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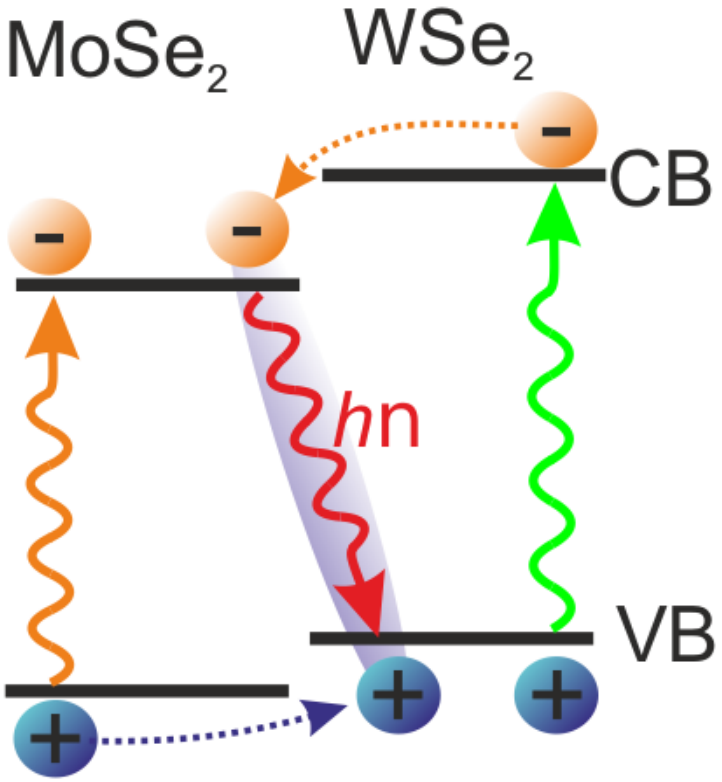

Modeling of interlayer excitons in van der Waals heterostructures

Simon Ovesen

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Gothenburg, Sweden 2017

Master's thesis 2017

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Author: Simon Ovesen

Supervisor: Ermin Malic, Department of Physics, Division of Condensed Matter Theory
Examiner: Ermin Malic, Department of Physics, Division of Condensed Matter Theory

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Department of Physics
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

Cover: Illustration of the formation and radiative decay of interlayer excitons. Taken from [1].

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Abstract

The field of TMD (Transition Metal Dichalcogenide) monolayers is an active one due to certain interesting properties such as a direct band gap, strong spin-orbit coupling and a remarkably large Coulomb interaction leading to strongly bound excitons. For technical applications heterostructures composed of stacked monolayers are also a huge topic of interest. Recent experimental studies of the photoluminescence of these structures show evidence of the existence of interlayer excitons.

The aim of this thesis is to propose a mechanism for the formation and dynamics of these interlayer excitons in a bilayer heterostructure. For this purpose the second quantization formalism and tight binding approach are employed. Aside from the free, optical, carrier-photon, carrier-phonon and Coulomb interactions that have already been studied for monolayers, a tunneling interaction that couples the two layers is also included. For the intralayer Coulomb potential the familiar Keldysh potential is used, while an extension of it derived here is used as the interlayer potential.

The Hamiltonian constructed from these contributions is then converted to the excitonic picture as opposed to the often used electron-hole picture. By using this excitonic Hamiltonian in the Heisenberg equation of motion, equations for the microscopic polarization and exciton densities are derived analytically and solved numerically. From these equations the physically measurable quantities absorption and photoluminescence are computed. Parameters used in the tunneling interaction are then varied to attempt to fit the results to the experimentally measured photoluminescence of an $MoSe_2$ - WSe_2 heterostructure.

Keywords: TMD, van der Waals, heterostructure, interlayer, exciton, tunneling.

Acknowledgements

First of I would like to thank my supervisor Ermin Malic. You have my sincerest gratitude for your continuous support and regular contact during the project. Next I would like to extend my thanks to the rest of the research group I have had the opportunity to be a part of, in particular to Malte Selig. You have always been there when I needed you, ready to lend your assistance with a positive attitude. Finally my last thanks go to the people closest to me, my friends and family.

Simon Ovesen, Gothenburg, 08-2017

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Introduction

Monolayers of TMD's (Transition Metal Dicalchogenides) have been a topic of much interest during the last years [2], [3]. They are semiconductors that display an indirect band gap in bulk, but when reduced to a single layer have direct ones at the high symmetry K and K' points of the first Brillouin zone [4], [5], [6]. Their small width leads to a significantly lessened screening of the Coulomb interaction, resulting in strongly bound excitons with binding energies of a few hundreds of meV's [7], [8], [6]. They also exhibit strong spin-orbit coupling, especially in the valence band. Being of the order of some hundreds of meV's as well means that two bright states for each excitonic energy level will appear, dubbed the A and B excitons.

Monolayer and bulk are not the only interesting states the TMD's can be used in however. Another area of much research is the properties of van der Waals heterostructures, structures created by stacking a few monolayers on top of each other. In recent studies of the photoluminescence of one such structure, the bilayer $MoSe_2$ - WSe_2, evidence of an interlayer exciton state, a state where the conduction electron resides in one layer and the corresponding hole in another, was found. This new state has a lower energy than the intralayer states due to the relative alignment of the two layers' band structures [1], [9]. The spectrum in question, in which the interlayer peak is about one order of magnitude larger than the largest intralayer peak, can be seen in Figure 1.1.

As will be seen later these results can not be explained through absorption only, as very few interlayer excitons are created optically. There therefore needs to exist some form of scattering process that couples inter- and intralayer densities. The purpose of this thesis is to investigate this process by proposing a tunneling interaction that couples the two layers, and see if it can be used to reproduce these results. To do this the Hamiltonian first needs to be constructed. Thereafter equations of motion for the microscopic polarization and exciton densities will be derived analytically and solved numerically.

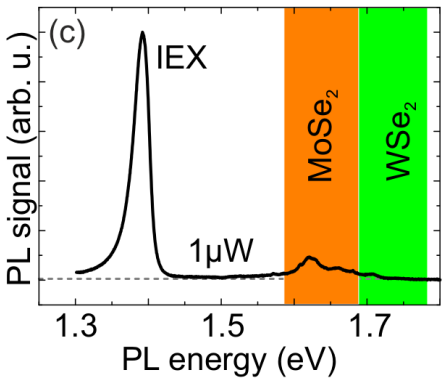

Figure 1.1: Experimentally measured photoluminescence of $MoSe_2$ - WSe_2 taken from [1]. The experiment was performed at a temperature of 4.5 K using an exciting pulse with a power of 1 μW, and integrated over a timespan of 2 ns. The colored areas represent the energy intervals where the intralayer peaks would normally appear. A small peak can be seen here for the energetically lower $MoSe_2$. Most of the excitons have however gathered in an even lower state centered at around 1.4 eV. Since this peak does not appear when examining the monolayers separately it is believed to correspond to an interlayer exciton state.

2

Theoretical basics

Before moving on to the main topic there are still some theoretical basics that need to be sorted out, which is precicely what this section is dedicated to.

2.1 Transition metal dichalcogenide

The structure of a monolayer transition metal dichalcogenide (TMD), both in real and reciprocal space, can be seen in Figure 2.1. It has the empirical formula MX_2 where M is a transition metal (here being either Mo or W) and X a chalcogenide (S or Se). The unit cell is composed of these three atoms, and together they create the same hexagonal structure that graphene has. There is difference in the out of plane direction though; while a layer of graphene is only one atom thick a TMD layer is slightly wider since the two X atoms are vertically stacked. The resulting thickness is then taken to be around the same as that of the lattice parameter a_0, being roughly 0.3 nm. This is still small enough that it can be neglected in most occasions though.

The lattice vectors can be expressed as

$$\boldsymbol{a}_1 = -\frac{a_0}{2}\begin{pmatrix}\sqrt{3}\\1\end{pmatrix}, \quad \boldsymbol{a}_2 = -a_0\begin{pmatrix}0\\1\end{pmatrix}, \tag{2.1}$$

using which we can construct a vector pointing to an arbitrary unit cell as

$$\boldsymbol{R} = \sum_i n_i \boldsymbol{a}_i \tag{2.2}$$

where $n_{1,2}$ are integers. We can also use these to create vectors that point from an M atom to a neighbouring X atom, turning out to be

$$\boldsymbol{b}_1 = \frac{1}{3}(\boldsymbol{a}_1 - 2\boldsymbol{a}_2) \tag{2.3}$$

$$\boldsymbol{b}_2 = \frac{1}{3}(\boldsymbol{a}_2 - 2\boldsymbol{a}_1) \tag{2.4}$$

$$\boldsymbol{b}_3 = \frac{1}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2). \tag{2.5}$$

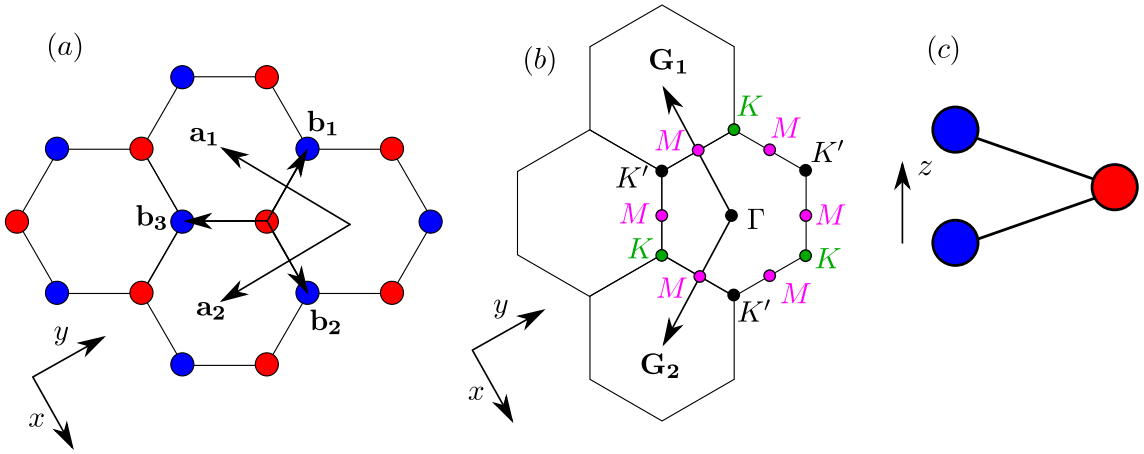

Figure 2.1: Figure showing the geometrical structure of a TMD monolayer in real (a) and reciprocal space (b). In real space the $\boldsymbol{a}$ vectors represent lattice vectors while the $\boldsymbol{b}$ vectors represent translation vectors from a metal to a dichalcogenide. The structure in the z direction can be seen in (c). In reciprocal space the $\boldsymbol{G}$ vectors are the reciprocal lattice vectors while the K, K', M and Γ points are high symmetry points.

One final use for the lattice vectors is so construct the reciprocal lattice vectors,

$$\boldsymbol{G}_1 = -\frac{\pi}{\sqrt{3}} \begin{pmatrix} 4\sqrt{3} \\ 0 \end{pmatrix} \tag{2.6}$$

$$\boldsymbol{G}_2 = -\frac{\pi}{\sqrt{3}} \begin{pmatrix} -2\sqrt{3} \\ 2 \end{pmatrix}. \tag{2.7}$$

All of these vectors can also be seen in Figure 2.1.

Aside from the physical structure, we also need to consider the electronic band structure. This, taken from DFT calculations [10], can be seen in Figure 2.2 where the high symmetry points Γ, M and K/K' points are marked. These mark points in reciprocal space where there is an unusually high symmetry, making Taylor approximations easier. Since this figure only shows a single slice of the Brillouine zone the points themselves are shown in Figure 2.1. In this thesis we will be focusing specifically on the K/K' points, since these contain a direct band gap. When we in the future use the words valence and conduction bands, it is the two bands related to this particular band gap that is referred to.

Another property of the K/K' points is that there is a significant spin-orbit splitting in the valence band. The split exists in the conduction band as well, but is about one order of magnitude smaller. This means that for two different excitons with identical properties but for the hole spin there will be a significant energy difference. These are called the A and B excitons for lower and higher energies respectively. The main difference between the K and K' points is that for the K point the A exciton will correspond to spin up and the B exciton to spin down, while the K' point has the opposite ordering. This effect is illustrated in Figure 2.3.

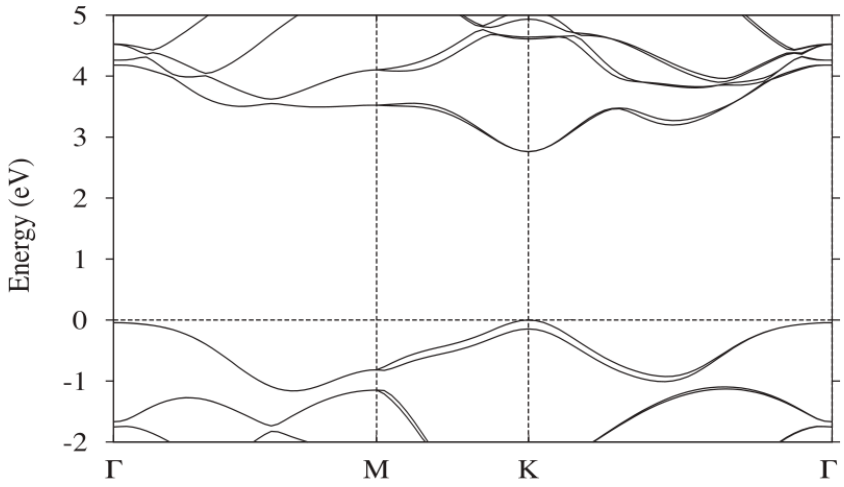

Figure 2.2: Figure showing the electronic band structure along a slice of the first Brillouin zone with the high symmetry points K, M and Γ marked. At the K point the direct band gap and spin-orbit splitting can be seen. The figure is taken from [10] and slightly modified.

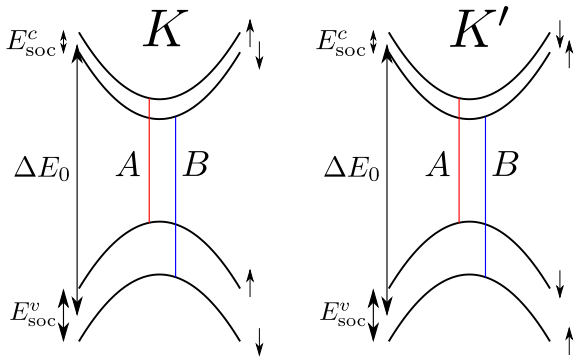

Figure 2.3: Here the difference in spin-orbit splitting between the K and K' points can be seen. The energies for the A and B excitons have been marked as well. Note that the figure is not scaled correctly, as the conduction splitting E^c_{soc} is significantly smaller than the valence splitting E^v_{soc}, which in turn is much smaller than the band gap energy without spin-orbit coupling ΔE_0.

Since there are three K points and three K' points in the Brillouine zone there are three ways to express their vector representations each, but the ones here are the opposite

$$\boldsymbol{K} = \frac{4\pi}{3a_0}\begin{pmatrix} 0 \\ -1 \end{pmatrix} \tag{2.8}$$

$$\boldsymbol{K} = \frac{4\pi}{3a_0}\begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{2.9}$$

2.2 Density matrix formalism

One quantity that is extremely useful when working with a statistical ensemble of quantum states is the density matrix operator

$$\rho \equiv \sum_i p_i |\phi_i\rangle\langle\phi_i|, \quad \text{with} \quad \sum_i p_i = 0 \tag{2.10}$$

where $|\phi_i\rangle$ are the possible states and p_i are the statistical probabilities of obtaining one of these states. Note that these probabilities simply arise due to lack of knowledge about the system, unlike the quantum mechanical uncertainty which is intrinsic to the system and can not be removed though increased knowledge.

There is a lot that can be said about this formalism, but for the purpose of this thesis we will restrict ourselves to some details about one specific case: a pure two-level system. The state for such a system looks like

$$|\phi\rangle = c_1|u_1\rangle + c_2|u_2\rangle, \tag{2.11}$$

where $|u_1\rangle$ and $|u_2\rangle$ are eigenstates in a suitable basis. In this case the density matrix looks like

$$\rho = |\phi\rangle\langle\phi| \tag{2.12}$$

$$= \begin{pmatrix} |c_1|^2 & c_1 c_2^* \\ c_1^* c_2 & |c_2|^2 \end{pmatrix} \tag{2.13}$$

$$\equiv \begin{pmatrix} f_1 & p_{12} \\ p_{12}^* & f_2 \end{pmatrix}. \tag{2.14}$$

As can be seen here the *population* f_i determines the probability of finding the state in state i, while the *microscopic polarization* $p_{1,2}$ is related to the coupling between the two states. These quantities are going to be very relevant for the rest of the thesis.

2.3 Second quantization

Decribing quantum mechanical multiparticle systems can be quite messy, with all of the symmetrization that is required. The formalism of second quantization greatly simplifies this process though, through the use of creation and annihilation operators $a_a^\dagger$ and a_a, Here the compound index a contains relevant information about the perticle in question, such as momentum or spin. A multiparticle state created from N single particle states $|\phi_{a_1}\rangle, \ldots, |\phi_{a_N}\rangle$ would then be expressed as

$$|\phi_{a_1}, \ldots, \phi_{a_N}\rangle = \frac{1}{N!} a_{a_1}^\dagger \ldots a_{a_N}^\dagger |0\rangle, \tag{2.15}$$

where $|0\rangle$ is a state describing the vacuum. The symmetrization is then automatically taken care of by the commutation relations of the creation and annihilation operator, which read

$$[a_{a_1}, a_{a_2}^\dagger] = \delta_{a_1 a_2} \tag{2.16}$$

for bosons and

$$\{a_{a_1}, a_{a_2}^\dagger\} = \delta_{a_1 a_2} \tag{2.17}$$

for fermions. Here $[,]$ represents a commutator while $\{,\}$ is an anticommutator.

Any physically relevant N-particle observable A_N can be expressed in terms of sums of one- and two-particle operators A_1^i and $A_2^{(i,j)}$ [11] as

$$A_N = \sum_{i=1}^{N} A_1^i + \frac{1}{2} \sum_{i,j}^{i \neq j} A_2^{(i,j)}, \tag{2.18}$$

which can then be expanded in terms of creation and annihilation operators as

$$A_N = \sum_{ab} \langle \phi_a | A_1 | \phi_b \rangle a_a^\dagger a_b + \frac{1}{2} \sum_{abcd} \langle \phi_a \phi_b | A_2 | \phi_d \phi_c \rangle a_a^\dagger a_b^\dagger a_d a_c. \tag{2.19}$$

One advantage of this formalism that will be taken advantage of here is that the Heisenberg equation of motion,

$$i\hbar \frac{d}{dt} . = [., H] \tag{2.20}$$

where H is the system's Hamiltonian, can be relatively easily evaluated if all operators are expressed in terms of creation and annihilation operators since the commutation relations for these are known and not too complicted.

Finally, the population and microscopic polarization quantities brought up in the previous subsection are in this formalism expressed as

$$f_a = \langle a_a^\dagger a_a \rangle \tag{2.21}$$

and

$$p_{ab} = \langle a_a^\dagger a_b \rangle. \tag{2.22}$$

2.3.1 A note about notation

In this thesis there will be a lot of different notation. If anything about the notation in later parts appears unclear it can therefore be a good idea to return to this segment, which covers the most basic notation.

There are three basic creation and annihilation operators that will be used in this thesis. The most prominent ones are the fermionic operators $a_a^{(\dagger)}$, used to describe electrons. In addition to those we also have the phonon operators $b_a^{(\dagger)}$ and photon operators $c_a^{(\dagger)}$, both being bosonic. In 3.2 we will also define excitonic operators $P_a^{(\dagger)}$, which we will approximate as bosons.

Taking the sheer number of different indices that will need to be used into account we will try to use compound indices as much as possible. What each index contains then depends on the type of operator it is assigned to: electronic operators have momentum $\boldsymbol{k}$, spin s and layer l, phonon operators have momentum $\boldsymbol{K}$, layer l and phonon mode α, photon operators have momentum $\boldsymbol{K}$ and polarity σ and excitonic operators have center of mass momentum $\boldsymbol{Q}$, energy state μ, hole spin s_h, hole layer l_h electron spin s_e and electron layer l_e. This means that the indices can be expanded as

$$a_a^{(\dagger)} = a_{\boldsymbol{k}}^{(\dagger)sl} \tag{2.23}$$

$$b_a^{(\dagger)} = b_{\boldsymbol{K}}^{(\dagger)l\alpha} \tag{2.24}$$

$$c_a^{(\dagger)} = c_{\boldsymbol{K}}^{(\dagger)\sigma} \tag{2.25}$$

$$P_a^{(\dagger)} = P_{\boldsymbol{Q}}^{(\dagger)\mu s_h l_h s_e l_e}. \tag{2.26}$$

Naturally this also applies to operator indices. If we for example had an arbitrary matrix element $A_{ab}a_a^\dagger a_a b_b$ then the operator indices would be expanded as $A_{\boldsymbol{k},\boldsymbol{K}}^{sll'\alpha}$.

Note that while the electrons, phonons and excitons are bound to the layers the photons are not, eaning that the photons' momenta exist in three dimensional space while the rest only occupy two. As a final remark, we will label fixed compound indices with numbers $1, 2, 3, \ldots$ while compound summation indices will be labeled with letters $a, b, c, \ldots$.

3

Constructing the Hamiltonian

This chapter will be dedicated to constructing the Hamiltonian that will be used in the Heisenberg equation of motion. The one we will use here has the form

$$H = H_0 + H_{c-f} + H_{c-\text{phot}} + H_{c-\text{phon}} + H_T + H_{c-c}, \tag{3.1}$$

where

$$H_0 = \sum_a \epsilon_a a_a^\dagger a_a + \sum_a \mathcal{E}_a b_a^\dagger b_a + \sum_a \hbar\omega_a c_a^\dagger c_a \equiv H_{0,c} + H_{0,\text{phon}} + H_{0,\text{phot}} \tag{3.2}$$

describes the (effective) free interaction where ϵ_a is the electron dispersion, $\mathcal{E}_a$ the phonon dispersion and $\hbar\omega_a$ the photon dispersion,

$$H_{c-f} = \sum_{ab} \boldsymbol{M}_{ab} \cdot \boldsymbol{A} a_a^\dagger a_b \tag{3.3}$$

describes the carrier-field interaction where $\boldsymbol{M}_{ab}$ is what is often refered to as the optical matrix element and $\boldsymbol{A}$ is the electromagnetic vector potential (treated classically),

$$H_{c-\text{phot}} = \sum_{abc} M_{abc} a_a^\dagger a_b (c_c \delta_{\lambda_c c} + c_{-c}^\dagger \delta_{\lambda_c v}) \tag{3.4}$$

describes the carrier-photon where M_{abc} is a sort of quantized optical matrix element and the energy concerving Kronecker δ's come from making a rotating wave approximation,

$$H_{c-\text{phon}} = \sum_{abc} g_{abc} a_a^\dagger a_b (b_c + b_{-c}^\dagger) \tag{3.5}$$

describes the electron-phonon interaction with coupling element g_{abc},

$$H_T = \sum_{ab} T_{ab} a_a^\dagger a_b \tag{3.6}$$

describes electron tunneling between the layers with tunneling element T_{ab} and

$$H_{c-c} = \frac{1}{2} \sum_{a,b,c,d} V_{cd}^{ab} a_a^\dagger a_b^\dagger a_d a_c \tag{3.7}$$

describes the carrier-carrier interaction where V_{cd}^{ab} is the coupling element describing the Coulomb interaction. We will use the semiclassical carrier-field interaction

to describe interaction with the exciting field and the carrier-photon interaction to describe the interaction with the rest of the field. Before proceeding we first want to find expressions for these coupling elements, which is done in the following subsections.

3.1 Computing the matrix elements

Before we start computing our matrix elements we need to come up with an expression for the wave functions involved. We start out by separating the spatial and spin dependencies as

$$\Psi^{as}(\boldsymbol{r}, \boldsymbol{s}) \equiv \Psi^{a}(\boldsymbol{r})\chi^{s}(\boldsymbol{s}), \tag{3.8}$$

where $\Psi^a(\boldsymbol{r})$ is a function in real space and $\chi^s(\boldsymbol{s})$ is a function in spin space. We then proceed to express the spatial wave function using the tight binding approximation, meaning that we assume that the electrons are so tightly bound to the ions of the crystals that they can be approximated using their respective atomic orbitals. The wave function can then be written as

$$\Psi^{a}(\boldsymbol{r}) = \sum_{i}^{M,X} C_i^a \Psi_i^a(\boldsymbol{r}) \tag{3.9}$$

$$= \frac{1}{\sqrt{V}} \sum_{i}^{M,X} C_i^a \sum_{\boldsymbol{R}_i} e^{i\boldsymbol{k}\cdot\boldsymbol{R}_i} \Phi_i^a(\boldsymbol{r} - \boldsymbol{R}_i), \tag{3.10}$$

where C_i^a are the so called tight binding coefficients, V is the volume (in this case area) of the sample, the i sums separates the two M and X sublattices, the $\boldsymbol{R}_i$ sum runs over all ions in the sublattice in question and Φ_i^a is the corresponding atomic wave function. From DFT studies of the band structures it has been discovered that around the $\boldsymbol{K}/\boldsymbol{K}'$ points the M atoms consists mostly of $d_0 = d_{z^2}$ orbital for the conduction band and $d_{\pm 2} = \frac{1}{\sqrt{2}}(d_{x^2+y^2} \pm i d_{xy})$ for the valence band, while both bands for the X atoms mostly contain $p_{\pm 1} = \frac{1}{\sqrt{2}}(p_x \pm i p_y)$ [12].

3.1.1 Electronic dispersion

The electronic despersion can be obtained by solving the free Schrödinger equation for the above expression of the wave function. Doing this (something that can be seen in D.1) and performing a Taylor expansion around the $\boldsymbol{K}/\boldsymbol{K}'$ point then results in

$$\epsilon^{\lambda sl}(\boldsymbol{k}) = (-1)^{\delta_{\lambda,v}} \left(\frac{\Delta E^{\lambda sl}}{2} + \frac{\hbar^2 \boldsymbol{k}^2}{2m^{\lambda sl}} \right), \tag{3.11}$$

where $\Delta E^{\lambda sl}$ is the energy of the λ band in the l layer with spin-orbit coupling taken into consideration and $m^{\lambda sl}$ is the correspinding effective mass, a meassure of the parabolic curvature. These values are taken from DFT calculations when taken on

their own. The ΔE parameters often appear as differences though, corresponding to band gaps, in which case more accurate experimental values will be used instead.

In finding the electronic dispersion, expressions for the tight binding coefficients can be obtained as well. These turn out to be

$$C_M^a(\boldsymbol{k}) = C_X^a(\boldsymbol{k}) g^a(\boldsymbol{k}), \tag{3.12}$$

$$C_X^a(\boldsymbol{k}) = \frac{(-1)^{\delta_{\lambda,v}}}{\sqrt{1 + |g^a(\boldsymbol{k})|^2}}, \tag{3.13}$$

$$g^a(\boldsymbol{k}) = \frac{t^a e(\boldsymbol{k})}{\frac{\Delta E^a}{2} - \epsilon^a(\boldsymbol{k})}, \tag{3.14}$$

where the hoping integral t^a is related to the effective mass as

$$\frac{\hbar^2 \boldsymbol{k}^2}{2m^{\lambda sl}} = \frac{3|t^{\lambda sl}|^2}{4\Delta E^{\lambda sl}} \left(\frac{\boldsymbol{k}}{a_0^l}\right)^2. \tag{3.15}$$

3.1.2 Phonon dispersion

A DFT calculation of the phonon dispersion in MoS_2 can be seen in Figure 3.1. In this figure we can clearly see that the different modes can be separated into two categories, one with lower energy and one with higher. These are called acoustic and optical phonon modes respectively.

For the purpose of this thesis we will be working in the long wavelength limit, meaning that we will assume that all phonons lie near the Γ point. Since the acoustic phonons have zero energy at this point we can assume a linear dispersion. This is the Debye approximation, meaning that the dispersion can be expressed as

$$\mathcal{E}_{\boldsymbol{q}}^A = \hbar v q \tag{3.16}$$

where v is the velocity of sound in the medium. We will also omit the out of plane ZA modes since they only couple to weak charge carriers [13], keeping the longitudinal and transverse modes LA and TA.

For the optical modes, modes that are non-zero at the Γ point, we will instead use a constant dispersion. This is an Einstein approximation. Here we will once again only use the longitudinal and transverse modes LO and TO.

3.1.3 Optical matrix element

The optical matrix element is given by

$$\boldsymbol{M}_{ab} = -\frac{i\hbar e_0}{m_0} \langle \Psi_a | \nabla | \Psi_b \rangle. \tag{3.17}$$

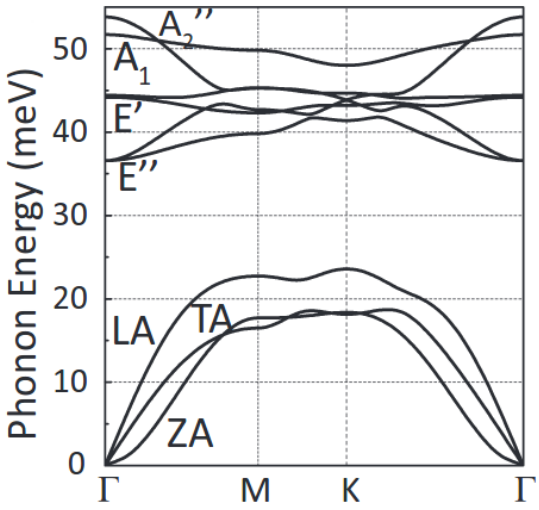

Figure 3.1: In this figure the phonon dispersion, taken from DFT calculations in [13], can be seen. The approximately linear dependence of the in-plane acoustic modes LA and TA near the Γ point can be seen at the bottom, while the more constant behaviour of the optical E' modes (corresponding to the in-plane modes LO and TO) can be seen higher up. In general the figure shows how the optical modes are of a higher energy than the acoustic ones.

By performing a number of approximations including the tight binding approximation and performing a Taylor approximation around the $\boldsymbol{K}/\boldsymbol{K}'$ points (done in D.2) we find that it can be written as

$$\boldsymbol{M}_{\boldsymbol{k}}^{vcsl_al_b}|_{\boldsymbol{K}} = M^{l_al_b}C_X^{vsl_a}(\boldsymbol{k})C_X^{csl_b}(\boldsymbol{k})\alpha^{csl_b}(\boldsymbol{k})ke^{-i\varphi_k}\begin{pmatrix}1\\ i\end{pmatrix}\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b}, \tag{3.18}$$

$$\boldsymbol{M}_{\boldsymbol{k}}^{vcsl_al_b}|_{\boldsymbol{K}'} = M^{l_al_b}C_X^{vsl_a}(\boldsymbol{k})C_X^{csl_b}(\boldsymbol{k})\alpha^{csl_b}(\boldsymbol{k})ke^{i\varphi_k}\begin{pmatrix}1\\ -i\end{pmatrix}\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b}, \tag{3.19}$$

where we for the second lines have expressed $\boldsymbol{k}$ in complex polar coordinates and used the notation

$$\boldsymbol{M}_{\boldsymbol{k}_a}^{\lambda_a\lambda_b s_a l_a l_b} \equiv \boldsymbol{M}_{\boldsymbol{k}_a\boldsymbol{k}_b}^{\lambda_a\lambda_b s_a s_b l_a l_b}\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b}. \tag{3.20}$$

The coefficient

$$\alpha^a(\boldsymbol{k}) = \frac{t^a}{\frac{\Delta E^a}{2} - \epsilon^a(\boldsymbol{k})} \tag{3.21}$$

is the $g^a(\boldsymbol{k})$ coefficient without the $e(\boldsymbol{k})$ factor and the intralayer $M^{l_al_b}$ parameters are chosen so that 10% of the incoming light gets absorbed, something that fits well with experimental results. The corresponding interlayer parameters were calculated using DFT and scaled in a similar manner, and ended up being about 1000 times smaller.

We can see that the optical matrix elements in this approximation are Jones vectors, and more specifically that the $\boldsymbol{K}$ point is optically active for right handed light

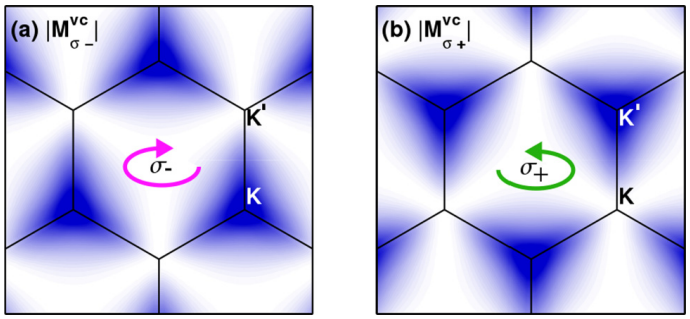

Figure 3.2: Here the optical matrix element projected to the right handed (a) and left handed (b) basis can be seen. Something that is clear from this is that the K point is optically active to right handed light while the K' point is the same for left handed light. Another aspect that can be seen is the element's iconic trigonal warping effect stemming from the electronic dispersion. The figure is taken from [6].

$\left(\sigma_- = \begin{pmatrix} 1 \\ -i \end{pmatrix}\right)$ while the $\boldsymbol{K}'$ point is active for left handed $\left(\sigma_+ = \begin{pmatrix} 1 \\ i \end{pmatrix}\right)$. This has been seen in DFT calculations, and can be seen in Figure 3.2.

We can also see that the optical interaction conserves not only spin but also momentum. This is a good approximation as the photon momentum is a lot smaller than that of the electrons.

3.1.4 Carrier photon matrix element

The carrier-photon matrix element can be expressed as

$$M_{abc} = \boldsymbol{M}_{\boldsymbol{k}_b}^{\lambda_a\lambda_b s_a l_a l_b} \cdot \boldsymbol{e}_{\boldsymbol{k}_{c\parallel}}^{\sigma_c} \sqrt{\frac{2\pi\hbar c^2}{\omega_{\boldsymbol{k}_c}^{\sigma_c} V}} \delta_{\boldsymbol{k}_a, \boldsymbol{k}_b + \boldsymbol{k}_{c\parallel}} \delta_{\lambda_a \bar{\lambda}_b} \delta_{s_a s_b} \equiv M_{\boldsymbol{k}_b, \boldsymbol{k}_{c\parallel}}^{\lambda_a\lambda_b s_a \sigma_c l_a l_b} \tag{3.22}$$

where $\boldsymbol{e}_{\boldsymbol{k}}^{\sigma}$ is the photon polarization vector, V the quantization volume and $\boldsymbol{k}_{\parallel}$ the in-plane component of the photon momentum. As with the optical element we neglect intraband transitions. Unlike the classical case however the electron momentum is not conserved, since the photon momentum is now included. We could go deeper into the quantization volume and photon dispersion, but for reasons you will see later it will not be needed.

3.1.5 Carrier phonon matrix element

In the tight binding approximation the carrier-phonon matrix element can be expressed as

$$g_{abc} = \sqrt{\frac{\Omega\hbar^2}{2M_\Omega^{l_a}\mathcal{E}_{\boldsymbol{q}}^{l\alpha}}} \sum_i^{M,X} \sum_l C_{i,\boldsymbol{k}_b+\boldsymbol{k}_c}^{l_a\lambda_a} C_{i,\boldsymbol{k}_b}^{l_a\lambda_a} \tilde{V}_{\boldsymbol{k}_c}^{l_a\lambda_a\alpha} \delta_{l_a l_b}^{l_b l_c} \delta_{\lambda_a\lambda_b} \delta_{s_a s_b} \delta_{\boldsymbol{k}_a, \boldsymbol{k}_b+\boldsymbol{k}_c} \equiv g_{\boldsymbol{k}_b, \boldsymbol{k}_c}^{\lambda_a l_a \alpha}, \tag{3.23}$$

where $\tilde{V}_{\boldsymbol{k}}^{l\lambda\alpha}$ is a deformation potential [13]. For the optical modes we use a zeroth order expansion $\tilde{V}_{\boldsymbol{k}}^{l\lambda\alpha_{\text{opt}}} = D_0^{l\lambda}$ while we use a first order expression $\tilde{V}_{\boldsymbol{k}}^{l\lambda\alpha_{\text{ac}}} = D_1^{l\lambda}|\boldsymbol{k}|$ for the acoustic modes. The D parameters were taken from DFT calculations. The δ functions come from spin- and momentum conservation and how we don't consider the possibility of phonons inducing either interband or interlayer transitions.

3.1.6 Tunneling matrix element

The tunneling matrix element is given by

$$T_{ab} = \langle \Psi_a | V_T | \Psi_b \rangle = \langle \Psi^{\lambda_a s_a l_a} | V_T | \Psi^{\lambda_b s_b l_b} \rangle \delta_{\lambda_a \lambda_b} \delta_{s_a s_b} \delta_{l_a \bar{l}_b}, \tag{3.24}$$

where the tunneling potential V_T is the static potential between the two layers. The conservation of band indices is not fundamental to the interaction, but is enforced here since energy conservation would be violated unless the interlayer band gap was zero or lower.

For the purpose of this thesis we will be using a potential on the form

$$V_T(\boldsymbol{r}) = V_{T,\boldsymbol{\rho}} V_{T,z} \tag{3.25}$$

where $V_{T,\boldsymbol{\rho}}$ is a slowly varying periodic potential in the in-plane direction with $\boldsymbol{\rho}$ as the in-plane spatial coordinate, and $V_{T,z}$ is the potential in the out of plane direction. We can then use the procedure that will be used for the Coulomb element in 3.1.7 to find

$$T_{ab} = \frac{1}{\Omega^l} \sum_{\boldsymbol{q}} V_{T,\boldsymbol{q}} \sum_i^{M,X} C_i^a C_{i/\bar{i}}^b \langle \Phi_i^a(\boldsymbol{r}) | e^{i\boldsymbol{q}\cdot\boldsymbol{r}} V_{T,z} | \Phi_{i/\bar{i}}^b(\boldsymbol{r} - \boldsymbol{R}) \rangle \delta_{\lambda_a \lambda_b} \delta_{s_a s_b} \delta_{l_a \bar{l}_b} \delta_{\boldsymbol{k}_a, \boldsymbol{k}_b + \boldsymbol{q}} \tag{3.26}$$

$$\equiv T_{\boldsymbol{k}_a \boldsymbol{k}_b}^{\lambda s l} \tag{3.27}$$

where once again the $i/\bar{i}$ corresponds to either AA or AB stacking and Φ are atomic orbitals. The $\langle \Phi_i^a(\boldsymbol{r}) | e^{i\boldsymbol{q}\cdot\boldsymbol{r}} V_{T,z} | \Phi_{i/\bar{i}}^b(\boldsymbol{r} - \boldsymbol{R}) \rangle$ integral will for the purpose of this thesis be taken as a single parameter. In the future it might be worth it to get a better approximation using for example DFT, but for now this is what we will have to deal with.

Finally, the $V_{T,\boldsymbol{q}}$ potential (the Fourier transform of $V_{T,\boldsymbol{\rho}}$) was given the form

$$V_{T,\boldsymbol{q}} = \frac{\pi L_C^2}{\left(1 + \frac{\boldsymbol{q}^2 L_C^2}{2}\right)} \tag{3.28}$$

where L_C is a correlation length that will be varied as a parameter. This expression was taken from [14].

3.1.7 Coulomb matrix element

The Coulomb matrix element is given by

$$V_{cd}^{ab} = \langle \Psi_a(\boldsymbol{r})\Psi_b(\boldsymbol{r}')|V(\boldsymbol{r}-\boldsymbol{r}')|\Psi_c(\boldsymbol{r})\Psi_d(\boldsymbol{r}')\rangle \tag{3.29}$$

where $V(\boldsymbol{r})$ is the Coulomb potential in real space. Using various steps written in D.3 this element to first order in $\boldsymbol{q}\cdot\boldsymbol{r}$ can be expressed as

$$V_{cd}^{ab} = \frac{1}{\Omega^2}\sum_{\boldsymbol{q}} V_{\boldsymbol{q}} \sum_{i,j}^{M,X} C_i^a C_i^c C_j^b C_j^d \tag{3.30}$$

$$\cdot (\delta_{l_a,l_c} + \langle \Phi_i^a(\boldsymbol{r})|e^{i\boldsymbol{q}\cdot\boldsymbol{r}}|\Phi_{i/\bar{i}}^c(\boldsymbol{r}-\boldsymbol{R})\rangle\delta_{l_a,\bar{l}_c})(\delta_{l_b,l_d} + \langle \Phi_j^a(\boldsymbol{r})|e^{i\boldsymbol{q}\cdot\boldsymbol{r}}|\Phi_{j/\bar{j}}^c(\boldsymbol{r}-\boldsymbol{R})\rangle\delta_{l_b,\bar{l}_d}) \tag{3.31}$$

$$\cdot \delta_{\lambda_a,\lambda_c}^{\lambda_b,\lambda_d}\delta_{s_a,s_c}^{s_b,s_d}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}}\delta_{\boldsymbol{k}_b,\boldsymbol{k}_d-\boldsymbol{q}}. \tag{3.32}$$

Here $V_{\boldsymbol{q}}$ is the Coulomb potential in Fourier space and the $i/\bar{i}$ index corresponds to AA or AB stacking. Unlike the spin conserving Kronecker delta the band conserving one is not fundamental, but has been enforced to neglect interband transitions since the band gap energy is much larger than the typical electron energies. We can also see that the total electron momentum is conserved, and the Fourier momentum $\boldsymbol{q}$ describes the momentum transferred between the scattering electrons.

We now have one final obstacle left, and that is to find an expression for the Fourier transformed Coulomb potential. For the intralayer case we can simply use the Keldysh potential, which looks like

$$V_{\boldsymbol{q}} = \frac{e_0^2}{\varepsilon_0(\varepsilon_1+\varepsilon_2)}\frac{1}{q(1+r_0 q)}, \quad r_0 = d\frac{\varepsilon}{\frac{1}{2}(\varepsilon_1+\varepsilon_2)} \tag{3.33}$$

where ε_1, ε_2 and ε are the relative permittivities of the over- and underlying substrates and the TMD itself, and d is the thickness of the layer. For the interlayer case further investigation is required, which will be explored in the following subsection.

3.1.7.1 Deriving the interlayer Coulomb potential

To find the interlayer Coulomb potential potential we examine a situation where we using cylindrical coordinates $(\boldsymbol{\rho}, z)$ have a point charge at the origin and relative permitivities

$$\epsilon(z) = \begin{pmatrix} \epsilon_1, & z > R + \frac{3}{2}d \\ \epsilon_{l_1}, & R+\frac{1}{2}d < z < R+\frac{3}{2}d \\ \epsilon_R, & \frac{1}{2}d < z < R+\frac{1}{2}d \\ \epsilon_{l_2}, & -\frac{1}{2}d < z < \frac{1}{2}d \\ \epsilon_2, & z < -\frac{1}{2}d \end{pmatrix}. \tag{3.34}$$

The physical meaning of this setup is that the lower TMD occupies the space $z \in \left[-\frac{1}{2}d, \frac{1}{2}d\right]$ where d is its thickness, and the upper TMD is placed at a distance R

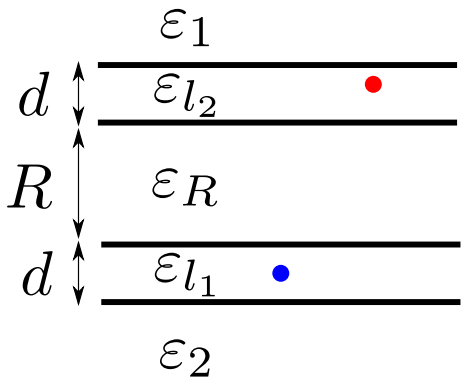

Figure 3.3: The purpose of this figure is to illustrate how the bilayer system is treated when deriving the extended Keldysh potential. The two layers are treated as homogenous slabs with infinite reach in the in-plane direction, thickness d and relative permittivity $\varepsilon_{l_{1,2}}$. They are surrounded by medium with permittivity $\varepsilon_{1,2}$ the R thick segment in between them has the permittivity ε_R. At the origin a point charge (blue) is placed. The extended Keldysh potential is then obtained by solving the Poisson equation for this setup with respect to a test charge in the other layer (red).

above it. It can be seen illustrated in Figure 3.3. To find the potential between two charges in the different layers we then place a point charge at the origin and calculate the potential for a test charge in the other layer. The Poisson equation then becomes

$$\nabla^2\phi(\boldsymbol{r}) = -\frac{e}{\epsilon(z)}\delta(\boldsymbol{r}). \tag{3.35}$$

We are however not interested in this basis. Instead we want to Fourier transform the x and y coordinates while keeping the z coordinate unchanged, giving

$$\left(-k^2 + \frac{\partial^2}{\partial z^2}\right)\phi(\boldsymbol{k}, z) = -\frac{e}{\epsilon(z)}\delta(z). \tag{3.36}$$

This equation has the solution

$$\phi(k,z) = \begin{pmatrix} F_2e^{-kz}, & z > R + \frac{3}{2}d \\ E_1e^{kz} + E_2e^{-kz}, & R + \frac{1}{2}d < z < R + \frac{3}{2}d \\ D_1e^{kz} + D_2e^{-kz}, & \frac{1}{2}d < z < R + \frac{1}{2}d \\ C_1e^{kz} + C_2e^{-kz}, & 0 < z < \frac{1}{2}d \\ B_1e^{kz} + B_2e^{-kz}, & -\frac{1}{2}d < z < 0 \\ A_1e^{kz}, & z < -\frac{1}{2}d \end{pmatrix}, \tag{3.37}$$

where the coefficients can be solved for using the boundary conditions

$$\phi|_{z^+} - \phi|_{z^-} = 0 \tag{3.38}$$

and

$$\epsilon\frac{\partial\phi}{\partial z}\bigg|_{z^+} - \epsilon\frac{\partial\phi}{\partial z}\bigg|_{z^-} = \begin{pmatrix} -e, & z = 0 \\ 0, & z \neq 0 \end{pmatrix}. \tag{3.39}$$

By solving the resulting equation system while using the approximations $\epsilon_1, \epsilon_2, \epsilon_R \ll \epsilon_{l_1}, \epsilon_{l_2}$, $kd \ll 1$ and neglecting the effect of different z values within the layers we then find our potential as

$$V_{\boldsymbol{k}} = e\phi\left(k, R + \frac{1}{2}d < z < R + \frac{3}{2}d\right) \tag{3.40}$$

$$= \frac{e^2}{\epsilon_0\left((\epsilon_1+\epsilon_2)\cosh(kR) + \frac{\epsilon_R^2+\epsilon_1\epsilon_2}{\epsilon_R}\sinh(kR)\right)} \tag{3.41}$$

$$\cdot \frac{e^{-kR}}{k\left(1 + d\frac{(\epsilon_{l_1}+\epsilon_{l_2})\cosh(kR)+\frac{\epsilon_{l_2}\epsilon_1+\epsilon_{l_1}\epsilon_2}{\epsilon_R}\sinh(kR)}{\frac{1}{2}\left((\epsilon_1+\epsilon_2)\cosh(kR)+\frac{\epsilon_R^2+\epsilon_1\epsilon_2}{\epsilon_R}\sinh(kR)\right)}k\right)}. \tag{3.42}$$

We can see that if we go from here to the monolayer case by letting $R \to 0$ and removing either ϵ_{l_1} or ϵ_{l_2} this expression reduces to the familiar Keldysh potential

$$V_{\boldsymbol{k},\text{Keldysh}} = \frac{e^2}{\epsilon_0(\epsilon_1+\epsilon_2)}\frac{1}{k(1+d\frac{\epsilon_{l_{1,2}}}{\frac{1}{2}(\epsilon_1+\epsilon_2)}k)} \tag{3.43}$$

If we instead let $R \to 0$ without removing a permittivity constant we end up with

$$V_{\boldsymbol{k},R\to 0} = \frac{e^2}{\epsilon_0(\epsilon_1+\epsilon_2)}\frac{1}{k(1+2d\frac{\frac{1}{2}(\epsilon_{l_1}+e_{l_2})}{\frac{1}{2}(\epsilon_1+\epsilon_2)}k)} \tag{3.44}$$

which is the same as a Keldysh potential with $d \to 2d$ and $\epsilon_{l_{1,2}} \to \frac{1}{2}(\epsilon_{l_1} + e_{l_2})$.

This potential as a function of $\boldsymbol{k}$ for different values of R can been seen in Figure 3.4.

3.2 Going to the pair operator picture

Using our newly evaluated matrix elements and the notation

$$v^{(\dagger)} \equiv a^{(\dagger)v}, \quad c^{(\dagger)} \equiv a^{(\dagger)c} \tag{3.45}$$

we can expand the free Hamiltonians to

$$H_{0,e} = \sum_{\boldsymbol{k}sl}(\epsilon_{\boldsymbol{k}}^{vsl} v_{\boldsymbol{k}}^{\dagger sl} v_{\boldsymbol{k}}^{sl} + \epsilon_{\boldsymbol{k}}^{csl} c_{\boldsymbol{k}}^{\dagger sl} c_{\boldsymbol{k}}^{sl}), \tag{3.46}$$

$$H_{0,\text{phon}} = \sum_{\boldsymbol{K}l\alpha} \mathcal{E}_{\boldsymbol{K}}^{l\alpha} b_{\boldsymbol{K}}^{\dagger l\alpha} b_{\boldsymbol{K}}^{l\alpha} \tag{3.47}$$

and

$$H_{0,\text{phot}} = \sum_{\boldsymbol{K}\sigma} \hbar\omega_{\boldsymbol{K}}^{\sigma} c_{\boldsymbol{K}}^{\dagger\sigma} c_{\boldsymbol{K}}^{\sigma}, \tag{3.48}$$

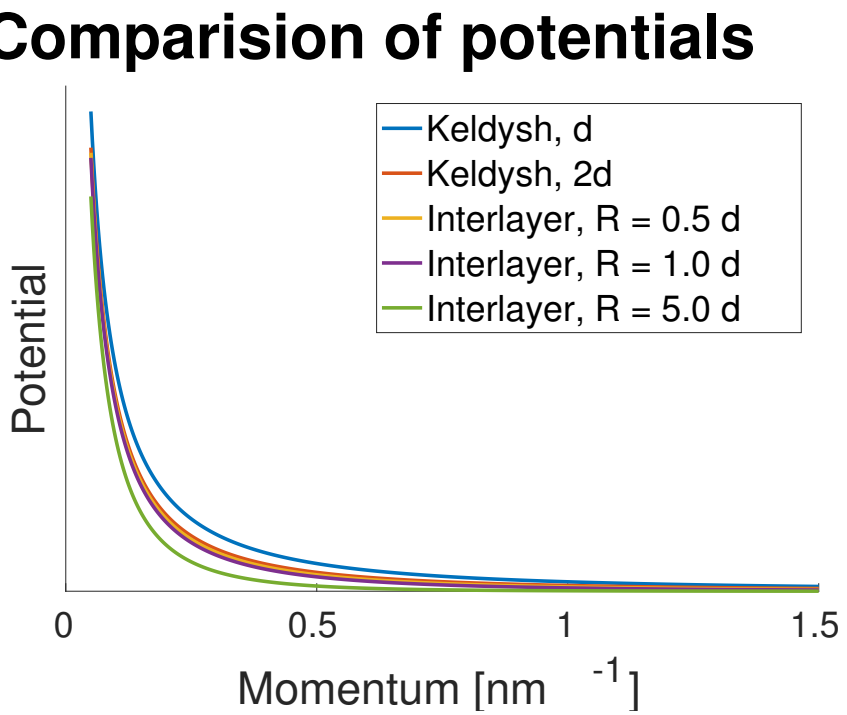

Figure 3.4: This figure shows how the extended Keldysh potential depends on the layer distance R. We can see that the potential gets smaller for larger R, and converges towards the Keldysh potential for a thickness of $2d$.

our carrier-field Hamiltonian to

$$H_{c-f} = \sum_{\boldsymbol{k}sl_al_b} (\boldsymbol{M}_{\boldsymbol{k}}^{vcsl_al_b} v_{\boldsymbol{k}}^{\dagger sl_a} c_{\boldsymbol{k}}^{sl_b} + \boldsymbol{M}_{\boldsymbol{k}}^{cvsl_al_b} c_{\boldsymbol{k}}^{\dagger sl_a} v_{\boldsymbol{k}}^{sl_b}), \tag{3.49}$$

the carrier-photon Hamiltonian to

$$H_{c-\text{phot}} = \sum_{\boldsymbol{k}\boldsymbol{K}sll'\sigma} (M_{\boldsymbol{k}+\boldsymbol{K}_\parallel,\boldsymbol{k}}^{cvs\sigma ll'} c_{\boldsymbol{k}+\boldsymbol{K}_\parallel}^{\dagger sl} v_{\boldsymbol{k}}^{sl'} c_{\boldsymbol{K}}^{\sigma} + M_{\boldsymbol{k}+\boldsymbol{K}_\parallel,\boldsymbol{k}}^{vcs\sigma ll'} v_{\boldsymbol{k}+\boldsymbol{K}_\parallel}^{\dagger sl} c_{\boldsymbol{k}}^{sl'} c_{-\boldsymbol{K}}^{\dagger\sigma}), \tag{3.50}$$

the carrier-phonon Hamiltonian as

$$H_{c-\text{phon}} = \sum_{\boldsymbol{k}\boldsymbol{q}sl\alpha} (g_{\boldsymbol{k},\boldsymbol{q}}^{cl\alpha} c_{\boldsymbol{k}+\boldsymbol{q}}^{\dagger sl} c_{\boldsymbol{k}}^{sl} + g_{\boldsymbol{k},\boldsymbol{q}}^{vl\alpha} v_{\boldsymbol{k}+\boldsymbol{q}}^{\dagger sl} v_{\boldsymbol{k}}^{sl})(b_{\boldsymbol{q}}^{l\alpha} + b_{-\boldsymbol{q}}^{\dagger l\alpha}), \tag{3.51}$$

the tunneling Hamiltonian as

$$H_T = \sum_{\boldsymbol{k}l} (T_{\boldsymbol{k}_a\boldsymbol{k}_b}^{csl} c_{\boldsymbol{k}_a}^{\dagger sl} c_{\boldsymbol{k}_b}^{s\neg l} + T_{\boldsymbol{k}_a\boldsymbol{k}_b}^{vsl} v_{\boldsymbol{k}_a}^{\dagger sl} v_{\boldsymbol{k}_b}^{s\neg l}) \tag{3.52}$$

and the Coulomb Hamiltonian as

$$H_{c-c} = \frac{1}{2} \sum_{\boldsymbol{k}_a\boldsymbol{k}_b\boldsymbol{q}s_as_bl_al_bl_cl_d} V_{\boldsymbol{k}_a,\boldsymbol{k}_b,\boldsymbol{q}}^{ccs_as_bl_al_bl_cl_d} c_{\boldsymbol{k}_a+\boldsymbol{q}}^{\dagger s_al_a} c_{\boldsymbol{k}_b-\boldsymbol{q}}^{\dagger s_bl_b} c_{\boldsymbol{k}_b}^{s_bl_d} c_{\boldsymbol{k}_a}^{s_al_c} \tag{3.53}$$

$$+ \frac{1}{2} \sum_{\boldsymbol{k}_a\boldsymbol{k}_b\boldsymbol{q}s_as_bl_al_bl_cl_d} V_{\boldsymbol{k}_a,\boldsymbol{k}_b,\boldsymbol{q}}^{vvs_as_bl_al_bl_cl_d} v_{\boldsymbol{k}_a+\boldsymbol{q}}^{\dagger s_al_a} v_{\boldsymbol{k}_b-\boldsymbol{q}}^{\dagger s_bl_b} v_{\boldsymbol{k}_b}^{s_bl_d} v_{\boldsymbol{k}_a}^{s_al_c} \tag{3.54}$$

$$+ \sum_{\boldsymbol{k}_a\boldsymbol{k}_b\boldsymbol{q}s_as_bl_al_bl_cl_d} V_{\boldsymbol{k}_a,\boldsymbol{k}_b,\boldsymbol{q}}^{cvs_as_bl_al_bl_cl_d} c_{\boldsymbol{k}_a+\boldsymbol{q}}^{\dagger s_al_a} v_{\boldsymbol{k}_b-\boldsymbol{q}}^{\dagger s_bl_b} v_{\boldsymbol{k}_b}^{s_bl_d} c_{\boldsymbol{k}_a}^{s_al_c} \tag{3.55}$$

$$\equiv H_{e-e} + H_{h-h} + H_{e-h} \tag{3.56}$$

where

$$V^{\lambda_a\lambda_b s_a s_b l_a l_b l_c l_d}_{\boldsymbol{k}_a,\boldsymbol{k}_b,\boldsymbol{q}} \equiv V^{ab}_{cd}\delta^{\lambda_b,\lambda_d}_{\lambda_a,\lambda_c}\delta^{s_b,s_d}_{s_a,s_c}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}}\delta_{\boldsymbol{k}_b,\boldsymbol{k}_d-\boldsymbol{q}} \tag{3.57}$$

and the three terms describe electron-electron, hole-hole and electron-hole interaction.

Normally we would have gone ahead and insert this into the Heisenberg equation. In this thesis we will use a slightly different approach however. First off we will need to define the pair operators

$$P^{s_h l_h s_e l_e}_{\boldsymbol{k}_h\boldsymbol{k}_e} \equiv v^{\dagger s_h l_h}_{\boldsymbol{k}_h} c^{s_e l_e}_{\boldsymbol{k}_e}, \quad P^{\dagger s_h l_h s_e l_e}_{\boldsymbol{k}_h\boldsymbol{k}_e} \equiv c^{\dagger s_e l_e}_{\boldsymbol{k}_e} v^{s_h l_h}_{\boldsymbol{k}_h} \tag{3.58}$$

which are basically the microscopic polarization in operator form. By using the relations

$$\sum_a v_a v_a^\dagger = \sum_a c_a^\dagger c_a = 1 \tag{3.59}$$

we can then form the conservation laws

$$c^{\dagger s_1 l_1}_{\boldsymbol{k}_1} c^{s_2 l_2}_{\boldsymbol{k}_2} = \sum_{\boldsymbol{k}_h s_h l_h} c^{\dagger s_1 l_1}_{\boldsymbol{k}_1} v^{s_h l_h}_{\boldsymbol{k}_h} v^{\dagger s_h l_h}_{\boldsymbol{k}_h} c^{s_2 l_2}_{\boldsymbol{k}_2} \tag{3.60}$$

$$= \sum_{\boldsymbol{k}_h s_h l_h} P^{\dagger s_h l_h s_1 l_1}_{\boldsymbol{k}_h\boldsymbol{k}_1} P^{s_h l_h s_2 l_2}_{\boldsymbol{k}_h\boldsymbol{k}_2} \tag{3.61}$$

and

$$v^{\dagger s_1 l_1}_{\boldsymbol{k}_1} v^{s_2 l_2}_{\boldsymbol{k}_2} = \delta^{l_1 l_2}_{s_1 s_2}\delta_{\boldsymbol{k}_1\boldsymbol{k}_2} - v^{s_2 l_2}_{\boldsymbol{k}_2} v^{\dagger s_1 l_1}_{\boldsymbol{k}_1} \tag{3.62}$$

$$= \delta^{l_1 l_2}_{s_1 s_2}\delta_{\boldsymbol{k}_1\boldsymbol{k}_2} - \sum_{\boldsymbol{k}_e s_e l_e} v^{s_2 l_2}_{\boldsymbol{k}_2} c^{\dagger s_e l_e}_{\boldsymbol{k}_e} c^{s_e l_e}_{\boldsymbol{k}_e} v^{\dagger s_1 l_1}_{\boldsymbol{k}_1} \tag{3.63}$$

$$= \delta^{l_1 l_2}_{s_1 s_2}\delta_{\boldsymbol{k}_1\boldsymbol{k}_2} - \sum_{\boldsymbol{k}_e s_e l_e} P^{\dagger s_2 l_2 s_e s_e}_{\boldsymbol{k}_2\boldsymbol{k}_e} P^{s_1 l_1 s_e l_e}_{\boldsymbol{k}_1\boldsymbol{k}_e}, \tag{3.64}$$

by which we can finally find the commutation relations

$$[P^{s_h l_h s_e s_e}_{\boldsymbol{k}_h\boldsymbol{k}_e} P^{\dagger s'_h l'_h s'_e l'_e}_{\boldsymbol{k}'_h\boldsymbol{k}'_e}] = [v^{\dagger s_h l_h}_{\boldsymbol{k}_h} c^{s_e l_e}_{\boldsymbol{k}_e}, c^{\dagger s'_e l'_e}_{\boldsymbol{k}'_e} v^{s'_h l'_h}_{\boldsymbol{k}'_h}] \tag{3.65}$$

$$= v^{\dagger s_h l_h}_{\boldsymbol{k}_h}[c^{s_e l_e}_{\boldsymbol{k}_e}, c^{\dagger s'_e l'_e}_{\boldsymbol{k}'_e}]v^{s'_h l'_h}_{\boldsymbol{k}'_h} + c^{\dagger s'_e l'_e}_{\boldsymbol{k}'_e}[v^{\dagger s_h l_h}_{\boldsymbol{k}_h}, v^{s'_h l'_h}_{\boldsymbol{k}'_h}]c^{s_e l_e}_{\boldsymbol{k}_e} \tag{3.66}$$

$$= v^{\dagger s_h l_h}_{\boldsymbol{k}_h}(2c^{s_e l_e}_{\boldsymbol{k}_e} c^{\dagger s'_e l'_e}_{\boldsymbol{k}'_e} - \{c^{s_e l_e}_{\boldsymbol{k}_e}, c^{\dagger s'_e l'_e}_{\boldsymbol{k}'_e}\})v^{s'_h l'_h}_{\boldsymbol{k}'_h} \tag{3.67}$$

$$+ c^{\dagger s'_e l'_e}_{\boldsymbol{k}'_e}(2v^{\dagger s_h l_h}_{\boldsymbol{k}_h} v^{s'_h l'_h}_{\boldsymbol{k}'_h} - \{v^{\dagger s_h l_h}_{\boldsymbol{k}_h}, v^{s'_h l'_h}_{\boldsymbol{k}'_h}\})c^{s_e l_e}_{\boldsymbol{k}_e} \tag{3.68}$$

$$= v^{\dagger s_h l_h}_{\boldsymbol{k}_h}(\delta^{l_e l'_e}_{s_e s'_e}\delta_{\boldsymbol{k}_e\boldsymbol{k}'_e} - 2c^{\dagger s'_e l'_e}_{\boldsymbol{k}'_e} c^{s_e l_e}_{\boldsymbol{k}_e})v^{s'_h l'_h}_{\boldsymbol{k}'_h} \tag{3.69}$$

$$+ c^{\dagger s'_e l'_e}_{\boldsymbol{k}'_e}(2v^{\dagger s_h l_h}_{\boldsymbol{k}_h} v^{s'_h l'_h}_{\boldsymbol{k}'_h} - \delta^{l_h l'_h}_{s_h s'_h}\delta_{\boldsymbol{k}_h\boldsymbol{k}'_h})c^{s_e l_e}_{\boldsymbol{k}_e} \tag{3.70}$$

$$= \delta^{l_e l'_e}_{s_e s'_e}\delta_{\boldsymbol{k}_e\boldsymbol{k}'_e} v^{\dagger s_h l_h}_{\boldsymbol{k}_h} v^{s'_h l'_h}_{\boldsymbol{k}'_h} \tag{3.71}$$

$$- \delta^{l_h l'_h}_{s_h s'_h}\delta_{\boldsymbol{k}_h\boldsymbol{k}'_h} c^{\dagger s'_e l'_e}_{\boldsymbol{k}'_e} c^{s_e l_e}_{\boldsymbol{k}_e} \tag{3.72}$$

$$= \delta^{l_e l'_e}_{s_e s'_e}\delta_{\boldsymbol{k}_e\boldsymbol{k}'_e}\delta^{l_h l'_h}_{s_h s'_h}\delta_{\boldsymbol{k}_h\boldsymbol{k}'_h} \tag{3.73}$$

$$- \delta^{l_e l'_e}_{s_e s'_e}\delta_{\boldsymbol{k}_e\boldsymbol{k}'_e}\sum_{\boldsymbol{k}''_e s''_e l''_e} P^{\dagger s_2 l_2 s''_e s''_e}_{\boldsymbol{k}_2\boldsymbol{k}''_e} P^{s_1 l_1 s''_e l''_e}_{\boldsymbol{k}_1\boldsymbol{k}''_e} \tag{3.74}$$

$$- \delta^{l_h l'_h}_{s_h s'_h}\delta_{\boldsymbol{k}_h\boldsymbol{k}'_h}\sum_{\boldsymbol{k}_h s_h l_h} P^{\dagger s''_h l''_h s_1 l_1}_{\boldsymbol{k}''_h\boldsymbol{k}_1} P^{s''_h l''_h s_2 l_2}_{\boldsymbol{k}''_h\boldsymbol{k}_2}. \tag{3.75}$$

While these relations work they are a bit messy. If we however keep them in the electron-hole picture and take the expectation value we find that

$$\langle [P^{s_h l_h s_e s_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} P^{\dagger s'_h l'_h s'_e l'_e}_{\boldsymbol{k}'_h \boldsymbol{k}'_e}] \rangle = \delta^{l_e l'_e}_{s_e s'_e} \delta_{\boldsymbol{k}_e \boldsymbol{k}'_e} \langle v^{\dagger s_h l_h}_{\boldsymbol{k}_h} v^{s'_h l'_h}_{\boldsymbol{k}'_h} \rangle - \delta^{l_h l'_h}_{s_h s'_h} \delta_{\boldsymbol{k}_h \boldsymbol{k}'_h} \langle c^{\dagger s'_e l'_e}_{\boldsymbol{k}'_e} c^{s_e l_e}_{\boldsymbol{k}_e} \rangle. \tag{3.76}$$

These quantities are densities (the populations from 2.2) meaning that we can extract δ functions from them for any non-matching quantum numbers (we aren't really interested in densities with different momenta for $a^\dagger$ and a for example). We can also use that the density of holes f_h can be expressed as $1 - f_v$ where $f_v \equiv \langle v^\dagger v \rangle$ (and similarily $f_c \equiv \langle c^\dagger c \rangle$), meaning that we can express the commutator expectation value as

$$\langle [P^{s_h l_h s_e s_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} P^{\dagger s'_h l'_h s'_e l'_e}_{\boldsymbol{k}'_h \boldsymbol{k}'_e}] \rangle = \delta^{l_e l'_e}_{s_e s'_e} \delta_{\boldsymbol{k}_e \boldsymbol{k}'_e} \delta^{l_h l'_h}_{s_h s'_h} \delta_{\boldsymbol{k}_h \boldsymbol{k}'_h} (f_v^{\boldsymbol{k}_h s_h l_h} - f_e^{\boldsymbol{k}_e s_e l_e}) \tag{3.77}$$

$$= \delta^{l_e l'_e}_{s_e s'_e} \delta_{\boldsymbol{k}_e \boldsymbol{k}'_e} \delta^{l_h l'_h}_{s_h s'_h} \delta_{\boldsymbol{k}_h \boldsymbol{k}'_h} (1 - f_h^{\boldsymbol{k}_h s_h l_h} - f_e^{\boldsymbol{k}_e s_e l_e}). \tag{3.78}$$

The phase-space filling term $(1 - f_h^{\boldsymbol{k}_h s_h l_h} - f_e^{\boldsymbol{k}_e s_e l_e})$ corresponds to Pauli blocking due to the fact that excitons are not bosons on the fundamental level, they are only composite bosons created by a pair of fermions. We will however be working in the low-excitation limit where the electron-hole densities are small enough that they can be neglected, which can also be interpreted as there being so few excitons that they won't be interacting to such a degree that their fermionic properties need to be accounted for. However you want to phrase it the consequence is that we within this approximation can assume that our pair operators have the purely bosonic commutation relations

$$[P^{s_h l_h s_e s_e}_{\boldsymbol{k}_h \boldsymbol{k}_e}, P^{\dagger s'_h l'_h s'_e l'_e}_{\boldsymbol{k}'_h \boldsymbol{k}'_e}] = \delta^{l_e l'_e}_{s_e s'_e} \delta_{\boldsymbol{k}_e \boldsymbol{k}'_e} \delta^{l_h l'_h}_{s_h s'_h} \delta_{\boldsymbol{k}_h \boldsymbol{k}'_h}. \tag{3.79}$$

With this out of the way we now want to convert our electron-hole Hamiltonian to this picture. For the free carrier part part we obtain

$$H_{0,c} = \sum_{\boldsymbol{k}_h s_h l_h} \epsilon^{v s_h l_h}_{\boldsymbol{k}_h} \left(\delta^{l_h l_h}_{s_h s_h} \delta_{\boldsymbol{k}_h \boldsymbol{k}_h} - \sum_{\boldsymbol{k}_e s_e l_e} P^{\dagger s_h l_h s_e s_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} P^{s_h l_h s_e l_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} \right) \tag{3.80}$$

$$+ \sum_{\boldsymbol{k}_e s_e l_e} \epsilon^{c s_e l_e}_{\boldsymbol{k}_e} \sum_{\boldsymbol{k}_h s_h l_h} P^{\dagger s_h l_h s_e l_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} P^{s_h l_h s_e l_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} \tag{3.81}$$

$$= \sum_{\boldsymbol{k}_h s_h l_h \boldsymbol{k}_e s_e l_e} (\epsilon^{c s_e l_e}_{\boldsymbol{k}_e} - \epsilon^{v s_h l_h}_{\boldsymbol{k}_h}) P^{\dagger s_h l_h s_e s_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} P^{s_h l_h s_e l_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} + \sum_{\boldsymbol{k}_h s_h l_h} \epsilon^{v s_h l_h}_{\boldsymbol{k}_h} \tag{3.82}$$

$$= \sum_{\boldsymbol{k}_h s_h l_h \boldsymbol{k}_e s_e l_e} \left(\frac{\hbar^2 \boldsymbol{k}_h^2}{2 m_h} + \frac{\hbar^2 \boldsymbol{k}_e^2}{2 m_e} + E_G^{s_h l_h s_e l_e} \right) P^{\dagger s_h l_h s_e s_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} P^{s_h l_h s_e l_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} + \sum_{\boldsymbol{k}_h s_h l_h} \epsilon^{v s_h l_h}_{\boldsymbol{k}_h} \tag{3.83}$$

where $E_G^{s_h l_h s_e l_e}$ is the total band gap energy and the last term can be ignored since it's a constant energy offset that doesn't contribute to any dynamics. We do not need to change the rest of the free Hamiltonian since it does not contain any electronic operators. Next we proceed to the carrier-field Hamiltonian

$$H_{c-f} = \sum_{\boldsymbol{k} s l_h l_e} \left(\boldsymbol{M}^{v c s l_h l_e}_{\boldsymbol{k}} P^{s l_h s l_e}_{\boldsymbol{k}, \boldsymbol{k}} + \boldsymbol{M}^{v c s l_h l_e}_{\boldsymbol{k}} P^{\dagger s l_h s s_e}_{\boldsymbol{k}, \boldsymbol{k}} \right) \tag{3.84}$$

the carrier-photon Hamiltonian

$$H_{c-\text{phot}} = \sum_{\boldsymbol{k}\boldsymbol{K}sl_hl_e\sigma} \left(M^{vcs\sigma l_h l_e}_{\boldsymbol{k},\boldsymbol{K}_\parallel} P^{sl_h sl_e}_{\boldsymbol{k}+\boldsymbol{K}_\parallel,\boldsymbol{k}} c^{\dagger\sigma}_{-\boldsymbol{K}} + M^{vcs\sigma l_h l_e}_{\boldsymbol{k},\boldsymbol{K}_\parallel} P^{\dagger sl_h sl_e}_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{K}_\parallel} c^{\sigma}_{\boldsymbol{K}} \right), \tag{3.85}$$

the carrier-phonon Hamiltonian

$$H_{c-\text{phon}} = \sum_{\boldsymbol{q}l_h\alpha} g^{vl_h\alpha}_{\boldsymbol{0},\boldsymbol{q}} (b^{l_h\alpha}_{\boldsymbol{q}} + b^{\dagger l_h\alpha}_{-\boldsymbol{q}}) \tag{3.86}$$

$$+ \sum_{\boldsymbol{k}_h\boldsymbol{k}_e\boldsymbol{q}s_hs_el_hl_e\alpha} (g^{cl_e\alpha}_{\boldsymbol{k}_e,\boldsymbol{q}} P^{\dagger s_h l_h s_e l_e}_{\boldsymbol{k}_h,\boldsymbol{k}_e+\boldsymbol{q}} P^{s_h l_h s_e l_e}_{\boldsymbol{k}_h,\boldsymbol{k}_e} (b^{l_e\alpha}_{\boldsymbol{q}} + b^{\dagger l_e\alpha}_{-\boldsymbol{q}}) \tag{3.87}$$

$$- g^{vl_h\alpha}_{\boldsymbol{k}_h,\boldsymbol{q}} P^{\dagger s_h l_h s_e l_e}_{\boldsymbol{k}_h,\boldsymbol{k}_e} P^{s_h l_h s_e l_e}_{\boldsymbol{k}_h+\boldsymbol{q},\boldsymbol{k}_e} (b^{l_h\alpha}_{\boldsymbol{q}} + b^{\dagger l_h\alpha}_{-\boldsymbol{q}})) \tag{3.88}$$

and the tunneling Hamiltonian

$$H_T = \sum_{\boldsymbol{k}_h\boldsymbol{k}_e\boldsymbol{k}'_e s_h l_h s_e l_e} T^{cs_e l_e}_{\boldsymbol{k}_e\boldsymbol{k}'_e} P^{\dagger s_h l_h s_e l_e}_{\boldsymbol{k}_h,\boldsymbol{k}_e} P^{s_h l_h s_e \neg l_e}_{\boldsymbol{k}_h,\boldsymbol{k}'_e} \tag{3.89}$$

$$- \sum_{\boldsymbol{k}_h\boldsymbol{k}'_h\boldsymbol{k}_e s_h l_h s_e l_e} T^{vs_h l_h}_{\boldsymbol{k}_h\boldsymbol{k}'_h} P^{\dagger s_h \neg l_h s_e l_e}_{\boldsymbol{k}'_h,\boldsymbol{k}_e} P^{s_h l_h s_e l_e}_{\boldsymbol{k}_h,\boldsymbol{k}_e}. \tag{3.90}$$

The Coulomb Hamiltonian is a bit more complicated due to involving 4 operators. This process is shown in D.3.1, and the results are

$$H_{e-e} = \frac{1}{2} \sum_{\boldsymbol{k}_e\boldsymbol{k}'_e\boldsymbol{k}_h\boldsymbol{k}'_h\boldsymbol{q}s_es'_es_hs'_hl_al'_bl_cl'_dl_hl'_h} V^{ccs_e s'_e l_a l'_b l_c l'_d}_{\boldsymbol{k}_e,\boldsymbol{k}'_e,\boldsymbol{q}} P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{k}_h,\boldsymbol{k}_e+\boldsymbol{q}} P^{\dagger s'_h l'_h s'_e l'_b}_{\boldsymbol{k}'_h,\boldsymbol{k}'_e-\boldsymbol{q}} P^{s'_h l'_h s'_e l'_d}_{\boldsymbol{k}'_h\boldsymbol{k}'_e} P^{s_h l_h s_e l_c}_{\boldsymbol{k}_h\boldsymbol{k}_e}, \tag{3.91}$$

$$H_{h-h} = \frac{1}{2} \sum_{\boldsymbol{k}_e\boldsymbol{k}'_e\boldsymbol{k}_h\boldsymbol{k}'_h\boldsymbol{q}s_es'_es_hs'_hs'_hl_el'_el_al'_bl_cl'_d} V^{vvs_h s_h s'_h l_c l'_d l_a l'_b}_{\boldsymbol{k}_h-\boldsymbol{q},\boldsymbol{k}'_h+\boldsymbol{q},\boldsymbol{q}} P^{\dagger s_h l_a s_e l_e}_{\boldsymbol{k}_h-\boldsymbol{q},\boldsymbol{k}_e} P^{\dagger s'_h l'_b s'_e l'_e}_{\boldsymbol{k}'_h+\boldsymbol{q},\boldsymbol{k}'_e} P^{s'_h l'_d s'_e l'_e}_{\boldsymbol{k}'_h,\boldsymbol{k}'_e} P^{s_h l_c s_e l_e}_{\boldsymbol{k}_h,\boldsymbol{k}_e} \tag{3.92}$$

and

$$H_{e-h} = - \sum_{\boldsymbol{k}_e\boldsymbol{k}'_e\boldsymbol{k}_h\boldsymbol{k}'_h\boldsymbol{q}s_es'_es_hs'_hl_el_al'_bl_cl'_dl'_h} V^{cvs_e s'_h l_a l'_d l_c l'_b}_{\boldsymbol{k}_e,\boldsymbol{k}'_h+\boldsymbol{q},\boldsymbol{q}} P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{k}_h,\boldsymbol{k}_e+\boldsymbol{q}} P^{\dagger s'_h l'_b s'_e l'_e}_{\boldsymbol{k}'_h+\boldsymbol{q},\boldsymbol{k}'_e} P^{s'_h l'_d s'_e l'_e}_{\boldsymbol{k}'_h,\boldsymbol{k}'_e} P^{s_h l_h s_e l_c}_{\boldsymbol{k}_h,\boldsymbol{k}_e}. \tag{3.93}$$

There are also some terms arising from the commutations on the form $\sum_a V_a P^\dagger_a P_a$. However, since these are on the same form as the free Hamiltonian what they end up doing is renormalizing the band gap energy. The value used for the band gap energy is taken from experiment, meaning that these terms can be ignored. There is one term that survives however, which we choose to call

$$H^0_{e-h} = - \sum_{\boldsymbol{k}_e\boldsymbol{k}_h\boldsymbol{q}s_es_hl_al_bl_cl_d} V^{cvs_e s_h l_a l_d l_c l_d}_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{q},\boldsymbol{q}} P^{\dagger s_h l_b s_e l_a}_{\boldsymbol{k}_h+\boldsymbol{q},\boldsymbol{k}_e+\boldsymbol{q}} P^{s_h l_d s_e l_c}_{\boldsymbol{k}_h,\boldsymbol{k}_e}. \tag{3.94}$$

Since the coupling element is significantly smaller for the interlayer coupling we will neglect it for this particular element, leading to

$$H^0_{e-h} = - \sum_{\boldsymbol{k}_e\boldsymbol{k}_h\boldsymbol{q}s_es_hl_el_hl_el_h} V^{cvs_e s_h l_e l_h l_e l_h}_{\boldsymbol{k}_e,\boldsymbol{k}_h+\boldsymbol{q},\boldsymbol{q}} P^{\dagger s_h l_h s_e l_e}_{\boldsymbol{k}_h+\boldsymbol{q},\boldsymbol{k}_e+\boldsymbol{q}} P^{s_h l_h s_e l_e}_{\boldsymbol{k}_h,\boldsymbol{k}_e}. \tag{3.95}$$

3.3 Going to the excitonic picture

We are however not done quite yet. First we will transform to center of mass coordinates using the coordinate transformations

$$\boldsymbol{k}_h = \boldsymbol{q} - \beta\boldsymbol{Q}, \boldsymbol{k}_e = \boldsymbol{q} + \alpha\boldsymbol{Q} \quad \Longleftrightarrow \quad \boldsymbol{q} = \alpha\boldsymbol{k}_h + \beta\boldsymbol{k}_e, \boldsymbol{Q} = \boldsymbol{k}_e - \boldsymbol{k}_h \tag{3.96}$$

with

$$\alpha = \frac{m_h}{m_h + m_e}, \quad \beta = \frac{m_e}{m_h + m_e}. \tag{3.97}$$

Here $\boldsymbol{q}$ can be interpreted as the relative momentum while $\boldsymbol{Q}$ is the center of mass momentum. The momentum dependent parts of the electronic band structure then becomes

$$\frac{\boldsymbol{k}_h^2}{2m_h} + \frac{\boldsymbol{k}_e^2}{2m_e} = \frac{(\boldsymbol{q} - \beta\boldsymbol{Q})^2}{2m_h} + \frac{(\boldsymbol{q} + \alpha\boldsymbol{Q})^2}{2m_e} \tag{3.98}$$

$$= \frac{1}{2}\left(\frac{1}{m_h} + \frac{1}{m_e}\right)\boldsymbol{q}^2 + \left(-\frac{\beta}{m_h} + \frac{\alpha}{m_e}\right)\boldsymbol{q}\cdot\boldsymbol{Q} + \frac{1}{2}\left(\frac{\beta^2}{m_h} + \frac{\alpha^2}{m_e}\right)\boldsymbol{Q}^2 \tag{3.99}$$

$$= \frac{1}{2}\left(\frac{1}{m_h} + \frac{1}{m_e}\right)\boldsymbol{q}^2 + \frac{1}{2}\frac{1}{m_h + m_e}\boldsymbol{Q}^2 \tag{3.100}$$

$$\equiv \frac{\boldsymbol{q}^2}{2m_r} + \frac{\boldsymbol{Q}^2}{2M}. \tag{3.101}$$

We then map our pair operators to a basis of complete functions $\varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e}$ as

$$P^{s_h l_h s_e l_e}_{\boldsymbol{k}_h, \boldsymbol{k}_e} = P^{s_h l_h s_e l_e}_{\boldsymbol{q}, \boldsymbol{Q}} = \sum_{\mu} \varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} P_{\boldsymbol{Q}}^{\mu s_h l_h s_e l_e}. \tag{3.102}$$

Using this expansion and coordinate system we now need to once again rewrite our Hamiltonian. The free electronic part turns out to be

$$H_{0,c} = \sum_{\boldsymbol{q}\boldsymbol{Q} s_h l_h s_e l_e} \left(\frac{\boldsymbol{q}^2}{2m_r} + \frac{\boldsymbol{Q}^2}{2M} + E_G^{s_h l_h s_e l_e}\right) P^{\dagger s_h l_h s_e s_e}_{\boldsymbol{q}, \boldsymbol{Q}} P^{s_h l_h s_e l_e}_{\boldsymbol{q}, \boldsymbol{Q}} \tag{3.103}$$

$$= \sum_{\boldsymbol{q}\boldsymbol{Q} s_h l_h s_e l_e \mu\nu} \left(\frac{\boldsymbol{q}^2}{2m_r} + \frac{\boldsymbol{Q}^2}{2M} + E_G^{s_h l_h s_e l_e}\right) \varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} \varphi_{\boldsymbol{q}}^{\nu s_h l_h s_e l_e} P^{\dagger \mu s_h l_h s_e s_e}_{\boldsymbol{Q}} P^{\nu s_h l_h s_e l_e}_{\boldsymbol{Q}}. \tag{3.104}$$

Before proceeding we take a look at the two-operator term from the electron-hole Coulomb interaction, which gains the form

$$H^0_{e-h} = -\sum_{\boldsymbol{q}\boldsymbol{Q} s_e s_h l_e l_h \boldsymbol{K}} V^{cvs_e s_h l_e l_h}_{\boldsymbol{q}+\alpha\boldsymbol{Q}, \boldsymbol{q}-\beta\boldsymbol{Q}+\boldsymbol{K}, \boldsymbol{K}} P^{\dagger s_h l_h s_e l_e}_{\boldsymbol{q}+\boldsymbol{K}, \boldsymbol{Q}} P^{s_h l_h s_e l_e}_{\boldsymbol{q}, \boldsymbol{Q}} \tag{3.105}$$

$$= -\sum_{\boldsymbol{q}\boldsymbol{Q} s_e s_h l_e l_h \boldsymbol{K}\mu\nu} V^{cvs_e s_h l_e l_h}_{\boldsymbol{q}+\alpha\boldsymbol{Q}, \boldsymbol{q}-\beta\boldsymbol{Q}+\boldsymbol{K}, \boldsymbol{K}} \varphi^{\mu s_h l_h s_e l_e}_{\boldsymbol{q}+\boldsymbol{K}} \varphi^{\nu s_h l_h s_e l_e}_{\boldsymbol{q}} P^{\dagger \mu s_h l_h s_e s_e}_{\boldsymbol{Q}} P^{\nu s_h l_h s_e l_e}_{\boldsymbol{Q}}. \tag{3.106}$$

If we now add these together we obtain

$$H_{0,c} + H^0_{e-h} \tag{3.107}$$

$$= \sum_{\boldsymbol{q}\boldsymbol{Q}s_h l_h s_e l_e \mu\nu} \left(\frac{\boldsymbol{q}^2}{2m_r} + \frac{\boldsymbol{Q}^2}{2M} + E_G^{s_h l_h s_e l_e} \right) \varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} \varphi_{\boldsymbol{q}}^{\nu s_h l_h s_e l_e} P_{\boldsymbol{Q}}^{\dagger \mu s_h l_h s_e s_e} P_{\boldsymbol{Q}}^{\nu s_h l_h s_e l_e} \tag{3.108}$$

$$- \sum_{\boldsymbol{q}\boldsymbol{Q}s_e s_h l_e l_h \boldsymbol{K}\mu\nu} V^{cvs_e s_h l_e l_h}_{\boldsymbol{q}+\alpha\boldsymbol{Q},\boldsymbol{q}-\beta\boldsymbol{Q}+\boldsymbol{K},\boldsymbol{k}} \varphi_{\boldsymbol{q}+\boldsymbol{K}}^{\mu s_h l_h s_e l_e} \varphi_{\boldsymbol{q}}^{\nu s_h l_h s_e l_e} P_{\boldsymbol{Q}}^{\dagger \mu s_h l_h s_e s_e} P_{\boldsymbol{Q}}^{\nu s_h l_h s_e l_e} \tag{3.109}$$

$$= \sum_{\boldsymbol{q}\boldsymbol{Q}s_h l_h s_e l_e \mu\nu} \left(\left(\frac{\boldsymbol{Q}^2}{2M} + E_G^{s_h l_h s_e l_e} \right) \varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} \right. \tag{3.110}$$

$$\left. + \frac{\boldsymbol{q}^2}{2m_r} \varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} - \sum_{\boldsymbol{K}} V^{cvs_e s_h l_e l_h}_{\boldsymbol{q}+\alpha\boldsymbol{Q},\boldsymbol{q}-\beta\boldsymbol{Q}+\boldsymbol{K},\boldsymbol{K}} \varphi_{\boldsymbol{q}+\boldsymbol{K}}^{\mu s_h l_h s_e l_e} \right) \tag{3.111}$$

$$\cdot \varphi_{\boldsymbol{q}}^{\nu s_h l_h s_e l_e} P_{\boldsymbol{Q}}^{\dagger \mu s_h l_h s_e s_e} P_{\boldsymbol{Q}}^{\nu s_h l_h s_e l_e}. \tag{3.112}$$

Now, the second row just so happens to have the shape of the left hand side of a time independent Schrödinger equation, meaning that we can choose our φ functions as solutions to

$$\frac{\boldsymbol{q}^2}{2m_r} \varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} - \sum_{\boldsymbol{K}} V^{cvs_e s_h l_e l_h}_{\boldsymbol{q}+\alpha\boldsymbol{Q},\boldsymbol{q}-\beta\boldsymbol{Q}+\boldsymbol{K},\boldsymbol{K}} \varphi_{\boldsymbol{q}+\boldsymbol{K}}^{\mu s_h l_h s_e l_e} = \tilde{E}_{\boldsymbol{Q}}^{\mu s_h l_h s_e l_e} \varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} \tag{3.113}$$

to simplify the expression greatly. Moreover, this is the so called Wannier equation that is used for describing excitons. In other words $\varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e}$ is an excitonic excitonic wave function with n, l and m quantum numbers compound into μ, $\tilde{E}_{\boldsymbol{Q}}^{\mu s_h l_h s_e l_e}$ its corresponding binding energy and $P_{\boldsymbol{Q}}^{(\dagger)\mu s_h l_h s_e s_e}$ is an excitonic annihilation (creation) operator. Inserting this then gives us

$$H_{0,c} + H^0_{e-h} \tag{3.114}$$

$$= \sum_{\boldsymbol{q}\boldsymbol{Q}s_h l_h s_e l_e \mu\nu} \left(\frac{\boldsymbol{Q}^2}{2M} + E_G^{s_h l_h s_e l_e} + \tilde{E}_{\boldsymbol{Q}}^{\mu s_h l_h s_e l_e} \right) \varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} \varphi_{\boldsymbol{q}}^{\nu s_h l_h s_e l_e} P_{\boldsymbol{Q}}^{\dagger \mu s_h l_h s_e s_e} P_{\boldsymbol{Q}}^{\nu s_h l_h s_e l_e}. \tag{3.115}$$

By using the orthonormalization condition

$$\sum_{\boldsymbol{q}} \varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} \varphi_{\boldsymbol{q}}^{\nu s_h l_h s_e l_e} = \delta_{\mu\nu} \tag{3.116}$$

we can then redefine the electronic part of the free Hamiltonian as

$$H_{0,c} = \sum_{\boldsymbol{Q}s_h l_h s_e l_e \mu} E_{\boldsymbol{Q}}^{\mu s_h l_h s_e l_e} P_{\boldsymbol{Q}}^{\dagger \mu s_h l_h s_e s_e} P_{\boldsymbol{Q}}^{\mu s_h l_h s_e l_e}, \tag{3.117}$$

where

$$E_{\boldsymbol{Q}}^{\mu s_h l_h s_e l_e} \equiv \frac{\boldsymbol{Q}^2}{2M} + E_G^{s_h l_h s_e l_e} + \tilde{E}_{\boldsymbol{Q}}^{\mu s_h l_h s_e l_e}. \tag{3.118}$$

With this out of the way we can now move on to the optical term,

$$H_{c-f} = \sum_{\boldsymbol{q}sl_hl_e} (\boldsymbol{M}_{\boldsymbol{q}}^{vc,s,l_al_b} P_{\boldsymbol{q},\boldsymbol{0}}^{sl_hsl_e} + \boldsymbol{M}_{\boldsymbol{q}}^{cv,s,l_al_b} P_{\boldsymbol{q},\boldsymbol{0}}^{\dagger sl_hss_e}) \tag{3.119}$$

$$= \sum_{\boldsymbol{q}sl_hl_e\mu} \left(\boldsymbol{M}_{\boldsymbol{q}}^{vc,s,l_hl_e} \varphi_{\boldsymbol{q}}^{\mu sl_hsl_e} P_{\boldsymbol{0}}^{\mu sl_hsl_e} + \boldsymbol{M}_{\boldsymbol{q}}^{cv,s,l_el_h} \varphi_{\boldsymbol{q}}^{\mu sl_hsl_e} P_{\boldsymbol{0}}^{\dagger \mu sl_hss_e}\right) \tag{3.120}$$

$$= \sum_{sl_hl_e\mu} \left(\boldsymbol{M}^{\mu s,l_hl_e} P_{\boldsymbol{0}}^{\mu sl_hsl_e} + \boldsymbol{M}^{\mu s,l_el_h} P_{\boldsymbol{0}}^{\dagger \mu sl_hss_e}\right), \tag{3.121}$$

where

$$\boldsymbol{M}^{\mu s,l_hl_e} \equiv \sum_{\boldsymbol{q}} \boldsymbol{M}_{\boldsymbol{q}}^{vc,s,l_hl_e} \varphi_{\boldsymbol{q}}^{\mu sl_hsl_e}, \tag{3.122}$$

the carrier-photon term

$$H_{c-\mathrm{phot}} = \sum_{\boldsymbol{q}\boldsymbol{K}sl_hl_e\sigma} (M_{\boldsymbol{q},\boldsymbol{K}_\parallel}^{cvs\sigma l_el_h} P_{\boldsymbol{q}+\beta\boldsymbol{K}_\parallel,\boldsymbol{K}_\parallel}^{\dagger sl_hsl_e} c_{\boldsymbol{K}}^{\sigma} + M_{\boldsymbol{q},\boldsymbol{K}_\parallel}^{vcs\sigma l_hl_e} P_{\boldsymbol{q}-\beta\boldsymbol{K}_\parallel,-\boldsymbol{K}_\parallel}^{sl_hsl_e} c_{-\boldsymbol{K}}^{\dagger\sigma}) \tag{3.123}$$

$$= \sum_{\boldsymbol{q}\boldsymbol{K}sl_hl_e\sigma\mu} \left(M_{\boldsymbol{q},\boldsymbol{K}_\parallel}^{cvs\sigma l_el_h} \varphi_{\boldsymbol{q}+\beta\boldsymbol{K}_\parallel}^{\mu sl_hsl_e} P_{\boldsymbol{K}_\parallel}^{\dagger \mu sl_hsl_e} c_{\boldsymbol{K}}^{\sigma} + M_{\boldsymbol{q},\boldsymbol{K}_\parallel}^{vcs\sigma l_hl_e} \varphi_{\boldsymbol{q}-\beta\boldsymbol{K}_\parallel}^{\mu sl_hsl_e} P_{-\boldsymbol{K}_\parallel}^{sl_hsl_e} c_{-\boldsymbol{K}}^{\dagger\sigma}\right) \tag{3.124}$$

$$\equiv \sum_{\boldsymbol{K}sl_hl_e\sigma\mu} \left(M_{\boldsymbol{K}_\parallel}^{vcs\sigma l_hl_e} P_{\boldsymbol{K}_\parallel}^{\dagger \mu sl_hsl_e} c_{\boldsymbol{K}}^{\sigma} + M_{-\boldsymbol{K}_\parallel}^{vcs\sigma l_hl_e} P_{\boldsymbol{K}_\parallel}^{sl_hsl_e} c_{\boldsymbol{K}}^{\dagger\sigma}\right) \tag{3.125}$$

where

$$M_{\boldsymbol{K}_\parallel}^{vcs\sigma l_hl_e} = \sum_{\boldsymbol{q}} M_{\boldsymbol{q},\boldsymbol{K}_\parallel}^{vcs\sigma l_hl_e} \varphi_{\boldsymbol{q}+\beta\boldsymbol{K}_\parallel}^{\mu sl_hsl_e}, \tag{3.126}$$

the carrier-phonon term

$$H_{c-\mathrm{phon}} \tag{3.127}$$

$$= \sum_{\boldsymbol{q}\boldsymbol{Q}\boldsymbol{K}s_hs_el_hl_e\alpha} (g_{\boldsymbol{q}+\alpha\boldsymbol{Q},\boldsymbol{K}}^{cl_e\alpha} P_{\boldsymbol{q}+\beta\boldsymbol{K},\boldsymbol{Q}+\boldsymbol{K}}^{\dagger s_hl_hs_el_e} P_{\boldsymbol{q},\boldsymbol{Q}}^{s_hl_hs_el_e} (b_{\boldsymbol{K}}^{l_e\alpha} + b_{-\boldsymbol{K}}^{\dagger l_e\alpha}) \tag{3.128}$$

$$- g_{\boldsymbol{q}-\beta\boldsymbol{Q},\boldsymbol{K}}^{vl_h\alpha} P_{\boldsymbol{q},\boldsymbol{Q}}^{\dagger s_hl_hs_el_e} P_{\boldsymbol{q}+\alpha\boldsymbol{K},\boldsymbol{Q}-\boldsymbol{K}}^{s_hl_hs_el_e} (b_{\boldsymbol{K}}^{l_h\alpha} + b_{-\boldsymbol{K}}^{\dagger l_h\alpha})) \tag{3.129}$$

$$= \sum_{\boldsymbol{q}\boldsymbol{Q}\boldsymbol{K}s_hs_el_hl_e\alpha\mu\mu'} \Big(g_{\boldsymbol{q}+\alpha\boldsymbol{Q}-\beta\boldsymbol{K},\boldsymbol{K}}^{cl_e\alpha} \varphi_{\boldsymbol{q}}^{\mu s_hl_hs_el_e} \varphi_{\boldsymbol{q}-\beta\boldsymbol{K}}^{\mu' s_hl_hs_el_e} P_{\boldsymbol{Q}+\boldsymbol{K}}^{\dagger \mu s_hl_hs_el_e} P_{\boldsymbol{Q}}^{\mu s_hl_hs_el_e} (b_{\boldsymbol{K}}^{l_e\alpha} + b_{-\boldsymbol{K}}^{\dagger l_e\alpha}) \tag{3.130}$$

$$- g_{\boldsymbol{q}-\beta\boldsymbol{Q}-\beta\boldsymbol{K},\boldsymbol{K}}^{vl_h\alpha} \varphi_{\boldsymbol{q}}^{\mu s_hl_hs_el_e} \varphi_{\boldsymbol{q}+\alpha\boldsymbol{K}}^{\mu' s_hl_hs_el_e} P_{\boldsymbol{Q}+\boldsymbol{K}}^{\dagger \mu s_hl_hs_el_e} P_{\boldsymbol{Q}}^{\mu' s_hl_hs_el_e} (b_{\boldsymbol{K}}^{l_h\alpha} + b_{-\boldsymbol{K}}^{\dagger l_h\alpha})\Big) \tag{3.131}$$

$$\equiv \sum_{\boldsymbol{Q}\boldsymbol{K}s_hs_el_hl_el\alpha\mu\mu'} g_{\boldsymbol{Q},\boldsymbol{K}}^{s_hl_hs_el_el\alpha\mu\mu'} P_{\boldsymbol{Q}+\boldsymbol{K}}^{\dagger \mu s_hl_hs_el_e} P_{\boldsymbol{Q}}^{\mu s_hl_hs_el_e} (b_{\boldsymbol{K}}^{l\alpha} + b_{-\boldsymbol{K}}^{\dagger l\alpha}) \tag{3.132}$$

where

$$g_{\boldsymbol{Q},\boldsymbol{K}}^{s_hl_hs_el_el\alpha\mu\mu'} \tag{3.133}$$

$$\equiv \sum_{\boldsymbol{q}} \varphi_{\boldsymbol{q}}^{\mu s_hl_hs_el_e} (g_{\boldsymbol{q}+\alpha\boldsymbol{Q}-\beta\boldsymbol{K},\boldsymbol{K}}^{cl_e\alpha} \varphi_{\boldsymbol{q}-\beta\boldsymbol{K}}^{\mu' s_hl_hs_el_e} \delta_{ll_e} - g_{\boldsymbol{q}-\beta\boldsymbol{Q}-\beta\boldsymbol{K},\boldsymbol{K}}^{vl_h\alpha} \varphi_{\boldsymbol{q}+\alpha\boldsymbol{K}}^{\mu' s_hl_hs_el_e} \delta_{ll_h}) \tag{3.134}$$

and the tunneling term

$$H_T = \sum_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{Q}\boldsymbol{Q}' s_h s_e l_h l_e} T^{cs_e l_e}_{\boldsymbol{q}+\alpha\boldsymbol{Q},\boldsymbol{q}'+\alpha\boldsymbol{Q}'} P^{\dagger s_h l_h s_e l_e}_{\boldsymbol{q},\boldsymbol{Q}} P^{s_h l_h s_e \bar{l}_e}_{\boldsymbol{q}',\boldsymbol{Q}'} \delta_{\boldsymbol{q}-\beta\boldsymbol{Q},\boldsymbol{q}'-\beta\boldsymbol{Q}'} \tag{3.135}$$

$$- \sum_{\boldsymbol{q}\boldsymbol{q}'\boldsymbol{Q}\boldsymbol{Q}' s_h s_e l_h l_e} T^{vs_h \bar{l}_h}_{\boldsymbol{q}'-\beta\boldsymbol{Q}',\boldsymbol{q}-\beta\boldsymbol{Q}} P^{\dagger s_h l_h s_e l_e}_{\boldsymbol{q},\boldsymbol{Q}} P^{s_h \bar{l}_h s_e l_e}_{\boldsymbol{q}',\boldsymbol{Q}'} \delta_{\boldsymbol{q}+\alpha\boldsymbol{Q},\boldsymbol{q}'+\alpha\boldsymbol{Q}'} \tag{3.136}$$

$$= \sum_{\boldsymbol{q}\boldsymbol{Q}\boldsymbol{Q}' s_h s_e l_h l_e \mu\mu'} T^{cs_e l_e}_{\boldsymbol{q}+\alpha\boldsymbol{Q},\boldsymbol{q}+\boldsymbol{Q}'-\beta\boldsymbol{Q}} \varphi^{\mu s_h l_h s_e l_e}_{\boldsymbol{q}} \varphi^{\mu' s_h s_e l_h \bar{l}_e}_{\boldsymbol{q}-\beta(\boldsymbol{Q}-\boldsymbol{Q}')} P^{\dagger \mu s_h l_h s_e l_e}_{\boldsymbol{Q}} P^{\mu' s_h l_h s_e \bar{l}_e}_{\boldsymbol{Q}'} \tag{3.137}$$

$$- \sum_{\boldsymbol{q}\boldsymbol{Q}\boldsymbol{Q}' s_h s_e l_h l_e \mu\mu'} T^{vs_h \bar{l}_h}_{\boldsymbol{q}-\boldsymbol{Q}'+\alpha\boldsymbol{Q},\boldsymbol{q}-\beta\boldsymbol{Q}} \varphi^{\mu s_h l_h s_e l_e}_{\boldsymbol{q}} \varphi^{\mu' s_h s_e \bar{l}_h l_e}_{\boldsymbol{q}+\alpha(\boldsymbol{Q}-\boldsymbol{Q}')} P^{\dagger \mu s_h l_h s_e l_e}_{\boldsymbol{Q}} P^{\mu' s_h \bar{l}_h s_e l_e}_{\boldsymbol{Q}'} \tag{3.138}$$

$$\equiv \sum_{\boldsymbol{Q}\boldsymbol{Q}' s_h s_e l_h l_e l'_h l'_e \mu\mu'} T^{s_h l_h s_e l_e \mu\mu'}_{\boldsymbol{Q},\boldsymbol{Q}'} P^{\dagger \mu s_h l_h s_e l_e}_{\boldsymbol{Q}} P^{\mu' s_h l'_h s_e l'_e}_{\boldsymbol{Q}'}, \tag{3.139}$$

where

$$T^{s_h s_e l_h l_e l'_h l'_e \mu\mu'}_{\boldsymbol{Q},\boldsymbol{Q}'} \tag{3.140}$$

$$\equiv \sum_{\boldsymbol{q}} \left(T^{cs_e l_e}_{\boldsymbol{q}+\boldsymbol{Q},\boldsymbol{q}+\boldsymbol{Q}'} \varphi^{\mu s_h l_h s_e l_e}_{\boldsymbol{q}+\beta\boldsymbol{Q}} \varphi^{\mu' s_h s_e l_h \bar{l}_e}_{\boldsymbol{q}+\beta\boldsymbol{Q}'} \delta^{l_e \bar{l}'_e}_{l_h l'_h} - T^{vs_h \bar{l}_h}_{\boldsymbol{q}-\boldsymbol{Q}',\boldsymbol{q}-\boldsymbol{Q}} \varphi^{\mu s_h l_h s_e l_e}_{\boldsymbol{q}-\alpha\boldsymbol{Q}} \varphi^{\mu' s_h s_e \bar{l}_h l_e}_{\boldsymbol{q}-\alpha\boldsymbol{Q}'} \delta^{l_e l'_e}_{l_h \bar{l}'_h} \right). \tag{3.141}$$

As usual the Coulomb term is a bit more complicated and therefore put in D.3.2, but the resulting expression is

$$H_{c-c} = \sum_{\boldsymbol{Q}\boldsymbol{Q}' s_h s_e s'_h s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e \boldsymbol{K} \mu\mu'\nu\nu'} V^{\mu\mu'\nu\nu' s_h s_e s'_h s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{\boldsymbol{Q},\boldsymbol{Q}',\boldsymbol{K}} \tag{3.142}$$

$$\cdot P^{\dagger \mu s_h l^a_h s_e l^a_e}_{\boldsymbol{Q}+\boldsymbol{K}} P^{\dagger \mu' s'_h l^b_h s'_e l^b_e}_{\boldsymbol{Q}'-\boldsymbol{K}} P^{\nu' s'_h l^d_h s'_e l^d_e}_{\boldsymbol{Q}'} P^{\nu s_h l^c_h s_e l^c_e}_{\boldsymbol{Q}}, \tag{3.143}$$

where

$$V^{\mu\mu'\nu\nu' s_h s_e s'_h s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{\boldsymbol{Q},\boldsymbol{Q}',\boldsymbol{K}} \equiv \frac{1}{4} V^{\mu\mu'\nu\nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{e-e,\boldsymbol{Q},\boldsymbol{Q}',\boldsymbol{K}} \tag{3.144}$$

$$+ \frac{1}{4} V^{\mu\mu'\nu\nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{h-h,\boldsymbol{Q},\boldsymbol{Q}',\boldsymbol{K}} \tag{3.145}$$

$$- \frac{1}{2} V^{\mu\mu'\nu\nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{e-h,\boldsymbol{Q},\boldsymbol{Q}',\boldsymbol{K}} \tag{3.146}$$

and

$$V^{\mu\mu'\nu\nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{e-e,\boldsymbol{Q},\boldsymbol{Q}',\boldsymbol{K}} \tag{3.147}$$

$$\equiv \sum_{\boldsymbol{q}\boldsymbol{q}'} V^{cc,s_e s'_e l_a l_b l_c l_d}_{\boldsymbol{q}+\alpha\boldsymbol{Q},\boldsymbol{q}'+\alpha\boldsymbol{Q}',\boldsymbol{K}} \varphi^{\mu s_h l^a_h s_e l^a_e}_{\boldsymbol{q}+\beta\boldsymbol{K}} \varphi^{\mu' s'_h l^b_h s'_e l^b_e}_{\boldsymbol{q}'-\beta\boldsymbol{K}'} \varphi^{\nu' s'_h l^b_h s'_e l^d_e}_{\boldsymbol{q}'} \varphi^{\nu s_h l^a_h s_e l^c_e}_{\boldsymbol{q}} \delta_{l^a_h l^c_h} \delta_{l^b_h l^d_h}, \tag{3.148}$$

$$V^{\mu\mu'\nu\nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{h-h,\boldsymbol{Q},\boldsymbol{Q}',\boldsymbol{K}} \tag{3.149}$$

$$\equiv \sum_{\boldsymbol{q}\boldsymbol{q}'} V^{vv,s_e s'_e l_c l_d l_a l_b}_{\boldsymbol{q}-\beta\boldsymbol{Q}-\boldsymbol{K},\boldsymbol{q}'-\beta\boldsymbol{Q}'+\boldsymbol{K},\boldsymbol{K}} \varphi^{\mu s_h l_a s_e l^a_e}_{\boldsymbol{q}-\alpha\boldsymbol{K}} \varphi^{\mu' s'_h l_b s'_e l^b_e}_{\boldsymbol{q}'+\alpha\boldsymbol{K}'} \varphi^{\nu' s'_h l_d s'_e l^b_e}_{\boldsymbol{q}'} \varphi^{\nu s_h l_c s_e l^a_e}_{\boldsymbol{q}} \delta_{l^a_e l^c_e} \delta_{l^b_e l^d_e}, \tag{3.150}$$

$$V^{\mu\mu'\nu\nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{e-h,\boldsymbol{Q},\boldsymbol{Q}',\boldsymbol{K}} \tag{3.151}$$

$$\equiv \sum_{\boldsymbol{q}\boldsymbol{q}'} V^{cv,s_e s'_h l_a l_d l_c l_b}_{\boldsymbol{q}+\alpha\boldsymbol{Q},\boldsymbol{q}'-\beta\boldsymbol{Q}'+\boldsymbol{K},\boldsymbol{K}} \varphi^{\mu s_h l^a_h s_e l^a_e}_{\boldsymbol{q}+\beta\boldsymbol{K}} \varphi^{\mu' s'_h l^b_h s'_e l^b_e}_{\boldsymbol{q}'+\alpha\boldsymbol{K}'} \varphi^{\nu' s'_h l^d_h s'_e l^b_e}_{\boldsymbol{q}'} \varphi^{\nu s_h l^a_h s_e l^c_e}_{\boldsymbol{q}} \delta_{l^a_h l^c_h} \delta_{l^b_e l^d_e}. \tag{3.152}$$

3.3.1 Solving the Wannier equation

In order to actually evaluate these new elements the Wannier equation

$$\frac{\boldsymbol{q}^2}{2m_r}\varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} - \sum_{\boldsymbol{K}} V^{cvs_e s_h l_e l_h}_{\boldsymbol{q}+\alpha\boldsymbol{Q},\boldsymbol{q}-\beta\boldsymbol{Q}+\boldsymbol{K},\boldsymbol{K}}\varphi_{\boldsymbol{q}+\boldsymbol{K}}^{\mu s_h l_h s_e l_e} = \tilde{E}_{\boldsymbol{Q}}^{\mu s_h l_h s_e l_e}\varphi_{\boldsymbol{q}}^{\mu s_h l_h s_e l_e} \tag{3.153}$$

will need to be solved. First off we assume that the effects of the center off mass momentum is negligible. Next we will restrict ourselves to states whose absolute values are isotropic, averaging over the angular dependency. If we look at the Bloch equation to be derived in 4.2, we can see that the dominant states are the ones in phase with the optical matrix element. We already know its phase from 3.1.3, meaning that we can write $\varphi_{\boldsymbol{q}} = \varphi_q e^{i\varphi_q}$ (for the K point, for the K' point the sign would be opposite). By also performing a shift of $\boldsymbol{K} \to \boldsymbol{K} - \boldsymbol{q}$ and multiplying by $e^{-i\varphi_q}$ we can then express the equation as

$$\tilde{E}^{\mu s_h l_h s_e l_e}\varphi_q^{\mu s_h l_h s_e l_e} = \frac{q^2}{2m_r}\varphi_q^{\mu s_h l_h s_e l_e} - \frac{1}{2\pi}\sum_{\varphi_q}\sum_{\boldsymbol{K}} V^{cvs_e s_h l_e l_h}_{\boldsymbol{q},\boldsymbol{K},\boldsymbol{K}-\boldsymbol{q}} e^{i(\varphi_k-\varphi_q)}\varphi_K^{\mu s_h l_h s_e l_e} \tag{3.154}$$

$$= \sum_K \left(\frac{q^2}{2m_r}\delta_{K,q} - \frac{1}{2\pi}\sum_{\varphi_q\varphi_K} V^{cvs_e s_h l_e l_h}_{\boldsymbol{q},\boldsymbol{K},\boldsymbol{K}-\boldsymbol{q}}\right) e^{i(\varphi_k-\varphi_q)}\varphi_K^{\mu s_h l_h s_e l_e} \tag{3.155}$$

$$\equiv \sum_K W_{qK}^{s_h l_h s_e l_e}\varphi_K^{\mu s_h l_h s_e l_e}. \tag{3.156}$$

This is an eigenvalue problem. When treating this numerically $W_{qK}^{s_h l_h s_e l_e}$ will be a matrix, meaning that the wave functions and energy levels can be obtained as eigenfunctions and eigenenergies of this matrix.

The resulting energies can be seen in Figure 3.5 which compares the intralayer energies for $MoSe_2$ and WSe_2 as well as the interlayer energies for $MoSe_2 - WSe_2$, while Figure 3.6 does a similar comparison of the wavefunctions for the first three s states. In these we can see that the interlayer binding energies are a fair bit smaller than the intralayer ones, meaning that the wavefunctions have smaller radii (in momentum space, in real space the opposite applies). These details aside, the wavefunctions look like you would expect two dimensional hydrogen-like wavefunctions would.

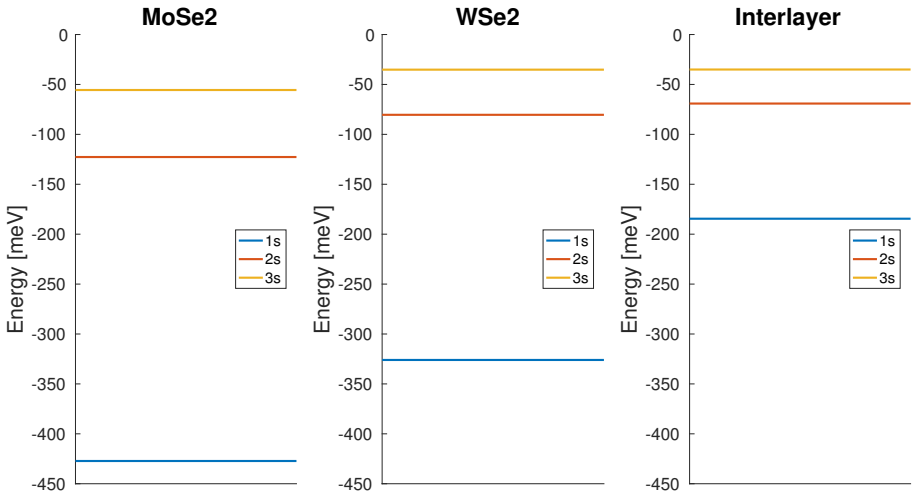

Figure 3.5: This figure displays the three lowest excitonic energy levels for the $MoSe_2$ and WSe_2 intralayer states and the energetically lower interlayer state, in that order. Here we can see that while the WSe_2 states are somewhat lower than their $MoSe_2$ counterparts, the interlayer states are lower than both of them. This can be explained by the spatial separation between the electron and hole.

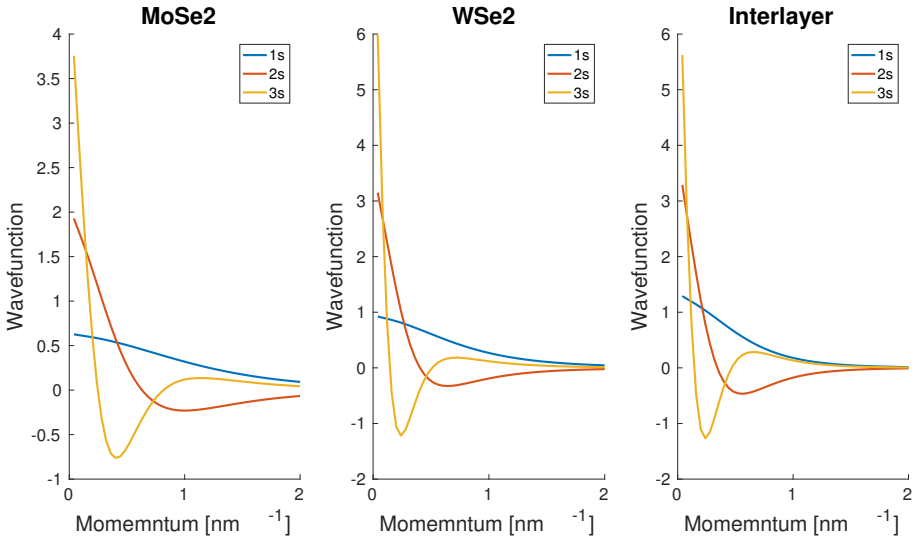

Figure 3.6: This figure displays the three lowest excitonic wavefunctions in momentum space for the $MoSe_2$ and WSe_2 intralayer states and the energetically lower interlayer state, in that order. By comparing this to Figure 3.5 we can see that a lower energy corresponds to a sharper wavefunction, meaning that the interlayer excitons are more delocalized in real space than the other two.

4

The Bloch equation

Now that the Hamiltonian has been constructed we can start finding equations of motion. We will start with deriving the Bloch equation, the equation of motion for the microscopic polarization, and then use it to calculate the absorption spectrum.

If we look at the definition for the Pair operators we find that

$$p^{s_h l_h s_e l_e}_{\boldsymbol{q},\boldsymbol{Q}} = \langle P^{s_h l_h s_e l_e}_{\boldsymbol{q},\boldsymbol{Q}} \rangle = \sum_\mu \varphi^{\mu s_h l_h s_e l_e}_{\boldsymbol{q}} \langle P^{\mu s_h l_h s_e l_e}_{\boldsymbol{Q}} \rangle \equiv \sum_\mu \varphi^{\mu s_h l_h s_e l_e}_{\boldsymbol{q}} p^{\mu s_h l_h s_e l_e}_{\boldsymbol{Q}}, \tag{4.1}$$

meaning that we can find the Bloch equation by finding the equation of motion for $\langle P^{\mu s_h l_h s_e l_e}_{\boldsymbol{Q}} \rangle$. To do this we first find the different contributions for all the different terms in the Hamiltonian.

4.1 Deriving the Bloch equation

Using compound indices the free electronic contribution is given by

$$i\hbar \frac{\partial}{\partial t} p_1 \bigg|_{H=H_{0,c}} = \langle \sum_a E_a [P_1, P_a^\dagger P_a] \rangle \tag{4.2}$$

$$= E_1 p_1 \tag{4.3}$$

while the free photon and phonon terms don't contribute at all since it commutes with the excitonic operators. After this we get the optical term

$$i\hbar \frac{\partial}{\partial t} p_1 \bigg|_{H=H_{e-f}} = \langle \sum_a \left[P_1, \boldsymbol{M}_a \cdot \boldsymbol{A} P_a + \boldsymbol{M}_a \cdot \boldsymbol{A} P_a^\dagger \right] \rangle \tag{4.4}$$

$$= \boldsymbol{M}_1 \cdot \boldsymbol{A} \tag{4.5}$$

and the photon term

$$i\hbar \frac{\partial}{\partial t} P_1 \bigg|_{H=H_{c-\text{phot}}} = \langle \sum_{ab} \left[P_1, M_{ab} P_a^\dagger c_b + M_{a-b} P_a c_{-b}^\dagger \right] \rangle \tag{4.6}$$

$$= \sum_a M_{1b} \langle c_b \rangle. \tag{4.7}$$

Aside from the differences between the semi-classical and quantum descriptions of the field interaction (the prescense of the photon momentum) we can here see yet another difference, that the polarization couples to the expectation value of the photon. We will therefore need to find an equation of motion for this quantity later on as well.

For the carrier-phonon contribution we get

$$i\hbar\frac{\partial}{\partial t}p_1\Big|_{H=H_{c-\text{phon}}} = \langle\sum_{abc} g_{abc}[P_1, P_a^\dagger P_b(b_c + b_{-c}^\dagger)]\rangle \tag{4.8}$$

$$= \sum_{ab} g_{1ab}(\langle p_a b_b\rangle + \langle p_a b_{-b}^\dagger\rangle) \tag{4.9}$$

$$\equiv \sum_{ab} g_{1ab}(S_{ab} + \tilde{S}_{a-b}) \tag{4.10}$$

where the so called phonon assisted polarizations that describe absorption and emission of phonons respectively are yet another set of quantities we will need to find equations of motion for.

The tunneling contribution then turns out to be

$$i\hbar\frac{\partial}{\partial t}p_1\Big|_{H=H_T} = \langle\sum_{ab} T_{ab}[P_1, P_a^\dagger P_b]\rangle \tag{4.11}$$

$$= \sum_a T_{1a}p_a \tag{4.12}$$

in which we can see that the tunneling couples intra andinterlayer polarizations. We now finally have the Coulomb contribution, and it should not come as a surprise that it is more complex than the rest. When approaching this like we did for the previous contributions we end up with

$$i\hbar\frac{\partial}{\partial t}p_1\Big|_{H=H_{c-c}} = \langle\sum_{abcd} V_{cd}^{ab}[P_1, P_a^\dagger P_b^\dagger P_c P_d]\rangle \tag{4.13}$$

$$= \sum_{abcd} V_{cd}^{ab}\langle(P_a^\dagger\delta_{1b} + \delta_{1a}P_b^\dagger)P_c P_d\rangle \tag{4.14}$$

$$= \sum_{abc}(V_{bc}^{a1}V_{bc}^{1a})\langle P_a^\dagger P_b P_c\rangle \tag{4.15}$$

$$= 2\sum_{abc} V_{bc}^{1a}\langle P_a^\dagger P_b P_c\rangle. \tag{4.16}$$

Here we can immediately identify a problem. The polarization couples to a 3-operator quantity. If we try doing the same for this quantity we find that it in turn couples to a 5-operator quantity, and by exprapolating this we find that a quantity with n operator couples to one with $n+2$ operators. To solve this problem we must find a way to close the equation. What we do here is a correlation expansion (see A),where we approximate

$$\langle P_a^\dagger P_b P_c\rangle \approx \langle P_a^\dagger P_b\rangle\langle P_c\rangle + \langle P_a^\dagger P_c\rangle\langle P_b\rangle + \langle P_b P_c\rangle\langle P_a^\dagger\rangle + \langle P_a^\dagger\rangle\langle P_b\rangle\langle P_c\rangle. \tag{4.17}$$

The $\langle P^\dagger P\rangle$ quantities are exciton densities, which we can neglect since we work in the low excitation limit. We can also neglect the $\langle P_b P_c\rangle$ term since it describes a kind of oscillation we will not be examining here, one where two excitons are simultaneously created or annihilated. Finally we can neglect $\langle P_a^\dagger\rangle\langle P_b\rangle\langle P_c\rangle$ as well, since it is to third order in p. In other words, in the approximation used here the aspects of the Coulomb interaction that are not responsible for the formation of excitons (the terms that were absorbed into H_0) vanish entirely.

4.1.1 Photon expectation value

We now have to find the corresponding equations for the photon expectation value and phonon assisted polarizations, starting with the former. Since only two terms contain photon operators and both have relatively simple forms it is easy to see that the equation of motion for the photon expectation value becomes

$$i\hbar\frac{\partial}{\partial t}\langle c_1\rangle = \sum_a \langle[c_1, \hbar\omega_a c_a^\dagger c_a]\rangle \tag{4.18}$$

$$+ \sum_{ab}\langle\Big[c_1, M_{ab}P_a^\dagger c_b + M_{ab}P_a c_{-b}^\dagger\Big]\rangle \tag{4.19}$$

$$= \hbar\omega_1\langle c_1\rangle + \sum_a M_{a1}p_a. \tag{4.20}$$

In other words it has one free term and one that couples back to the polarization.

4.1.2 Phonon assisted polarizations

Now we finally have the phonon assisted polarizations, starting with S_1. For all contributions aside from the phonon related ones we can use our previous results to trivially obtain

$$i\hbar\frac{\partial}{\partial t}S_{12}\bigg|_{H=H_{0,c}} = E_1 S_{12}, \tag{4.21}$$

$$i\hbar\frac{\partial}{\partial t}S_{12}\bigg|_{H=H_{c-f}} = \boldsymbol{M}_1\langle b_2\rangle, \tag{4.22}$$

$$i\hbar\frac{\partial}{\partial t}S_{12}\bigg|_{H=H_{c-\mathrm{phot}}} = \sum_a M_{1a}\langle c_a b_2\rangle \tag{4.23}$$

$$i\hbar\frac{\partial}{\partial t}S_{12}\bigg|_{H=H_T} = \sum_a T_{1a}S_{a2}. \tag{4.24}$$

and

$$i\hbar\frac{\partial}{\partial t}S_{12}\bigg|_{H=H_{c-c}} = 0 \tag{4.25}$$

For the purpose of this thesis we will only be interested in incoherent phonons, meaning that we can neglect $\langle b^{(\dagger)} \rangle$ and with is the optical contribution. For the photon term we instead have the $\langle cb^{(\dagger)} \rangle$ expectation value. This describes phonon-assisted absorption. While this is an interesting topic that deserves it's own investigation, it lies beyond the scope of this thesis and will therefore be ignored.

Now it is time to proceed to the terms containing phonon operators, starting with the free phonon contribution

$$i\hbar \frac{\partial}{\partial t} S_{12} \Big|_{H=H_{0,p}} = \langle \sum_a \mathcal{E}_a P_1 [b_2, b_a^\dagger b_a] \rangle \tag{4.26}$$

$$= \mathcal{E}_2 S_{12}. \tag{4.27}$$

The more complicated carrier-phonon term then becomes

$$i\hbar \frac{\partial}{\partial t} S_{12} \Big|_{H=H_{c-\text{phon}}} \tag{4.28}$$

$$= \langle \sum_{abc} g_{abc} [P_1 b_2, P_a^\dagger P_b (b_c + b_{-c}^\dagger)] \rangle \tag{4.29}$$

$$= \sum_{abc} g_{abc} \langle (P_1 [b_2, b_{-c}^\dagger] P_a^\dagger P_b + [P_1, P_a^\dagger] P_b (b_c + b_{-c}^\dagger) b_2) \rangle \tag{4.30}$$

$$= \sum_{ab} \langle (g_{ab-2} P_1 P_a^\dagger P_b + g_{1ab} P_a (b_b + b_{-b}^\dagger) b_2) \rangle \tag{4.31}$$

$$= \sum_{ab} \langle (g_{ab-2} P_b \delta_{a1} + g_{ab-2} P_a^\dagger P_b P_1 + g_{1ab} P_a (b_b b_2 + b_2 b_{-b}^\dagger) - g_{1ab} P_a \delta_{-b2}) \rangle \tag{4.32}$$

$$= \sum_{ab} (g_{ab-2} \langle P_a^\dagger P_b P_1 \rangle + g_{1ab} (\langle P_a b_b b_2 \rangle + \langle P_a b_2 b_{-b}^\dagger \rangle)). \tag{4.33}$$

As for the Coulomb contribution we now ignore the term that is cubic in P. When taking the expectation value we then make use of the Born approximation by separating the exciton and phonon expectation values as $\langle P_1 b_2^{(\dagger)} b_3^{(\dagger)} \rangle \approx \langle P_1 \rangle \langle b_2^{(\dagger)} b_3^{(\dagger)} \rangle$. We also neglect the $\langle b_1 b_2 \rangle$ terms since we are once again not interested in coherent phonon effects, and identify $\langle b_1 b_2^\dagger \rangle = (1 + n_1)\delta_{12}$ where n_1 is the phonon density. Doing this then leads to

$$i\hbar \frac{\partial}{\partial t} S_{12} \Big|_{H=H_{c-\text{phon}}} = \sum_a g_{1a-2} p_a (1 + n_2). \tag{4.34}$$

Using the same method for $\tilde{S}_{12}$ with $\langle b_1^\dagger b_2 \rangle = n_1 \delta_{12}$ and neglecting $\langle b_1^\dagger b_2^\dagger \rangle$ we get

$$i\hbar \frac{\partial}{\partial t} \widetilde{S}_{12} \Big|_{H=H_{c-\text{phon}}} = \sum_{ab} (-g_{ab2} \langle P_a^\dagger P_b P_1 \rangle + g_{1ab} (\langle P_a b_2^\dagger b_b^\dagger \rangle + \langle P_a b_2^\dagger b_b \rangle)), \tag{4.35}$$

leading to

$$i\hbar \frac{\partial}{\partial t} \tilde{S}_{12} \Big|_{H=H_{c-\text{phon}}} = \sum_a g_{1a2} p_a n_2. \tag{4.36}$$

For the free phonon term we get

$$i\hbar\frac{\partial}{\partial t}\tilde{S}_{12}\bigg|_{H=H_{0,p}} = -\mathcal{E}_2\tilde{S}_{12}, \tag{4.37}$$

while the rest of the terms can be obtained by simply exchanging b with $b^\dagger$ and S with $\tilde{S}$.

4.2 Simplifying the Bloch equation

Now that all the individual terms of the Bloch equation have been derived we can put them together to find

$$i\hbar\frac{\partial}{\partial t}p_1 = E_1 p_1 + \boldsymbol{M}_1\cdot\boldsymbol{A} + \sum_a M_{1a}\langle c_a\rangle + \sum_{ab} g_{1ab}(S_{ab} + \tilde{S}_{a-b}) + \sum_a T_{1a}p_a, \tag{4.38}$$

where the photon expectation value is given by

$$i\hbar\frac{\partial}{\partial t}\langle c_1\rangle = \hbar\omega_1\langle c_1\rangle + \sum_a M_{a1}p_a \tag{4.39}$$

and the phonon assisted polarizations follow

$$i\hbar\frac{\partial}{\partial t}S_{12} = (E_1 + \mathcal{E}_2)S_{12} + \sum_a g_{1a-2}p_a(1+n_2) + \sum_a T_{1a}S_{a2} \tag{4.40}$$

and

$$i\hbar\frac{\partial}{\partial t}\tilde{S}_{12} = (E_1 - \mathcal{E}_2)S_{12} + \sum_a g_{1a2}p_a n_2 + \sum_a T_{1a}\tilde{S}_{a2}. \tag{4.41}$$

These could be solved numerically as they stand. They can however still be simplified further to a good approximation by solving all but the Bloch equation using the Markov approximation (see B). Doing this results in

$$\langle c_1\rangle \approx \frac{\pi}{i\hbar}\sum_a M_{a1}p_a\delta(\hbar\omega_1 - E_a), \tag{4.42}$$

$$S_{12} \approx \frac{\pi}{i\hbar}\sum_a g_{1a-2}p_a(1+n_2)\delta(E_1 - E_a + \mathcal{E}_2) + \frac{\pi}{i\hbar}\sum_a T_{1a}S_{a2}\delta(E_1 - E_a) \tag{4.43}$$

and

$$\tilde{S}_{12} \approx \frac{\pi}{i\hbar}\sum_a g_{1a2}p_a n_2\delta(E_1 - E_a - \mathcal{E}_2) + \frac{\pi}{i\hbar}\sum_a T_{1a}\tilde{S}_{a2}\delta(E_1 - E_a). \tag{4.44}$$

If we now look at how the tunneling elements look we can see that the delta function for the tunneling contributions contain a difference between intra and interlayer energies. Since the difference in band gap energy is too large to be compensated for by a shift in excitonic energy level without a huge momentum transfer we can safely omit the tunneling terms for the phonon-assisted polarizations.

By inserting these solutions we then obtain

$$i\hbar\frac{\partial}{\partial t}p_1 = E_1 p_1 + \boldsymbol{M}_1 \cdot \boldsymbol{A} + \frac{\pi}{i\hbar}\sum_{ab} M_{1b}M_{ab}p_a\delta(E_a - \hbar\omega_b) \tag{4.45}$$

$$+ \frac{\pi}{i\hbar}\sum_{abc} g_{1ac}g_{ab-c}p_b(1+n_c)\delta(E_a - E_b + \mathcal{E}_c) + \frac{\pi}{i\hbar}\sum_{abc} g_{1ac}g_{ab-c}p_b n_c\delta(E_a - E_b - \mathcal{E}_c) \tag{4.46}$$

$$+ \sum_a T_{1a}p_a, \tag{4.47}$$

where we have used that $\mathcal{E}$ and n only depends on the magnitude of the momentum.

Before we solve this there is one final step we can take. We already decided to handle the exciting field classically and the rest quantum mechanically, but at this moment it is constructive to examine how the optical part would look if we treated the entire field classically. By solving Maxwell's equations (see C) we can see that that the total field can be written in the Fourier basis as

$$\boldsymbol{A}(\omega) = \boldsymbol{A}_0(\omega) + \frac{ic\mu_0}{\omega}\boldsymbol{j}(\omega). \tag{4.48}$$

Using second quantization the current can be expressed as

$$\boldsymbol{j}(\omega) = \frac{e_0}{2m_0}\langle \boldsymbol{p} - e_0\boldsymbol{A}\rangle + c.c. \tag{4.49}$$

$$= \frac{e_0}{2m_0}\sum_a \langle\phi_a|\boldsymbol{p} - e_0\boldsymbol{A}|\phi_b\rangle\langle a_a^\dagger a_b\rangle + c.c. \tag{4.50}$$

where e_0 and m_0 are the carge and mass of the electron [11]. When Coulomb interaction is included the $\boldsymbol{A}$ term becomes relatively small [11], and will therefore be neglected. By using that $\boldsymbol{p} = -i\hbar\nabla$ we can now identify the optical matrix element to obtain

$$\boldsymbol{j}(\omega) = \sum_a \mathrm{Im}(\boldsymbol{M}_a p_a(\omega)). \tag{4.51}$$

If we insert these results into our optical term and only consider the non-exciting part of the field we see that it ends up looking like

$$i\hbar\frac{\partial}{\partial t}p_1\bigg|_{\mathrm{Opt,non-exc}} = \boldsymbol{M}_1 \cdot \left(\frac{ic\mu_0}{\omega}\sum_a \mathrm{Re}\left(\boldsymbol{M}_a p_a\right)\right) \tag{4.52}$$

$$\approx -\frac{ic\mu_0}{\omega}\sum_a \boldsymbol{M}_1\boldsymbol{M}_a p_a \tag{4.53}$$

$$\equiv -i\hbar\sum_a \gamma_{\mathrm{rad}}^{1a}p_a\delta_{s_{e_1}s_{h_1}}\delta_{\boldsymbol{Q}_1,\boldsymbol{0}} \tag{4.54}$$

where we have used the rotating wave approximation to neglect off-resonant terms. The whole point of this exercise is that if we recall that the photon coupling element also conserves spin and use that the photon momentum is relatively small we can see that this term and the photon term have roughly the same form. Since this form is much easier to calculate and has given results consistent with experiment in past

studies we can simply replace the photon term with this expression, which gives us our final form for the Bloch equation

$$\frac{\partial}{\partial t}p_1 = \frac{1}{i\hbar}E_1 p_1 + \frac{1}{i\hbar}\boldsymbol{M}_1 \cdot \boldsymbol{A}_0 - \sum_a \gamma_{\text{rad}}^{1a} p_a \delta_{s_{e_1} s_{h_1}} \delta_{\boldsymbol{Q}_1,\boldsymbol{0}} \tag{4.55}$$

$$- \frac{\pi}{i\hbar^2}\sum_{abc\pm} g_{1ac} g_{bac} p_b \left(\frac{1}{2} \pm \frac{1}{2} + n_c\right)\delta(E_a - E_b \pm \mathcal{E}_c) \tag{4.56}$$

$$+ \frac{1}{i\hbar}\sum_a T_{1a} p_a. \tag{4.57}$$

Here the $\pm$ index is an 'operator index" that is either $+$ or $-$. Now that we have reached this final form it is finally time to expand the indices. Since all of our terms but the free one which is purely imaginary contain a factor $\delta_{s_h s_e}$ we can also simplify our notation to only include one spin index, resulting in

$$\frac{\partial}{\partial t} p_{\boldsymbol{Q}_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} \tag{4.58}$$

$$= \frac{1}{i\hbar} E_{\boldsymbol{Q}_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} p_{\boldsymbol{Q}_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} + \frac{1}{i\hbar}\boldsymbol{M}^{\mu_1 s_1 l_{h_1} l_{e_1}} \cdot \boldsymbol{A}_0 - \sum_{\mu s l_h l_e} \gamma_{\text{rad}}^{\mu_1 s_1 l_{h_1} l_{e_1}, \mu s l_h l_e} p_{\boldsymbol{0}}^{\mu s l_h l_e} \delta_{\boldsymbol{Q}_1,\boldsymbol{0}} \tag{4.59}$$

$$- \frac{\pi}{\hbar^2}\sum_{\boldsymbol{K} l\alpha\mu\nu\pm} g_{\boldsymbol{Q}_1-\boldsymbol{K},\boldsymbol{K}}^{s_1 l_{h_1} l_{e_1} l\alpha\mu_1\mu} g_{\boldsymbol{Q}_1-\boldsymbol{K},\boldsymbol{K}}^{s_1 l_{h_1} l_{e_1} l\alpha\nu\mu} p_{\boldsymbol{Q}_1}^{\nu s_1 l_{h_1} l_{e_1}} \tag{4.60}$$

$$\cdot \left(\frac{1}{2} \pm \frac{1}{2} + n_{\boldsymbol{K}}^{l\alpha}\right)\delta\left(E_{\boldsymbol{Q}_1-\boldsymbol{K}}^{\mu s_1 l_{h_1} l_{e_1}} - E_{\boldsymbol{Q}_1}^{\nu s_1 l_{h_1} l_{e_1}} \pm \mathcal{E}_{\boldsymbol{K}}^{l\alpha}\right) \tag{4.61}$$

$$+ \sum_{\boldsymbol{Q} l_h l_e \mu} T_{\boldsymbol{Q}_1,\boldsymbol{Q}}^{s_1 l_{h_1} l_{e_1} l_h l_e \mu_1 \mu} p_{\boldsymbol{Q}}^{\mu s_1 l_h l_e}. \tag{4.62}$$

We can now take the time to go over the different terms one by one. The first one results in free oscillation. The second will be real and positive in our definition of the optical matrix element, exciting the polarization using an initial pulse $\boldsymbol{A}_0(t)$. The third term, being mostly real and negative, will lead to radiative dephasing. In a similar way the third term will lead to non-radiative dephasing by the means of emission and absorption of phonons respectively. Finally the last term will couple intra and interlayer polarizations to each other. The imaginary part will lead to a frequency offset in the absorption.

4.3 Solving the Bloch equation

To solve this equation we have used the Runge-Kutta method implemented in the C programming language. The system was solved on a 100×100 grid in polar coordinates. To account for uncertainty the phonon delta functions were implemented as Lorentzians. The widths that were used for these were the non-radiative dephasing

rates found in the Bloch equation as

$$\frac{\partial}{\partial t} p_{\boldsymbol{Q}_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} \Big|_{H=H_{c-\mathrm{phon}}} \tag{4.63}$$

$$= \frac{\pi}{\hbar^2} \sum_{\boldsymbol{K} l\alpha\mu\nu\pm} g_{\boldsymbol{Q}_1-\boldsymbol{K},\boldsymbol{K}}^{s_1 l_{h_1} l_{e_1} l\alpha\mu_1\mu} g_{\boldsymbol{Q}_1-\boldsymbol{K},\boldsymbol{K}}^{s_1 l_{h_1} l_{e_1} l\alpha\nu\mu} p_{\boldsymbol{Q}_1}^{\nu s_1 l_{h_1} l_{e_1}} \tag{4.64}$$

$$\cdot \left(\frac{1}{2} \pm \frac{1}{2} + n_{\boldsymbol{K}}^{l\alpha}\right) \delta\left(E_{\boldsymbol{Q}_1-\boldsymbol{K}}^{\mu s_1 l_{h_1} l_{e_1}} - E_{\boldsymbol{Q}_1}^{\nu s_1 l_{h_1} l_{e_1}} \pm \mathcal{E}_{\boldsymbol{K}}^{l\alpha}\right) \tag{4.65}$$

$$\equiv \sum_{\nu} \gamma_{\mathrm{non-rad}}^{\boldsymbol{Q}_1 s_1 l_{h_1} l_{e_1} \mu_1 \nu} p_{\boldsymbol{Q}_1}^{\nu s_1 l_{h_1} l_{e_1}}. \tag{4.66}$$

However these have to satisfy

$$\gamma_{\mathrm{non-rad}}^{\boldsymbol{Q}_1 s_1 l_{h_1} l_{e_1} \mu_1 \nu} \tag{4.67}$$

$$= \frac{\pi}{\hbar^2} \sum_{\boldsymbol{K} l\alpha\mu\pm} g_{\boldsymbol{Q}_1-\boldsymbol{K},\boldsymbol{K}}^{s_1 l_{h_1} l_{e_1} l\alpha\mu_1\mu} g_{\boldsymbol{Q}_1-\boldsymbol{K},\boldsymbol{K}}^{s_1 l_{h_1} l_{e_1} l\alpha\nu\mu} \left(\frac{1}{2} \pm \frac{1}{2} + n_{\boldsymbol{K}}^{l\alpha}\right) \delta\left(E_{\boldsymbol{Q}_1-\boldsymbol{K}}^{\mu s_1 l_{h_1} l_{e_1}} - E_{\boldsymbol{Q}_1}^{\nu s_1 l_{h_1} l_{e_1}} \pm \mathcal{E}_{\boldsymbol{K}}^{l\alpha}\right) \tag{4.68}$$

while also being a part of the delta functions. To get around this the dephasing rates were solved iteratively with a suitable initial value until they had converged.

We then assumed that the total phonon population was already in equilibrium. This means that the phonon densities could be treated as Bose-Einstein distributions. Finally we treated $\boldsymbol{A}_0(t)$ as a δ function.

As for the integrals we calculated them as Riemann sums in polar coordinates, meaning that for an arbitrary sum over momentum space we get

$$\sum_{\boldsymbol{k}} f(\boldsymbol{k}) = \frac{1}{(2\pi)^2} \int k dk \int d\varphi f(k,\varphi) \to \frac{1}{(2\pi)^2} \Delta k \Delta\varphi \sum_{n}^{N_n} \sum_{m}^{N_m} k_n f(k_n, \varphi_n), \tag{4.69}$$

where $\Delta k = \frac{k_{\max}}{N_k}$ and $\Delta\varphi = \frac{2\pi}{N_m}$ are the discretized differentials and $k_n = n\Delta k$ and $\varphi_m = m\Delta\varphi$ are the discretized momenta and angles.

Finally we made use of the fact that the K/K' points being isotropic implies that the polarization is also isotropic. By averaging the angular dependence we could then simplify the Bloch equation to

$$\frac{\partial}{\partial t} p_{Q_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} \tag{4.70}$$

$$= \frac{1}{i\hbar} E_{Q_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} p_{Q_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} + \frac{1}{i\hbar} \boldsymbol{M}^{\mu_1 s_1 l_{h_1} l_{e_1}} \cdot \boldsymbol{A}_0 - \sum_{\mu s l_h l_e} \gamma_{\mathrm{rad}}^{\mu_1 s_1 l_{h_1} l_{e_1}, \mu s l_h l_e} p_Q^{\mu s l_h l_e} \delta_{Q_1,0} \tag{4.71}$$

$$- \sum_{\nu} \frac{1}{2\pi} \sum_{\varphi_{Q1}} \gamma_{\mathrm{non-rad}}^{\boldsymbol{Q}_1 s_1 l_{h_1} l_{e_1} \mu_1 \nu} p_{Q_1}^{\nu s_1 l_{h_1} l_{e_1}} \tag{4.72}$$

$$+ \sum_{\boldsymbol{Q} l_h l_e \mu} \frac{1}{2\pi} \sum_{\varphi_{Q_1}} T_{\boldsymbol{Q}_1,\boldsymbol{Q}}^{s_1 l_{h_1} l_{e_1} l_h l_e \mu_1 \mu} p_Q^{\mu s_1 l_h l_e}. \tag{4.73}$$

The point of doing this is that now the angular dependency can be included into the definition of the matrix elements. While this makes the computation of these take more time it greatly improves the time needed for the Runge-Kutta method since the angular summation now only needs to be performed once and not once for every timestep.

We also chose to neglect the tunneling contribution. This can be motivated by the fact that our tunneling element in this model is mostly real, meaning that only a very small part of it will drive the creation of new polarizations. The imaginary part will only contribute to the oscillations, shifting the position in Fourier space. Combined with the fact that the interlayer optical matrix element is relatively small this means that the tunneling term will have a correspondingly small effect on the intralayer polarization while the interlayer one will be so small that a frequency shift would not affect the overall dynamics anyway. It may be an interesting topic to examine in the future though.

4.3.1 Calculating the absorption

It is now time to finally use our newly calculated polarizations to calculate the absorption spectrum of the TMD. In Appendix C we derive the classical absorption coefficient to be

$$\alpha(\omega) \propto \mathrm{Im}\left(\frac{j(\omega)}{\omega A(\omega)}\right). \tag{4.74}$$

We also showed that the current can be expressed as

$$\boldsymbol{j}(\omega) = \mathrm{Im}(\boldsymbol{M}_a p_a(\omega)). \tag{4.75}$$

Inserting this into the absorption coefficient then finally results in

$$\alpha(\omega) \propto \frac{\mathrm{Im}\left(\sum_a \mathrm{Im}(\boldsymbol{M}_a p_a(\omega))\right)}{\omega A(\omega)} \tag{4.76}$$

$$= -\frac{\mathrm{Re}\left(\sum_{sl_h l_e \mu} \boldsymbol{M}_{\boldsymbol{0}}^{\mu s l_h l_e} p_{\boldsymbol{0}}^{\mu s l_h s l_e}(\omega)\right)}{\omega A(\omega)}. \tag{4.77}$$

The result for the three first energy levels at room temperature can be seen in Figure 4.1. There are a number of aspects we can observe here. We can see the spin-orbit splitting in the significant energy difference between the A and B excitons. We can also see how the WSe-WSe excitons have slightly higher energies than the MoSe-MoSe ones, and how the absorption gets smaller for higher excitonic energy levels. This can be attributed to how the shape of the excitonic wavefunctions when projecting the optical matrix element to the excitonic picture. Finally we can see that the absorption is significantly lower for the interlayer excitons, meaning that, as predicted, the experimental results can not be replicated using optical excitation alone.

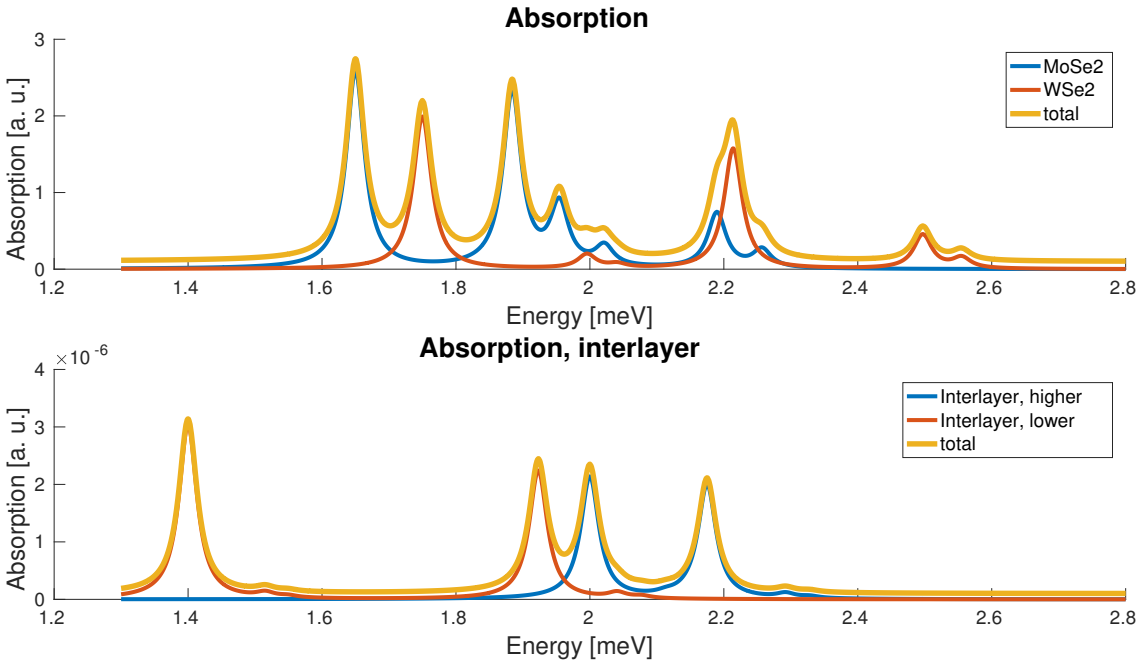

Figure 4.1: In the upper figure the absorption spectrum for the three lowest excitonic energy states at room temperature can be seen. The large spin-orbit coupling clearly separates the A from the B excitons. It can also be seen that the absorption greatly lessens for higher energy levels, meaning that most excitons will be created at the ground state. Due to the huge difference in magnitude the interlayer peaks can not be seen in this figure. They are therefore shown isolated in the lower one instead. Since the purpose of this figure is to highlight these aspects without going into the finer aspects we have chosen to use the same linewidth for all peaks. The total spectrum has also been raised by a tiny amount to more easily distinguish the components.

5

The exciton density equation

It is now time to do what we just did for the polarization $p_1 \equiv \langle P_1 \rangle$ for the exciton density $N_1 \equiv \langle P_1^\dagger P_1 \rangle$, starting with the more general $N_{12} \equiv \langle P_1^\dagger P_2 \rangle$. This is however the total density. What we are interested in is the incoherent part of it, obtained by subtracting the coherent part from the total density as $\delta N_{12} \equiv \langle P_1^\dagger P_2 \rangle - \langle P_1^\dagger \rangle \langle P_2 \rangle = N_{12} - p_1 p_2$. In other words the incoherent density is nothing but the correlation term in a correlation expansion. In the way we can define $\delta S_{12} \equiv \langle P_1 b_2 \rangle - \langle P_1 \rangle \langle b_2 \rangle$,

but since we neglect the $\langle b \rangle$ terms we get $\delta S_{12} = S_{12}$.

Now, when it comes to finding the actual equations we can save a lot of time by making use of a couple of tricks. First off, we see that

$$i\hbar \frac{\partial}{\partial t} P_1^\dagger = -\left(i\hbar \frac{\partial}{\partial t} P_1 \right)^\dagger . \tag{5.1}$$

We then use the Leibniz rule to find

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \delta N_{12} &= i\hbar \frac{\partial}{\partial t} (\langle P_1^\dagger P_2 \rangle - \langle P_1^\dagger \rangle \langle P_2 \rangle) && (5.2) \\ &= \langle i\hbar \frac{\partial}{\partial t} (P_1^\dagger) P_2 \rangle + \langle P_1^\dagger i\hbar \frac{\partial}{\partial t} P_2 \rangle - \left(i\hbar \frac{\partial}{\partial t} (\langle P_1^\dagger \rangle) \langle P_2 \rangle + \langle P_1^\dagger \rangle i\hbar \frac{\partial}{\partial t} \langle P_2 \rangle \right) && (5.3) \\ &= \langle P_1^\dagger i\hbar \frac{\partial}{\partial t} P_2 \rangle - \langle \left(i\hbar \frac{\partial}{\partial t} P_1 \right)^\dagger P_2 \rangle - \left(\langle P_1^\dagger \rangle i\hbar \frac{\partial}{\partial t} \langle P_2 \rangle - \left(i\hbar \frac{\partial}{\partial t} \langle P_1 \rangle \right) \langle P_2 \rangle \right). && (5.4) \end{aligned}$$

By doing this we can find the equations of motion directly from our results in the previous section.

5.1 Constructing the contributions

Using the above tricks we can now easily find the free contribution

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\delta N_{12}\bigg|_{H=H_{0,c}} &= (E_2 - E_1)N_{12} - (E_2 - E_1)p_1 p_2 \\ &= (E_2 - E_1)\delta N_{12} \end{aligned} \tag{5.5}$$

and the optical

$$i\hbar\frac{\partial}{\partial t}\delta N_{12}\bigg|_{H=H_{c-f}} = \boldsymbol{M}_2 \cdot \boldsymbol{A}p_1 - \boldsymbol{M}_1 \cdot \boldsymbol{A}p_2 - (\boldsymbol{M}_2 \cdot \boldsymbol{A}p_1 - \boldsymbol{M}_1 \cdot \boldsymbol{A}p_2) \tag{5.6}$$

$$= 0, \tag{5.7}$$

which apparently disappears. The photon contribution then turns out to be

$$i\hbar\frac{\partial}{\partial t}\delta N_{12}\bigg|_{H=H_{c-\mathrm{phot}}} \tag{5.8}$$

$$= \sum_a M_{2a}\langle P_1^\dagger c_a\rangle - \sum_a M_{1a}\langle P_2 c_a^\dagger\rangle - \left(\sum_a M_{2a}p_1\langle c_a\rangle - \sum_a M_{1a}p_2\langle c_a\rangle\right) \tag{5.9}$$

$$= \sum_a M_{2a}\langle P_1 c_a^\dagger\rangle - \sum_a M_{1a}\langle P_2 c_a^\dagger\rangle - \left(\sum_a M_{2a}(p_1\langle c_a^\dagger\rangle) - \sum_a M_{1a}p_2\langle c_a^\dagger\rangle\right) \tag{5.10}$$

$$\equiv \sum_a \left(M_{2a}\delta\tilde{\mathcal{T}}_{1a} - M_{1a}\delta\tilde{\mathcal{T}}_{2a}\right), \tag{5.11}$$

where $\delta\tilde{\mathcal{T}}_{ab} \equiv \langle P_a c_b^\dagger\rangle - \langle P_a\rangle\langle c_b^\dagger\rangle$ is the incoherent part of the *photon assisted polarization*. In a similar but slightly more complex way the phonon contribution

becomes

$$
\begin{aligned}
&i\hbar\frac{\partial}{\partial t}\delta N_{12}\Big|_{H=H_{c-\mathrm{phon}}} && (5.12)\\
&= \sum_{ab} g_{2ab}(\langle P_1^\dagger P_a b_b\rangle + \langle P_1^\dagger P_a b_{-b}^\dagger\rangle) - \sum_{ab} g_{1ab}(\langle P_a^\dagger b_{-b} P_2\rangle + \langle P_a^\dagger b_b^\dagger P_2\rangle) && (5.13)\\
&- \left(\sum_{ab} g_{2ab}(\langle P_1^\dagger\rangle\langle P_a b_b\rangle + \langle P_1^\dagger\rangle\langle P_a b_{-b}^\dagger\rangle) - \sum_{ab} g_{1ab}(\langle P_a^\dagger b_{-b}\rangle\langle P_2\rangle + \langle P_a^\dagger b_b^\dagger\rangle\langle P_2\rangle)\right) && (5.14)\\
&= \left(\sum_{ab} g_{2ab}(\langle P_1^\dagger P_a b_b\rangle + \langle P_1^\dagger P_a b_{-b}^\dagger\rangle) - \sum_{ab} g_{1ab}(\langle P_a^\dagger P_2 b_{-b}\rangle + \langle P_a^\dagger P_2 b_b^\dagger\rangle)\right. && (5.15)\\
&- \left(\sum_{ab} g_{2ab}(\langle P_1^\dagger\rangle\langle P_a b_b\rangle + \langle P_1^\dagger\rangle\langle P_a b_{-b}^\dagger\rangle) - \sum_{ab} g_{1ab}(\langle P_a^\dagger\rangle\langle P_2 b_{-b}\rangle + \langle P_a^\dagger\rangle\langle P_2 b_b^\dagger\rangle)\right) && (5.16)\\
&\left.- \left(\sum_{ab} g_{2ab}(\langle P_a\rangle\langle P_1^\dagger b_b\rangle + \langle P_a\rangle\langle P_1^\dagger b_{-b}^\dagger\rangle) - \sum_{ab} g_{1ab}(\langle P_2\rangle\langle P_a^\dagger b_{-b}\rangle + \langle P_2\rangle\langle P_a^\dagger b_b^\dagger\rangle)\right)\right) && (5.17)\\
&+ \left(\sum_{ab} g_{2ab}(\langle P_a\rangle\langle P_1^\dagger b_b\rangle + \langle P_a\rangle\langle P_1^\dagger b_{-b}^\dagger\rangle) - \sum_{ab} g_{1ab}(\langle P_a^\dagger\rangle\langle P_2 b_{-b}\rangle + \langle P_a^\dagger\rangle\langle P_2 b_b^\dagger\rangle)\right) && (5.18)\\
&\equiv \sum_{ab} g_{2ab}(O_{1ab} + \tilde{O}_{1a-b}) - \sum_{ab} g_{1ab}(O_{a2-b} + \tilde{O}_{a2b}) && (5.19)\\
&+ \sum_{ab} g_{2ab}\left(\langle P_a\rangle\langle P_1 b_b^\dagger\rangle + \langle P_a\rangle\langle P_1 b_{-b}\rangle\right) - \sum_{ab} g_{1ab}(\langle P_a^\dagger\rangle\langle P_2 b_{-b}\rangle + \langle P_a^\dagger\rangle\langle P_2 b_b^\dagger\rangle) && (5.20)\\
&= \sum_{ab} g_{2ab}(\delta O_{1ab} + \delta\tilde{O}_{1a-b}) - \sum_{ab} g_{1a-b}(\delta O_{a2b} + \delta\tilde{O}_{a2-b}) && (5.21)\\
&+ \sum_{ab} g_{2ab} p_a\left(\delta\tilde{S}_{1b} + \delta S_{1-b}\right) - \sum_{ab} g_{1a-b} p_a(\delta S_{2b} + \delta\tilde{S}_{2-b}) && (5.22)
\end{aligned}
$$

where $\delta O_{abc} \equiv \langle P_a^\dagger P_b b_c\rangle - \langle P_a^\dagger\rangle\langle P_b b_c\rangle - \langle P_b\rangle\langle P_a^\dagger b_c\rangle$ and $\delta\tilde{O}_{abc} \equiv \langle P_a^\dagger P_b b_c^\dagger\rangle - \langle P_a^\dagger\rangle\langle P_b b_c^\dagger\rangle - \langle P_b\rangle\langle P_a^\dagger b_c^\dagger\rangle$ are the incoherent parts of the *phonon assisted densities*. We then have the tunneling contribution

$$
\begin{aligned}
i\hbar\frac{\partial}{\partial t}\delta N_{12}\Big|_{H=H_T} &= \sum_a T_{2a}\langle P_1^\dagger P_a\rangle - \sum_a T_{1a}\langle P_a^\dagger P_2\rangle && (5.23)\\
&- \left(\sum_a T_{2a}\langle P_1^\dagger\rangle\langle P_a\rangle - \sum_a T_{1a}\langle P_a^\dagger\rangle\langle P_2\rangle\right) && (5.24)\\
&= \sum_a T_{2a}\delta N_{1a} - \sum_a T_{1a}\delta N_{a2} && (5.25)
\end{aligned}
$$

and finally the Coulomb term

$$i\hbar\frac{\partial}{\partial t}\delta N_{12}\bigg|_{H=H_{c-c}} = 2\sum_{abc} V_{bc}^{2a}\langle P_1^\dagger P_a^\dagger P_b P_c\rangle - 2\sum_{abc} V_{bc}^{1a}\langle P_b^\dagger P_c^\dagger P_a P_2\rangle \tag{5.26}$$

$$- \left(2\sum_{abc} V_{bc}^{2a}\langle P_1^\dagger\rangle\langle P_a^\dagger P_b P_c\rangle - 2\sum_{abc} V_{bc}^{1a}\langle P_b^\dagger P_c^\dagger P_a\rangle\langle P_2\rangle\right) \tag{5.27}$$

$$\approx 0. \tag{5.28}$$

Here we have we once again neglected higher order terms. Before proceeding to put these together we first have to find the corresponding equations for the photon- and phonon assisted quantities.

5.1.1 Photon assisted polarization

Similar to how we handled the phonon assisted polarization we can easily find the contributions from all non-photon related terms to be

$$i\hbar\frac{\partial}{\partial t}\delta\tilde{\mathcal{T}}_{12}\bigg|_{H=H_{0,c}} = E_1\langle P_1 c_2^\dagger\rangle - E_1\langle P_1\rangle\langle c_2^\dagger\rangle \tag{5.29}$$

$$= E_1\tilde{\mathcal{T}}_{12}, \tag{5.30}$$

$$i\hbar\frac{\partial}{\partial t}\delta\tilde{\mathcal{T}}_{12}\bigg|_{H=H_{e-f}} = \boldsymbol{M}_1\cdot\boldsymbol{A}\langle c_2^\dagger\rangle - \boldsymbol{M}_1\cdot\boldsymbol{A}\langle c_2^\dagger\rangle \tag{5.31}$$

$$= 0, \tag{5.32}$$

$$i\hbar\frac{\partial}{\partial t}\delta\tilde{\mathcal{T}}_{12}\bigg|_{H=H_{c-\mathrm{phon}}} \tag{5.33}$$

$$= \sum_{ab} g_{1ab}(\langle P_a b_b c_2^\dagger\rangle + \langle P_a b_{-b}^\dagger c_2^\dagger\rangle) - \sum_{ab} g_{1ab}(\langle P_a b_b\rangle\langle c_2^\dagger\rangle + \langle P_a b_{-b}^\dagger\rangle\langle c_2^\dagger\rangle) \tag{5.34}$$

$$= \sum_{ab} g_{1ab}(\delta\langle P_a b_b c_2^\dagger\rangle + \delta\langle P_a b_{-b}^\dagger c_2^\dagger\rangle) \tag{5.35}$$

$$\approx 0, \tag{5.36}$$

$$i\hbar\frac{\partial}{\partial t}\delta\tilde{\mathcal{T}}_{12}\bigg|_{H=H_T} = \sum_a T_{1a}\langle P_a c_2^\dagger\rangle - \sum_a T_{1a}\langle P_a\rangle\langle c_2^\dagger\rangle \tag{5.37}$$

$$= \sum_a T_{1a}\delta\tilde{\mathcal{T}}_{a2} \tag{5.38}$$

and

$$i\hbar\frac{\partial}{\partial t}\delta\tilde{\mathcal{T}}_{12}\bigg|_{H=H_{c-c}} = 2\sum_{abc} V_{bc}^{1a}\langle P_a^\dagger P_b P_c c_2^\dagger\rangle - 2\sum_{abc} V_{bc}^{1a}\langle P_a^\dagger P_b P_c\rangle\langle c_2^\dagger\rangle \tag{5.39}$$

$$\approx 0 \tag{5.40}$$

where we have neglected the incoherent parts of the phonon assisted absorption quantities $\langle P_a b_b^{(\dagger)} c_2^\dagger \rangle$ and the higher order terms of the Coulomb interaction. For the remaining two terms we get

$$i\hbar\frac{\partial}{\partial t}\delta\tilde{\mathcal{T}}_{12}\bigg|_{H=H_{0,\mathrm{phot}}} = \delta\langle\sum_a \hbar\omega_a[P_1 c_2^\dagger, c_a^\dagger c_a]\rangle \tag{5.41}$$

$$= -\hbar\omega_2\delta\langle P_1 c_2^\dagger\rangle \tag{5.42}$$

$$= -\hbar\omega_2\delta\tilde{\mathcal{T}}_{12} \tag{5.43}$$

and

$$i\hbar\frac{\partial}{\partial t}\delta\tilde{\mathcal{T}}_{12}\bigg|_{H=H_{c-\mathrm{phot}}} = \delta\langle\sum_{ab}\left[P_1 c_2^\dagger, M_{ab}P_a c_{-b}^\dagger + M_{ab}P_a^\dagger c_{-b}\right]\rangle \tag{5.44}$$

$$= \sum_{ab} M_{ab}\delta\langle P_1[c_2^\dagger, c_b]P_a^\dagger + [P_1, P_a^\dagger]c_b c_2^\dagger\rangle \tag{5.45}$$

$$= -\sum_a M_{a2}\delta\langle P_1 P_a^\dagger\rangle \tag{5.46}$$

$$+\sum_a M_{1a}\delta\langle c_a c_2^\dagger\rangle \tag{5.47}$$

$$= -\sum_a M_{a2}\delta\langle P_a^\dagger P_1\rangle \tag{5.48}$$

$$- M_{12} \tag{5.49}$$

$$+\sum_a M_{1a}\delta\langle c_2^\dagger c_a\rangle \tag{5.50}$$

$$+ M_{12} \tag{5.51}$$

$$\approx -\sum_a M_{a2}\delta N_{a1}. \tag{5.52}$$

The first term simply adds an oscillating term to the free part, and in the second one we have neglected the $\delta\langle c_2^\dagger c_{-a}\rangle$ term since we are only interested in coherent photon densities.

5.1.2 Phonon assisted densities

For the terms containing only excitonic operators this can be handled the usual way, giving

$$i\hbar\frac{\partial}{\partial t}\delta O_{123}\bigg|_{H=H_{0,c}} = (E_2 - E_1)\delta O_{123}, \tag{5.53}$$

$$i\hbar\frac{\partial}{\partial t}\delta O_{123}\Big|_{H=H_{c-f}} = i\hbar\frac{\partial}{\partial t}(\langle P_1^\dagger P_2 b_3\rangle - \langle P_1^\dagger\rangle\langle P_2 b_3\rangle - \langle P_2\rangle\langle P_1^\dagger b_3\rangle)\Big|_{H=H_{c-f}} \tag{5.54}$$
$$= \boldsymbol{M}_2\cdot\boldsymbol{A}\langle P_1^\dagger b_3\rangle - \boldsymbol{M}_1\cdot\boldsymbol{A}\langle P_2 b_3\rangle \tag{5.55}$$
$$- \Big(\boldsymbol{M}_2\cdot\boldsymbol{A}\langle P_1^\dagger\rangle\langle b_3\rangle - \boldsymbol{M}_1\cdot\boldsymbol{A}\langle P_2 b_3\rangle\Big) \tag{5.56}$$
$$- \Big(\boldsymbol{M}_2\cdot\boldsymbol{A}\langle P_1^\dagger b_3\rangle - \boldsymbol{M}_1\cdot\boldsymbol{A}\langle P_2\rangle\langle b_3\rangle\Big) \tag{5.57}$$
$$\approx 0 \tag{5.58}$$

where we have once again neglected the $\langle b^{(\dagger)}\rangle$ terms,

$$i\hbar\frac{\partial}{\partial t}\delta O_{123}\Big|_{H=H_{c-\mathrm{phot}}} = i\hbar\frac{\partial}{\partial t}(\langle P_1^\dagger P_2 b_3\rangle - \langle P_1^\dagger\rangle\langle P_2 b_3\rangle - \langle P_2\rangle\langle P_1^\dagger b_3\rangle)\Big|_{H=H_{c-f}} \tag{5.59}$$
$$= \sum_a M_{2a}\langle P_1^\dagger c_a b_3\rangle - \sum_a M_{1a}\langle P_2 c_a^\dagger b_3\rangle \tag{5.60}$$
$$- \left(\sum_a M_{2a}\langle P_1^\dagger\rangle\langle c_a b_3\rangle - \sum_a M_{1a}\langle c_a^\dagger\rangle\langle P_2 b_3\rangle\right) \tag{5.61}$$
$$- \left(\sum_a M_{2a}\langle c_a\rangle\langle P_1^\dagger b_3\rangle - \sum_a M_{1a}\langle P_2\rangle\langle c_a^\dagger b_3\rangle\right) \tag{5.62}$$
$$= \sum_a M_{2a}\delta\langle P_1^\dagger c_a b_3\rangle - \sum_a M_{1a}\delta\langle P_2 c_a^\dagger b_3\rangle \tag{5.63}$$
$$\approx 0, \tag{5.64}$$

where we have neglected phonon assisted absorption and emission as usual,

$$i\hbar\frac{\partial}{\partial t}\delta O_{123}\Big|_{H=H_T} = i\hbar\frac{\partial}{\partial t}(\langle P_1^\dagger P_2 b_3\rangle - \langle P_1^\dagger\rangle\langle P_2 b_3\rangle - \langle P_2\rangle\langle P_1^\dagger b_3\rangle)\Big|_{H=H_T} \tag{5.65}$$
$$= \sum_a T_{2a}\langle P_1^\dagger P_a b_3\rangle - \sum_a T_{1a}\langle P_a^\dagger P_2 b_3\rangle \tag{5.66}$$
$$- \left(\sum_a T_{2a}\langle P_1^\dagger\rangle\langle P_a b_3\rangle - \sum_a T_{1a}\langle P_a^\dagger\rangle\langle P_2 b_3\rangle\right) \tag{5.67}$$
$$- \left(\sum_a T_{2a}\langle P_a\rangle\langle P_1^\dagger b_3\rangle - \sum_a T_{1a}\langle P_2\rangle\langle P_a^\dagger b_3\rangle\right) \tag{5.68}$$
$$= \sum_a T_{2a}\delta O_{1a3} - \sum_a T_{1a}\delta O_{a23} \tag{5.69}$$

and

$$i\hbar\frac{\partial}{\partial t}\delta O_{123}\Big|_{H=H_{c-c}} = i\hbar\frac{\partial}{\partial t}(\langle P_1^\dagger P_2 b_3\rangle - \langle P_1^\dagger\rangle\langle P_2 b_3\rangle - \langle P_2\rangle\langle P_1^\dagger b_3\rangle)\Big|_{H=H_T} \tag{5.70}$$
$$= 2\sum_{abc} V_{bc}^{2a}\langle P_1^\dagger P_a^\dagger P_b P_c b_3\rangle - 2\sum_{abc} V_{bc}^{1a}\langle P_b^\dagger P_c^\dagger P_a P_2 b_3\rangle \tag{5.71}$$
$$- \left(2\sum_{abc} V_{bc}^{2a}\langle P_1^\dagger\rangle\langle P_a^\dagger P_b P_c b_3\rangle - 2\sum_{abc} V_{bc}^{1a}\langle P_b^\dagger P_c^\dagger P_a\rangle\langle P_2 b_3\rangle\right) \tag{5.72}$$
$$- \left(2\sum_{abc} V_{bc}^{2a}\langle P_1^\dagger b_3\rangle\langle P_a^\dagger P_b P_c\rangle - 2\sum_{abc} V_{bc}^{1a}\langle P_b^\dagger P_c^\dagger P_a b_3\rangle\langle P_2\rangle\right) \tag{5.73}$$
$$\approx 0. \tag{5.74}$$

For the free phonon part we predictably get

$$i\hbar\frac{\partial}{\partial t}\delta O_{123}\Big|_{H=H_{0,\mathrm{phon}}} = \mathcal{E}_3\delta O_{123} \tag{5.75}$$

while the phonon term is more complicated. Deriving it is going to take a few steps, but all of them will be variants of tricks we have used before. First off we have

$$i\hbar\frac{\partial}{\partial t}\delta O_{123}\Big|_{H=H_{c-\mathrm{phon}}} \tag{5.76}$$

$$= i\hbar\frac{\partial}{\partial t}(\langle P_1^\dagger P_2 b_3\rangle - \langle P_1^\dagger\rangle\langle P_2 b_3\rangle - \langle P_2\rangle\langle P_1^\dagger b_3\rangle)\Big|_{H=H_{c-\mathrm{phon}}} \tag{5.77}$$

$$= \left(\langle i\hbar\frac{\partial}{\partial t}(P_1^\dagger P_2)b_3\rangle + \langle P_1^\dagger P_2 i\hbar\frac{\partial}{\partial t}b_3\rangle\right)\Big|_{H=H_{c-\mathrm{phon}}} \tag{5.78}$$

$$- \left(i\hbar\frac{\partial}{\partial t}(\langle P_1^\dagger\rangle)\langle P_2 b_3\rangle + \langle P_1^\dagger\rangle i\hbar\frac{\partial}{\partial t}\langle P_2 b_3\rangle\right)\Big|_{H=H_{c-\mathrm{phon}}} \tag{5.79}$$

$$- \left(i\hbar\frac{\partial}{\partial t}(\langle P_2\rangle)\langle P_1^\dagger b_3\rangle + \langle P_2\rangle i\hbar\frac{\partial}{\partial t}\langle P_1^\dagger b_3\rangle\right)\Big|_{H=H_{c-\mathrm{phon}}} \tag{5.80}$$

$$= \sum_{ab} g_{2ab}(\langle P_1^\dagger P_a b_b b_3\rangle + \langle P_1^\dagger P_a b_{-b}^\dagger b_3\rangle) - \sum_{ab} g_{1ab}(\langle P_a^\dagger P_2 b_{-b} b_3\rangle + \langle P_a^\dagger P_2 b_b^\dagger b_3\rangle) \tag{5.81}$$

$$+ \sum_{ab} g_{ab-3}\langle P_1^\dagger P_2 P_a^\dagger P_b\rangle \tag{5.82}$$

$$- \left(\sum_{ab} g_{2ab}(\langle P_1^\dagger\rangle\langle P_a b_b b_3\rangle + \langle P_1^\dagger\rangle\langle P_a b_3 b_{-b}^\dagger\rangle) - \sum_{ab} g_{1ab}\left(\langle P_a b_b\rangle\langle P_2 b_3\rangle + \langle P_a b_{-b}^\dagger\rangle\langle P_2 b_3\rangle\right)\right) \tag{5.83}$$

$$- \left(\sum_{ab} g_{2ab}(\langle P_a b_b\rangle\langle P_1^\dagger b_3\rangle + \langle P_a b_{-b}^\dagger\rangle\langle P_1^\dagger b_3\rangle) - \sum_{ab} g_{1ab}\left(\langle P_2\rangle\langle P_a b_3^\dagger b_b\rangle + \langle P_2\rangle\langle P_a b_3^\dagger b_{-b}^\dagger\rangle\right)\right) \tag{5.84}$$

$$= \sum_{ab} g_{2ab}(\langle P_1^\dagger P_a b_b b_3\rangle + \langle P_1^\dagger P_a b_3 b_{-b}^\dagger\rangle) - \sum_{ab} g_{1ab}(\langle P_a^\dagger P_2 b_{-b} b_3\rangle + \langle P_a^\dagger P_2 b_b^\dagger b_3\rangle) \tag{5.85}$$

$$+ \sum_{ab} g_{ab-3}\langle P_1^\dagger P_a^\dagger P_2 P_b\rangle + \sum_a g_{2a-3}\langle P_1^\dagger P_a\rangle - \sum_a g_{2a-3}\langle P_1^\dagger P_a\rangle \tag{5.86}$$

$$- \left(\sum_{ab} g_{2ab}(\langle P_1^\dagger\rangle\langle P_a b_b b_3\rangle + \langle P_1^\dagger\rangle\langle P_a b_3 b_{-b}^\dagger\rangle) - \sum_{ab} g_{1ab}\left(\langle P_2\rangle\langle P_a b_3^\dagger b_b\rangle + \langle P_2\rangle\langle P_a b_3^\dagger b_{-b}^\dagger\rangle\right)\right) \tag{5.87}$$

$$- \left(\sum_{ab} g_{2ab}\left(\langle P_a b_b\rangle\langle P_1 b_3^\dagger\rangle + \langle P_a b_{-b}^\dagger\rangle\langle P_1 b_3^\dagger\rangle\right) - \sum_{ab} g_{1ab}\left(\langle P_a b_b\rangle\langle P_2 b_3\rangle + \langle P_a b_{-b}^\dagger\rangle\langle P_2 b_3\rangle\right)\right). \tag{5.88}$$

Now it is time to perform a correlation expansion of our 4-operator quantity

$$\langle P_1^\dagger P_2 b_3 b_4\rangle \approx \langle P_1^\dagger P_2\rangle\langle b_3 b_4\rangle + \langle P_1^\dagger b_3\rangle\langle P_2 b_4\rangle + \langle P_1^\dagger b_4\rangle\langle P_2 b_3\rangle, \tag{5.89}$$

while we use the same Born approximation as before for

$$\langle P_1 b_2 b_3\rangle \approx \langle P_1\rangle\langle b_2 b_3\rangle. \tag{5.90}$$

We then neglect the $\langle b_1 b_2\rangle$ and $\langle b_1^\dagger b_2^\dagger\rangle$ terms because we are only interested in incoherent phonons, and then we finally neglect the $\langle P_1^\dagger P_a^\dagger P_2 P_b\rangle$ term. Doing all of this then results in

$$i\hbar\frac{\partial}{\partial t}\delta O_{123}\bigg|_{H=H_{c-\text{phon}}} \tag{5.91}$$

$$\approx \sum_{ab} g_{2ab}(\langle P_1^\dagger P_a\rangle - \langle P_1^\dagger\rangle\langle P_a\rangle)\langle b_3 b_{-b}^\dagger\rangle - \sum_{ab} g_{1ab}(\langle P_a^\dagger P_2\rangle - \langle P_a^\dagger\rangle\langle P_2\rangle)\langle b_b^\dagger b_3\rangle \tag{5.92}$$

$$+ \sum_{ab} g_{2ab}(\langle P_1^\dagger b_b\rangle\langle P_a b_3\rangle + \langle P_1^\dagger b_3\rangle\langle P_a b_b\rangle) - \sum_{ab} g_{1ab}(\langle P_a^\dagger b_3\rangle\langle P_2 b_{-b}\rangle + \langle P_a^\dagger b_{-b}\rangle\langle P_2 b_3\rangle) \tag{5.93}$$

$$+ \sum_{ab} g_{2ab}(\langle P_1^\dagger b_{-b}^\dagger\rangle\langle P_a b_3\rangle + \langle P_1^\dagger b_3\rangle\langle P_a b_{-b}^\dagger\rangle) - \sum_{ab} g_{1ab}(\langle P_a^\dagger b_3\rangle\langle P_2 b_b^\dagger\rangle + \langle P_a^\dagger b_b^\dagger\rangle\langle P_2 b_3\rangle) \tag{5.94}$$

$$- \left(\sum_{ab} g_{2ab}\left(\langle P_a b_b\rangle\langle P_1 b_3^\dagger\rangle + \langle P_a b_{-b}^\dagger\rangle\langle P_1 b_3^\dagger\rangle\right) - \sum_{ab} g_{1ab}\left(\langle P_a b_b\rangle\langle P_2 b_3\rangle + \langle P_a b_{-b}^\dagger\rangle\langle P_2 b_3\rangle\right)\right) \tag{5.95}$$

$$= \sum_{ab} g_{2ab}\delta N_{1a}\langle b_3 b_{-b}^\dagger\rangle - \sum_{ab} g_{1ab}\delta N_{a2}\langle b_b^\dagger b_3\rangle \tag{5.96}$$

$$+ \sum_{ab} g_{2ab}\left(\widetilde{S}_{1b}S_{a3}\right) - \sum_{ab} g_{1ab}\left(\tilde{S}_{a3}S_{2-b}\right) \tag{5.97}$$

$$+ \sum_{ab} g_{2ab}\left(S_{1-b}S_{a3}\right) - \sum_{ab} g_{1ab}\left(\tilde{S}_{a3}\tilde{S}_{2b}\right), \tag{5.98}$$

which once again can be simplified further by identifying $\langle b_1^\dagger b_2\rangle = n_1\delta_{12}$ and $\langle b_1 b_2^\dagger\rangle = (1+n_1)\delta_{12}$ to obtain our final expression,

$$i\hbar\frac{\partial}{\partial t}\delta O_{123}\bigg|_{H=H_{c-\text{phon}}} \tag{5.99}$$

$$= \sum_{ab} g_{2ab}\left(\widetilde{S}_{1b}S_{a3} + S_{1-b}S_{a3} + \delta N_{1a}(1+n_3)\delta_{b-3}\right) - \sum_{ab} g_{1ab}\left(\tilde{S}_{a3}S_{2-b} + \tilde{S}_{a3}\tilde{S}_{2b} + \delta N_{a2}n_3\delta_{b3}\right). \tag{5.100}$$

For $\tilde{O}$ we get the same expressions (with $\tilde{O}$ instead of O) for the non-phonon related terms, while the rest in the same way become

$$i\hbar\frac{\partial}{\partial t}\delta\tilde{O}_{123}\bigg|_{H=H_{0,\text{phon}}} = -\mathcal{E}_3\delta\tilde{O}_{123} \tag{5.101}$$

and

$$i\hbar\frac{\partial}{\partial t}\delta\tilde{O}_{123}\bigg|_{H=H_{c-\text{phon}}} = \sum_{ab} g_{2ab}\left(S_{1b}\tilde{S}_{a3} + \tilde{S}_{1-b}\tilde{S}_{a3} + \delta N_{1a}n_3\delta_{b3}\right) \tag{5.102}$$

$$- \sum_{ab} g_{1ab}\left(S_{a3}\tilde{S}_{2-b} + S_{a3}S_{2b} + \delta N_{a2}(1+n_3)\delta_{b-3}\right). \tag{5.103}$$

5.2 Simplifying the density equation

We now have arrived at the equation

$$
\begin{aligned}
i\hbar\frac{\partial}{\partial t}\delta N_{12} &= (E_2 - E_1)\delta N_{12} && (5.104)\\
&+ \sum_a \left(M_{2a}\delta\tilde{\mathcal{T}}_{1a} - M_{1a}\delta\tilde{\mathcal{T}}_{2a}\right) && (5.105)\\
&+ \sum_{ab} g_{2ab}(\delta O_{1ab} + \delta\tilde{O}_{1a-b}) - \sum_{ab} g_{1a-b}(\delta O_{a2b} + \delta\tilde{O}_{a2-b}) && (5.106)\\
&+ \sum_{ab} g_{2ab}p_a\left(\delta\tilde{S}_{1b} + \delta S_{1-b}\right) - \sum_{ab} g_{1a-b}p_a(\delta S_{2b} + \delta\tilde{S}_{2-b}) && (5.107)\\
&+ \sum_a T_{2a}\delta N_{1a} - \sum_a T_{1a}\delta N_{a2}, && (5.108)
\end{aligned}
$$

where the photon assisted polarization follows

$$
\begin{aligned}
i\hbar\frac{\partial}{\partial t}\delta\tilde{\mathcal{T}}_{12} &= (E_1 - \hbar\omega_2)\delta\tilde{\mathcal{T}}_{12} && (5.109)\\
&- \sum_a M_{a2}\delta N_{a1} && (5.110)\\
&+ \sum_a T_{1a}\delta\tilde{\mathcal{T}}_{a2} && (5.111)
\end{aligned}
$$

and the phonon assisted densities obey

$$
\begin{aligned}
i\hbar\frac{\partial}{\partial t}\delta O_{123} &= (E_2 - E_1 + \mathcal{E}_3)\delta O_{123} && (5.112)\\
&+ \sum_{ab} g_{2ab}\left(\widetilde{S}_{1b}S_{a3} + S_{1-b}S_{a3} + \delta N_{1a}(1+n_3)\delta_{b-3}\right) && (5.113)\\
&- \sum_{ab} g_{1ab}\left(\tilde{S}_{a3}S_{2-b} + \tilde{S}_{a3}\tilde{S}_{2b} + \delta N_{a2}n_3\delta_{b3}\right) && (5.114)\\
&+ \sum_a T_{2a}\delta O_{1a3} - \sum_a T_{1a}\delta O_{a23} && (5.115)
\end{aligned}
$$

and

$$
\begin{aligned}
i\hbar\frac{\partial}{\partial t}\delta\tilde{O}_{123} &= (E_2 - E_1 - \mathcal{E}_3)\delta\tilde{O}_{123} && (5.116)\\
&+ \sum_{ab} g_{2ab}\left(S_{1b}\tilde{S}_{a3} + \tilde{S}_{1-b}\tilde{S}_{a3} + \delta N_{1a}n_3\delta_{b3}\right) && (5.117)\\
&- \sum_{ab} g_{1ab}\left(S_{a3}\tilde{S}_{2-b} + S_{a3}S_{2b} + \delta N_{a2}(1+n_3)\delta_{b-3}\right) && (5.118)\\
&+ \sum_a T_{2a}\delta\tilde{O}_{1a3} - \sum_a T_{1a}\delta\tilde{O}_{a23}. && (5.119)
\end{aligned}
$$

Like we did for the phonon assisted polarizations in 4.1.2 we will now proceed to find approximate expressions for the photon assisted polarization and the phonon assisted densities. Just like earlier the tunneling contributions will be neglected since the delta functions will contain interlayer energy differences, which are relatively

large compared to the contents of the other delta functions. The terms containing the phonon assisted polarizations will be neglected as well since the final expression would contain a product of three delta functions. Using these modifications we then end up with

$$\delta\tilde{\mathcal{T}}_{12} \approx -\frac{\pi}{i\hbar}\sum_a M_{a2}\delta N_{a1}\delta(E_a - \hbar\omega_2) \tag{5.120}$$

$$\delta O_{123} \approx \frac{\pi}{i\hbar}\sum_a g_{2a-3}\delta N_{1a}(1+n_3)\delta(E_2 - E_a + \mathcal{E}_3) \tag{5.121}$$

$$-\frac{\pi}{i\hbar}\sum_a g_{1a3}\delta N_{a2}n_3\delta(E_a - E_1 + \mathcal{E}_3) \tag{5.122}$$

and

$$\delta\tilde{O}_{123} \approx \frac{\pi}{i\hbar}\sum_a g_{2a3}\delta N_{1a}n_3\delta(E_2 - E_a - \mathcal{E}_3) \tag{5.123}$$

$$-\frac{\pi}{i\hbar}\sum_a g_{1a-3}\delta N_{a2}(1+n_3)\delta(E_a - E_1 - \mathcal{E}_3). \tag{5.124}$$

Inserting this into the density equation then results in

$$\frac{\partial}{\partial t}\delta N_{12} \tag{5.125}$$

$$= \frac{1}{i\hbar}(E_2 - E_1)\delta N_{12} \tag{5.126}$$

$$-\frac{\pi}{\hbar^2}\sum_{ab}\left(M_{2a}M_{ab}\delta N_{a1} + M_{1b}M_{ab}\delta N_{a2}\right)\delta(E_a - \hbar\omega_b) \tag{5.127}$$

$$-\frac{\pi}{\hbar^2}\sum_{abc} g_{2ac}\left(g_{ab-c}\delta N_{1b}(1+n_c)\delta(E_a - E_b + \mathcal{E}_c) - g_{1bc}\delta N_{ba}n_c\delta(E_b - E_1 + \mathcal{E}_c)\right) \tag{5.128}$$

$$-\frac{\pi}{\hbar^2}\sum_{abc} g_{2ac}\left(g_{ab-c}\delta N_{1b}n_{-c}\delta(E_a - E_b - \mathcal{E}_{-c}) - g_{1bc}\delta N_{ba}(1+n_{-c})\delta(E_b - E_1 - \mathcal{E}_{-c})\right) \tag{5.129}$$

$$-\frac{\pi}{\hbar^2}\sum_{abc} g_{1a-c}\left(g_{2b-c}\delta N_{ab}(1+n_c)\delta(E_2 - E_b + \mathcal{E}_c) - g_{abc}\delta N_{b2}n_c\delta(E_b - E_a + \mathcal{E}_c)\right) \tag{5.130}$$

$$-\frac{\pi}{\hbar^2}\sum_{abc} g_{1a-c}\left(g_{2b-c}\delta N_{ab}n_{-c}\delta(E_2 - E_b - \mathcal{E}_{-c}) - g_{abc}\delta N_{b2}(1+n_{-c})\delta(E_b - E_a - \mathcal{E}_{-c})\right) \tag{5.131}$$

$$+\frac{\pi}{\hbar^2}\sum_{abc} g_{2ac}p_a\left(g_{1bc}p_b n_c\delta(E_1 - E_b - \mathcal{E}_c) + g_{1bc}p_b(1+n_{-c})\delta(E_1 - E_b + \mathcal{E}_{-c})\right) \tag{5.132}$$

$$+\frac{\pi}{\hbar^2}\sum_{abc} g_{1a-c}p_a(g_{2b-c}p_b(1+n_c)\delta(E_2 - E_b + \mathcal{E}_c) + g_{2b-c}p_b n_{-c}\delta(E_2 - E_b - \mathcal{E}_{-c})) \tag{5.133}$$

$$+\frac{1}{i\hbar}\sum_a T_{2a}\delta N_{1a} - \frac{1}{i\hbar}\sum_a T_{1a}\delta N_{a2}. \tag{5.134}$$

What we normally would like to do now is to focus only on densities by enforcing $\delta N_{12} = \delta N_1 \delta_{12}$. If we do this for the tunneling terms they will disappear though, since we would obtain factors like $\delta_{l_1 l_2}\delta_{l_1 \bar{l}_2}$. To circumvent this we treat the coupled equations

$$i\hbar \frac{\partial}{\partial t}\delta N_{12}\bigg|_{H=H_0+H_T} = (E_2 - E_1)\delta N_{12} \tag{5.135}$$

$$+ \sum_a T_{2a}\delta N_{1a} - \sum_a T_{1a}\delta N_{a2} \tag{5.136}$$

and

$$i\hbar \frac{\partial}{\partial t}\delta N_1\bigg|_{H=H_0+H_T} = \sum_a T_{1a}\delta N_{1a} - \sum_a T_{1a}\delta N_{a1} \tag{5.137}$$

$$= 2i\sum_a \mathrm{Im}(T_{1a}\delta N_{1a}) \tag{5.138}$$

separately. By using a Markov approximation to find an approximate solution to (5.135) we get

$$\delta N_{12}|_{H_0+H_T} \approx \frac{\pi}{i\hbar}\sum_a T_{2a}\delta N_{1a}\delta(E_2 - E_a) - \frac{\pi}{i\hbar}\sum_a T_{1a}\delta N_{a2}\delta(E_a - E_1). \tag{5.139}$$

By inserting this into (5.137) and now enforcing $\delta N_{12} = \delta N_1 \delta_{12}$ then gives us

$$i\hbar \frac{\partial}{\partial t}\delta N_1\bigg|_{H=H_0+H_T} \approx 2i\sum_{ab}\mathrm{Im}\left(T_{1a}\frac{\pi}{i\hbar}\left(T_{ab}\delta N_{1b}\delta(E_a - E_b) - T_{1b}\delta N_{ba}\delta(E_b - E_1)\right)\right) \tag{5.140}$$

$$= -\frac{2\pi i}{\hbar}\sum_a \mathrm{Im}\left(T_{1a}\left(T_{a1}\delta N_1 - T_{1a}\delta N_a\right)\right)\delta(E_a - E_1) \tag{5.141}$$

$$= \frac{2\pi i}{\hbar}\sum_a |T_{1a}|^2(\delta N_a - \delta N_1)\delta(E_a - E_1). \tag{5.142}$$

An interesting fact is that this is the same expression that would have been obtained using Fermi's golden rule.

With this out of the way we can now finally obtain

$$\frac{\partial}{\partial t}\delta N_1 = -\frac{2\pi}{\hbar^2}\sum_a |M_{1a}|^2 \delta N_1 \delta(E_1 - \hbar\omega_a) \tag{5.143}$$

$$- \frac{\pi}{\hbar^2}\sum_{ab} |g_{1ab}|^2 (\delta N_1(1+n_b)\delta(E_a - E_1 + \mathcal{E}_b) - \delta N_a n_b \delta(E_a - E_1 + \mathcal{E}_b)) \tag{5.144}$$

$$- \frac{\pi}{\hbar^2}\sum_{ab} |g_{1ab}|^2 (\delta N_1 n_b \delta(E_a - E_1 - \mathcal{E}_b) - \delta N_a(1+n_b)\delta(E_a - E_1 - \mathcal{E}_b)) \tag{5.145}$$

$$- \frac{\pi}{\hbar^2}\sum_{ab} |g_{1ab}|^2 (\delta N_a(1+n_b)\delta(E_1 - E_a + \mathcal{E}_b) - \delta N_1 n_b \delta(E_1 - E_a + \mathcal{E}_b)) \tag{5.146}$$

$$- \frac{\pi}{\hbar^2}\sum_{ab} |g_{1ab}|^2 (\delta N_a n_b \delta(E_1 - E_a - \mathcal{E}_b) - \delta N_1(1+n_b)\delta(E_1 - E_a - \mathcal{E}_b)) \tag{5.147}$$

$$+ \frac{\pi}{\hbar^2}\sum_{abc} g_{1ac} g_{1bc} p_a p_b (n_c \delta(E_1 - E_b - \mathcal{E}_c) + (1+n_c)\delta(E_1 - E_b + \mathcal{E}_c)) \tag{5.148}$$

$$+ \frac{\pi}{\hbar^2}\sum_{abc} g_{1ac} g_{1bc} p_a p_b ((1+n_c)\delta(E_1 - E_b + \mathcal{E}_c) + n_c \delta(E_1 - E_b - \mathcal{E}_c)) \tag{5.149}$$

$$+ \frac{2\pi}{\hbar^2}\sum_a |T_{1a}|^2 (\delta N_a - \delta N_1)\delta(E_a - E_1). \tag{5.150}$$

If we now look at the first term we can see that it is strikingly similar to a term we had in the Bloch equation in 4.2. In fact, we can perform the same approximation here and use

$$\frac{2\pi}{\hbar^2}\sum_a |M_{1a}|^2 \delta N_1 \delta(E_1 - \hbar\omega_a) \approx 2\gamma_{\text{rad}}^{11} \delta N_1 \delta_{s_{e_1} s_{h_1}} \delta_{\boldsymbol{Q}_1, \mathbf{0}} \tag{5.151}$$

We also introduce a new index that we simply call "$\pm$", which takes on the "values" $+$ and $-$. By doing this we can contract our density equation to

$$\frac{\partial}{\partial t}\delta N_1 = -2\gamma_{\text{rad}}^{11} \delta N_1 \delta_{s_{e_1} s_{h_1}} \delta_{\boldsymbol{Q}_1, \mathbf{0}} \tag{5.152}$$

$$- \frac{2\pi}{\hbar^2}\sum_{ab\pm} |g_{1ab}|^2 \delta N_1 \left(\frac{1}{2} \pm \frac{1}{2} + n_b\right) \delta(E_a - E_1 \pm \mathcal{E}_b) \tag{5.153}$$

$$+ \frac{2\pi}{\hbar^2}\sum_{ab\pm} |g_{1ab}|^2 \delta N_a \left(\frac{1}{2} \pm \frac{1}{2} + n_b\right) \delta(E_1 - E_a \pm \mathcal{E}_b) \tag{5.154}$$

$$+ \frac{2\pi}{\hbar^2}\sum_{abc\pm} \text{Re}\left(g_{1ac} g_{1bc} p_a p_b\right) \left(\frac{1}{2} \pm \frac{1}{2} + n_b\right) \delta(E_1 - E_b \pm \mathcal{E}_c) \tag{5.155}$$

$$+ \frac{2\pi}{\hbar^2}\sum_a |T_{1a}|^2 (\delta N_a - \delta N_1)\delta(E_a - E_1). \tag{5.156}$$

Now that we have gotten this far it is finally time to expand the indices. As we do not have any processes that do not conserve the spin we can shorten our notation

to only include a single spin index instead of one for the electron and one for the hole. Doing this leads to the exciton density equation:

$$\frac{\partial}{\partial t}\delta N_{\boldsymbol{Q}_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} \tag{5.157}$$

$$= -2\gamma_{\text{rad}}^{\mu_1 s_1 l_{h_1} l_{e_1}} \delta N_{\boldsymbol{0}}^{\mu_1 s_1 l_{h_1} l_{e_1}} \delta_{\boldsymbol{Q}_1,\boldsymbol{0}} \tag{5.158}$$

$$- \frac{2\pi}{\hbar^2} \sum_{\boldsymbol{K} l\alpha\mu\pm} \left| g_{\boldsymbol{Q}_1+\boldsymbol{K},-\boldsymbol{K}}^{s_1 l_{h_1} l_{e_1} l\alpha\mu_1\mu} \right|^2 \delta N_{\boldsymbol{Q}_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} \left(\frac{1}{2} \pm \frac{1}{2} + n_{\boldsymbol{K}}^{l\alpha} \right) \delta \left(E_{\boldsymbol{Q}_1+\boldsymbol{K}}^{\mu s_1 l_{h_1} l_{e_1}} - E_{\boldsymbol{Q}_1}^{\mu s_1 l_{h_1} l_{e_1}} \pm \mathcal{E}_{\boldsymbol{K}}^{l\alpha} \right) \tag{5.159}$$

$$+ \frac{2\pi}{\hbar^2} \sum_{\boldsymbol{K} l\alpha\mu\pm} \left| g_{\boldsymbol{Q}_1+\boldsymbol{K},-\boldsymbol{K}}^{s_1 l_{h_1} l_{e_1} l\alpha\mu_1\mu} \right|^2 \delta N_{\boldsymbol{Q}_1+\boldsymbol{K}}^{\mu s_1 l_{h_1} l_{e_1}} \left(\frac{1}{2} \pm \frac{1}{2} + n_{\boldsymbol{K}}^{l\alpha} \right) \delta \left(E_{\boldsymbol{Q}_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} - E_{\boldsymbol{Q}_1+\boldsymbol{K}}^{\mu s_1 l_{h_1} l_{e_1}} \pm \mathcal{E}_{\boldsymbol{K}}^{l\alpha} \right) \tag{5.160}$$

$$+ \frac{2\pi}{\hbar^2} \sum_{\boldsymbol{K} l\alpha\mu\nu\pm} \text{Re} \left(g_{\boldsymbol{Q}_1+\boldsymbol{K},-\boldsymbol{K}}^{s_1 l_{h_1} l_{e_1} l\alpha\mu_1\mu} g_{\boldsymbol{Q}_1+\boldsymbol{K},-\boldsymbol{K}}^{s_1 l_{h_1} l_{e_1} l\alpha\mu_1\nu} p_{\boldsymbol{Q}_1+\boldsymbol{K}}^{\mu s_1 l_{h_1} l_{e_1}} p_{\boldsymbol{Q}_1+\boldsymbol{K}}^{\nu s_1 l_{h_1} l_{e_1}} \right) \tag{5.161}$$

$$\cdot \left(\frac{1}{2} \pm \frac{1}{2} + n_{\boldsymbol{K}}^{l\alpha} \right) \delta \left(E_{\boldsymbol{Q}_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} - E_{\boldsymbol{Q}_1+\boldsymbol{K}}^{\nu s_1 l_{h_1} l_{e_1}} \pm \mathcal{E}_{\boldsymbol{K}}^{l\alpha} \right) \tag{5.162}$$

$$+ \frac{2\pi}{\hbar^2} \sum_{\boldsymbol{Q} l_h l_e \mu} \left| T_{\boldsymbol{Q}_1,\boldsymbol{Q}}^{s_1 l_{h_1} l_{e_1} l_h l_e \mu_1 \mu} \right|^2 \left(\delta N_{\boldsymbol{Q}}^{\mu s_1 l_h l_e} - \delta N_{\boldsymbol{Q}_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} \right) \delta \left(E_{\boldsymbol{Q}}^{\mu s_1 l_h l_e} - E_{\boldsymbol{Q}_1}^{\mu_1 s_1 l_{h_1} l_{e_1}} \right). \tag{5.163}$$

Now, after all this work, we can finally start analyzing the equation. We can see that the first row describes radiative decay of the exciton densities. The next two rows describe exciton-phonon scattering while the fourth row shows how incoherent exciton densities can form from the non-radiative decay of coherent densities. Finally the last row describes how inter and intralayer excitons will form from intra- and interlayer ones through tunneling.

5.3 Solving the density equation

For solving the density equation numerically the same methods as for the Bloch equation were used. For the tunneling matrix element some further simplifications were made however. Without DFT input we have to resort to using the overlap integral $M_T^{ab} \equiv \langle \Phi_a | e^{i(\boldsymbol{k}_b - \boldsymbol{k}_a)\cdot \boldsymbol{r}} | \Phi_b \rangle$ and correlation length L_C as parameters. Since we wanted as few parameters as possible we ignored the index dependence of M_T, reducing the number of parameters to two. We will also restrict ourselves to the lowest excitonic energy states for the sake of saving computation time (we have seen in the absorption spectrum that a relatively small number of these get absorbed and the increasing sharpness of the wavefunctions means that the matrix elements will decrease in size), and A excitons. The reason for excluding the B excitons is that without including either spin flipping or intervalley processes we have no way for them to decay to the ground state,which is what the rest of the thesis will be all about. This is definitely something that could be worth looking into in the future though.

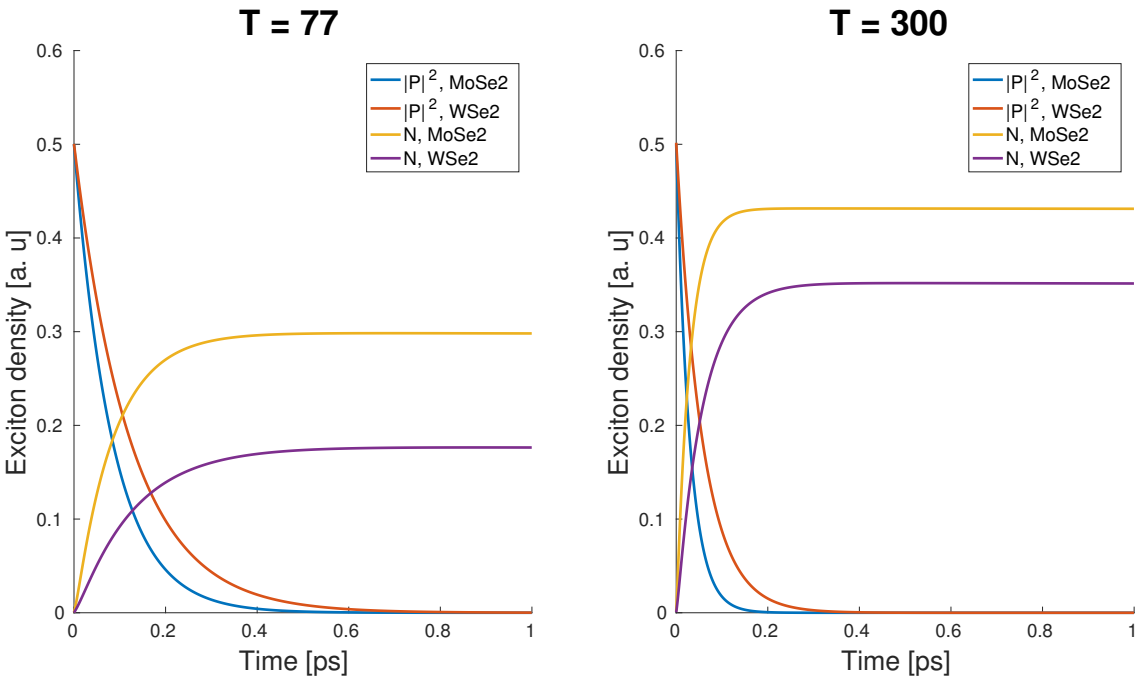

Figure 5.1: In this figure the total number of intralayer exciton densities can be seen plotted against time for temperatures $T = 300, 77\,\mathrm{K}$. Here we can see how most of the coherent densities dephase into incoherent ones at a rate that lessens with the temperature. The missing number have been lost to radiative dephasing. We can also see that an equilibrium is reached within a timescale of hundreds of fs.

In 5.1 we have have plotted the total number (normalized) of intralayer excitons against time, separated into layers and coherency, for the temperatures $T = 300, 77\,\mathrm{K}$ and without the tunneling. We can see here that the system reaches an equilibrium within a timespan of hundreds of fs. We can also see how the incoherent excitons are created as the coherent ones disappear. The total number of incoherent excitons do not match that of the coherent ones however. The missing number corresponds to those that have decayed radiatively.

In Figure 5.2 we have a similar set of graphs. Here we have not integrated over the momentum however, in order to see how the excitons' momentum distribution looks. We have left out the coherent excitons, since these are zero for $Q \neq 0$ with the tunneling neglected. In these we can see that the exciton densities are centered around $Q = 0$, decreasing with larger momenta. This can be easily explained by looking at the electronic dispersion, since $Q = 0$ is the energetic minimum. We can also see that the distribution becomes narrower for lower temperatures, which can be explained by the phonon occupation decreasing making it harder to absorb phonons (the terms containing $n_{\boldsymbol{K}}$) while not affecting the emission that much (the terms containing $1 + n_{\boldsymbol{K}}$).

The experiment we are trying to predict was performed at $T = 4.5\,\mathrm{K}$, a temperature low enough that it is not a bad approximation to say that for the purpose of calculating the tunneling element all excitons can be assumed to lie at zero momentum.

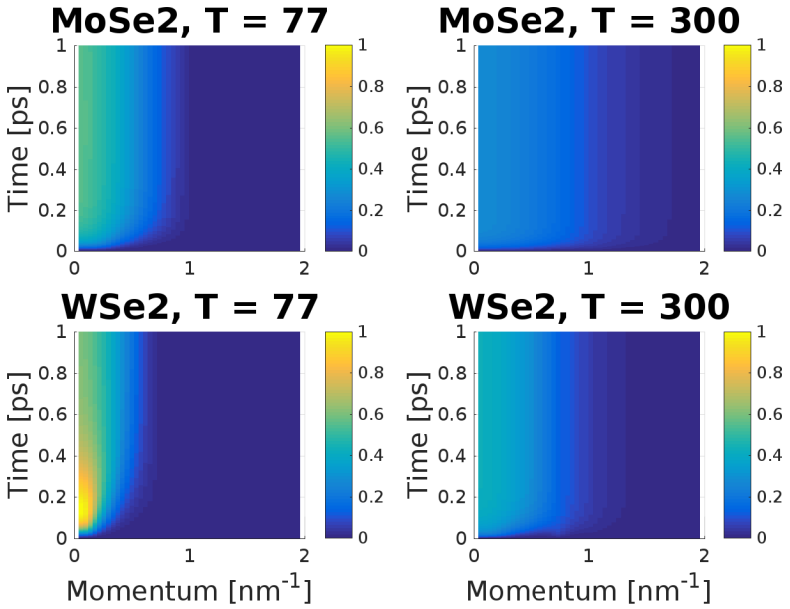

Figure 5.2: In this figure the incoherent intralayer exciton densities can be seen plotted against time and momentum for temperatures $T = 300, 77\,\mathrm{K}$. Here we can see that the densities increase with lower Q, and that the distribution gets narrower for lower temperatures.

In other words we can reduce the effective element to

$$\left|T^{s_1 l_{h_1} l_{e_1} l_h l_e \mu_1 \mu}_{\boldsymbol{Q}_{0_1}, \boldsymbol{Q}_0}\right|^2 \left(\delta N^{\mu s_1 l_h l_e}_{\boldsymbol{Q}} - \delta N^{\mu_1 s_1 l_{h_1} l_{e_1}}_{\boldsymbol{Q}_1}\right) \delta\left(E^{\mu s_1 l_h l_e}_{\boldsymbol{Q}} - E^{\mu_1 s_1 l_{h_1} l_{e_1}}_{\boldsymbol{Q}_1}\right), \tag{5.164}$$

where $\boldsymbol{Q}_{0_1}$ and $\boldsymbol{Q}_0$ are the lowest possible momenta that obey the energy conservation enforced by the delta function. By consequence one of them will be zero while the other will be as low as it can be. These momenta will therefore be uniquely determined by the spin, layer and energy level indices.

The part of the tunneling Hamiltonian that involves L_C is given by

$$\frac{\pi L_C^2}{\left(1 + \frac{\boldsymbol{q}^2 L_C^2}{2}\right)^{\frac{3}{2}}}. \tag{5.165}$$

If we then look at the full element in the excitonic picture we can then see that this $\boldsymbol{q}$ is precisely the difference between these two momenta, meaning that for a fixed set of spin, layer and energy level indices this will be a constant. If we then assume that $\frac{\boldsymbol{q}^2 L_C^2}{2}$ is significantly larger than 1 we can finally find

$$M_T \frac{\pi L_C^2}{\left(1 + \frac{\boldsymbol{q}^2 L_C^2}{2}\right)^{\frac{3}{2}}} \approx \frac{M_T}{L_C} \frac{2^{\frac{2}{3}} \pi}{q^3}, \tag{5.166}$$

meaning that we can treat $\frac{M_T}{L_C}$ as a single parameter as long as L_C is large enough. The relevant momenta turn out to be a bit over $2\,\mathrm{nm}^{-1}$, meaning that a value as small as $L_C = 2\,\mathrm{nm}$ does not give too bad of an approximation.

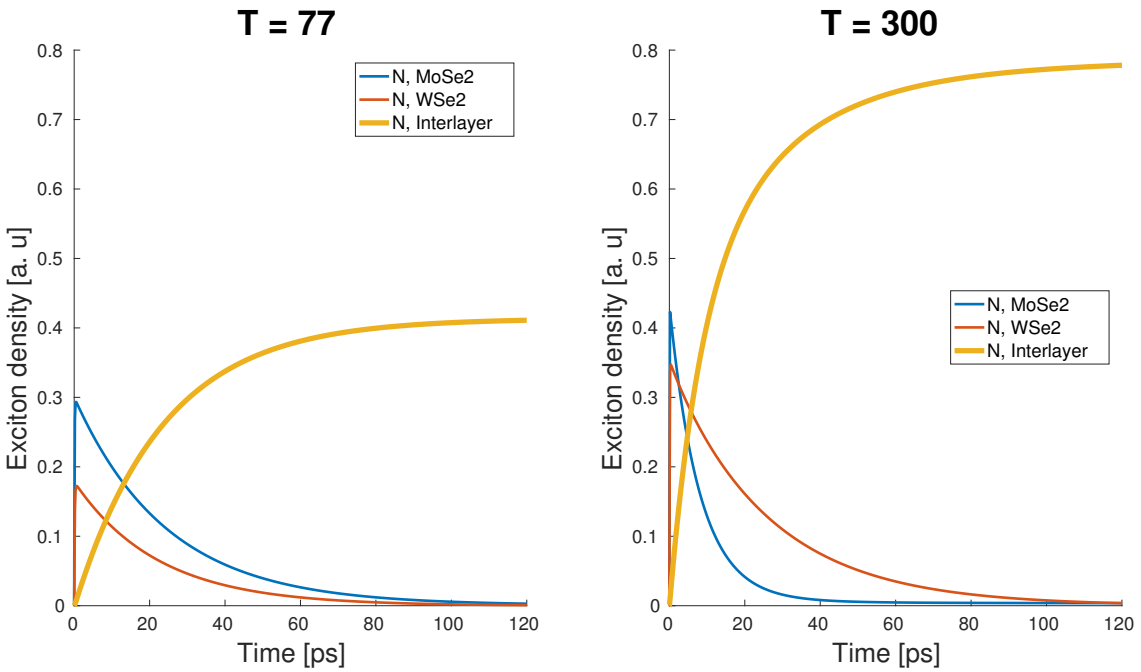

Figure 5.3: In this figure the total number of exciton densities can be seen plotted against time for temperatures $T = 300, 77\,\mathrm{K}$. Here we can see how the intralayer densities eventually get transformed into interlayer densities (specifically the energetically lower one) through tunneling, at a much larger timescale (about 100 ps) than the one for the phonon scattering. We can also see another interesting detail. For $T = 77\,\mathrm{K}$ the intralayer excitons decay at similar rates, while the $MoSe_2$ one clearly decays faster for $T = 300\,\mathrm{K}$. This can be explained by looking at Figure 5.5. There we can see that while the WSe_2 and interlayer dispersions have similar curvatures, the one for $MoSe_2$ is a bit lower. This means that for higher $\boldsymbol{Q}$ the momentum transfer will be smaller, meaning that the tunnelling matrix element will be larger. Since, as we can see in Figure 5.2, the states with higher momenta are more populated for higher temperatures, this effect gets more pronounced for $T = 300\,\mathrm{K}$ than $77\,\mathrm{K}$

The results for $\frac{M_T}{L_C} = 2\,{}^{\mathrm{meV}}/_{\mathrm{nm}}$ can be seen in Figures 5.3 and 5.4. These have the same structure as Figures 5.1 and 5.2, but now have the two interlayer densities added as well. Unlike the previous case, we can now clearly see how the intralayer densities decrease as the interlayer ones increase. It is however done at a much slower pace than the phonon scattering, requiring a timescale in the order of 100 ps.

There is also an important asymmetry at work here. The tunneling element is symmetric, but at equilibrium we have all excitons gathered at the energetically lowest state, lower interlayer one. The reason for this is rather simple. While the tunneling element is symmetric the phonon element is not. As we have seen in the case where we did not include the tunneling, the excitons tend to gather at zero momentum. We also know that the equilibration time due to phonon scattering is much faster than the one due to tunneling, meaning that most excitons that have tunneled from an energetically higher state will scatter to a momentum too low

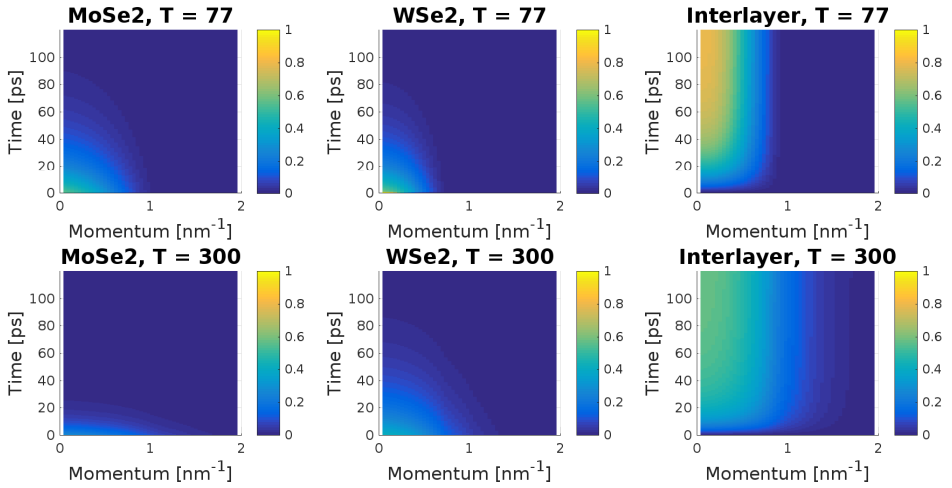

Figure 5.4: In this figure the incoherent exciton densities can be seen plotted against time and momentum for temperatures $T = 300, 77\,\mathrm{K}$. Here we can see how the interlayer densities slowly emerge through tunneling as the intralayer ones vanish. Only the energetically lower one gets populated though, which is as expected.

to tunnel back. Therefore they will all eventually end up at the lowest possible state in due time, provided that the temperature is not high enough to have a significant population at the momenta required for tunneling. This process can be seen illustrated in Figure 5.5.

5.3.1 Calculating the photoluminescence

We now want to use our solutions to both the Bloch and density equations to calculate the photoluminescence of the system. The intensity intensity can be written as

$$I(t) \propto \sum_a \frac{\partial}{\partial t} \langle c_a^\dagger c_a \rangle. \tag{5.167}$$

In other words we wave one more equation of motion to calculate, the one for the total photon density $\langle c_1^\dagger c_2 \rangle$. This can be easily accomplished using (4.39) and

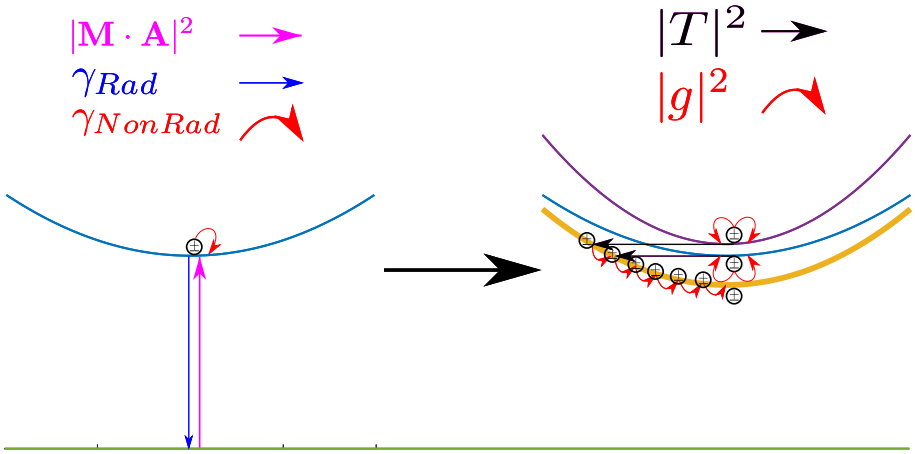

Figure 5.5: This figure is meant to illustrate how the optically excited coherent intralayer excitons end up in a specific incoherent interlayer exciton state. As the figure on the left (which only contains the dispersion for the $MoSe_2$ exciton) illustrates, the process starts with coherent excitons being excited optically, after which they dephase. Some do this radiatively, but the ones that do it through phonon scattering end up as incoherent densities. At this state there are practically only intralayer densities, since the interlayer optical matrix element is relatively small. The right figure (where the WSe_2 and lower interlayer excitons have been added) then shows how the newly formed incoherent excitons start decaying to energetically lower states. The higher ones tunnel to lower ones, after which they quickly scatter to lower momenta. This continues until they have all ended up in the lowest possible state, the WSe - MoSe interlayer one. During this time some zero momentum excitons decay radiatively, but this is not shown to avoid the figure getting cluttered.

(5.120), giving us

$$i\hbar\frac{\partial}{\partial t}\langle c_1^\dagger c_2\rangle = \langle c_1^\dagger \frac{\partial}{\partial t} c_2\rangle - \langle \left(\frac{\partial}{\partial t} c_1\right)^\dagger c_2\rangle \tag{5.168}$$

$$= \hbar\omega_2\langle c_1^\dagger c_2\rangle + \sum_a M_{a2}\langle P_a c_1^\dagger\rangle \tag{5.169}$$

$$- \hbar\omega_1\langle c_1^\dagger c_2\rangle - \sum_a M_{a1}\langle P_a^\dagger c_2\rangle \tag{5.170}$$

$$= (\hbar\omega_2 - \hbar\omega_1)\langle c_1^\dagger c_2\rangle + \sum_a M_{a2}\tilde{\mathcal{T}}_{a1} - \sum_a M_{a1}\tilde{\mathcal{T}}_{a2} \tag{5.171}$$

$$\approx (\hbar\omega_2 - \hbar\omega_1)\langle c_1^\dagger c_2\rangle \tag{5.172}$$

$$- \frac{\pi}{i\hbar}\sum_{ab} M_{a2}M_{b1}N_{ba}\delta(E_b - \hbar\omega_1) - \frac{\pi}{i\hbar}\sum_a M_{a1}M_{b2}N_{ba}\delta(E_b - \hbar\omega_2), \tag{5.173}$$

or in our case with $1 = 2$ and $N_{ab} = N_a\delta_{ab}$,

$$\frac{\partial}{\partial t}\langle c_1^\dagger c_1\rangle = \frac{\pi}{\hbar^2}\sum_a M_{a1}M_{a1}N_a\delta(E_a - \hbar\omega_1) + \frac{\pi}{\hbar^2}\sum_a M_{a1}M_{a1}N_a\delta(E_a - \hbar\omega_1) \tag{5.174}$$

$$= \frac{2\pi}{\hbar^2}\sum_a |M_{a1}|^2 N_a\delta(E_a - \hbar\omega_1) \tag{5.175}$$

$$= \frac{2\pi}{\hbar^2}\sum_a |M_{a1}|^2(|p_a|^2 + \delta N_a)\delta(E_a - \hbar\omega_1). \tag{5.176}$$

We can now finally obtain our intensity by inserting this into (5.167), resulting in

$$I(t) \propto \frac{2\pi}{\hbar^2}\sum_{ab} |M_{ab}|^2(|p_a|^2 + \delta N_a)\delta(E_a - \hbar\omega_b) \tag{5.177}$$

$$= \frac{2\pi}{\hbar^2}\sum_{\boldsymbol{Q}\boldsymbol{K}\sigma l_h l_e} |M_{\boldsymbol{Q}}^{l_h l_e\sigma}|^2(|p_{\boldsymbol{Q}}^{l_h l_e}(t)|^2 + \delta N_{\boldsymbol{Q}}^{l_h l_e}(t))\delta(E_{\boldsymbol{Q}}^{l_h l_e} - \hbar\omega_{\boldsymbol{K}}^\sigma)\delta_{\boldsymbol{Q},\boldsymbol{K}_\parallel}. \tag{5.178}$$

This is however not the form of the intensity we are after. Since this form contains a sum over the photon momentum, which is related to it's energy through the dispersion relation $h\omega_{\boldsymbol{K}} = \hbar c|\boldsymbol{K}|$ we can express the sum as a sum over frequency instead. By then choosing to examine the integrand we obtain the *time resolved photoluminescence*,

$$I(t,\omega) \propto \sum_{\boldsymbol{Q}\sigma l_h l_e} |M_{\boldsymbol{Q}}^{l_h l_e\sigma}|^2(|p_{\boldsymbol{Q}}^{l_h l_e}(t)|^2 + \delta N_{\boldsymbol{Q}}^{l_h l_e}(t))\delta(E_{\boldsymbol{Q}}^{l_h l_e} - \hbar\omega^\sigma)\delta_{\boldsymbol{Q},\boldsymbol{K}(\omega)_\parallel}. \tag{5.179}$$

We then use that the photon momentum is relatively small and perform the same approximation as before, leading to

$$I(t,\omega) \propto \sum_{l_h l_e} \gamma_{\text{rad}}^{l_{h_1} l_{e_1}}(|p_{\boldsymbol{0}}^{l_h l_e}(t)|^2 + \delta N_{\boldsymbol{0}}^{l_h l_e}(t))\delta(E_{\boldsymbol{0}}^{l_h l_e} - \hbar\omega). \tag{5.180}$$

By integrating this over time we then obtain the *time integrated photoluminescence*,

$$I(\omega) \propto \int_0^t \sum_{l_h l_e} \gamma_{\text{rad}}^{l_{h_1} l_{e_1}}(|p_{\boldsymbol{0}}^{l_h l_e}(t)|^2 + \delta N_{\boldsymbol{0}}^{l_h l_e}(t))\delta(E_{\boldsymbol{0}}^{l_h l_e} - \hbar\omega)\,\mathrm{d}t\,. \tag{5.181}$$

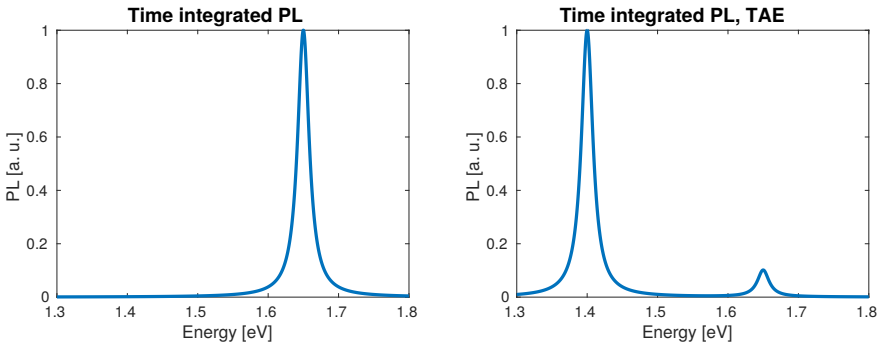

Figure 5.6: The left figure shows the calculated photoluminescence at 77 K for $\frac{M_T}{L_C} = 2\,{}^{\mathrm{meV}}/_{\mathrm{nm}}$, in which the interlayer peak can not be seen. For the right one an approximate form of tunneling assisted emission with $L_C = 2\,\mathrm{nm}$ has been applied, managing to give the interlayer peak a boost big enough to approximately replicate the amplitude difference seen in Figure 1.1. Note that the linewidth used is purely phenomenological. The one computed by this model was much too small, but that is also to be expected since various processes that would have contributed to it (such as the experimentally measurement time dependent redshift of the peak position [1] and intervalley coupling) have not been included.

In both cases the δ functions will be treated as Lorentzians with appropriate linewidths.

As we have stated before, the goal has been to try to recreate Figure 1.1. However, the code used turned out to be unstable for temperatures that low. For that reason we had to settle for $T = 77\,\mathrm{K}$ a temperature that has been shown to give stable results in the past [15]. This means that our approximation of viewing M_T and L_C as a single parameter is not as valid as it could have optimally been, but it will still have to do for now. As we will see soon, it is not the only approximation we have had to make. For the same value as before ($\frac{M_T}{L_C} = 2\,{}^{\mathrm{meV}}/_{\mathrm{nm}}$) the spectrum shown in the left part of 5.6. As we can see the interlayer peak is completely overshadowed by the intralayer one. The plan was to then increase $\frac{M_T}{L_C}$ until it appeared and see if the resulting value seemed physical or not. However, the code once again turned unstable. More specifically, the solution from the Runge-Kutta method started diverging for larger values.

Instead our attention was turned towards a different direction. When doing intervalley physics it is possible for a phonon moving an exciton from a dark state (a state that can not decay radiatively) to a bright one before decaying in a process called phonon-assisted emission. In loose term this makes the emission depend on $|gM_{\mathrm{bright}}|^2$ instead of $|M_{\mathrm{dark}}|^2 \approx 0$. Similarly, one possible way to increase the interlayer photoluminescence would be to introduce tunneling-assisted emission, where the exciton tunnels to an intralayer state before decaying. To test this possibility we let $\gamma_{\mathrm{Rad,inter}} \to |T_{0,0}|^2\gamma_{\mathrm{Rad,intra}}$. For low momenta the $\frac{M_T}{L_C}$ approximation does not work however. Instead we end up with $M_T L_C^2 = \frac{M_T}{L_C} L_C^3$, meaning that we have to choose a value for L_C. We decided to go with $L_C = 2$, meaning that the corresponding value for M_T would be 4 meV. Whether these are physically plausible or not is

hard to tell at the moment, but we can still make some inferences.

In the paper we got the L_C model from, [14], they they examined values from $L_C = 2\,\text{nm}$ to $10\,\text{nm}$. They meant for actual values to come from experiment, but if they were somewhat accurate in their guesses then this value works, if a bit low. As for M_T it is harder to say. At the very least we can probably assume that it is not too large however, since it is an interlayer integral.

Anyway, using these values the right part of Figure 5.6 was computed. As we can see, the amplitude ratio in Figure 1.1 was able to be approximately replicated. The linewidth is however much smaller than the experiment shows (the one used in the figure is purely phenomenological). One possible reason for this is that they in the time resolved photoluminescence observe a significant redshift over time, which would broaden the peak in the spectrum. They hypothesize that this is due to the excitons interacting with each other. This interaction is something that we neglected when we ignored most of the Coulomb interaction and treated the excitons as pure bosons, meaning that investigating these aspects further might give new insight into this phenomenon. The fact that we have not included intervalley coupling could be a contributing factor as well.

Note that this result should not be taken as definite. Aside from the linewidth, there are a few too many uncertainties in the way it was computed to take as absolute. One way to get a more precise result would be to reduce the number of parameters by obtaining an approximate value for M_T, for example using DFT. A proper investigation into the tunneling-assisted emission is needed too, since the current form is nothing but an estimation of what it might look like. Finally it would be good if the stability of the code would be improved for lower temperatures, since what applies for $77\,\text{K}$ may not be at all applicable for $4.5\,\text{K}$. If this can not be accomplished another idea could be to calculate for example the peak amplitude ratio for a variety if temperatures and see if a curve can be fit to the results, allowing us to extrapolate to lower temperatures. The results do however show that the model is very much capable of reproducing the experiment, even if the details remain to be sorted out.

6

Conclusions

The purpose of this thesis was to propose a theoretical model for interlayer coupling to recreate the results found in [1], specifically Figure 1.1. To this end a tunneling Hamiltonian based on [14] was implemented, along with terms for free, carrier-field, carrier-photon- carrier-phonon and carrier-carrier interaction. Normally the equations of motion would be derived in the electron-hole picture and then projected onto the excitonic basis. Here we chose the relatively new approach of projecting the Hamiltonian itself onto that basis instead. While this made the coupling elements more complicated it greatly simplified the deriving of the equations, since the number of operators get reduced. Everything related to the Wannier equation gets absorbed into the elements as well. Later on it was discovered however that treating the excitons as bosons may have neglected dynamics needed to explain the results. It is possible to construct the excitonic Hamiltonian without using this approximation, but the commutation relations get so complicated that the advantages of using this formalism may get overshadowed. Looking further into using this formalism may therefore be needed.

As for the actual results, the densities looked promising. We could observe how the intralayer densities slowly decreased as the energetically lower interlayer one increased when the tunneling was applied. The actual photoluminescence was not as successful though. The observed peak amplitude ratio was able to be replicated, but an approximation of how tunneling assisted emission might look had to be implemented to accomplish this, along with having two free parameters to vary. On top of this the parameters and temperature could not be varied to the extent we had intended due to computational difficulties. Thus no definitive statements can be said about the results at the moment.

They do however show that the model allows for a potential recreation of the experiment in the future. Further investigation is definitely needed, but it is not unreasonable to conclude that promising results may be reached later on.

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A

The correlation expansion

When doing multiparticle physics it is not unusual to encounter expectation values of multiple operators. We will here use the notation

$$\langle n \rangle \equiv \langle A_1 A_2 \dots A_n \rangle, \tag{A.1}$$

where $A_{1,\dots,n}$ are arbitrary operators, making $\langle n \rangle$ an n-operator quantity. A common method for evaluating this is by performing a correlation expansion. It is possible to express this expectation value as

$$\langle n \rangle = \langle n \rangle_\Sigma + (\langle n-2 \rangle_\Sigma \delta\langle 2 \rangle)_\Sigma + \dots + (\langle 1 \rangle \delta\langle n-1 \rangle)_\Sigma + \delta\langle n \rangle, \tag{A.2}$$

where the Σ index indicates a summation over all possible permutations and $\delta\langle n \rangle$ is an n-particle correlation function. For example we could express a three-operator quantity as

$$\begin{aligned}
\langle 3 \rangle &= \langle 3 \rangle_\Sigma + (\langle 1 \rangle \delta\langle 2 \rangle)_\Sigma + \delta\langle 3 \rangle && \text{(A.3)}\\
&= \langle A_1 A_2 \rangle \langle A_3 \rangle + \langle A_1 A_3 \rangle \langle A_2 \rangle + \langle A_2 A_3 \rangle \langle A_1 \rangle + \langle A_1 \rangle \langle A_2 \rangle \langle A_3 \rangle && \text{(A.4)}\\
&+ \langle A_1 \rangle \delta\langle A_2 A_3 \rangle + \langle A_2 \rangle \delta\langle A_1 A_3 \rangle + \langle A_3 \rangle \delta\langle A_1 A_2 \rangle && \text{(A.5)}\\
&+ \delta\langle A_1 A_2 A_3 \rangle. && \text{(A.6)}
\end{aligned}$$

This may look overly complicated, but it is often necessary if expressions for quantities of lower number are not known but not for higher. It can also be used as an approximation if certain terms can be neglected. Finally it can be used to separate quantities into *coherent* and *incoherent* terms. For example, a density $\langle a^\dagger a \rangle$ where $a^{(\dagger)}$ is a general annihilation (creation) operator can be written as

$$\langle a^\dagger a \rangle = \langle a^\dagger \rangle \langle a \rangle + \delta\langle a^\dagger a \rangle. \tag{A.7}$$

Here the two terms can be interpreted as the coherent and incoherent parts of the density.

B

The Markov approximation

A differential equation on the form

$$\frac{\partial}{\partial t}f(t) = \frac{i}{\hbar}E_f f(t) + g(t) \tag{B.1}$$

can be solved using formal integration as

$$f(t) = \int_{-\infty}^{t} dt' g(t') e^{\frac{i}{\hbar}E_f(t-t')}, \tag{B.2}$$

which using the variable transformation $s \equiv t - t'$ becomes

$$f(t) = \int_{0}^{\infty} ds g(t-s) e^{\frac{i}{\hbar}E_f s}. \tag{B.3}$$

By then using a rotating wave approximation to write $g(t)$ as

$$g(t) = g_{\text{slow}}(t) e^{\frac{i}{\hbar}E_g t} \tag{B.4}$$

where $g_{\text{slow}}(t)$ is the slowly oscillating part of $g(t)$ we obtain

$$f(t) = e^{iE_g t} \int_{0}^{\infty} ds g_{\text{slow}}(t-s) e^{\frac{i}{\hbar}(E_f - E_g)s}. \tag{B.5}$$

We now perform the final step, the actual Markov approximation, and say that since $g_{\text{slow}}(t)$ changes slowly relative to the exponential function we can extract it from the integral. Doing this then finally results in

$$f(t) \approx g_{\text{slow}}(t) e^{iE_g t} \int_{0}^{\infty} ds e^{\frac{i}{\hbar}(E_f - E_g)s} \tag{B.6}$$

$$= g(t)\pi\delta(E_f - E_g). \tag{B.7}$$

C

Classical electrodynamics

The dynamics of an electric wave propagating through a medium is given by the telegrapher's equation,

$$\left(\nabla^2 - \frac{n^2}{c^2}\frac{\partial^2}{\partial t^2}\right)\boldsymbol{E}(\boldsymbol{r},t) = \mu_0\sigma\frac{\partial}{\partial t}\boldsymbol{E}(\boldsymbol{r},t) \tag{C.1}$$

where $n = n(\omega)$ is the refractive index and σ the conductivity. By assuming a plane wave solution on the form $\boldsymbol{E}_0 e^{i(kz-\omega t)}$ we then obtain the dispersion relation

$$k^2 = \frac{\omega^2}{c^2}\left(n + i\frac{\sigma}{\epsilon_0\omega}\right) \equiv \frac{\omega^2}{c^2}\tilde{\epsilon}^2, \tag{C.2}$$

where $\tilde{\epsilon} \equiv \epsilon' + i\epsilon''$ is a complex relative permitivity. Since this quantity is complex the wave vector $k \equiv k' + ik''$ has to be complex as well. Inserting this into the above expression and using the assumptions $\epsilon' \gg \epsilon''$ and $n \approx \sqrt{\epsilon'}$ then yields

$$k' = \frac{\omega}{c}\sqrt{\epsilon'} \tag{C.3}$$

$$k'' = \frac{\omega}{c}\frac{\epsilon''}{2\sqrt{\epsilon'}}. \tag{C.4}$$

By using the Beer-Lambert law for the intensity $I(z)$ along with the definition of the absorption coefficient $\alpha(\omega)$ we then obtain

$$I(z) = |\boldsymbol{E}(z)|^2 = E_0 e^{-2k''z} \equiv E_0 e^{-\alpha(\omega)z}, \tag{C.5}$$

meaning that we now have an expression for the absorption coefficient,

$$\alpha(\omega) = \frac{\omega}{c}\frac{\epsilon''(\omega)}{\sqrt{\epsilon'(\omega)}}. \tag{C.6}$$

We now assume a weak ω-dependency in $\epsilon'(\omega)$ meaning that we can treat it as constant, giving

$$\alpha(\omega) \propto \omega\epsilon''(\omega) = \omega\,\mathrm{Im}(\tilde{\epsilon}). \tag{C.7}$$

We now need an alternative way of expressing ϵ'', which we will find by examining the relationship between the electric field $\boldsymbol{E}$, the displacement field $\boldsymbol{P}$ and the macroscopic polarization $\boldsymbol{P}$ which is given by

$$\boldsymbol{D} = \epsilon_0\boldsymbol{E} + \boldsymbol{P}. \tag{C.8}$$

If we assume the material to be linear, homogeneous and isotropic we can write $\boldsymbol{D}$ in the frequency domain as

$$\boldsymbol{D}(\omega) = \tilde{\epsilon}(\omega)\epsilon_0 \boldsymbol{E}(\omega). \tag{C.9}$$

In other words the polarization becomes parallel to the electric field, and we get

$$P(\omega) = \epsilon_0(\tilde{\epsilon}(\omega) - 1)E(\omega) \equiv \epsilon_0 \chi(\omega) E(\omega), \tag{C.10}$$

where $\chi(\omega)$ is the optical susceptibility. By solving for χ and expressing it in terms of the current $\boldsymbol{j}$ and vector potential $\boldsymbol{A}$ using the relations $\boldsymbol{j} = \partial_t \boldsymbol{P}$ and $\boldsymbol{E} = \partial_t \boldsymbol{A}$ (in the Coulomb gauge) we then obtain

$$\chi(\omega) = \frac{j(\omega)}{\epsilon_0 \omega^2 A(\omega)}. \tag{C.11}$$

Using this we can finally obtain a working expression for the absorption coefficient,

$$\alpha(\omega) \propto \omega \,\mathrm{Im}(\chi(\omega)) \propto \mathrm{Im}\left(\frac{j(\omega)}{\omega A(\omega)}\right). \tag{C.12}$$

This will be needed for later, when we calculate the absorption spectra for different heterostructures.

We still have one more quantity that we want to calculate however. By assuming a linear relation $\boldsymbol{j} = \sigma \boldsymbol{E}$ and that $\boldsymbol{E}$ propagates in the z direction we can transform (C.1) into

$$\left(\frac{\partial^2}{\partial z^2} - \frac{n^2}{c^2}\frac{\partial^2}{\partial t^2}\right)\boldsymbol{E}(z,t) = \mu_0 \frac{\partial}{\partial t}\boldsymbol{j}(z,t), \tag{C.13}$$

and by looking at a specific polarization we can find the solution

$$E(t) = E_0\left(t - \frac{z}{c}\right) - \frac{c\mu_0}{2} j\left(t - \frac{|z - z_0|}{c}\right). \tag{C.14}$$

Here E_0 is the incident field (the homogenous solution), j the resulting current (inhomogenous solution) and z_0 the z coordinate of the surface of the medium. If we now once again use that $E = \partial t A$ and perform a Fourier transform we then finally end up with

$$A(\omega) = A_0(\omega) + \frac{c\mu_0}{2} j(\omega). \tag{C.15}$$

D

Computing the matrix elements

This section contains calculations of some of the matrix elements from 3, specifically the ones that were deemed too long to keep in the main text.

D.1 Electronic dispersion

To calculate the electronic band structure we start by inserting our wave function into the Schrödinger equation, obtaining

$$H \sum_{i}^{M,X} C_i^a |\Psi_i^a\rangle - \epsilon^a \sum_{i}^{M,X} C_i^a |\Psi_i^a\rangle = 0. \tag{D.1}$$

If we then proceed to move H into the sum and multiply with $\langle\Psi_M^a|$ from the left we end up with

$$(\langle\Psi_M^a|H|\Psi_M^a\rangle - \epsilon^a\langle\Psi_M^a|\Psi_M^a\rangle)C_M^a + (\langle\Psi_M^a|H|\Psi_X^a\rangle - \epsilon^a\langle\Psi_M^a|\Psi_X^a\rangle)C_X^a = 0, \tag{D.2}$$

and if we instead use $\langle\Psi_X^a|$ we get

$$(\langle\Psi_X^a|H|\Psi_M^a\rangle - \epsilon^a\langle\Psi_X^a|\Psi_M^a\rangle)C_M^a + (\langle\Psi_X^a|H|\Psi_X^a\rangle - \epsilon^a\langle\Psi_X^a|\Psi_X^a\rangle)C_X^a = 0. \tag{D.3}$$

If we use the notation

$$H_{ij} \equiv \langle\Psi_i|H|\Psi_j\rangle, \quad S_{ij} \equiv \langle\Psi_i|\Psi_j\rangle \tag{D.4}$$

(surpressing the a indices for the moment) we can then express these equations as a single matrix equation

$$\begin{pmatrix} H_{MM} - \epsilon S_{MM} & H_{MX} - \epsilon S_{MX} \\ H_{XM} - \epsilon S_{XM} & H_{XX} - \epsilon S_{XX} \end{pmatrix} \begin{pmatrix} C_M \\ C_X \end{pmatrix} = 0. \tag{D.5}$$

Since we want this equation to have a non-trivial solution we need the matrix to have a determinant of 0, giving us the condition

$$(H_{MM} - \epsilon S_{MM})(H_{XX} - \epsilon S_{XX}) - (H_{XM} - \epsilon S_{XM})(H_{MX} - \epsilon S_{MX}) = 0, \tag{D.6}$$

which has the solution

$$\epsilon = -\frac{A}{2} \pm \sqrt{\frac{A^2}{4} - B} \tag{D.7}$$

where

$$A = \frac{H_{MM}S_{XX} + H_{XX}S_{MM} - 2\,\mathrm{Re}(H_{MX}S_{XM})}{|S_{MX}|^2 - S_{MM}S_{XX}} \tag{D.8}$$

and

$$B = \frac{|H_{MX}|^2 - H_{MM}H_{XX}}{|S_{MX}|^2 - S_{MM}S_{XX}}. \tag{D.9}$$

We now need to evaluate the overlap integrals. By using the tight binding approximation we find

$$H_{MX} = \frac{1}{V}\sum_{\boldsymbol{R}_M,\boldsymbol{R}_X} e^{i\boldsymbol{k}\cdot(\boldsymbol{R}_X-\boldsymbol{R}_M)}\langle\Phi_M(\boldsymbol{r}-\boldsymbol{R}_M)|H|\Phi_X(\boldsymbol{r}-\boldsymbol{R}_X)\rangle. \tag{D.10}$$

By then using a nearest neighbour approximation we can write $\boldsymbol{R}_X = \boldsymbol{R}_M + \boldsymbol{b}_i$, where the $\boldsymbol{b}_i$ vectors are defined in 2.1, we find

$$H_{MX} = \frac{1}{V}\sum_{\boldsymbol{R}_M,\boldsymbol{b}_i} e^{i\boldsymbol{k}\cdot\boldsymbol{b}_i}\langle\Phi_M(\boldsymbol{r}-\boldsymbol{R}_M)|H|\Phi_X(\boldsymbol{r}-\boldsymbol{R}_M-\boldsymbol{b}_i)\rangle, \tag{D.11}$$

which after a $\boldsymbol{r} \to \boldsymbol{r} + \boldsymbol{R}_M$ shift reduces to

$$H_{MX} = \frac{N}{V}\sum_{\boldsymbol{b}_i} e^{i\boldsymbol{k}\cdot\boldsymbol{b}_i}\langle\Phi_M(\boldsymbol{r})|H|\Phi_X(\boldsymbol{r}-\boldsymbol{b}_i)\rangle \tag{D.12}$$

where N is the number of M atoms. If we separate the parts that depend on $\boldsymbol{k}$ and the ones that don't we can define

$$e(\boldsymbol{k}) \equiv \sum_{\boldsymbol{b}_i} e^{i\boldsymbol{k}\cdot\boldsymbol{b}_i} \tag{D.13}$$

and

$$t = \frac{N}{V}\langle\Phi_M(\boldsymbol{r})|H|\Phi_X(\boldsymbol{r}-\boldsymbol{b}_i)\rangle \tag{D.14}$$

to write H^a_{MX} as

$$H_{MX}(\boldsymbol{k}) = e(\boldsymbol{k})t, \tag{D.15}$$

where we have neglected any differences in what $\boldsymbol{b}_i$ is used for t. By doing the same for the rest of the integrals and assuming that the Ψ_i wave functions are orthonormal we then end up with

$$H_{XM} = H_{MX} = e(\boldsymbol{k})t \tag{D.16}$$

$$H_{MM} = \frac{N}{V}\langle\Phi_M|H|\Phi_M\rangle \equiv \alpha_0 \tag{D.17}$$

$$H_{XX} = \frac{N}{V}\langle\Phi_X|H|\Phi_X\rangle \equiv \beta_0 \tag{D.18}$$

$$S_{MM} = S_{XX} = 1 \tag{D.19}$$

$$S_{MX} = S_{XM} = 0. \tag{D.20}$$

Inserting these into our definitions of A and B then leads to

$$A = -(\alpha_0 + \beta_0) \tag{D.21}$$

and

$$B = \alpha_0^2\beta_0^2 - |e(\boldsymbol{k})|^2|t|^2, \tag{D.22}$$

which gives the band structure the form

$$\epsilon^a(\boldsymbol{k}) = \frac{\alpha_0^a + \beta_0^a}{2} \pm \sqrt{\frac{(\alpha_0^a - \beta_0^a)^2}{4} + |e(\boldsymbol{k})|^2|t^a|^2} \tag{D.23}$$

$$\equiv E_0^a \pm \sqrt{\left(\frac{\Delta E^a}{2}\right)^2 + |e(\boldsymbol{k})|^2|t^a|^2}. \tag{D.24}$$

We now do a Taylor expansion around the $\boldsymbol{K}/\boldsymbol{K}'$ points to lowest non-zero order in $\boldsymbol{k}$, which results in

$$\epsilon^a(\boldsymbol{k}) = E_0^a \pm \left(\frac{\Delta E^a}{2} + \frac{3|t^a|^2}{4\Delta E^a}\left(\frac{\boldsymbol{k}}{a_0^a}\right)^2\right), \tag{D.25}$$

which if we expand our a index into band λ, spin s and layer l can be expressed as

$$\epsilon^{\lambda sl}(\boldsymbol{k}) = E_0^{\lambda sl} \pm \left(\frac{\Delta E^{\lambda sl}}{2} + \frac{3|t^{\lambda sl}|^2}{4\Delta E^{\lambda sl}}\left(\frac{\boldsymbol{k}}{a_0^l}\right)^2\right) \tag{D.26}$$

We can now finally start interpreting this expression. First we can see that this is a parabolic approximation of the band structure, meaning that we can define an effective mass $m^{\lambda sl}$ that fulfills

$$\frac{\hbar^2\boldsymbol{k}^2}{2m^{\lambda sl}} = \frac{3|t^{\lambda sl}|^2}{4\Delta E^{\lambda sl}}\left(\frac{\boldsymbol{k}}{a_0^l}\right)^2. \tag{D.27}$$

By taking this effective mass from either experiment or DFT we can therefore eliminate the need for computing the $t^{\lambda sl}$ integrals. Using this approximation we can also easily see that the $+$ and $-$ corresponds to the conduction and valence bands, meaning that we can write the dispersion as

$$\epsilon^{\lambda sl}(\boldsymbol{k}) = E_0^{\lambda sl} + (-1)^{\delta_{\lambda,v}}\left(\frac{\Delta E^{\lambda sl}}{2} + \frac{\hbar^2\boldsymbol{k}^2}{2m^{\lambda sl}}\right). \tag{D.28}$$

Since the sign is now λ dependent we can now absorb $E_0^{\lambda sl}$ into $\Delta E^{\lambda sl}$, leaving us with our final expression

$$\epsilon^{\lambda sl}(\boldsymbol{k}) = (-1)^{\delta_{\lambda,v}}\left(\frac{\Delta E^{\lambda sl}}{2} + \frac{\hbar^2\boldsymbol{k}^2}{2m^{\lambda sl}}\right). \tag{D.29}$$

Now we only have $\Delta E^{\lambda sl}$ left, which can be interpreted as the band gap energy. Giving an exact value for this isn't that easy though, since the band gap depends on the properties of both the valence and conduction bands. What we can do is make

use of the fact that constant energy offsets don't contribute to dynamics. We are therefore only interested in energy differences, meaning that we can define

$$E_G^{s_c s_v l_c l_v} \equiv \Delta E^{cs_c l_c} - \Delta E^{vs_v l_v}, \tag{D.30}$$

which is something we can take from experiment. The spin dependency is easy to find an expression for. Going by Figure 2.3, we can see that it can be written as

$$\Delta E^{\lambda sl} = \Delta E_0^l \pm E_{\text{soc}}^{\lambda l}, \tag{D.31}$$

where $E_{\text{soc}}^{\lambda sl}$ is the offset due to spin-orbit coupling and the sign depends on the spin and valley (K or K' point).

Now that the dispersion has been evaluated we can move on to find expressions for the tight binding coefficients. By inserting (D.29) into (D.5) and solving it we obtain the expressions

$$C_M^a(\boldsymbol{k}) = C_S^a(\boldsymbol{k}) g^a(\boldsymbol{k}), \tag{D.32}$$

$$C_S^a(\boldsymbol{k}) = \frac{(-1)^{\delta_{\lambda,v}}}{\sqrt{1 + |g^a(\boldsymbol{k})|^2}}, \tag{D.33}$$

$$g^a(\boldsymbol{k}) = \frac{t^a e^a(\boldsymbol{k})}{\frac{\Delta E^a}{2} - \epsilon^a(\boldsymbol{k})}. \tag{D.34}$$

D.2 Optical matrix element

Using the tight binding approximation and the fact that the spin dependent parts of the wave functions are orthonormal we can write the optical matrix element as

$$\boldsymbol{M}_{ab} = -\frac{i\hbar e_0}{m_0} \langle \Psi_a | \nabla | \Psi_b \rangle \tag{D.35}$$

$$= -\frac{i\hbar e_0}{m_0} \frac{1}{V} \sum_{i,j}^{M,X} C_i^a C_j^b \sum_{\boldsymbol{R}_i, \boldsymbol{R}_j} e^{i(\boldsymbol{k}_b \cdot \boldsymbol{R}_j - \boldsymbol{k}_a \cdot \boldsymbol{R}_i)} \langle \Phi_i^a(\boldsymbol{r} - \boldsymbol{R}_i) | \nabla | \Phi_j^b(\boldsymbol{r} - \boldsymbol{R}_j) \rangle \delta_{s_a, s_b}. \tag{D.36}$$

After performing a variable transformation $\boldsymbol{R}_j \to \boldsymbol{R}_i + \boldsymbol{T}$ and shifting $\boldsymbol{r} \to \boldsymbol{r} + \boldsymbol{R}_i$ we can rewrite it as

$$\boldsymbol{M}_{ab} = -\frac{i\hbar e_0}{m_0} \frac{1}{V} \sum_{i,j}^{M,X} C_i^a C_j^b \sum_{\boldsymbol{R}_i, \boldsymbol{T}} e^{i\boldsymbol{R}_i(\boldsymbol{k}_b - \boldsymbol{k}_a)} e^{i\boldsymbol{k}_b \cdot \boldsymbol{T}} \langle \Phi_i^a(\boldsymbol{r}) | \nabla | \Phi_j^b(\boldsymbol{r} - \boldsymbol{T}) \rangle \delta_{s_a, s_b}. \tag{D.37}$$

Part of this expression can be written as

$$\sum_{\boldsymbol{R}_i} e^{i\boldsymbol{R}_i \cdot (\boldsymbol{k}_b - \boldsymbol{k}_a)} = N \sum_{\boldsymbol{G}} \delta_{\boldsymbol{G}, \boldsymbol{k}_b - \boldsymbol{k}_a}, \tag{D.38}$$

where the inclusion of the reciprocal lattice vectors comes from the periodicity of the lattice. We will however only consider the case where $\boldsymbol{G} = \boldsymbol{0}$, leading to

$$\boldsymbol{M}_{ab} = -\frac{i\hbar e_0}{m_0}\frac{N}{V}\sum_{i,j}^{M,X} C_i^a C_j^b \sum_{\boldsymbol{T}} e^{i\boldsymbol{k}_b\cdot\boldsymbol{T}}\langle\Phi_i^a(\boldsymbol{r})|\nabla|\Phi_j^b(\boldsymbol{r}-\boldsymbol{T})\rangle\delta_{s_a,s_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b}. \tag{D.39}$$

As we can see, this physically means that we neglect any momentum transfer from the exciting field, which is reasonable since the photon momenta for the frequencies used are much smaller than the relevant electron momenta.

It is now time to expand our compound indices. First we shorten our notation by defining

$$\boldsymbol{M}_{\boldsymbol{k}_a}^{\lambda_a\lambda_b s_a l_a l_b} \equiv \boldsymbol{M}_{\boldsymbol{k}_a\boldsymbol{k}_b}^{\lambda_a\lambda_b s_a s_b l_a l_b}\delta_{s_a s_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b} \tag{D.40}$$

We then neglect intraband transitions. We therefore only need to calculate

$$\begin{aligned}
\boldsymbol{M}_{\boldsymbol{k}_a}^{vcsll} = -\frac{i\hbar e_0}{m_0}\frac{1}{\Omega^l}\Bigg(& C_M^{vsl}C_M^{csl}\sum_{\boldsymbol{T}} e^{i\boldsymbol{k}_b\cdot\boldsymbol{T}}\langle\Phi_M^{vl}(\boldsymbol{r})|\nabla|\Phi_M^{cl}(\boldsymbol{r}-\boldsymbol{T})\rangle && \text{(D.41)}\\
&+ C_M^{vsl}C_X^{csl}\sum_{\boldsymbol{T}} e^{i\boldsymbol{k}_b\cdot\boldsymbol{T}}\langle\Phi_M^{vl}(\boldsymbol{r})|\nabla|\Phi_X^{cl}(\boldsymbol{r}-\boldsymbol{T})\rangle && \text{(D.42)}\\
&+ C_X^{vsl}C_M^{csl}\sum_{\boldsymbol{T}} e^{i\boldsymbol{k}_b\cdot\boldsymbol{T}}\langle\Phi_X^{vl}(\boldsymbol{r})|\nabla|\Phi_M^{cl}(\boldsymbol{r}-\boldsymbol{T})\rangle && \text{(D.43)}\\
&+ C_X^{vsl}C_X^{csl}\sum_{\boldsymbol{T}} e^{i\boldsymbol{k}_b\cdot\boldsymbol{T}}\langle\Phi_X^{vl}(\boldsymbol{r})|\nabla|\Phi_X^{cl}(\boldsymbol{r}-\boldsymbol{T})\rangle\Bigg)\delta_{s_a s_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b} && \text{(D.44)}
\end{aligned}$$

where $\Omega = \frac{V}{N}$ is the volume (area) of a single unit cell.

We will now proceed to make a nearest neighbour approximation, which means that we will need to treat the intra and interlayer case somewhat differently. If we start with the intralayer case we can eliminate the on site $\boldsymbol{T} = 0$ case for parity reasons, leaving us with $\boldsymbol{T} = \pm\boldsymbol{b}_i$ and the MX and XM terms. In other words we get

$$\begin{aligned}
\boldsymbol{M}_{\boldsymbol{k}}^{vcsll} = -\frac{i\hbar e_0}{m_0}\frac{1}{\Omega}\Bigg(& C_M^{vsl}C_X^{csl}\sum_{\boldsymbol{b}_i} e^{i\boldsymbol{k}\cdot\boldsymbol{b}_i}\langle\Phi_M^{vl}(\boldsymbol{r})|\nabla|\Phi_X^{cl}(\boldsymbol{r}-\boldsymbol{b}_i)\rangle && \text{(D.45)}\\
&+ C_X^{vsl}C_M^{csl}\sum_{\boldsymbol{b}_i} e^{-i\boldsymbol{k}\cdot\boldsymbol{b}_i}\langle\Phi_X^{vl}(\boldsymbol{r})|\nabla|\Phi_M^{cl}(\boldsymbol{r}+\boldsymbol{b}_i)\rangle\Bigg)\delta_{s_a s_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b}. && \text{(D.46)}
\end{aligned}$$

We now need to find a way to evaluate the integrals. It is possible to show that for graphene they can be expressed as

$$\langle\Phi_M^{vl}(\boldsymbol{r})|\nabla|\Phi_X^{cl}(\boldsymbol{r}\mp\boldsymbol{b}_i)\rangle = \pm\frac{\boldsymbol{b}_i}{|\boldsymbol{b}_i|}M^{ll} \tag{D.47}$$

due to the xy rotational symmetry and z antisymmetry of the relevant $2p_z$ orbitals. In TMD's this doesn't really work anymore however, since different orbitals with different symmetries are involved. They are however similar enough that it can be

used as an approximation, which leads us to

$$\boldsymbol{M}_{\boldsymbol{k}}^{vcsll} = -\frac{i\hbar e_0}{m_0}\frac{1}{\Omega}\left(C_M^{vsl}C_X^{csl}\sum_{\boldsymbol{b}_i} e^{i\boldsymbol{k}\cdot\boldsymbol{b}_i}\frac{\boldsymbol{b}_i}{|\boldsymbol{b}_i|}\ M^{ll} - C_X^{vsl}C_M^{csl}\sum_{\boldsymbol{b}_i} e^{-i\boldsymbol{k}\cdot\boldsymbol{b}_i}\frac{\boldsymbol{b}_i}{|\boldsymbol{b}_i|}M^{ll}\right)\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b} \tag{D.48}$$

$$= -\frac{i\hbar e_0}{m_0}\frac{1}{\Omega}\frac{1}{|\boldsymbol{b}|}M^{ll}\sum_{\boldsymbol{b}_i}\left(e^{i\boldsymbol{k}\cdot\boldsymbol{b}_i}C_M^{vsl}C_X^{csl} - e^{-i\boldsymbol{k}\cdot\boldsymbol{b}_i}C_X^{vsl}C_M^{csl}\right)\boldsymbol{b}_i\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b}, \tag{D.49}$$

where $|\boldsymbol{b}|$ refers to the size of any of the $\boldsymbol{b}_i$ vectors. We then rewrite the tight binding coefficients as

$$C_M(\boldsymbol{k}) = C_X(\boldsymbol{k})g(\boldsymbol{k}) \equiv C_X(\boldsymbol{k})\alpha(\boldsymbol{k})\sum_{\boldsymbol{b}_i} e^{i\boldsymbol{k}\cdot\boldsymbol{b}_i}, \tag{D.50}$$

giving us

$$\boldsymbol{M}_{\boldsymbol{k}}^{vcsll} \tag{D.51}$$

$$= -\frac{i\hbar e_0}{m_0}\frac{1}{\Omega}\frac{1}{|\boldsymbol{b}|}M^{ll}\sum_{\boldsymbol{b}_i,\boldsymbol{b}_j}\left(C_X^{vsl}C_X^{csl}\alpha^{vsl}e^{i\boldsymbol{k}\cdot(\boldsymbol{b}_i-\boldsymbol{b}_j)} - C_X^{vsl}C_X^{csl}\alpha^{csl}e^{i\boldsymbol{k}\cdot(\boldsymbol{b}_j-\boldsymbol{b}_i)}\right)\boldsymbol{b}_i\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b}. \tag{D.52}$$

By looking at our expressions for the tight binding coefficients we can see that $|\alpha^c| \gg |\alpha^v|$, meaning that we can throw away the first term. We then perform a Taylor expansion around the K/K' points to end up with

$$\boldsymbol{M}_{\boldsymbol{k}}^{vcsll} = \frac{i\hbar e_0}{m_0}\frac{1}{\Omega}\frac{1}{|\boldsymbol{b}|}M^{ll}C_X^{vsl}C_X^{csl}\alpha^{csl}\sum_{\boldsymbol{b}_i,\boldsymbol{b}_j} e^{i\boldsymbol{K}/\boldsymbol{K}'\cdot(\boldsymbol{b}_j-\boldsymbol{b}_i)}(i\boldsymbol{k}\cdot\boldsymbol{b}_j - i\boldsymbol{k}\cdot\boldsymbol{b}_i)\boldsymbol{b}_i\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b}, \tag{D.53}$$

which after inserting the actual expressions for $\boldsymbol{b}_i$ and $\boldsymbol{K}/\boldsymbol{K}'$ results in

$$\boldsymbol{M}_{\boldsymbol{k}}^{vcsll}|_{\boldsymbol{K}} = \frac{\hbar e_0}{m_0}\frac{1}{\Omega^l}\frac{1}{|\boldsymbol{b}|}M^{ll}\frac{3\sqrt{3}}{4a_0^l}C_X^{vsl}C_X^{csl}\alpha^{csl}(k_x - ik_y)(\hat{\boldsymbol{x}} + i\hat{\boldsymbol{y}})\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b} \tag{D.54}$$

$$= \frac{\hbar e_0}{m_0}\frac{1}{\Omega^l}\frac{1}{|\boldsymbol{b}|}M^{ll}\frac{3\sqrt{3}}{4a_0^l}C_X^{vsl}C_X^{csl}\alpha^{csl}ke^{-i\varphi_k}\begin{pmatrix}1\\ i\end{pmatrix}\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b}, \tag{D.55}$$

$$\boldsymbol{M}_{\boldsymbol{k}}^{vcsll}|_{\boldsymbol{K}'} = \frac{\hbar e_0}{m_0}\frac{1}{\Omega^l}\frac{1}{|\boldsymbol{b}|}M^{ll}\frac{3\sqrt{3}}{4a_0^l}C_X^{vsl}C_X^{csl}\alpha^{csl}(k_x + ik_y)(\hat{\boldsymbol{x}} - i\hat{\boldsymbol{y}})\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b} \tag{D.56}$$

$$= \frac{\hbar e_0}{m_0}\frac{1}{\Omega^l}\frac{1}{|\boldsymbol{b}|}M^{ll}\frac{3\sqrt{3}}{4a_0^l}C_X^{vsl}C_X^{csl}\alpha^{csl}ke^{i\varphi_k}\begin{pmatrix}1\\ -i\end{pmatrix}\delta_{s_as_b}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_b} \tag{D.57}$$

where we for the second lines have expressed $\boldsymbol{k}$ in complex polar coordinates. It is known from experiment that TMD's absorb around 10% of incoming light, meaning that all of the prefactors can be absorbed into M^{ll} which is then chosen to fit this number.

For the interlayer case the situation is a bit more complicated since we now need to consider the displacement in the z direction. While it should be possible to make a similar but more extensive analysis for this case, what we decided to do instead

was to request external help in calculating the matrix element itself using DFT. By then assuming a similar shape as the one for the interlayer case we could find an estimate for $M^{ll'}, l \neq l'$ as

$$M^{ll'} \approx 10^{-3} M^{ll}.$$

D.3 Coulomb matrix element

Using the Fourier transform

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{q}} V_{\boldsymbol{q}} e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \tag{D.58}$$

where $V(\boldsymbol{r})$ and $V_{\boldsymbol{q}}$ are the Coulomb potentials in real and Fourier space we can express the Coulomb matrix element as

$$\begin{aligned} V_{cd}^{ab} &= \langle \Psi_a(\boldsymbol{r})\Psi_b(\boldsymbol{r}')|V(\boldsymbol{r}-\boldsymbol{r}')|\Psi_c(\boldsymbol{r})\Psi_d(\boldsymbol{r}')\rangle && \text{(D.59)} \\ &= \sum_{\boldsymbol{q}} V_{\boldsymbol{q}} \langle \Psi_a|e^{i\boldsymbol{q}\cdot\boldsymbol{r}}|\Psi_c\rangle\langle\Psi_b|e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}|\Psi_d\rangle && \text{(D.60)} \\ &\equiv \sum_{\boldsymbol{q}} V_{\boldsymbol{q}} \Gamma_{ac}(\boldsymbol{q})\Gamma_{bd}(-\boldsymbol{q}). && \text{(D.61)} \end{aligned}$$

Using the same steps as for the optical matrix element (use the orthonormality of the spin wave functions, make a tight binding approximation and rewrite $\boldsymbol{R}_j \to \boldsymbol{R}_i + \boldsymbol{T}$) we can then express the overlap integrals as

$$\Gamma_{ac}(\boldsymbol{q}) = \frac{1}{V}\sum_{i,j}^{M,X} C_i^a C_j^c \sum_{\boldsymbol{R}_i,\boldsymbol{T}} e^{i\boldsymbol{R}_i\cdot(\boldsymbol{k}_c-\boldsymbol{k}_a)} e^{i\boldsymbol{k}_c\cdot\boldsymbol{T}} \langle \Phi_i^a(\boldsymbol{r}-\boldsymbol{R}_i)|e^{i\boldsymbol{q}\cdot\boldsymbol{r}}|\Phi_j^c(\boldsymbol{r}-\boldsymbol{R}_i-\boldsymbol{T})\rangle \delta_{s_a,s_c} \tag{D.62}$$

$$= \frac{1}{V}\sum_{i,j}^{M,X} C_i^a C_j^c \sum_{\boldsymbol{R}_i,\boldsymbol{T}} e^{i\boldsymbol{R}_i\cdot(\boldsymbol{k}_c-\boldsymbol{k}_a+\boldsymbol{q})} e^{i\boldsymbol{k}_c\cdot\boldsymbol{T}} \langle \Phi_i^a(\boldsymbol{r})|e^{i\boldsymbol{q}\cdot\boldsymbol{r}}|\Phi_j^c(\boldsymbol{r}-\boldsymbol{T})\rangle \delta_{s_a,s_c}. \tag{D.63}$$

We once again identify the δ function as

$$\sum_{\boldsymbol{R}_i} e^{i\boldsymbol{R}_i\cdot(\boldsymbol{k}_c-\boldsymbol{k}_a+\boldsymbol{q})} = \sum_{\boldsymbol{G}} \delta_{\boldsymbol{G},\boldsymbol{k}_c-\boldsymbol{k}_a+\boldsymbol{q}} \tag{D.64}$$

and neglect any contributions from $\boldsymbol{G} \neq \boldsymbol{0}$, leading to

$$\Gamma_{ac}(\boldsymbol{q}) = \frac{1}{\Omega}\sum_{i,j}^{M,X} C_i^a C_j^c \sum_{\boldsymbol{T}} e^{i\boldsymbol{k}_c\cdot\boldsymbol{T}} \langle \Phi_i^a(\boldsymbol{r})|e^{i\boldsymbol{q}\cdot\boldsymbol{r}}|\Phi_j^c(\boldsymbol{r}-\boldsymbol{T})\rangle \delta_{s_a,s_c}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}}. \tag{D.65}$$

We now Taylor expand the $e^{i\boldsymbol{q}\cdot\boldsymbol{r}}$ exponential to first order and examine the two terms separately. The first one is a simple overlap integral,

$$\Gamma_{ac}^0(\boldsymbol{q}) = \frac{1}{\Omega}\sum_{i,j}^{M,X} C_i^a C_j^c \sum_{\boldsymbol{T}} e^{i\boldsymbol{k}_c\cdot\boldsymbol{T}} \langle \Phi_i^a(\boldsymbol{r})|\Phi_j^c(\boldsymbol{r}-\boldsymbol{T})\rangle \delta_{s_a,s_c}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}}. \tag{D.66}$$

Using a nearest neighbour approximation (with the nearest neighbour here being the on-site (at least in the in-plane meaning) interaction $\boldsymbol{T} = 0$, $i = j$) we end up with

$$\Gamma^0_{ac}(\boldsymbol{q})|_{\text{intra}} = \frac{1}{\Omega}\sum_i^{M,X} C_i^a C_i^c \langle \Phi_i^a | \Phi_i^c \rangle \delta_{l_a,l_c}\delta_{s_a,s_c}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}} \tag{D.67}$$

$$= \frac{1}{\Omega}\sum_i^{M,X} C_i^a C_i^c \delta_{\lambda_a,\lambda_c}\delta_{l_a,l_c}\delta_{s_a,s_c}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}} \tag{D.68}$$

and

$$\Gamma^0_{ac}(\boldsymbol{q})|_{\text{inter}} = \frac{1}{\Omega} e^{i\boldsymbol{k}_c\cdot\boldsymbol{R}} \sum_i^{M,X} C_i^a C_{i/\bar{i}}^c \langle \Phi_i^a(\boldsymbol{r}) | \Phi_{i/\bar{i}}^c(\boldsymbol{r}-\boldsymbol{R})\rangle \delta_{l_a,\bar{l}_c}\delta_{s_a,s_c}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}}, \tag{D.69}$$

where $\delta_{l_a,\bar{l}_c}$ is meant to signify that $l_a \neq l_c$, $i/\bar{i}$ means that one type of atom couples to either the same type or a different type depending on stacking and $\boldsymbol{R} = R\hat{\boldsymbol{z}}$ is the vector connecting the two layers.

Before we approach the first order term we first need to bring up something called the $\boldsymbol{p}$-$\boldsymbol{r}$ relations. Using the fact that the optical component of the Hamiltonian can be expressed both in terms of $\boldsymbol{M}\cdot\boldsymbol{A}$ and $\boldsymbol{d}\cdot\boldsymbol{E}$ it is possible to find the relationship

$$\langle \Phi_i^a(\boldsymbol{r})|\boldsymbol{r}|\Phi_j^c(\boldsymbol{r}-\boldsymbol{T})\rangle = \frac{\hbar}{m_0}\frac{1}{\Delta\omega^{ca}}\langle \Phi_i^a(\boldsymbol{r})|\nabla|\Phi_j^c(\boldsymbol{r}-\boldsymbol{T})\rangle, \tag{D.70}$$

where $\Delta\omega^{ca} \equiv \omega^c - \omega^a$ is the transition frequency between the two states. Using this relationship we can now express the first order term as

$$\Gamma^1_{ac}(\boldsymbol{q}) \tag{D.71}$$

$$= \frac{1}{\Omega}\sum_{i,j}^{M,X} C_i^a C_j^c \sum_{\boldsymbol{T}} e^{i\boldsymbol{k}_c\cdot\boldsymbol{T}} \langle \Phi_i^a(\boldsymbol{r})|i\boldsymbol{q}\cdot\boldsymbol{r}|\Phi_j^c(\boldsymbol{r}-\boldsymbol{T})\rangle \delta_{s_a,s_c}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}} \tag{D.72}$$

$$= \frac{1}{\Delta\omega^{ca}}\frac{-1}{e_0}\boldsymbol{q}\cdot\left(\left(-\frac{i\hbar e_0}{m_0}\right)\frac{1}{\Omega}\sum_{i,j}^{M,X} C_i^a C_j^c \sum_{\boldsymbol{T}} e^{i\boldsymbol{k}_c\cdot\boldsymbol{T}}\langle \Phi_i^a(\boldsymbol{r})|\nabla|\Phi_j^c(\boldsymbol{r}-\boldsymbol{T})\rangle \delta_{s_a,s_c}\delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}}\right) \tag{D.73}$$

$$= -\frac{1}{e_0\Delta\omega^{ca}}\boldsymbol{q}\cdot\boldsymbol{M}^{\lambda_a\lambda_c s_a s_c l_a l_c}_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}}, \tag{D.74}$$

meaning that in the end we get

$$V_{cd}^{ab} \tag{D.75}$$
$$= \sum_{\boldsymbol{q}} V_{\boldsymbol{q}} \tag{D.76}$$
$$\cdot \left(\frac{1}{\Omega} \sum_{i}^{M,X} C_i^a C_{\bar{i}}^c (\delta_{\lambda_a,\lambda_c} \delta_{l_a,l_c} + \langle \Phi_i^a(\boldsymbol{r}) | \Phi_{\bar{i}/\bar{i}}^c(\boldsymbol{r} - \boldsymbol{R}) \rangle \delta_{l_a,\bar{l}_c}) - \frac{1}{e_0 \Delta\omega^{ca}} \boldsymbol{q} \cdot \boldsymbol{M}_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}}^{\lambda_a \lambda_c s_a s_c l_a l_c} \right) \tag{D.77}$$
$$\cdot \left(\frac{1}{\Omega} \sum_{j}^{M,X} C_j^b C_{\bar{j}}^d (\delta_{\lambda_b,\lambda_d} \delta_{l_b,l_d} + \langle \Phi_j^a(\boldsymbol{r}) | \Phi_{\bar{j}/\bar{j}}^c(\boldsymbol{r} - \boldsymbol{R}) \rangle \delta_{l_b,\bar{l}_d}) + \frac{1}{e_0 \Delta\omega^{bd}} \boldsymbol{q} \cdot \boldsymbol{M}_{\boldsymbol{k}_b,\boldsymbol{k}_d-\boldsymbol{q}}^{\lambda_b \lambda_d s_b s_d l_b l_d} \right) \tag{D.78}$$
$$\cdot \delta_{s_a,s_c}^{s_b,s_d} \delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}} \delta_{\boldsymbol{k}_b,\boldsymbol{k}_d-\boldsymbol{q}}. \tag{D.79}$$

Here we can see that for the intralayer case we can neglect the first order term in the case of intraband transitions. For the purposes of this thesis those are the only types of transitions we will consider, because interband transitions requires larger energies than those of typical Coulomb interactions due to the large band gap.

As usual the situation is more complex for the interlayer case. On one hand we know that the optical matrix elements are really small, but on the other hand we need to calculate the $\langle \Phi_i^a(\boldsymbol{r}) | \Phi_{i/\bar{i}}^c(\boldsymbol{r} - \boldsymbol{R}) \rangle$ overlap integral to be able to compare them. This could be done using DFT, but since we need external help with that anyway we might as well calculate the whole of $\langle \Phi_i^a(\boldsymbol{r}) | e^{i\boldsymbol{q}\cdot\boldsymbol{r}} | \Phi_{i/\bar{i}}^c(\boldsymbol{r} - \boldsymbol{R}) \rangle$ instead. Using this input we then in this approach end up with

$$V_{cd}^{ab} = \frac{1}{\Omega^2} \sum_{\boldsymbol{q}} V_{\boldsymbol{q}} \sum_{i,j}^{M,X} C_i^a C_i^c C_j^b C_j^d \tag{D.80}$$
$$\cdot (\delta_{l_a,l_c} + \langle \Phi_i^a(\boldsymbol{r}) | e^{i\boldsymbol{q}\cdot\boldsymbol{r}} | \Phi_{\bar{i}/\bar{i}}^c(\boldsymbol{r} - \boldsymbol{R}) \rangle \delta_{l_a,\bar{l}_c})(\delta_{l_b,l_d} + \langle \Phi_j^a(\boldsymbol{r}) | e^{i\boldsymbol{q}\cdot\boldsymbol{r}} | \Phi_{\bar{j}/\bar{j}}^c(\boldsymbol{r} - \boldsymbol{R}) \rangle \delta_{l_b,\bar{l}_d}) \tag{D.81}$$
$$\cdot \delta_{\lambda_a,\lambda_c}^{\lambda_b,\lambda_d} \delta_{s_a,s_c}^{s_b,s_d} \delta_{\boldsymbol{k}_a,\boldsymbol{k}_c+\boldsymbol{q}} \delta_{\boldsymbol{k}_b,\boldsymbol{k}_d-\boldsymbol{q}}. \tag{D.82}$$

D.3.1 Going to the pair operator picture

To convert the Coulomb Hamiltonian to the pair operator picture we start off by rearranging the terms as

$$H_{c-c} = \frac{1}{2}\sum_{\boldsymbol{k}_e\boldsymbol{k}'_e\boldsymbol{q}s_es'_el_al_bl_cl_d} V^{ccs_es'_el_al_bl_cl_d}_{\boldsymbol{k}_e,\boldsymbol{k}'_e,\boldsymbol{q}} c^{\dagger s_el_a}_{\boldsymbol{k}_e+\boldsymbol{q}} c^{\dagger s'_el_b}_{\boldsymbol{k}'_e-\boldsymbol{q}} c^{s'_el_d}_{\boldsymbol{k}'_e} c^{s_el_c}_{\boldsymbol{k}_e} \tag{D.83}$$

$$+\frac{1}{2}\sum_{\boldsymbol{k}_h\boldsymbol{k}'_h\boldsymbol{q}s_hs'_hl_al_bl_cl_d} V^{vvs_hs'_hl_al_bl_cl_d}_{\boldsymbol{k}_h,\boldsymbol{k}'_h,\boldsymbol{q}} v^{\dagger s_hl_a}_{\boldsymbol{k}_h+\boldsymbol{q}} v^{\dagger s'_hl_b}_{\boldsymbol{k}'_h-\boldsymbol{q}} v^{s'_hl_d}_{\boldsymbol{k}'_h} v^{s_hl_c}_{\boldsymbol{k}_h} \tag{D.84}$$

$$+\sum_{\boldsymbol{k}_e\boldsymbol{k}'_h\boldsymbol{q}s_es'_hl_al_bl_cl_d} V^{cvs_es'_hl_al_bl_cl_d}_{\boldsymbol{k}_e,\boldsymbol{k}'_h,\boldsymbol{q}} c^{\dagger s_el_a}_{\boldsymbol{k}_e+\boldsymbol{q}} v^{\dagger s'_hl_b}_{\boldsymbol{k}'_h-\boldsymbol{q}} v^{s'_hl_d}_{\boldsymbol{k}'_h} c^{s_el_c}_{\boldsymbol{k}_e} \tag{D.85}$$

$$=-\frac{1}{2}\sum_{\boldsymbol{k}_e\boldsymbol{q}s_el_al_bl_d} V^{ccs_es_el_al_bl_bl_d}_{\boldsymbol{k}_e,\boldsymbol{k}_e+\boldsymbol{q},\boldsymbol{q}} c^{\dagger s_el_a}_{\boldsymbol{k}_e+\boldsymbol{q}} c^{s_el_d}_{\boldsymbol{k}_e+\boldsymbol{q}} \tag{D.86}$$

$$+\frac{1}{2}\sum_{\boldsymbol{k}_e\boldsymbol{k}'_e\boldsymbol{q}s_es'_el_al_bl_cl_d} V^{ccs_es'_el_al_bl_cl_d}_{\boldsymbol{k}_e,\boldsymbol{k}'_e,\boldsymbol{q}} c^{\dagger s_el_a}_{\boldsymbol{k}_e+\boldsymbol{q}} c^{s_el_c}_{\boldsymbol{k}_e} c^{\dagger s'_el_b}_{\boldsymbol{k}'_e-\boldsymbol{q}} c^{s'_el_d}_{\boldsymbol{k}'_e} \tag{D.87}$$

$$-\frac{1}{2}\sum_{\boldsymbol{k}_h\boldsymbol{q}s_hl_al_bl_d} V^{vvs_hs_hl_al_bl_bl_d}_{\boldsymbol{k}_h,\boldsymbol{k}_h+\boldsymbol{q},\boldsymbol{q}} v^{\dagger s_hl_a}_{\boldsymbol{k}_h+\boldsymbol{q}} v^{s_hl_d}_{\boldsymbol{k}_h+\boldsymbol{q}} \tag{D.88}$$

$$+\frac{1}{2}\sum_{\boldsymbol{k}_h\boldsymbol{k}'_h\boldsymbol{q}s_hs'_hl_al_bl_cl_d} V^{vvs_hs'_hl_al_bl_cl_d}_{\boldsymbol{k}_h,\boldsymbol{k}'_h,\boldsymbol{q}} v^{\dagger s_hl_a}_{\boldsymbol{k}_h+\boldsymbol{q}} v^{s_hl_c}_{\boldsymbol{k}_h} v^{\dagger s'_hl_b}_{\boldsymbol{k}'_h-\boldsymbol{q}} v^{s'_hl_d}_{\boldsymbol{k}'_h} \tag{D.89}$$

$$+\sum_{\boldsymbol{k}_e\boldsymbol{k}'_hs_es'_hl_al_bl_c} V^{cvs_es'_hl_al_bl_cl_b}_{\boldsymbol{k}_e,\boldsymbol{k}'_h,\boldsymbol{0}} c^{\dagger s_el_a}_{\boldsymbol{k}_e} c^{s_el_c}_{\boldsymbol{k}_e} \tag{D.90}$$

$$-\sum_{\boldsymbol{k}_e\boldsymbol{k}'_h\boldsymbol{q}s_es'_hl_al_bl_cl_d} V^{cvs_es'_hl_al_bl_cl_d}_{\boldsymbol{k}_e,\boldsymbol{k}'_h,\boldsymbol{q}} c^{\dagger s_el_a}_{\boldsymbol{k}_e+\boldsymbol{q}} c^{s_el_c}_{\boldsymbol{k}_e} v^{s'_hl_d}_{\boldsymbol{k}'_h} v^{\dagger s'_hl_b}_{\boldsymbol{k}'_h-\boldsymbol{q}} \tag{D.91}$$

$$=-\frac{1}{2}\sum_{\boldsymbol{k}_e\boldsymbol{q}s_el_al_bl_d} V^{ccs_es_el_al_bl_bl_d}_{\boldsymbol{k}_e-\boldsymbol{q},\boldsymbol{k}_e,\boldsymbol{q}} c^{\dagger s_el_a}_{\boldsymbol{k}_e} c^{s_el_d}_{\boldsymbol{k}_e} \tag{D.92}$$

$$-\frac{1}{2}\sum_{\boldsymbol{k}_h\boldsymbol{q}s_hl_al_bl_d} V^{vvs_hs_hl_al_bl_bl_d}_{\boldsymbol{k}_h-\boldsymbol{q},\boldsymbol{k}_h,\boldsymbol{q}} v^{\dagger s_hl_a}_{\boldsymbol{k}_h} v^{s_hl_d}_{\boldsymbol{k}_h} \tag{D.93}$$

$$+\sum_{\boldsymbol{k}_e\boldsymbol{k}'_hs_es'_hl_al_bl_c} V^{cvs_es'_hl_al_bl_cl_b}_{\boldsymbol{k}_e,\boldsymbol{k}'_h,\boldsymbol{0}} c^{\dagger s_el_a}_{\boldsymbol{k}_e} c^{s_el_c}_{\boldsymbol{k}_e} \tag{D.94}$$

$$+\frac{1}{2}\sum_{\boldsymbol{k}_e\boldsymbol{k}'_e\boldsymbol{q}s_es'_el_al_bl_cl_d} V^{ccs_es'_el_al_bl_cl_d}_{\boldsymbol{k}_e,\boldsymbol{k}'_e,\boldsymbol{q}} c^{\dagger s_el_a}_{\boldsymbol{k}_e+\boldsymbol{q}} c^{s_el_c}_{\boldsymbol{k}_e} c^{\dagger s'_el_b}_{\boldsymbol{k}'_e-\boldsymbol{q}} c^{s'_el_d}_{\boldsymbol{k}'_e} \tag{D.95}$$

$$+\frac{1}{2}\sum_{\boldsymbol{k}_h\boldsymbol{k}'_h\boldsymbol{q}s_hs'_hl_al_bl_cl_d} V^{vvs_hs'_hl_al_bl_cl_d}_{\boldsymbol{k}_h,\boldsymbol{k}'_h,\boldsymbol{q}} v^{\dagger s_hl_a}_{\boldsymbol{k}_h+\boldsymbol{q}} v^{s_hl_c}_{\boldsymbol{k}_h} v^{\dagger s'_hl_b}_{\boldsymbol{k}'_h-\boldsymbol{q}} v^{s'_hl_d}_{\boldsymbol{k}'_h} \tag{D.96}$$

$$-\sum_{\boldsymbol{k}_e\boldsymbol{k}'_h\boldsymbol{q}s_es'_hl_al_bl_cl_d} V^{cvs_es'_hl_al_bl_cl_d}_{\boldsymbol{k}_e,\boldsymbol{k}'_h,\boldsymbol{q}} c^{\dagger s_el_a}_{\boldsymbol{k}_e+\boldsymbol{q}} c^{s_el_c}_{\boldsymbol{k}_e} v^{s'_hl_d}_{\boldsymbol{k}'_h} v^{\dagger s'_hl_b}_{\boldsymbol{k}'_h-\boldsymbol{q}} \tag{D.97}$$

The first three terms are all of the form $\sum_a \tilde{\epsilon}_a a^\dagger_a a_a$, meaning that all they do is renormalize the band structure. However, since we are going to be using experimental values for quantities like the band gap they will automatically be included there, meaning that we can simply ignore them. We then proceed by inserting our

conservation laws for the electron-electron interaction,

$$H_{e-e} = \frac{1}{2} \sum_{\boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{q} s_e s'_e l_a l_b l_c l_d} V^{ccs_e s'_e l_a l_b l_c l_d}_{\boldsymbol{k}_e, \boldsymbol{k}'_e, \boldsymbol{q}} c^{\dagger s_e l_a}_{\boldsymbol{k}_e + \boldsymbol{q}} c^{s_e l_c}_{\boldsymbol{k}_e} c^{\dagger s'_e l_b}_{\boldsymbol{k}'_e - \boldsymbol{q}} c^{s'_e l_d}_{\boldsymbol{k}'_e} \tag{D.98}$$

$$= \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{q} s_h s'_h s_e s'_e l_a l_b l_c l_d l_h l'_h} V^{ccs_e s'_e l_a l_b l_c l_d}_{\boldsymbol{k}_e, \boldsymbol{k}'_e, \boldsymbol{q}} P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{k}_h, \boldsymbol{k}_e + \boldsymbol{q}} P^{s_h l_h s_e l_c}_{\boldsymbol{k}_h, \boldsymbol{k}_e} P^{\dagger s'_h l'_h s'_e l_b}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e - \boldsymbol{q}} P^{s'_h l'_h s'_e l_d}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} \tag{D.99}$$

$$= \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}_e \boldsymbol{q} s_h s_e l_a l_b l_d l_h} V^{ccs_e s_e l_a l_b l_b l_d}_{\boldsymbol{k}_e - \boldsymbol{q}, \boldsymbol{k}_e, \boldsymbol{q}} P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{k}_h, \boldsymbol{k}_e} P^{s_h l_h s_e l_d}_{\boldsymbol{k}_h, \boldsymbol{k}_e} \tag{D.100}$$

$$+ \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{q} s_h s'_h s_e s'_e l_a l_b l_c l_d l_h l'_h} V^{ccs_e s'_e l_a l_b l_c l_d}_{\boldsymbol{k}_e, \boldsymbol{k}'_e, \boldsymbol{q}} P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{k}_h, \boldsymbol{k}_e + \boldsymbol{q}} P^{\dagger s'_h l'_h s'_e l_b}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e - \boldsymbol{q}} P^{s'_h l'_h s'_e l_d}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} P^{s_h l_h s_e l_c}_{\boldsymbol{k}_h, \boldsymbol{k}_e}. \tag{D.101}$$

The first term can now be thrown away for the same reason as before, leaving us with

$$H_{e-e} = \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{q} s_h s'_h s_e s'_e l_a l_b l_c l_d l_h l'_h} V^{ccs_e s'_e l_a l_b l_c l_d}_{\boldsymbol{k}_e, \boldsymbol{k}'_e, \boldsymbol{q}} P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{k}_h, \boldsymbol{k}_e + \boldsymbol{q}} P^{\dagger s'_h l'_h s'_e l_b}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e - \boldsymbol{q}} P^{s'_h l'_h s'_e l_d}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} P^{s_h l_h s_e l_c}_{\boldsymbol{k}_h, \boldsymbol{k}_e}. \tag{D.102}$$

Now we proceed to do the same for the hole-hole interaction,

$$H_{h-h} \tag{D.103}$$

$$= \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{q} s_h s'_h l_a l_b l_c l_d} V^{vvs_h l_a l_b l_c l_d}_{\boldsymbol{k}_h, \boldsymbol{k}'_h, \boldsymbol{q}} v^{\dagger s_h l_a}_{\boldsymbol{k}_h + \boldsymbol{q}} v^{s_h l_c}_{\boldsymbol{k}_h} v^{\dagger s'_h l_b}_{\boldsymbol{k}'_h - \boldsymbol{q}} v^{s'_h l_d}_{\boldsymbol{k}'_h} \tag{D.104}$$

$$= \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{q} s_h s'_h l_a l_b l_c l_d} V^{vvs_h s'_h l_a l_b l_c l_d}_{\boldsymbol{k}_h, \boldsymbol{k}'_h, \boldsymbol{q}} \tag{D.105}$$

$$\cdot \left(\delta^{l_a l_c}_{s_h s_h} \delta_{\boldsymbol{k}_h + \boldsymbol{q}, \boldsymbol{k}_h} - \sum_{\boldsymbol{k}_e s_e l_e} P^{\dagger s_h l_c s_e l_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} P^{s_h l_a s_e l_e}_{\boldsymbol{k}_h + \boldsymbol{q}, \boldsymbol{k}_e} \right) \tag{D.106}$$

$$\cdot \left(\delta^{l_b l_d}_{s'_h s'_h} \delta_{\boldsymbol{k}'_h - \boldsymbol{q}, \boldsymbol{k}'_h} - \sum_{\boldsymbol{k}'_e s'_e l'_e} P^{\dagger s'_h l_d s'_e l'_e}_{\boldsymbol{k}'_h \boldsymbol{k}'_e} P^{s'_h l_b s'_e l'_e}_{\boldsymbol{k}'_h - \boldsymbol{q}, \boldsymbol{k}'_e} \right) \tag{D.107}$$

$$= \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h s_h s'_h l_a l_b} V^{vvs_h s'_h l_a l_b l_a l_b}_{\boldsymbol{k}_h, \boldsymbol{k}'_h, \boldsymbol{0}} \tag{D.108}$$

$$- \frac{1}{2} \sum_{\boldsymbol{k}'_e \boldsymbol{k}_h \boldsymbol{k}'_h s_h s'_h s'_e l_a l_b l_d l'_e} V^{vvs_h s'_h l_a l_b l_a l_d}_{\boldsymbol{k}_h, \boldsymbol{k}'_h, \boldsymbol{0}} P^{\dagger s'_h l_d s'_e l'_e}_{\boldsymbol{k}'_h \boldsymbol{k}'_e} P^{s'_h l_b s'_e l'_e}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} \tag{D.109}$$

$$- \frac{1}{2} \sum_{\boldsymbol{k}_e \boldsymbol{k}_h \boldsymbol{k}'_h s_e s_h s'_h l_a l_b l_b l_c l_e} V^{vvs_h s'_h l_a l_b l_c l_b}_{\boldsymbol{k}_h, \boldsymbol{k}'_h, \boldsymbol{0}} P^{\dagger s_h l_c s_e l_e}_{\boldsymbol{k}_h \boldsymbol{k}_e} P^{s_h l_a s_e l_e}_{\boldsymbol{k}_h, \boldsymbol{k}_e} \tag{D.110}$$

$$+ \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{q} s_h s'_h s_e s'_e l_a l_b l_c l_d l_e l'_e} V^{vvs_h s'_h l_a l_b l_c l_d}_{\boldsymbol{k}_h, \boldsymbol{k}'_h, \boldsymbol{q}} P^{\dagger s_h l_c s_e l_e}_{\boldsymbol{k}_h, \boldsymbol{k}_e} P^{s_h l_a s_e l_e}_{\boldsymbol{k}_h + \boldsymbol{q}, \boldsymbol{k}_e} P^{\dagger s'_h l_d s'_e l'_e}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} P^{s'_h l_b s'_e l'_e}_{\boldsymbol{k}'_h - \boldsymbol{q}, \boldsymbol{k}'_e}. \tag{D.111}$$

As usual we ignore the constant and energy renormalizing terms and continue with

$$H_{h-h} = \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{q} s_h s'_h s_e s'_e l_a l_b l_c l_d l_e l'_e} V^{vvs_h s'_h l_a l_b l_c l_d}_{\boldsymbol{k}_h, \boldsymbol{k}'_h, \boldsymbol{q}} P^{\dagger s_h l_c s_e l_e}_{\boldsymbol{k}_h, \boldsymbol{k}_e} P^{s_h l_a s_e l_e}_{\boldsymbol{k}_h + \boldsymbol{q}, \boldsymbol{k}_e} P^{\dagger s'_h l_d s'_e l'_e}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} P^{s'_h l_b s'_e l'_e}_{\boldsymbol{k}'_h - \boldsymbol{q}, \boldsymbol{k}'_e} \tag{D.112}$$

$$= \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{k}_e s_h s_e l_a l_b l_c l_e} V^{vvs_h s'_h l_a l_b l_c l_a}_{\boldsymbol{k}_h, \boldsymbol{k}_h + \boldsymbol{q}, \boldsymbol{q}} P^{\dagger s_h l_c s_e l_e}_{\boldsymbol{k}_h, \boldsymbol{k}_e} P^{s_h l_b s_e l_e}_{\boldsymbol{k}_h, \boldsymbol{k}_e} \tag{D.113}$$

$$+ \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{q} s_h s'_h s_e s'_e l_a l_b l_c l_d l_e l'_e} V^{vvs_h s'_h l_a l_b l_c l_d}_{\boldsymbol{k}_h, \boldsymbol{k}'_h, \boldsymbol{q}} P^{\dagger s_h l_c s_e l_e}_{\boldsymbol{k}_h, \boldsymbol{k}_e} P^{\dagger s'_h l_d s'_e l'_e}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} P^{s'_h l_b s'_e l'_e}_{\boldsymbol{k}'_h - \boldsymbol{q}, \boldsymbol{k}'_e} P^{s_h l_a s_e l_e}_{\boldsymbol{k}_h + \boldsymbol{q}, \boldsymbol{k}_e}. \tag{D.114}$$

After once again throwing away the first term and shifting the indices $\boldsymbol{k}_h \to \boldsymbol{k}_h - \boldsymbol{q}$, $\boldsymbol{k}'_h \to \boldsymbol{k}'_h + \boldsymbol{q}$, $l_a \leftrightarrow l_c$, $l_b \leftrightarrow l_d$ for convenience we finally end up with

$$H_{h-h} = \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{q} s_h s'_h s_e s'_e l_a l_b l_c l_d l_e l'_e} V^{vvs_h s'_h l_c l_d l_a l_b}_{\boldsymbol{k}_h - \boldsymbol{q}, \boldsymbol{k}'_h + \boldsymbol{q}, \boldsymbol{q}} P^{\dagger s_h l_a s_e l_e}_{\boldsymbol{k}_h - \boldsymbol{q}, \boldsymbol{k}_e} P^{\dagger s'_h l_b s'_e l'_e}_{\boldsymbol{k}'_h + \boldsymbol{q}, \boldsymbol{k}'_e} P^{s'_h l_d s'_e l'_e}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} P^{s_h l_c s_e l_e}_{\boldsymbol{k}_h, \boldsymbol{k}_e}. \tag{D.115}$$

Now for the final term, the electron-hole interaction

$$H_{e-h} = - \sum_{\boldsymbol{k}_e \boldsymbol{k}'_h \boldsymbol{q} s_e s'_h l_a l_b l_c l_d} V^{cvs_e s'_h l_a l_b l_c l_d}_{\boldsymbol{k}_e, \boldsymbol{k}'_h, \boldsymbol{q}} c^{\dagger s_e l_a}_{\boldsymbol{k}_e + \boldsymbol{q}} c^{s_e l_c}_{\boldsymbol{k}_e} v^{s'_h l_d}_{\boldsymbol{k}'_h} v^{\dagger s'_h l_b}_{\boldsymbol{k}'_h - \boldsymbol{q}} \tag{D.116}$$

$$= - \sum_{\boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{q} s_e s'_e s_h s'_h l_a l_b l_c l_d l_h l'_e} V^{cvs_e s'_h l_a l_b l_c l_d}_{\boldsymbol{k}_e, \boldsymbol{k}'_h, \boldsymbol{q}} P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{k}_h, \boldsymbol{k}_e + \boldsymbol{q}} P^{s_h l_h s_e l_c}_{\boldsymbol{k}_h \boldsymbol{k}_e} P^{\dagger s'_h l_d s'_e l'_e}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} P^{s'_h l_b s'_e l'_e}_{\boldsymbol{k}'_h - \boldsymbol{q}, \boldsymbol{k}'_e} \tag{D.117}$$

$$= - \sum_{\boldsymbol{k}_e \boldsymbol{k}_h \boldsymbol{q} s_e s_h l_a l_b l_c l_d} V^{cvs_e s_h l_a l_b l_c l_d}_{\boldsymbol{k}_e, \boldsymbol{k}_h, \boldsymbol{q}} P^{\dagger s_h l_c s_e l_a}_{\boldsymbol{k}_h, \boldsymbol{k}_e + \boldsymbol{q}} P^{s_h l_b s_e l_d}_{\boldsymbol{k}_h - \boldsymbol{q}, \boldsymbol{k}_e} \tag{D.118}$$

$$- \sum_{\boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{q} s_e s'_e s_h s'_h l_a l_b l_c l_d l_h l'_e} V^{cvs_e s'_h l_a l_b l_c l_d}_{\boldsymbol{k}_e, \boldsymbol{k}'_h, \boldsymbol{q}} P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{k}_h, \boldsymbol{k}_e + \boldsymbol{q}} P^{\dagger s'_h l_d s'_e l'_e}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} P^{s'_h l_b s'_e l'_e}_{\boldsymbol{k}'_h - \boldsymbol{q}, \boldsymbol{k}'_e} P^{s_h l_h s_e l_c}_{\boldsymbol{k}_h \boldsymbol{k}_e}. \tag{D.119}$$

This time we can see that the first term does more than simply renormalize the energy. We will cover what it does in more detail later on, but for now we will simply shift the index $\boldsymbol{k}_h \to \boldsymbol{k}_h + \boldsymbol{q}$, call it

$$H^0_{e-h} \equiv - \sum_{\boldsymbol{k}_e \boldsymbol{k}_h \boldsymbol{q} s_e s_h l_a l_b l_c l_d} V^{cvs_e s_h l_a l_b l_c l_d}_{\boldsymbol{k}_e, \boldsymbol{k}_h + \boldsymbol{q}, \boldsymbol{q}} P^{\dagger s_h l_c s_e l_a}_{\boldsymbol{k}_h + \boldsymbol{q}, \boldsymbol{k}_e + \boldsymbol{q}} P^{s_h l_b s_e l_d}_{\boldsymbol{k}_h, \boldsymbol{k}_e} \tag{D.120}$$

and move on. For the remaining term we will perform the same index shift (but for $\boldsymbol{k}'_h$) as well as $l_b \leftrightarrow l_d$ to find

$$H_{e-h} = \sum_{\boldsymbol{k}_e \boldsymbol{k}'_e \boldsymbol{k}_h \boldsymbol{k}'_h \boldsymbol{q} s_e s'_e s_h s'_h l_a l_b l_c l_d l_h l'_e} V^{cvs_e s'_h l_a l_d l_c l_b}_{\boldsymbol{k}_e, \boldsymbol{k}'_h + \boldsymbol{q}, \boldsymbol{q}} P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{k}_h, \boldsymbol{k}_e + \boldsymbol{q}} P^{\dagger s'_h l_b s'_e l'_e}_{\boldsymbol{k}'_h + \boldsymbol{q}, \boldsymbol{k}'_e} P^{s'_h l_d s'_e l'_e}_{\boldsymbol{k}'_h, \boldsymbol{k}'_e} P^{s_h l_h s_e l_c}_{\boldsymbol{k}_h \boldsymbol{k}_e}. \tag{D.121}$$

D.3.2 Going to the excitonic picture

It is now finally time to convert the Coulomb element to the excitonic picture (the H^0_{e-h} element excluded since it is handled in the main text). Taking the terms one at a time we get

$$H_{e-e} \tag{D.122}$$
$$= \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}_e \boldsymbol{k}'_h \boldsymbol{k}'_e \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_h l'_h} V^{ccs_e s'_e l_a l_b l_c l_d}_{\boldsymbol{k}_e, \boldsymbol{k}'_e, \boldsymbol{K}} \tag{D.123}$$
$$\cdot P^{\dagger s_h l_h s_e l_a}_{\alpha \boldsymbol{k}_h + \beta(\boldsymbol{k}_e + \boldsymbol{K}), \boldsymbol{k}_e + \boldsymbol{q} - \boldsymbol{k}_h} P^{\dagger s'_h l'_h s'_e l_b}_{\alpha \boldsymbol{k}'_h + \beta(\boldsymbol{k}'_e - \boldsymbol{K}), \boldsymbol{k}'_e - \boldsymbol{K} - \boldsymbol{k}'_h} P^{s'_h l'_h s'_e l_d}_{\alpha \boldsymbol{k}'_h + \beta \boldsymbol{k}'_e, \boldsymbol{k}'_e - \boldsymbol{k}'_h} P^{s_h l_h s_e l_c}_{\alpha \boldsymbol{k}_h + \beta \boldsymbol{k}_e, \boldsymbol{k}_e - \boldsymbol{k}_h} \tag{D.124}$$
$$= \frac{1}{2} \sum_{\boldsymbol{q} \boldsymbol{q}' \boldsymbol{Q} \boldsymbol{Q}' \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_h l_h} V^{ccs_e s'_e l_a l_b l_c l_d}_{\boldsymbol{q} + \alpha \boldsymbol{Q}, \boldsymbol{q}' + \alpha \boldsymbol{Q}', \boldsymbol{K}} \tag{D.125}$$
$$\cdot P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{q} + \beta \boldsymbol{K}, \boldsymbol{Q} + \boldsymbol{K}} P^{\dagger s'_h l'_h s'_e l_b}_{\boldsymbol{q}' - \beta \boldsymbol{K}, \boldsymbol{Q}' - \boldsymbol{K}} P^{s'_h l'_h s'_e l_d}_{\boldsymbol{q}', \boldsymbol{Q}'} P^{s_h l_h s_e l_c}_{\boldsymbol{q}, \boldsymbol{Q}} \tag{D.126}$$
$$= \frac{1}{2} \sum_{\boldsymbol{q} \boldsymbol{q}' \boldsymbol{Q} \boldsymbol{Q}' \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_h l'_h \mu \mu' \nu \nu'} V^{ccs_e s'_e l_a l_b l_c l_d}_{\boldsymbol{q} + \alpha \boldsymbol{Q}, \boldsymbol{q}' + \alpha \boldsymbol{Q}', \boldsymbol{K}} \tag{D.127}$$
$$\cdot \varphi^{\mu s_h l_h s_e l_a}_{\boldsymbol{q} + \beta \boldsymbol{K}} \varphi^{\mu' s'_h l'_h s'_e l_b}_{\boldsymbol{q}' - \beta \boldsymbol{K}} \varphi^{\nu' s'_h l'_h s'_e l_d}_{\boldsymbol{q}'} \varphi^{\nu s_h l_h s_e l_c}_{\boldsymbol{q}} \tag{D.128}$$
$$\cdot P^{\dagger \mu s_h l_h s_e l_a}_{\boldsymbol{Q} + \boldsymbol{K}} P^{\dagger \mu' s'_h l'_h s'_e l_b}_{\boldsymbol{Q}' - \boldsymbol{K}} P^{\nu' s'_h l'_h s'_e l_d}_{\boldsymbol{Q}'} P^{\nu s_h l_h s_e l_c}_{\boldsymbol{Q}} \tag{D.129}$$
$$\equiv \frac{1}{2} \sum_{\boldsymbol{q} \boldsymbol{q}' \boldsymbol{Q} \boldsymbol{Q}' \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_h l'_h \mu \mu' \nu \nu'} V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e l_a l_b l_c l_d}_{e-e, \boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \tag{D.130}$$
$$\cdot P^{\dagger \mu s_h l_h s_e l_a}_{\boldsymbol{Q} + \boldsymbol{K}} P^{\dagger \mu' s'_h l'_h s'_e l_b}_{\boldsymbol{Q}' - \boldsymbol{K}} P^{\nu' s'_h l'_h s'_e l_d}_{\boldsymbol{Q}'} P^{\nu s_h l_h s_e l_c}_{\boldsymbol{Q}}, \tag{D.131}$$

$$H_{h-h} \tag{D.132}$$
$$= \frac{1}{2} \sum_{\boldsymbol{k}_h \boldsymbol{k}_e \boldsymbol{k}'_h \boldsymbol{k}'_e \boldsymbol{K} s_{h,} s_e s'_h s'_e l_h l_e l'_h l'_e} V^{vv, s_h s'_h l_c l_d l_a l_b}_{\boldsymbol{k}_h - \boldsymbol{K}, \boldsymbol{k}'_h + \boldsymbol{K}, \boldsymbol{K}} \tag{D.133}$$
$$\cdot P^{\dagger s_h l_h s_e l_a}_{\alpha(\boldsymbol{k}_h - \boldsymbol{K}) + \beta \boldsymbol{k}_e, \boldsymbol{k}_e - \boldsymbol{k}_h + \boldsymbol{K}} P^{\dagger s'_h l'_h s'_e l_b}_{\alpha(\boldsymbol{k}'_h + \boldsymbol{K}) + \beta \boldsymbol{k}'_e, \boldsymbol{k}'_e - \boldsymbol{k}'_h - \boldsymbol{K}} P^{s'_h l'_h s'_e l_d}_{\alpha \boldsymbol{k}'_h + \beta \boldsymbol{k}'_e, \boldsymbol{k}'_e - \boldsymbol{k}'_h} P^{s_h l_h s_e l_c}_{\alpha \boldsymbol{k}_h + \beta \boldsymbol{k}_e, \boldsymbol{k}_e - \boldsymbol{k}_h} \tag{D.134}$$
$$= \frac{1}{2} \sum_{\boldsymbol{q} \boldsymbol{q}' \boldsymbol{Q} \boldsymbol{Q}' \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_e l'_e} V^{vv, s_h s'_h l_c l_d l_a l_b}_{\boldsymbol{q} - \beta \boldsymbol{Q} - \boldsymbol{K}, \boldsymbol{q}' - \beta \boldsymbol{Q}' + \boldsymbol{K}, \boldsymbol{K}} \tag{D.135}$$
$$\cdot P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{q} - \alpha \boldsymbol{K}, \boldsymbol{Q} + \boldsymbol{K}} P^{\dagger s'_h l'_h s'_e l_b}_{\boldsymbol{q}' + \alpha \boldsymbol{K}, \boldsymbol{Q}' - \boldsymbol{K}} P^{s'_h l'_h s'_e l_d}_{\boldsymbol{q}', \boldsymbol{Q}'} P^{s_h l_h s_e l_c}_{\boldsymbol{q}, \boldsymbol{Q}} \tag{D.136}$$
$$= \frac{1}{2} \sum_{\boldsymbol{q} \boldsymbol{q}' \boldsymbol{Q} \boldsymbol{Q}' \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_e l'_e \mu \mu' \nu \nu'} V^{vv, s_h s'_h l_c l_d l_a l_b}_{\boldsymbol{q} - \beta \boldsymbol{Q} - \boldsymbol{K}, \boldsymbol{q}' - \beta \boldsymbol{Q}' + \boldsymbol{K}, \boldsymbol{K}} \tag{D.137}$$
$$\cdot \varphi^{\mu s_h l_h s_e l_a}_{\boldsymbol{q} - \alpha \boldsymbol{K}} \varphi^{\mu' s'_h l'_h s'_e l_b}_{\boldsymbol{q}' + \alpha \boldsymbol{K}} \varphi^{\nu' s'_h l'_h s'_e l_d}_{\boldsymbol{q}'} \varphi^{\nu s_h l_h s_e l_c}_{\boldsymbol{q}} \tag{D.138}$$
$$\cdot P^{\dagger \mu s_h l_h s_e l_a}_{\boldsymbol{Q} + \boldsymbol{K}} P^{\dagger \mu' s'_h l'_h s'_e l_b}_{\boldsymbol{Q}' - \boldsymbol{K}} P^{\nu' s'_h l'_h s'_e l_d}_{\boldsymbol{Q}'} P^{\nu s_h l_h s_e l_c}_{\boldsymbol{Q}} \tag{D.139}$$
$$\equiv \frac{1}{2} \sum_{\boldsymbol{q} \boldsymbol{q}' \boldsymbol{Q} \boldsymbol{Q}' \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_e l_e \mu \mu' \nu \nu'} V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e l_h l_e l'_h l'_e}_{h-h, \boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \tag{D.140}$$
$$\cdot P^{\dagger \mu s_h l_h s_e l_a}_{\boldsymbol{Q} + \boldsymbol{K}} P^{\dagger \mu' s'_h l'_h s'_e l_b}_{\boldsymbol{Q}' - \boldsymbol{K}} P^{\nu' s'_h l'_h s'_e l_d}_{\boldsymbol{Q}'} P^{\nu s_h l_h s_e l_c}_{\boldsymbol{Q}} \tag{D.141}$$

and

$$H_{e-h} \tag{D.142}$$
$$= - \sum_{\boldsymbol{k}_h \boldsymbol{k}_e \boldsymbol{k}'_h \boldsymbol{k}'_e \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_h l'_e} V^{cvs_e s'_h s'_h l_a l_d l_c l_b}_{\boldsymbol{k}_e, \boldsymbol{k}'_h + \boldsymbol{K}, \boldsymbol{K}} \tag{D.143}$$
$$\cdot P^{\dagger s_h l_h s_e l_a}_{\alpha \boldsymbol{k}_h + \beta(\boldsymbol{k}_e + \boldsymbol{K}), \boldsymbol{k}_e + \boldsymbol{K} - \boldsymbol{k}_h} P^{\dagger s'_h l'_h s'_e l_b}_{\alpha(\boldsymbol{k}'_h + \boldsymbol{K}) + \beta \boldsymbol{k}'_e, \boldsymbol{k}'_e - \boldsymbol{k}'_h - \boldsymbol{K}} P^{s'_h l'_h s'_e l_d}_{\alpha \boldsymbol{k}'_h + \beta \boldsymbol{k}'_e, \boldsymbol{k}'_e - \boldsymbol{k}'_h} P^{s_h l_h s_e l_c}_{\alpha \boldsymbol{k}_h + \beta \boldsymbol{k}_e, \boldsymbol{k}_e - \boldsymbol{k}_h} \tag{D.144}$$
$$= - \sum_{\boldsymbol{q} \boldsymbol{q}' \boldsymbol{Q} \boldsymbol{Q}' \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_h l'_e} V^{cvs_e s'_h s'_h l_a l_d l_c l_b}_{\boldsymbol{q} + \alpha \boldsymbol{Q}, \boldsymbol{q}' - \beta \boldsymbol{Q}' + \boldsymbol{K}, \boldsymbol{K}} \tag{D.145}$$
$$\cdot P^{\dagger s_h l_h s_e l_a}_{\boldsymbol{q} + \beta \boldsymbol{K}, \boldsymbol{Q} + \boldsymbol{K}} P^{\dagger s'_h l'_h s'_e l_b}_{\boldsymbol{q}' + \alpha \boldsymbol{K}, \boldsymbol{Q}' - \boldsymbol{K}} P^{s'_h l'_h s'_e l_d}_{\boldsymbol{q}', \boldsymbol{Q}'} P^{s_h l_h s_e l_c}_{\boldsymbol{q}, \boldsymbol{Q}} \tag{D.146}$$
$$= - \sum_{\boldsymbol{q} \boldsymbol{q}' \boldsymbol{Q} \boldsymbol{Q}' \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_h l'_e \mu \mu' \nu \nu'} V^{cvs_e s'_h s'_h l_a l_d l_c l_b}_{\boldsymbol{q} + \alpha \boldsymbol{Q}, \boldsymbol{q}' - \beta \boldsymbol{Q}' + \boldsymbol{K}, \boldsymbol{K}} \tag{D.147}$$
$$\cdot \varphi^{\mu s_h l_h s_e l_a}_{\boldsymbol{q} + \beta \boldsymbol{K}} \varphi^{\mu' s'_h l'_h s'_e l_b}_{\boldsymbol{q}' + \alpha \boldsymbol{K}} \varphi^{\nu' s'_h l'_h s'_e l_d}_{\boldsymbol{q}'} \varphi^{\nu s_h l_h s_e l_c}_{\boldsymbol{q}} \tag{D.148}$$
$$\cdot P^{\dagger \mu s_h l_h s_e l_a}_{\boldsymbol{Q} + \boldsymbol{K}} P^{\dagger \mu' s'_h l'_h s'_e l_b}_{\boldsymbol{Q}' - \boldsymbol{K}} P^{\nu' s'_h l'_h s'_e l_d}_{\boldsymbol{Q}'} P^{\nu s_h l_h s_e l_c}_{\boldsymbol{Q}} \tag{D.149}$$
$$\equiv -\frac{1}{2} \sum_{\boldsymbol{Q} \boldsymbol{Q}' \boldsymbol{K} s_h s_e s'_h s'_e l_a l_b l_c l_d l_h l'_e \mu \mu' \nu \nu'} V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e l_h l_e l'_h l'_e}_{e-h, \boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \tag{D.150}$$
$$\cdot P^{\dagger \mu s_h l_h s_e l_a}_{\boldsymbol{Q} + \boldsymbol{K}} P^{\dagger \mu' s'_h l'_h s'_e l_b}_{\boldsymbol{Q}' - \boldsymbol{K}} P^{\nu' s'_h l'_h s'_e l_d}_{\boldsymbol{Q}'} P^{\nu s_h l_h s_e l_c}_{\boldsymbol{Q}}. \tag{D.151}$$

We therefore get

$$H_{c-c} = \sum_{\boldsymbol{Q} \boldsymbol{Q}' s_h s_e s'_h s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e \boldsymbol{K} \mu \mu' \nu \nu'} V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{\boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \tag{D.152}$$
$$\cdot P^{\dagger \mu s_h l^a_h s_e l^a_e}_{\boldsymbol{Q} + \boldsymbol{K}} P^{\dagger \mu' s'_h l^b_h s'_e l^b_e}_{\boldsymbol{Q}' - \boldsymbol{K}} P^{\nu' s'_h l^d_h s'_e l^d_e}_{\boldsymbol{Q}'} P^{\nu s_h l^c_h s_e l^c_e}_{\boldsymbol{Q}}, \tag{D.153}$$

where

$$V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{\boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \equiv \frac{1}{4} V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{e-e, \boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \tag{D.154}$$
$$+ \frac{1}{4} V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{h-h, \boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \tag{D.155}$$
$$- \frac{1}{2} V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{e-h, \boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \tag{D.156}$$

and

$$V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{e-e, \boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \tag{D.157}$$
$$\equiv \sum_{\boldsymbol{q} \boldsymbol{q}'} V^{cc, s_e s'_e l_a l_b l_c l_d}_{\boldsymbol{q} + \alpha \boldsymbol{Q}, \boldsymbol{q}' + \alpha \boldsymbol{Q}', \boldsymbol{K}} \varphi^{\mu s_h l^a_h s_e l^a_e}_{\boldsymbol{q} + \beta \boldsymbol{K}} \varphi^{\mu' s'_h l^b_h s'_e l^b_e}_{\boldsymbol{q}' - \beta \boldsymbol{K}'} \varphi^{\nu' s'_h l^b_h s'_e l^d_e}_{\boldsymbol{q}'} \varphi^{\nu s_h l^a_h s_e l^c_e}_{\boldsymbol{q}} \delta_{l^a_h l^c_h} \delta_{l^b_h l^d_h}, \tag{D.158}$$
$$V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{h-h, \boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \tag{D.159}$$
$$\equiv \sum_{\boldsymbol{q} \boldsymbol{q}'} V^{vv, s_e s'_e l_c l_d l_a l_b}_{\boldsymbol{q} - \beta \boldsymbol{Q} - \boldsymbol{K}, \boldsymbol{q}' - \beta \boldsymbol{Q}' + \boldsymbol{K}, \boldsymbol{K}} \varphi^{\mu s_h l_a s_e l^a_e}_{\boldsymbol{q} - \alpha \boldsymbol{K}} \varphi^{\mu' s'_h l_b s'_e l^b_e}_{\boldsymbol{q}' + \alpha \boldsymbol{K}'} \varphi^{\nu' s'_h l_d s'_e l^b_e}_{\boldsymbol{q}'} \varphi^{\nu s_h l_c s_e l^a_e}_{\boldsymbol{q}} \delta_{l^a_e l^c_e} \delta_{l^b_e l^d_e}, \tag{D.160}$$
$$V^{\mu \mu' \nu \nu' s_h s_e s'_h s'_e s'_e l^a_h l^b_h l^c_h l^d_h l^a_e l^b_e l^c_e l^d_e}_{e-h, \boldsymbol{Q}, \boldsymbol{Q}', \boldsymbol{K}} \tag{D.161}$$
$$\equiv \sum_{\boldsymbol{q} \boldsymbol{q}'} V^{cv, s_e s'_h l_a l_d l_c l_b}_{\boldsymbol{q} + \alpha \boldsymbol{Q}, \boldsymbol{q}' - \beta \boldsymbol{Q}' + \boldsymbol{K}, \boldsymbol{K}} \varphi^{\mu s_h l^a_h s_e l^a_e}_{\boldsymbol{q} + \beta \boldsymbol{K}} \varphi^{\mu' s'_h l^b_h s'_e l^b_e}_{\boldsymbol{q}' + \alpha \boldsymbol{K}'} \varphi^{\nu' s'_h l^d_h s'_e l^b_e}_{\boldsymbol{q}'} \varphi^{\nu s_h l^a_h s_e l^c_e}_{\boldsymbol{q}} \delta_{l^a_h l^c_h} \delta_{l^b_e l^d_e}. \tag{D.162}$$