10}$$

2) Compute the Cholesky factorization

$$M = LL^T \tag{11}$$

3) Construct W

$$W = L^t J_n L \tag{12}$$

where J_n is the skew-symmetric matrix

$$J_n = \begin{pmatrix} 0 & I \\ -I & 0 \end{pmatrix}$$

4) Compute the spectral decomposition

$$-iW = \begin{pmatrix} Z_+ & Z_- \end{pmatrix} \begin{pmatrix} \Lambda_+ & 0 \\ 0 & -\Lambda_+ \end{pmatrix} \begin{pmatrix} Z_+ \\ Z_- \end{pmatrix}^* \tag{13}$$

5) Set

$$\begin{pmatrix} X_1 \\ X_2 \end{pmatrix} = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} QLZ_+\Lambda_+^{-1/2} \tag{14}$$

where the BSE hamiltonian eigenvalue problem is

$$H \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} = \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} \Lambda_+ \tag{15}$$

1.3 Macroscopic dielectric function

Diagonalized the BSE hamiltonian, the macroscopic dielectric function can be then evaluated as

$$\epsilon_M(\omega) = 1 - \lim_{q\to 0} \frac{8\pi}{|\boldsymbol{q}|^2\Omega} \sum_{vc\sigma\boldsymbol{k}} \sum_{v'c'\sigma'\boldsymbol{k'}} \rho_{c'v'\sigma'}(\boldsymbol{k'q0})(\rho_{cv\sigma}(\boldsymbol{kq0}))^* \sum_{\lambda} \frac{A^\lambda_{cv\boldsymbol{k}}(A^\lambda_{c'v'\boldsymbol{k'}})^*}{\omega - E_\lambda}$$

where A^λ are the eigenstates of the BSE hamiltonian and E_λ the respective eigenvalues.

2 The TDDFT approach

asfaslfa