Linear Response Signatures of Collective Excitations

Quantum Matter Summer School - Materials & Concepts

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Contents

1 Introduction: Mean-field theory, Ground state and Excitations

Let us consider we have a system of interacting electrons, described by the Hamiltonian H. Besides perturbation theory, one of the simplest ways of described an interacting system is through a self-consistent mean field theory. Let us assume that after achieving self-consistency, the diagonalized mean field Hamiltonian can be written as

$$H_{MF} = \sum_a \epsilon_a^{MF} c_a^\dagger c_a \tag{1}$$

where the operator $c_a^\dagger$ creates a particle in the mean-field single particle states a, which has energy ϵ_a^{MF}. The mean-field ground state with N particles is thus given by

$$|\Omega\rangle_{MF} = c_N^\dagger ... c_1^\dagger |0\rangle \tag{2}$$

where $|0\rangle$ represents the state with zero particles and we have ordered the states such that $\epsilon_1 \le \epsilon_2 \le ... \le \epsilon_N$. Since in mean-field theory we are approximating an interacting system by a system of independent particles, we would naivelly expect that an excited state is obtained by removing an electron from one of the occupied states in $|\Omega\rangle_{MF}$ and promote it to an excited state. Such a state is written in terms of creation/annhilation operators as

$$|e, o\rangle = c_e^\dagger c_o |\Omega\rangle_{MF} \tag{3}$$

where the index o labels a state that is occupied in $|\Omega\rangle_{MF}$ and e labbels a state that is empty in $|\Omega\rangle_{MF}$, and such a state would have energy $\epsilon_e^{MF} - \epsilon_o^{MF} + E_\Omega^{MF}$ where E_Ω^{MF} is the ground state energy. However there are excitations that cannot be approximated in a such a way. One such exemple are excitons in insulators, which have energies bellow the quasiparticle (mean-field) bandgap. Another example are plasmon-polaritons in metals. These kind of collective excitations emerge due to the residual interaction between the excited electron and the remaning hole.

There are several well established ways to describe this kind of excitation. One of these approaches, commonly employed in Quantum Chemistry, is the so called Configuration Interaction Singles (CIS). In terms of creation/annhilation operators, this consists in writing the excited state as a linear combination

$$|X\rangle = \sum_{\substack{e\in\text{empty} \\ o\in\text{occupied}}} \Psi^X_{e,o} c^\dagger_e c_o |\Omega\rangle_{MF}.$$ (4)

The coefficcients $\Psi^X_{o,e}$ are obtained by solving the eigenvalue equation

$$\sum_{e_2,o_2} \langle e_1, o_1| H |e_2, o_2\rangle \Psi^X_{e_2,o_2} = E_X \Psi^X_{e_1,o_1}.$$ (5)

Another way to describe collective excitation is via Many-Body Perturbation Theory, by resumming an infinite series of ladder and bubble diagramms in the two-particle propagator, which leads to the so called Bethe-Salpeter equation (BSE). Another possibility is using time-dependent Density Functional Theory (TDDFT).

The above discussion might make the reader believe that the innabibilty in describing collective excitations might indicate a breakdown of mean-field theory. It turns out that is not case. Mean-field theory is perfectly capable of describing collective excitations. It is only *ground-state mean field theory* that does not capture these excitations. This should not surprise us as variational mean-field theory is based on the minimization of the energy (at zero temperature) or of the free energy (at finite temperature). As such, it only gives reliable results for the quantities which we are minimizing. If one instead describes the system using time-dependent mean-field theory, collective excitations naturally emerge. It turns out that linear response time-dependent mean-field theory is actually equivalent to the BSE and to CIS (actually CIS is only reobtained if a futher approximation, the so called Tamm-Dancoff approximation, is performed).

In this notes we will see how collective excitations are capture within time-dependent mean-field theory. We will focus on excitations of insulators, so we will use time-dependent Hartree-Fock (TDHF) theory. But the collective excitations of other kinds of materials can be described in a similar way. For exemple, the collective modes of superconductors can be described using time-dependent BCS theory.

2 Time-dependent Hartree Fock theory

Let us consider a sistem of electrons whose equilibirum state is described by the equilibirum Hamiltonian H_{eq}, which in a given basis, can be written as

$$H_{\text{eq}} = \sum_{ab} h_{ab} c^\dagger_a c_b + \frac{1}{2} \sum_{abcd} V^{ab}_{cd} c^\dagger_a c^\dagger_b c_c c_d,$$ (6)

where

$$h_{ab} = \int d^3\mathbf{r} \phi^*_a(\mathbf{r}) \left[\frac{\mathbf{p}^2}{2m} + U(\mathbf{r}) \right] \phi_b(\mathbf{r}),$$ (7)

$$V^{ab}_{cd} = \int d^3\mathbf{r} d^3\mathbf{r}' \phi^*_a(\mathbf{r}) \phi^*_b(\mathbf{r}') V(\mathbf{r} - \mathbf{r}') \phi_c(\mathbf{r}') \phi_d(\mathbf{r}),$$ (8)

where $c^\dagger_a (c_a)$ creates (annihilates) an electron in the state described by the wavefunction $\phi_a(\mathbf{r})$. $U(\mathbf{r})$ is a static potential (for example the lattice potential) and $V(\mathbf{r} - \mathbf{r}')$ is the electron-electron interaction. Notice that the interaction matrix elements obbey the symmetries

$$V^{ab}_{cd} = V^{ba}_{dc},$$ (9)

$$\left(V^{ab}_{cd}\right)^* = V^{dc}_{ba} = V^{cd}_{ab}.$$ (10)

To the equilibirum Hamiltonian we add a perturbation, which is switched on for $t > t_0$, which is described by a one-particle term:

$$H_{\text{d}}(t) = \sum_{ab} B_{ab} c^\dagger_a c_b F(t)$$ (11)

where B_{ab} are matrix elements of a one-particle operator which couples to the time-depedant external "force" $F(t)$, which will drive the system out-of-equilibrium. Examples of perturbation can be the charge density coupled to a

scalar potential, the dipole moment coupled to an electric field, or a current density coupled to a vector potential. The full Hamiltonian is thus given by

$$H(t) = H_{\text{eq}} + H_{\text{d}}(t). \tag{12}$$

The response of the system to the external "force" can be monitored by measuring different observables. We will focus on one-particle quantites of the form

$$A = \sum_{ab} A_{ab} c_a^\dagger c_b. \tag{13}$$

The expectation value of A can be written as

$$\langle A \rangle (t) = \sum_{ab} A_{ab} \left\langle c_a^\dagger(t) c_b(t) \right\rangle. \tag{14}$$

Defining the one-particle reduced density matrix

$$\rho_{ba}(t) = \left\langle c_a^\dagger(t) c_b(t) \right\rangle, \tag{15}$$

with the operators in the Heisenberg picture, we can write

$$\langle A \rangle (t) = \sum_{ab} A_{ab} \rho_{ba}(t) = \text{Tr}\left[\boldsymbol{A} \cdot \boldsymbol{\rho}(t) \right]. \tag{16}$$

We will formulate our time-dependant Hartee-Fock theory with the reduced density matrix as the central object. To determine $\langle A \rangle (t)$ we will study the equation of motion of the reduced density matrix. We have that

$$\frac{d}{dt} \rho_{ab}(t) = \left\langle \frac{dc_b^\dagger(t)}{dt} c_a(t) \right\rangle + \left\langle c_b^\dagger(t) \frac{dc_a(t)}{dt} \right\rangle. \tag{17}$$

Using the Heisenberg equation of motion, we have that

$$\begin{aligned}
\frac{dc_a}{dt} &= \frac{i}{\hbar} [H, c_a] \\
&= \frac{i}{\hbar} \sum_{\alpha\beta} \left[(h_{\alpha\beta} + B_{\alpha\beta} F(t)) c_\alpha^\dagger c_\beta, c_a \right] + \frac{i}{\hbar} \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \left[V_{\gamma\delta}^{\alpha\beta} c_\alpha^\dagger c_\beta^\dagger c_\gamma c_\delta, c_a \right].
\end{aligned} \tag{18}$$

Using the equal-time anti-commutation relations for fermions $\left\{ c_a, c_b^\dagger \right\} = c_a c_b^\dagger + c_b^\dagger c_a = \delta_{ab}$, and the properties

$$[AB, C] = A[B, C] + [A, C]B, \tag{19}$$
$$[AB, C] = A\{B, C\} - \{A, C\}B. \tag{20}$$

we obtain

$$\frac{dc_a}{dt} = -\frac{i}{\hbar} \sum_\beta (h_{a\beta} + B_{a\beta} F(t)) c_\beta + \frac{i}{\hbar} \frac{1}{2} \sum_{\beta\gamma\delta} \left(V_{\gamma\delta}^{\beta a} - V_{\gamma\delta}^{a\beta} \right) c_\beta^\dagger c_\gamma c_\delta. \tag{21}$$

Taking the Hermitian conjugate, we obtain

$$\frac{dc_b^\dagger}{dt} = \frac{i}{\hbar} \sum_\alpha (h_{\alpha b} + B_{\alpha b} F(t)) c_\alpha^\dagger + \frac{i}{\hbar} \frac{1}{2} \sum_{\alpha\beta\gamma} \left(V_{\gamma b}^{\alpha\beta} - V_{b\gamma}^{\alpha\beta} \right) c_\alpha^\dagger c_\beta^\dagger c_\gamma. \tag{22}$$

The equation of motion for the reduced density matrix, thus becomes

$$\begin{aligned}
\frac{d}{dt} \rho_{ab}(t) &= \frac{i}{\hbar} \sum_\alpha (h_{\alpha b} + B_{\alpha b} F(t)) \left\langle c_\alpha^\dagger(t) c_a(t) \right\rangle + \frac{i}{\hbar} \frac{1}{2} \sum_{\alpha\beta\gamma} \left(V_{\gamma b}^{\alpha\beta} - V_{b\gamma}^{\alpha\beta} \right) \left\langle c_\alpha^\dagger(t) c_\beta^\dagger(t) c_\gamma(t) c_a(t) \right\rangle \\
&\quad - \frac{i}{\hbar} \sum_\beta (h_{a\beta} + B_{a\beta} F(t)) \left\langle c_b^\dagger(t) c_\beta(t) \right\rangle + \frac{i}{\hbar} \frac{1}{2} \sum_{\beta\gamma\delta} \left(V_{\gamma\delta}^{\beta a} - V_{\gamma\delta}^{a\beta} \right) \left\langle c_b^\dagger(t) c_\beta^\dagger(t) c_\gamma(t) c_\delta(t) \right\rangle.
\end{aligned} \tag{23}$$

Within a mean-field Hartree-Fock approximation, we make the factorization

$$\left\langle c_\alpha^\dagger(t) c_\beta^\dagger(t) c_\gamma(t) c_a(t) \right\rangle \simeq \left\langle c_\alpha^\dagger(t) c_a(t) \right\rangle \left\langle c_\beta^\dagger(t) c_\gamma(t) \right\rangle - \left\langle c_\alpha^\dagger(t) c_\gamma(t) \right\rangle \left\langle c_\beta^\dagger(t) c_a(t) \right\rangle. \tag{24}$$

3

Doing this we obtain

$$\frac{d}{dt}\rho_{ab}(t) = -\frac{i}{\hbar}\sum_\beta \left(h_{a\beta} + B_{a\beta}F(t)\right)\rho_{\beta b}(t) - \frac{i}{\hbar}\frac{1}{2}\sum_\alpha \left(\sum_{\beta\gamma} V_{\gamma\alpha}^{a\beta}\rho_{\gamma\beta}(t) - \sum_{\beta\gamma} V_{\alpha\gamma}^{a\beta}\rho_{\gamma\beta}(t)\right)\rho_{\alpha b}(t)$$
$$+ \frac{i}{\hbar}\sum_\alpha \rho_{a\alpha}(t)\left(h_{\alpha b} + B_{\alpha b}F(t)\right) + \frac{i}{\hbar}\sum_\beta \rho_{a\beta}(t)\left(\sum_{\alpha\gamma} V_{\gamma b}^{\beta\alpha}\rho_{\gamma\alpha}(t) - \sum_{\alpha\gamma} V_{b\gamma}^{\beta\alpha}\rho_{\gamma\alpha}(t)\right). \tag{25}$$

Defining the Hartree and Fock self-energies as

$$\Sigma_{ab}^H[\rho] = \sum_{cd} V_{cb}^{ad}\rho_{cd}, \tag{26}$$

$$\Sigma_{ab}^F[\rho] = -\sum_{cd} V_{bc}^{ad}\rho_{cd}, \tag{27}$$

the previous equations can be written in a very compact form

$$i\hbar\frac{d}{dt}\boldsymbol{\rho}(t) = [\boldsymbol{H}_{\text{TDHF}}(t), \boldsymbol{\rho}(t)], \tag{28}$$

$$\boldsymbol{H}_{\text{TDHF}}(t) = \boldsymbol{h} + \boldsymbol{B}F(t) + \boldsymbol{\Sigma}^H[\boldsymbol{\rho}(t)] + \boldsymbol{\Sigma}^F[\boldsymbol{\rho}(t)]. \tag{29}$$

where $\boldsymbol{H}_{\text{TDHF}}(t)$ is the mean-field time-dependent Hartree-Fock Hamiltonian.

Notice that in general the single-particle Hamiltonian already has its origin in a mean-field calculation. Therefore, in order to avoid a double counting of interaction effects, one should subtract from the self-energies the contribution from equilibrium:

$$\boldsymbol{\Sigma}^{H/F}[\boldsymbol{\rho}(t)] \rightarrow \boldsymbol{\Sigma}^{H/F}[\boldsymbol{\rho}(t)] - \boldsymbol{\Sigma}^{H/F}[\boldsymbol{\rho}_0] = \boldsymbol{\Sigma}^{H/F}[\boldsymbol{\rho}(t) - \boldsymbol{\rho}_0], \tag{30}$$

where $\boldsymbol{\rho}_0 = \boldsymbol{\rho}(t_0)$ is the equilibrium reduced density matrix. Notice that in the last equality of the above equation, we used the linearity of the Hartree/Fock self-energies on the density matrix.

3   Linear response theory within TDHF

We can solve Eqs. (28) and (29) in order to obtain the full response due to the external "force" $F(t)$. However, very frequently, one is interested in the regime where the "force" is weak and the system responds linearly to the "force". This is the so-called linear response regime. In this regime, the expected value of A can be written as

$$\langle A\rangle(t) = \int_{-\infty}^{+\infty} dt' \chi_{AB}(t - t')F(t'), \tag{31}$$

where $\chi_{AF}(t - t')$ is a generalized susceptibility. Making a Fourier transform, we obtain

$$\langle A\rangle(\omega) = \chi_{AB}(\omega)F(\omega).$$

Our goal will be to determine $\chi_{AB}(\omega)$ within the TDHF approximation. To do so we multiply the driving "force" $F(t)$ by a formall expansion parameter λ $F(t) \rightarrow \lambda F(t)$ and assume that the reduced density matrix can be expanded in powers of λ:

$$\boldsymbol{\rho}(t) = \sum_n \lambda^n \boldsymbol{\rho}^{(n)}(t). \tag{32}$$

We insert the above expansion into the TDHF equation (28), taking into account that the TDHF Hamiltonian also depends on $\boldsymbol{\rho}(t)$. To linear order in λ we obtain

$$i\hbar\frac{d}{dt}\boldsymbol{\rho}^{(1)}(t) = \left[\boldsymbol{h}, \boldsymbol{\rho}^{(1)}(t)\right] + \left[\boldsymbol{\Sigma}^H\left[\boldsymbol{\rho}^{(1)}(t)\right] + \boldsymbol{\Sigma}^F\left[\boldsymbol{\rho}^{(1)}(t)\right], \boldsymbol{\rho}^{(0)}\right] + \left[\boldsymbol{B}F(t), \boldsymbol{\rho}^{(0)}\right],$$

Recalling the definition of the Hartree/Fock self-energies

$$\Sigma_{ab}^H[\rho] = \sum_{cd} V_{cb}^{ad}\rho_{cd}, \tag{33}$$

$$\Sigma_{ab}^F[\rho] = -\sum_{cd} W_{bc}^{ad}\rho_{cd}, \tag{34}$$

4

(in the Fock term we represent the interaction with W instead of V, anticipating that in the Fock term the interaction should be screened, while in the Hartree it should not), we obtain more explicilty

$$i\hbar\frac{d}{dt}\rho_{ab}^{(1)}(t) - \sum_c \left(h_{ac}\rho_{cb}^{(1)}(t) - \rho_{ac}^{(1)}(t)h_{cb}\right) = \sum_{ced}\left[\left(V_{ec}^{ad} - W_{ce}^{ad}\right)\rho_{cb}^{(0)} - \rho_{ac}^{(0)}\left(V_{eb}^{cd} - W_{be}^{cd}\right)\right]\rho_{ed}^{(1)}(t)$$

$$+ \sum_c \left(B_{ac}\rho_{cb}^{(0)} - \rho_{ac}^{(0)}B_{cb}\right)F(t).$$

The above equation is linear in $\rho_{ab}^{(1)}(t)$. Expanding both the force and the correction to the density matrix in a Fourier transform in time,

$$F(t) = \int \frac{d\omega}{2\pi}e^{-i\omega t}F(\omega)$$

$$\rho_{ab}^{(1)}(t) = \int \frac{d\omega}{2\pi}e^{-i\omega t}\rho_{ab}^{(1)}(\omega)$$

we obtain

$$\hbar\omega\rho_{ab}^{(1)}(\omega) - \sum_c \left(h_{ac}\rho_{cb}^{(1)}(\omega) - \rho_{ac}^{(1)}(\omega)h_{cb}\right) = \sum_{ced}\left[\left(V_{ec}^{ad} - W_{ce}^{ad}\right)\rho_{cb}^{(0)} - \rho_{ac}^{(0)}\left(V_{eb}^{cd} - W_{be}^{cd}\right)\right]\rho_{ed}^{(1)}(\omega)$$

$$+ \sum_c \left(B_{ac}\rho_{cb}^{(0)} - \rho_{ac}^{(0)}B_{cb}\right)F(\omega). \tag{35}$$

We can rewrite the above equation as

$$\sum_{cd}\left(\hbar\omega\delta_{ac}\delta_{bd} - H_{ab,cd}\right)\rho_{cd}^{(1)}(\omega) = \bar{J}_{ab}(\omega) \tag{36}$$

where

$$H_{ab,cd} = \left(h_{ac}\delta_{bd} - \delta_{ac}h_{db}\right) + \sum_e\left(V_{ce}^{ad} - W_{ec}^{ad}\right)\rho_{eb}^{(0)} - \sum_e \rho_{ae}^{(0)}\left(V_{cb}^{ed} - W_{bc}^{ed}\right), \tag{37}$$

$$J_{ab}(\omega) = \sum_c \left(B_{ac}\rho_{cb}^{(0)} - \rho_{ac}^{(0)}B_{cb}\right)F(\omega). \tag{38}$$

The previous equations greatly simplify if we work in the basis that diagonalizes $\boldsymbol{h}$, in which case $h_{ab} = \epsilon_a\delta_{ab}$ and $\rho_{ab}^{(0)} = f_a\delta_{ab}$, since in that case we obtain

$$H_{ab,cd} = (\epsilon_a - \epsilon_b)\,\delta_{ac}\delta_{bd} + (f_b - f_a)\left(V_{cb}^{ad} - W_{bc}^{ad}\right), \tag{39}$$

$$J_{ab}(\omega) = (f_b - f_a)\,B_{ab}F(\omega). \tag{40}$$

We can further simplify the problem at zero temperature, in which case the occupations, f_a, are either 0 or 1. To see that we split $\rho_{ab}^{(1)}(\omega)$ into elements involving only empty states, occupied states or one empty state and another occupied states. Representing empty states via e_i and occupied states via o_i, we obtain

$$\begin{bmatrix} \omega\delta_{e_1e_3}\delta_{e_2e_4} - H_{e_1e_2,e_3e_4} & -H_{e_1e_2,e_3o_4} & -H_{e_1e_2,o_3e_4} & -H_{e_1e_2,o_3o_4} \\ -H_{e_1o_2,e_3e_4} & \omega\delta_{e_1e_3}\delta_{o_2o_4} - H_{e_1o_2,e_3o_4} & -H_{e_1o_2,o_3e_4} & -H_{e_1o_2,o_3o_4} \\ -H_{e_1e_2,o_3e_4} & -H_{o_1e_2,e_3o_4} & \omega\delta_{o_1o_3}\delta_{e_2e_4} - H_{o_1e_2,o_3e_4} & H_{o_1e_2,o_3o_4} \\ -H_{e_1e_2,o_3o_4} & -H_{e_1o_2,o_3o_4} & -H_{o_1e_2,o_3o_4} & \omega\delta_{o_1o_3}\delta_{o_2o_4} - H_{o_1o_2,o_3o_4} \end{bmatrix}\begin{bmatrix} \rho_{e_3e_4}^{(1)} \\ \rho_{e_3o_4}^{(1)} \\ \rho_{o_3e_4}^{(1)} \\ \rho_{o_3o_4}^{(1)} \end{bmatrix} = \begin{bmatrix} J_{e_1e_2} \\ J_{e_1o_2} \\ J_{o_1e_1} \\ J_{o_1o_1} \end{bmatrix} \tag{41}$$

It is easy to see that at zero temperature, the previous equation simplifies to

$$\begin{bmatrix} \omega\delta_{e_1e_3}\delta_{e_2e_4} - H_{e_1e_2,e_3e_4} & 0 & 0 & 0 \\ -H_{e_1o_2,e_3e_4} & \omega\delta_{e_1e_3}\delta_{o_2o_4} - H_{e_1o_2,e_3o_4} & -H_{e_1o_2,o_3e_4} & -H_{e_1o_2,o_3o_4} \\ -H_{e_1e_2,o_3e_4} & -H_{o_1e_2,e_3o_4} & \omega\delta_{o_1o_3}\delta_{e_2e_4} - H_{o_1e_2,o_3e_4} & H_{o_1e_2,o_3o_4} \\ 0 & 0 & 0 & \omega\delta_{o_1o_3}\delta_{o_2o_4} - H_{o_1o_2,o_3o_4} \end{bmatrix}\begin{bmatrix} \rho_{e_3e_4}^{(1)} \\ \rho_{e_3o_4}^{(1)} \\ \rho_{o_3e_4}^{(1)} \\ \rho_{o_3o_4}^{(1)} \end{bmatrix} = \begin{bmatrix} 0 \\ J_{e_1o_2} \\ J_{o_1e_2} \\ 0 \end{bmatrix} \tag{42}$$

5

From which we obtain

$$\rho^{(1)}_{e_3 e_4} = \rho^{(1)}_{o_3 o_4} = 0,$$

and the problem is thus reduced to

$$\left[\begin{array}{cc} \omega \delta_{e_1 e_3} \delta_{o_2 o_4} - H_{e_1 o_2, e_3 o_4} & -H_{e_1 o_2, o_3 e_4} \\ -H_{o_1 e_2, e_3 o_4} & \omega \delta_{o_1 o_3} \delta_{e_2 e_4} - H_{o_1 e_2, o_3 e_4} \end{array} \right] \left[\begin{array}{c} \rho^{(1)}_{e_3 o_4} \\ \rho^{(1)}_{o_3 e_4} \end{array} \right] = \left[\begin{array}{c} J_{e_1 o_2} \\ J_{o_1 e_2} \end{array} \right]. \tag{43}$$

For convinience in the second line we will make the replacement $o_1 e_2 \to o_2 e_1$ and $o_3 e_4 \to o_4 e_3$), such the above matrix equations reads

$$\left[\begin{array}{cc} \omega \delta_{e_1 e_3} \delta_{o_2 o_4} - H_{e_1 o_2, e_3 o_4} & -H_{e_1 o_2, o_4 e_3} \\ -H_{o_2 e_1, e_3 o_4} & \omega \delta_{o_1 o_4} \delta_{e_2 e_3} - H_{o_2 e_1, o_4 e_3} \end{array} \right] \left[\begin{array}{c} \rho^{(1)}_{e_3 o_4} \\ \rho^{(1)}_{o_4 e_3} \end{array} \right] = \left[\begin{array}{c} J_{e_1 o_2} \\ J_{o_2 e_1} \end{array} \right]. \tag{44}$$

The above representation is useful to notice the following symmetries

$$\begin{aligned} H_{e_1 o_2, e_3 o_4} &= (\epsilon_{e_1} - \epsilon_{o_2}) \delta_{e_1 e_3} \delta_{o_2 o_4} + \left(V^{e_1 o_4}_{e_3 o_2} - W^{e_1 o_4}_{o_2 e_3} \right) \equiv R_{e_1 o_2, e_3 o_4} \\ &= \left[(\epsilon_{e_1} - \epsilon_{o_2}) \delta_{e_1 e_3} \delta_{o_2 o_4} + \left(V^{e_3 o_2}_{e_1 o_4} - W^{e_3 o_2}_{o_4 e_1} \right) \right]^* = R^*_{e_3 o_4, e_1 o_2} \\ H_{o_2 e_1, o_4 e_3} &= (\epsilon_{o_2} - \epsilon_{e_1}) \delta_{o_2 o_4} \delta_{e_1 e_3} - \left(V^{o_2 e_3}_{o_4 e_1} - W^{o_2 e_3}_{e_1 o_4} \right) \\ &= - \left[(\epsilon_{e_1} - \epsilon_{o_2}) \delta_{e_1 e_3} \delta_{o_2 o_4} + \left(V^{e_1 o_4}_{e_3 o_2} - W^{e_1 o_4}_{o_2 e_3} \right) \right]^* = -R^*_{e_1 o_2, e_3 o_4} \end{aligned}$$

for the diagonal blocks and

$$\begin{aligned} H_{e_1 o_2, o_4 e_3} &= \left(V^{e_1 e_3}_{o_4 o_2} - W^{e_1 e_3}_{o_2 o_4} \right) \equiv C_{e_1 o_2, o_4 e_3} = C_{e_3 o_4, o_2 e_1} \\ H_{o_2 e_1, e_3 o_4} &= - \left(V^{o_2 o_4}_{e_3 e_1} - W^{o_2 o_4}_{e_1 e_3} \right) = - \left(V^{e_3 e_1}_{o_2 o_4} - W^{e_3 e_1}_{o_4 o_2} \right)^* = -C^*_{e_3 o_4, o_2 e_1}. \end{aligned}$$

for the off-diagonal blocks. Therefore, we obtain the following linear problem

$$\left[\begin{array}{cc} \omega \boldsymbol{I} - \boldsymbol{R} & -\boldsymbol{C} \\ \boldsymbol{C}^\dagger & \omega \boldsymbol{I} + \boldsymbol{R}^* \end{array} \right] \left[\begin{array}{c} \boldsymbol{\rho}^{(1)}_{eo}(\omega) \\ \boldsymbol{\rho}^{(1)}_{oe}(\omega) \end{array} \right] = \left[\begin{array}{c} \boldsymbol{B}_{eo} \\ -\boldsymbol{B}_{oe} \end{array} \right] F(\omega). \tag{45}$$

From which we read the electron-hole Hamiltonian

$$\boldsymbol{H}_{eh} = \left[\begin{array}{cc} \boldsymbol{R} & \boldsymbol{C} \\ -\boldsymbol{C}^\dagger & -\boldsymbol{R}^* \end{array} \right]. \tag{46}$$

This is usually refered to as the Bethe-Salpeter Hamiltonian. The linear response is thus given by

$$\left[\begin{array}{c} \boldsymbol{\rho}^{(1)}_{eo}(\omega) \\ \boldsymbol{\rho}^{(1)}_{oe}(\omega) \end{array} \right] = \left[\begin{array}{cc} \omega \boldsymbol{I} - \boldsymbol{R} & -\boldsymbol{C} \\ \boldsymbol{C}^\dagger & \omega \boldsymbol{I} + \boldsymbol{R}^* \end{array} \right]^{-1} \left[\begin{array}{c} \boldsymbol{B}_{eo} \\ -\boldsymbol{B}_{oe} \end{array} \right] F(\omega). \tag{47}$$

The expected value of A can thus be written as

$$\begin{aligned} \langle A \rangle (\omega) &= \sum_{ab} A_{ab} \rho^{(1)}_{ba}(\omega) \\ &= \sum_{e_1 o_2} \left(A_{o_2 e_1} \rho^{(1)}_{e_1 o_2}(\omega) + A_{e_1 o_2} \rho^{(1)}_{o_2 e_1}(\omega) \right) \\ &= \sum_{e_1 o_2} \left(A^*_{e_1 o_2} \rho^{(1)}_{e_1 o_2}(\omega) + A^*_{o_2 e_1} \rho^{(1)}_{o_2 e_1}(\omega) \right) \\ &= \left[\begin{array}{cc} \boldsymbol{A}_{eo} & \boldsymbol{A}_{oe} \end{array} \right]^\dagger \cdot \left[\begin{array}{c} \boldsymbol{\rho}^{(1)}_{eo}(\omega) \\ \boldsymbol{\rho}^{(1)}_{oe}(\omega) \end{array} \right] \\ &= \left[\begin{array}{cc} \boldsymbol{A}_{eo} & \boldsymbol{A}_{oe} \end{array} \right]^\dagger \cdot \left[\begin{array}{cc} \omega \boldsymbol{I} - \boldsymbol{R} & -\boldsymbol{C} \\ \boldsymbol{C}^\dagger & \omega \boldsymbol{I} + \boldsymbol{R}^* \end{array} \right]^{-1} \left[\begin{array}{c} \boldsymbol{B}_{eo} \\ -\boldsymbol{B}_{oe} \end{array} \right] F(\omega). \end{aligned} \tag{48}$$

Comparing this with

$$\langle A \rangle (\omega) = \chi_{AB}(\omega) F(\omega). \tag{49}$$

we obtain the generalized susceptibility

$$\chi_{AB}(\omega) = \left[\begin{array}{cc} \boldsymbol{A}_{eo} & \boldsymbol{A}_{oe} \end{array} \right]^\dagger \cdot \left[\begin{array}{cc} \omega \boldsymbol{I} - \boldsymbol{R} & -\boldsymbol{C} \\ \boldsymbol{C}^\dagger & \omega \boldsymbol{I} + \boldsymbol{R}^* \end{array} \right]^{-1} \left[\begin{array}{c} \boldsymbol{B}_{eo} \\ -\boldsymbol{B}_{oe} \end{array} \right]. \tag{50}$$

4 Linear response eigenvalue problem

From the previous section, obtaining the linear response within TDHF requires solving the linear problem

$$\left(\omega \begin{bmatrix} I & 0 \\ 0 & I \end{bmatrix} - \begin{bmatrix} R & C \\ -C^\dagger & -R^* \end{bmatrix} \right) \begin{bmatrix} \rho_{eo}^{(1)}(\omega) \\ \rho_{oe}^{(1)}(\omega) \end{bmatrix} = \begin{bmatrix} B_{eo} \\ -B_{oe} \end{bmatrix} F(\omega).$$

This can be done by solving the eigenvalue problem

$$\begin{bmatrix} R & C \\ -C^\dagger & -R^* \end{bmatrix} \begin{bmatrix} \Psi_{eo}^\lambda \\ \Psi_{oe}^\lambda \end{bmatrix} = E_\lambda \begin{bmatrix} \Psi_{eo}^\lambda \\ \Psi_{oe}^\lambda \end{bmatrix}.$$

This problem is sometimes refered to as linear response eigenvalue problem. Notice that the above eigenproblem does not involve Hermitian matrices. However, if we multiply the above equation by

$$\begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}$$

it becomes an hermitian generalized eigenvalue problem

$$\begin{bmatrix} R & C \\ C^\dagger & R^* \end{bmatrix} \begin{bmatrix} \Psi_{eo}^\lambda \\ \Psi_{oe}^\lambda \end{bmatrix} = E_\lambda \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \begin{bmatrix} \Psi_{eo}^\lambda \\ \Psi_{oe}^\lambda \end{bmatrix}. \tag{51}$$

4.1 Properties of the linear response eigenvalue problem

is positive defined, then the eigenvalues are real. This is a general property of a generalized eigenvalue problem of the form

4.2 Generalized susceptibility in terms of collective excitations

If we expand

$$\begin{bmatrix} \rho_{eo}^{(1)}(\omega) \\ \rho_{oe}^{(1)}(\omega) \end{bmatrix} = \sum_\lambda g(\omega) \begin{bmatrix} \Psi_{eo}^\lambda \\ \Psi_{oe}^\lambda \end{bmatrix},$$

then we obtain

$$\sum_\lambda g(\omega) \left(\omega \begin{bmatrix} I & 0 \\ 0 & I \end{bmatrix} - \begin{bmatrix} R & C \\ -C^\dagger & -R^* \end{bmatrix} \right) \begin{bmatrix} \Psi_{eo}^\lambda \\ \Psi_{oe}^\lambda \end{bmatrix} = \begin{bmatrix} B_{eo} \\ -B_{oe} \end{bmatrix} F(\omega)$$

$$\Rightarrow \sum_\lambda g(\omega) \left(\omega - E^\lambda \right) \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \begin{bmatrix} \Psi_{eo}^\lambda \\ \Psi_{oe}^\lambda \end{bmatrix} = \begin{bmatrix} B_{eo} \\ B_{oe} \end{bmatrix} F(\omega).$$

Contracting with $\begin{bmatrix} \Psi_{eo}^\lambda & \Psi_{oe}^\lambda \end{bmatrix}^\dagger$ we obtain

$$g(\omega) = \frac{\mathrm{sign}\left(E^\lambda\right)}{(\omega - E^\lambda)} \begin{bmatrix} \Psi_{eo}^\lambda & \Psi_{oe}^\lambda \end{bmatrix}^\dagger \begin{bmatrix} B_{eo} \\ B_{oe} \end{bmatrix} F(\omega),$$

such that

$$\begin{bmatrix} \rho_{eo}^{(1)}(\omega) \\ \rho_{oe}^{(1)}(\omega) \end{bmatrix} = \sum_\lambda \begin{bmatrix} \Psi_{eo}^\lambda \\ \Psi_{oe}^\lambda \end{bmatrix} \frac{\mathrm{sign}\left(E^\lambda\right)}{(\omega - E^\lambda)} \begin{bmatrix} \Psi_{eo}^\lambda & \Psi_{oe}^\lambda \end{bmatrix}^\dagger \cdot \begin{bmatrix} B_{eo} \\ B_{oe} \end{bmatrix} F(\omega).$$

The generalized susceptibility thus reads

$$\chi_{AB}(\omega) = \begin{bmatrix} A_{eo} & A_{oe} \end{bmatrix}^\dagger \cdot \begin{bmatrix} \rho_{eo}^{(1)}(\omega) \\ \rho_{oe}^{(1)}(\omega) \end{bmatrix}$$

$$= \begin{bmatrix} A_{eo} & A_{oe} \end{bmatrix}^\dagger \cdot \left(\sum_\lambda \begin{bmatrix} \Psi_{eo}^\lambda \\ \Psi_{oe}^\lambda \end{bmatrix} \frac{\mathrm{sign}\left(E^\lambda\right)}{(\omega - E^\lambda)} \begin{bmatrix} \Psi_{eo}^\lambda & \Psi_{oe}^\lambda \end{bmatrix}^\dagger \right) \cdot \begin{bmatrix} B_{eo} \\ B_{oe} \end{bmatrix}. \tag{52}$$

Notice that in the above equation has poles at E^λ, and as such these are energies of the collective excitations. Therefore, we interpret Ψ^λ as the wavefunctions of the collective excitations.

5 Derivation of Wannier equation for excitonic problem

How we will apply the previous general formalism to the case of excitons in a cristalline insulator/semiconductor. In particular, we will see how the linear response eigenvalue problem, which describes excitons, can be approximated by an hidrogenoid problem, the Wannier equation.

5.1 Electron-electron interaction for Bloch states

We will start by studying the form of the electron-electron interaction in a crystal. In terms of field operators, we have

$$H_{e-e} = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \Psi_\sigma^\dagger(\mathbf{r}_1) \Psi_{\sigma'}^\dagger(\mathbf{r}_2) V(\mathbf{r}_1 - \mathbf{r}_2) \Psi_{\sigma'}(\mathbf{r}_2) \Psi_\sigma(\mathbf{r}_1). \tag{53}$$

Assuming that the non-interacting Hamiltonian is diagonal in spin and expanding the field operators in terms of Bloch states

$$\Psi_\sigma(\mathbf{r}) = \sum_{\mathbf{k}n} \psi_{\mathbf{k}n}(\mathbf{r}) c_{\mathbf{k}n\sigma}, \tag{54}$$

we obtain

$$H_{e-e} = \sum_{\{\mathbf{k}_i n_i \sigma_i\}} V_{\mathbf{k}_3 n_3 \sigma_3, \mathbf{k}_4 n_4 \sigma_4}^{\mathbf{k}_1 n_1 \sigma_1, \mathbf{k}_2 n_2 \sigma_2} c_{\mathbf{k}_1 n_1 \sigma_1}^\dagger c_{\mathbf{k}_2 n_2 \sigma_2}^\dagger c_{\mathbf{k}_2 n_3 \sigma_3} c_{\mathbf{k}_4 n_4 \sigma_4}, \tag{55}$$

where

$$V_{\mathbf{k}_3 n_3 \sigma_3, \mathbf{k}_4 n_4 \sigma_4}^{\mathbf{k}_1 n_1 \sigma_1, \mathbf{k}_2 n_2 \sigma_2} = \delta_{\sigma_1, \sigma_4} \delta_{\sigma_2 \sigma_3} V_{\mathbf{k}_3 n_3, \mathbf{k}_4 n_4}^{\mathbf{k}_1 n_1, \mathbf{k}_2 n_2}, \tag{56}$$

$$V_{\mathbf{k}_3 n_3, \mathbf{k}_4 n_4}^{\mathbf{k}_1 n_1, \mathbf{k}_2 n_2} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \psi_{\mathbf{k}_1 n_1}^*(\mathbf{r}_1) \psi_{\mathbf{k}_2 n_2}^*(\mathbf{r}_2) V(\mathbf{r}_1 - \mathbf{r}_2) \psi_{\mathbf{k}_3 n_3}(\mathbf{r}_2) \psi_{\mathbf{k}_4 n_4}(\mathbf{r}_1). \tag{57}$$

Now let us study the matrix elements $V_{\mathbf{k}_3 n_3, \mathbf{k}_4 n_4}^{\mathbf{k}_1 n_1, \mathbf{k}_2 n_2}$. Writing the electron-electron interaction potential as a Fourier transform

$$V(\mathbf{r}) = \int \frac{d\mathbf{q}}{(2\pi)^D} e^{i\mathbf{q}\cdot\mathbf{r}} V(\mathbf{q}), \tag{58}$$

we obtain

$$V_{\mathbf{k}_3 n_3, \mathbf{k}_4 n_4}^{\mathbf{k}_1 n_1, \mathbf{k}_2 n_2} = \int \frac{d\mathbf{q}}{(2\pi)^D} V(\mathbf{q}) \varrho_{\mathbf{k}_1 n_1, \mathbf{k}_4 n_4}(\mathbf{q}) \varrho_{\mathbf{k}_2 n_2, \mathbf{k}_3 n_3}(-\mathbf{q}).$$

where

$$\varrho_{\mathbf{k}_1 n_1, \mathbf{k}_4 n_4}(\mathbf{q}) = \int d\mathbf{r}_1 \psi_{\mathbf{k}_1 n_1}^*(\mathbf{r}_1) e^{i\mathbf{q}\cdot\mathbf{r}_1} \psi_{\mathbf{k}_4 n_4}(\mathbf{r}_1).$$

we will now write the integral over $\mathbf{r}_1(\mathbf{r}_2)$ as a sum of integrations over each unit cell,

$$\int d\mathbf{r}_1 = \sum_{\mathbf{R}_1} \int_{\text{u.c.}} d\mathbf{x}_1, \tag{59}$$

such that $\mathbf{r}_1 = \mathbf{R}_1 + \mathbf{x}_1$, where $\mathbf{R}_1$ is a Bravais lattice site and $\mathbf{x}_1$ is a position within the unit cell. Doing this we obtain

$$\varrho_{\mathbf{k}_1 n_1, \mathbf{k}_4 n_4}(\mathbf{q}) = \sum_{\mathbf{R}_1} \int d\mathbf{x}_1 \psi_{\mathbf{k}_1 n_1}^*(\mathbf{R}_1 + \mathbf{x}_1) e^{i\mathbf{q}\cdot(\mathbf{R}_1 + \mathbf{x}_1)} \psi_{\mathbf{k}_4 n_4}(\mathbf{R}_1 + \mathbf{x}_1)$$

$$= \sum_{\mathbf{R}_1} e^{i(\mathbf{k}_4 + \mathbf{q} - \mathbf{k}_1)\cdot\mathbf{R}_1} \int d\mathbf{x}_1 \psi_{\mathbf{k}_1 n_1}^*(\mathbf{x}_1) e^{i\mathbf{q}\cdot\mathbf{x}_1} \psi_{\mathbf{k}_4 n_4}(\mathbf{x}_1).$$

where we used the property of Bloch state $\psi_{\mathbf{k}n}(\mathbf{R} + \mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}n}(\mathbf{r})$. Performing the sum over $\mathbf{R}_1$ we obtain

$$\sum_{\mathbf{R}_1} e^{i(\mathbf{q} - \mathbf{k}_1 + \mathbf{k}_4)\cdot\mathbf{R}_1} = N \sum_{\mathbf{G}_1} \delta_{\mathbf{q} - \mathbf{k}_1 + \mathbf{k}_4, \mathbf{G}_1}.$$

Notice what the above equations tells us: we have that up to a reciprocal lattice vector $\mathbf{k}_1 = \mathbf{k}_4 + \mathbf{q}$. Since $\mathbf{k}_1$ is in the 1BZ, we can write

$$\sum_{\mathbf{R}_1} e^{i(\mathbf{q} - \mathbf{k}_1 + \mathbf{k}_4)\cdot\mathbf{R}_1} = N \delta_{\mathbf{k}_1, \{\mathbf{k}_4 + \mathbf{q}\}},$$

where $\{\mathbf{p}\}$ is the restriction of $\mathbf{p}$ to the 1BZ, defined such that $\mathbf{p} = \{\mathbf{p}\} + \mathbf{G_p}$, where $\mathbf{G_p}$ is a reciprocal lattice vector. Notice that by definition $\{\mathbf{p} + \mathbf{G}\} = \{\mathbf{p}\}$. Therefore, we obtain

$$\varrho_{\mathbf{k}_1 n_1, \mathbf{k}_4 n_4}(\mathbf{q}) = \delta_{\mathbf{k}_1, \{\mathbf{k}_4+\mathbf{q}\}} N \int d\mathbf{x}_1 \psi^*_{\mathbf{k}_1 n_1}(\mathbf{x}_1) e^{i\mathbf{q}\cdot\mathbf{x}_1} \psi_{\mathbf{k}_4 n_4}(\mathbf{x}_1)$$

$$= \delta_{\mathbf{k}_1, \{\mathbf{k}_4+\mathbf{q}\}} \varrho_{\mathbf{k}_1 n_1, \mathbf{k}_4 n_4}(\mathbf{q}).$$

Therefore, the electron-electron interaction Hamiltonian can be written as

$$V^{\mathbf{k}_1 n_1, \mathbf{k}_2 n_2}_{\mathbf{k}_3 n_3, \mathbf{k}_4 n_4} = \int \frac{d\mathbf{q}}{(2\pi)^D} V(\mathbf{q}) \delta_{\mathbf{k}_1, \{\mathbf{k}_4+\mathbf{q}\}} \delta_{\mathbf{k}_2, \{\mathbf{k}_3-\mathbf{q}\}} \varrho_{\mathbf{k}_1 n_1, \mathbf{k}_4 n_4}(\mathbf{q}) \varrho_{\mathbf{k}_2 n_2, \mathbf{k}_3 n_3}(-\mathbf{q}) \tag{60}$$

where $\{\mathbf{q}\}$ is the rescriction of a vector $\mathbf{q}$ to the 1BZ, i.e. any vector $\mathbf{q}$ can be decomposed as $\mathbf{q} = \{\mathbf{q}\} + \mathbf{G_q}$, where $\mathbf{G_q}$ is a point in the reciprocal lattice. Therefore, we can write

$$V^{\mathbf{k}_1 n_1, \mathbf{k}_2 n_2}_{\mathbf{k}_3 n_3, \mathbf{k}_4 n_4} = \int \frac{d\mathbf{q}}{(2\pi)^D} V(\mathbf{q}) \delta_{\mathbf{k}_1, \{\mathbf{k}_4+\mathbf{q}\}} \delta_{\mathbf{k}_2, \{\mathbf{k}_3-\mathbf{q}\}} \varrho_{\mathbf{k}_1 n_1, \mathbf{k}_4 n_4}(\mathbf{q}) \varrho_{\mathbf{k}_2 n_2, \mathbf{k}_3 n_3}(-\mathbf{q}) \tag{61}$$

where

$$\varrho_{\mathbf{k}_1 n_1, \mathbf{k}_4 n_4}(\mathbf{q}) = \int d\mathbf{r}_1 \psi^*_{\mathbf{k}_1 n_1}(\mathbf{r}_1) e^{i\mathbf{q}\cdot\mathbf{r}_1} \psi_{\mathbf{k}_4 n_4}(\mathbf{r}_1). \tag{62}$$

We can therefore write

$$H_{e-e} = \int \frac{d\mathbf{p}}{(2\pi)^D} V(\mathbf{p}) \sum_{\{n_i\}} \sum_{\mathbf{k}\sigma, \mathbf{k}'\sigma'} V(\mathbf{p}) \varrho_{\mathbf{k}_1 n_1, \mathbf{k}_4 n_4}(\mathbf{p}) \varrho_{\mathbf{k}_2 n_2, \mathbf{k}_3 n_3}(-\mathbf{p}+\mathbf{G}) c^\dagger_{\{\mathbf{k}+\mathbf{p}\}n_1\sigma_1} c^\dagger_{\{\mathbf{k}'-\mathbf{p}\}n_2\sigma_2} c_{\mathbf{k}'n_3\sigma_3} c_{\mathbf{k}n_4\sigma_4}. \tag{63}$$

5.2 Tamm-Dancoff approximation

The Tamm-Dancoff approximation consists in neglecting the blocks $\boldsymbol{C}$ in the linear response eigenvalue problem, which is thus reduced to the problem of diagonalizing the $\boldsymbol{R}$ block. In terms of Bloch states, we want to solve

$$\sum_{\mathbf{k}'c_3 v_4} \left(\omega \delta_{\mathbf{k},\mathbf{k}'} \delta_{c_1,c_3} \delta_{v_2,v_4} - R_{\{\mathbf{k}+\mathbf{Q}\}c_1, \mathbf{k}v_2; \{\mathbf{k}'+\mathbf{Q}\}c_3, \mathbf{k}'v_4} \right) \rho^{(1)}_{\{\mathbf{k}'+\mathbf{Q}\}c_3, \mathbf{k}'v_4}(\omega) = J_{\{\mathbf{k}+\mathbf{Q}\}c_1, \mathbf{k}v_2}(\omega, \mathbf{p}), \tag{64}$$

where we have exploited the crystalline translation invariance.

The ressonant block of the electron-hole Hamiltonian is given by

$$R_{\{\mathbf{k}+\mathbf{Q}\}c_1, \mathbf{k}v_2; \{\mathbf{k}'+\mathbf{Q}\}c_3, \mathbf{k}'v_4} = \left(\epsilon_{\{\mathbf{k}+\mathbf{Q}\}c_1} - \epsilon_{\mathbf{k}v_2} \right) \delta_{\mathbf{k},\mathbf{k}'} \delta_{c_1,c_3} \delta_{v_2,v_4} - \left(W^{\{\mathbf{k}+\mathbf{Q}\}c_1, \mathbf{k}'v_4}_{\mathbf{k}v_2, \{\mathbf{k}'+\mathbf{Q}\}c_3} - V^{\mathbf{k}'v_4, \{\mathbf{k}+\mathbf{Q}\}c_1}_{\mathbf{k}v_2, \{\mathbf{k}'+\mathbf{Q}\}c_3} \right). \tag{65}$$

Notice that the interaction term that has origin in the Fock self-energy gives origin to an attrative interaction between electron an hole, while the Hartree term contributes with a repulsive term. (Somewaht confusingly, in the literature on exctions ther term involving W is refered as the direct electron-hole interaction term, while V is refereed to as the exchange electron-hole interaction term). We will focus on the Fock term, while discarding the Hartree term (which leads to a small correction in the exciton energy levels). We will further assume that we have only one conduction and one valence bands. Therefore, the linear response eigenvalue problem reduces to-

$$\left(\epsilon_{\{\mathbf{k}+\mathbf{Q}\}c} - \epsilon_{\mathbf{k}v} \right) \Psi^\lambda_{\mathbf{k}cv}(\mathbf{Q}) - \sum_{\mathbf{k}'} W^{\{\mathbf{k}+\mathbf{Q}\}c, \mathbf{k}'v}_{\mathbf{k}v, \{\mathbf{k}'+\mathbf{Q}\}c} \Psi^\lambda_{\mathbf{k}'cv}(\mathbf{Q}) = E_\lambda \Psi^\lambda_{\mathbf{k}cv}(\mathbf{Q}), \tag{66}$$

where

$$W^{\{\mathbf{k}+\mathbf{Q}\}c, \mathbf{k}'v}_{\mathbf{k}v, \{\mathbf{k}'+\mathbf{Q}\}c} = \frac{1}{V} \sum_{\mathbf{G}} \varrho_{\{\mathbf{k}+\mathbf{Q}\}c, \{\mathbf{k}'+\mathbf{Q}\}c}(\{\mathbf{k}-\mathbf{k}'\}+\mathbf{G}) W(\{\mathbf{k}-\mathbf{k}'\}+\mathbf{G}) \varrho_{\mathbf{k}'v, \mathbf{k}v}(-\{\mathbf{k}-\mathbf{k}'\}-\mathbf{G}). \tag{67}$$

5.3   Wannier equation

We will now assume that our system is a direct band gap insulator, and approximate the bandstructure close to the band gap as a parabolic band:

$$\epsilon_{\mathbf{k}c} \simeq \frac{\hbar^2 \mathbf{k}^2}{2m_c} + \frac{1}{2}E_{\text{gap}}$$

$$\epsilon_{\mathbf{k}v} \simeq -\frac{\hbar^2 \mathbf{k}^2}{2m_v} - \frac{1}{2}E_{\text{gap}}$$

where $m_{c/v}$ is the effective mass. We will also assume that small momenta are relevant and thus negelct umklapp processes. Forthermore, we also approximate

$$\varrho_{\{\mathbf{k}+\mathbf{Q}\}c,\{\mathbf{k}'+\mathbf{Q}\}c}\left(\{\mathbf{k}-\mathbf{k}'\}+\mathbf{G}\right) \simeq \varrho_{\mathbf{k}c,\mathbf{k}c}\left(\mathbf{0}\right) = 1$$

$$\varrho_{\mathbf{k}'v,\mathbf{k}v}\left(-\{\mathbf{k}-\mathbf{k}'\}-\mathbf{G}\right) \simeq \varrho_{\mathbf{k}v,\mathbf{k}v}\left(\mathbf{0}\right) = 1.$$

We therefore obtain

$$\left(E_{\text{gap}} + \frac{\hbar^2\left(\mathbf{k}+\mathbf{Q}\right)^2}{2m_{c/v}} + \frac{\hbar^2\mathbf{k}^2}{2m_v}\right)\Psi_{\mathbf{k}cv}^{\lambda}(\mathbf{Q}) - \frac{1}{V}\sum_{\mathbf{k}'}W\left(\mathbf{k}-\mathbf{k}'\right)\Psi_{\mathbf{k}'cv}^{\lambda}(\mathbf{Q}) = E_{\lambda}\Psi_{\mathbf{k}cv}^{\lambda}(\mathbf{Q}). \tag{68}$$

Focusing on exciton with zero center of mass momentum, $\mathbf{Q} = \mathbf{0}$ and introducing the reduced mass of the electron-hole pair as

$$\frac{1}{m_{eff}} = \frac{1}{m_c} + \frac{1}{m_c}, \tag{69}$$

we obtain the Wannier equation in momentum space

$$\left(E_{\text{gap}} + \frac{\hbar^2\mathbf{k}^2}{2m_{eff}}\right)\Psi_{\mathbf{k}cv}^{\lambda}(\mathbf{0}) - \int\frac{d\mathbf{k}'}{(2\pi)^D}W\left(\mathbf{k}-\mathbf{k}'\right)\Psi_{\mathbf{k}'cv}^{\lambda}(\mathbf{0}) = E_{\lambda}\Psi_{\mathbf{k}cv}^{\lambda}(\mathbf{0}). \tag{70}$$

Making a Fourier transform to real space

$$\Psi_{\mathbf{k}cv}^{\lambda}(\mathbf{0}) = \int d\mathbf{r}\,e^{-i\mathbf{k}\cdot\mathbf{r}}\Psi_{cv}^{\lambda}(\mathbf{r}),$$

we obtain the Wannier equation in real space

$$\left(E_{\text{gap}} - \frac{\hbar^2}{2m_{eff}}\nabla^2 - W\left(\mathbf{r}\right)\right)\Psi_{cv}^{\lambda}(\mathbf{r}) = E_{\lambda}\Psi_{\mathbf{k}cv}^{\lambda}(\mathbf{0}).$$

which is nothing more than the Wannier equation for a hidrogenoid atom.