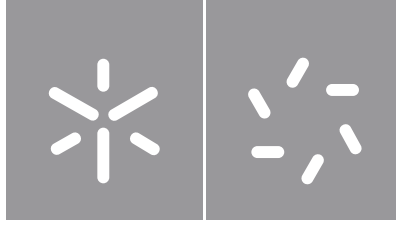


Universidade do Minho
Escola de Ciências

João Carlos Gomes Henriques

Excitons in two dimensional materials



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Excitons in two dimensional materials

Master Thesis

Physics

Work developed under the supervision of:

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*To my mother
and in memory of my father*

STATEMENT OF INTEGRITY

I hereby declare having conducted this academic work with integrity. I confirm that I have not used plagiarism or any form of undue use of information or falsification of results along the process leading to its elaboration.

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Resumo

Excitões em materiais bidimensionais

Nesta dissertação são exploradas algumas das principais propriedades óticas de dicalcogenetos de metais de transição (TMDs) devido a efeitos excitônicos.

Na primeira parte do texto dedicamo-nos ao estudo do caso de uma camada de MoS_2 perto de um material magnético. Aí, vimos que, devido à proximidade com o material magnético, a simetria de inversão temporal do TMD é quebrada, originando uma resposta de Hall finita mesmo na ausência de um campo magnético externo. Nessa mesma secção, calculamos a condutividade ótica do sistema quer no regime de partícula única, quer no excitónico, estudando o efeito da polarização da luz incidente. Em ambos os casos verificou-se a excitação seletiva do vale K ou K' quando luz circularmente polarizada é usada.

Na secção seguinte dedicamo-nos ao estudo dos estados- p , uma classe de excitões que, devido a regras de seleção, não aparece em espectros óticos resultantes de excitações interbanda, mas que pode ser estudada em experiências do tipo *pump-probe*. Partindo de uma expressão microscópica para a polarizabilidade, estudamos como o laser *pump* pode povoar o estado $1s$, enquanto que o *probe* induz transições do $1s$ para a série- p .

As duas secções finais são dedicadas ao estudo da interação de excitões com fonões A_1 , calculamos a largura espectral da ressonância $1s$ em vários TMDs e observamos que naqueles com molibdénio a largura cresce linearmente com a temperatura, com uma correção exponencial a temperaturas elevadas, enquanto que para TMDs com tungsténio esta rapidamente se afasta da dependência linear. Nessas secções estudamos ainda como o acoplamento com fonões produz um desvio para o vermelho da ressonância do estado $1s$, e como esta adquire uma forma assimétrica.

Palavras-chave: condutividade, dicalcogenetos de metais de transição, excitões, fonões, largura espectral

Abstract

Excitons in two dimensional materials

In this dissertation we explore some of the main optical properties of transition metal dichalcogenides due to excitonic effects.

In the first part of the text we study the case of a monolayer of MoS_2 near a magnetic material. There, we find that due to the proximity with the magnetic material, the time reversal symmetry in the TMD is broken, which leads to a finite Hall response even in the absence of an external magnetic field. In the same section, we compute the optical conductivity of the system both in the single particle picture and when excitons are accounted for, studying the effect of exciting the system with different light polarizations. In both cases a valley selective response when circularly polarized light is used was found, with either the K or K' valleys being excited.

In the following section we focus on the p -states, a class of excitons which does not appear in interband optical excitation due to selection rules, but can be studied in pump-probe experiments. Starting from the microscopic definition of the polarizability, we studied how a pump laser can populate the $1s$ state, while a probe induces transitions from the $1s$ to the p -series.

The final two sections of the dissertation are dedicated to the study of the interaction of excitons with phonons. There, we compute the homogeneous linewidth of the $1s$ resonance in different TMDs at finite temperature, and find that in TMDs with molybdenum the linewidth increases linearly with temperature, with an exponential correction at higher temperatures, while for TMDs with tungsten the linewidth deviates from a linear dependence even at low temperatures. Furthermore, we also studied how the coupling with phonons produces a red-shift of the $1s$ absorption peak and leads the formation of phonon sidebands, which are responsible for an asymmetrical broadening of the resonance.

Keywords: conductivity, excitons, linewidth, phonons, transition metal dichalcogenides

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Introduction

The history of two dimensional (2D) materials dates back to the decade of 1920 when Linus Pauling studied the structure of layered materials, in particular transition metal dichalcogenides (TMDs) [2]. From that point onward, and throughout the entire 20th century, the study of layered materials evolved, and by the late 1960s dozens of these systems were known [3, 4]. Before the turn of the century, some works started to appear where the isolation of ultrathin layers from bulk materials was achieved using adhesive tapes [5, 6].

The biggest milestone in the field of 2D materials came in 2004, when Novoselov *et al.* were able to isolate and characterize a single layer of graphene by removing it from bulk graphite with scotch tape [7]. The experimental realization of graphene, a gapless monolayer of carbon atoms with novel physical properties resulting from its reduced dimensionality, propelled the research on this field. This rediscovered interest in layered systems inevitably lead to many findings, both in fundamental physics as well as in techniques and applications. Since the isolation of graphene a large number of 2D materials has been studied (see Fig. 1), examples of which are monolayer hexagonal-boron nitride (hBN), phosphorene and monolayer TMDs, the same materials studied by Pauling nearly a century before. While graphene does not boast an energy gap between its valence and conduction bands, making it a semi-metal, hBN, a material with an identical structure to graphene but made of boron and nitrogen atoms, presents a huge band gap of approximately 6 to 7 eV, making it an insulator. This material is known for its outstanding chemical stability in the monolayer form [9] and is often seen as an ideal substrate for other 2D materials [10]; on its own, hBN also presents promising optical properties, especially in the ultra-violet region of the electromagnetic spectrum [11–13]. Regarding phosphorene, a highly anisotropic 2D material which may be obtained by isolating a single layer of black phosphorus [14], we highlight its small band gap which may vary from 0.3 (the value for the bulk) to 2 eV [15], making it a semi-conductor, and its high carrier mobility [8]. As a result of its anisotropy, phosphorene presents exotic mechanical properties (e.g. a negative Poisson ration [16]), and displays dichroism [17], that is, the rate at which light is absorbed depends strongly on how it

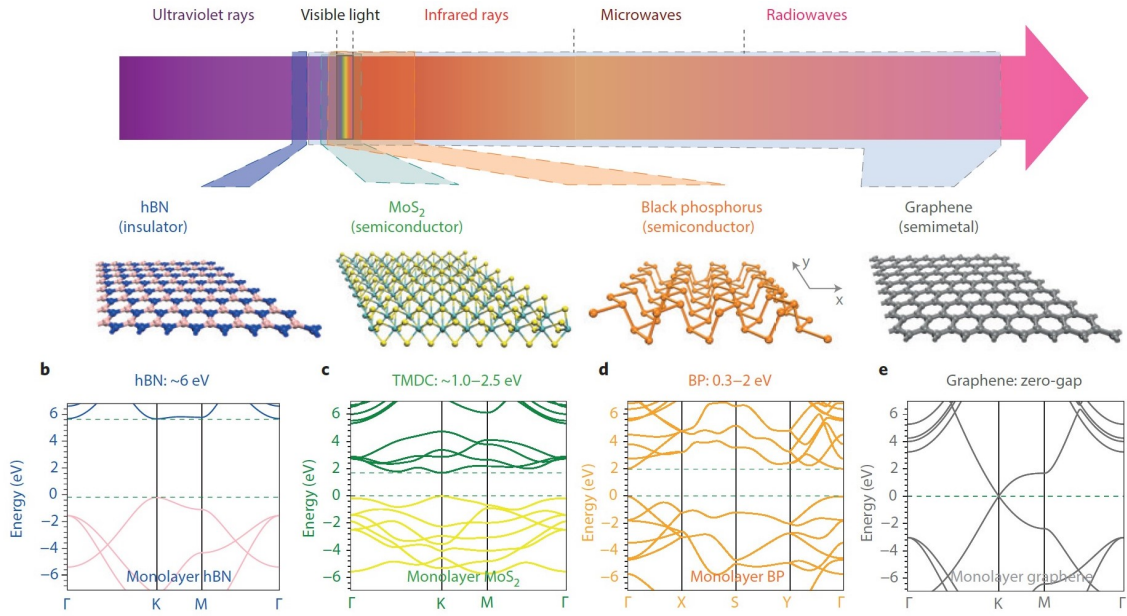


Figure 1: **2D materials.** Schematic representation of four 2D materials with the respective band structure and the relevant region of the electromagnetic spectrum for their optical properties. Taken from Ref. [8]

is polarized. At last, TMD monolayers are direct band gap semiconductors, with a gap of approximately 1 to 2 eV. Due to their current relevance in the field of 2D materials, especially the group VI semiconducting dichalcogenides, these will be the most prominent materials throughout this dissertation, and as such a more in depth description of their properties is given below.

Group VI semiconducting dichalcogenides are usually presented in the form MX_2 , with $M=Mo, W$ and $X=S, Se, Te$. Regarding the crystal structure, a TMD monolayer is composed of three planes of atoms, with two layers of chalcogens encapsulating a layer with the metal atoms. Its unit cell presents the structure of a trigonal prism with the vertices occupied with the chalcogens, while a single metal atom sits in the center of the prism. When seen from above, the monolayer resembles the honeycomb lattice found in graphene and hBN (see Fig. 2). In bulk crystals these monolayers are stacked, with each layer weakly connected to the ones surrounding it through van-der-Waals bondings [3]. Contrary to the bulk crystals, which are described by the D_{6h} point group, the monolayers present the symmetry of the D_{3h} point group [18]. This difference is a result of the loss of inversion symmetry in the monolayer form, something which is recovered when an even number of layers is stacked. As we mentioned before, TMDs are direct gap semiconductors, however it is important to note that this is only strictly true in the monolayer case, since in the respective bulk crystals the band gap has an indirect nature [19]. As the number of layers is reduced the indirect band gap increases, and the system experiences a crossover from indirect to direct band gap when going from a bilayer to a single layer of TMD, as can be seen in Fig. 2 [4]. The direct band gap in the monolayer limit allows for a much more efficient coupling with light, making these systems more

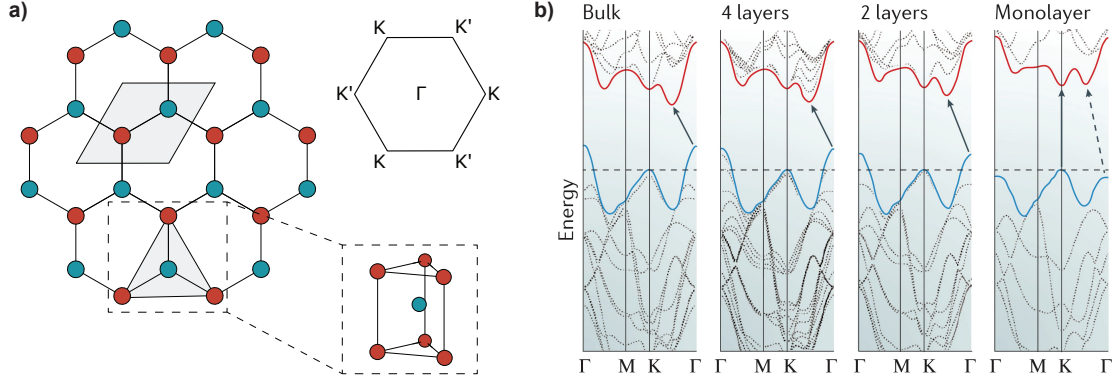


Figure 2: **Lattice and bands of a TMD.** a) Representation of the lattice of a TMD (both top and side view), and its Brillouin zone with the Dirac valleys (K and K') and the zone center (Γ point) identified. b) Band structure of a TMD from bulk to monolayer, with the band gap identified by the solid arrow. Taken from Ref. [4]

appealing than their bulk counterparts for optical applications, such as phototransistors and sensors [20, 21]. Furthermore, as opposed to many conventional three dimensional III-V and II-VI semiconductors, the direct band gap of a TMD monolayer is not located in the center of the Brillouin zone, but rather on its vertices, commonly called the Dirac valleys. The vertices of the Brillouin zone are also referred to as the K and K' points, being inequivalent and linked through time reversal symmetry [22]. Another important aspect of the band structure of TMDs is the large spin-orbit effect that appears in these materials due to the heavy *d*-orbitals of the metal atoms [23–25]. This effect is responsible for a splitting of hundreds of meV between the spin up and spin down states in the valence band, while the splitting in the conduction band is only of a few meV in materials with Mo, and few tens of meV in materials with W. Moreover, the relative shift between spin up and spin down states in the conduction band has different signs depending on the type of transition metal. At last, we note that due to the orbital composition of the conduction and valence bands in the K and K' points, TMDs present circular dichroism [22, 26], i.e. left and right circularly polarized light interact preferentially with either the K or the K' point. This valley selective excitation, combined with the strong spin-orbit coupling, makes these materials useful in the field of valleytronics [27].

Besides all the aforementioned properties, the 2D character of monolayer TMDs combined with the reduced dielectric screening is responsible for the appearance of many body effects, such as the formation of excitons. When radiation with an appropriate energy shines on the monolayer, an electron may be promoted from the valence to the conduction band, leaving in its place a hole. Since an electron is a negatively charged particle, and a hole can be interpreted as an effective one with positive charge, these two particles interact through an electrostatic potential [28]. This situation clearly resembles that of the hydrogen atom, where the Coulomb potential mediates the interaction between a proton and an electron, originating the bound states which make up the Rydberg series. Likewise, when the electron and

hole interact in a TMD, a bound state, which we term exciton, may be created. Although excitons are not exclusive to 2D materials, what truly sets them apart from the 3D case is the value of their binding energies. While in conventional 3D semiconductors excitons present binding energies in the order of a few tens of meV, which makes them vulnerable to thermal dissociation, in 2D systems excitons may acquire binding energies in excess of 500 meV, making them robust structures even at room temperature [28]. The optical properties of monolayer TMDs are intimately related with their excitonic response, since excitons originate a much stronger light-matter coupling than interband transitions [22]. The main signature of the presence of excitons is the appearance of sharp resonances inside the energy gap in e.g. absorption measurements, schematically depicted in Fig. 3. These resonances correspond to the excitation of different exciton states

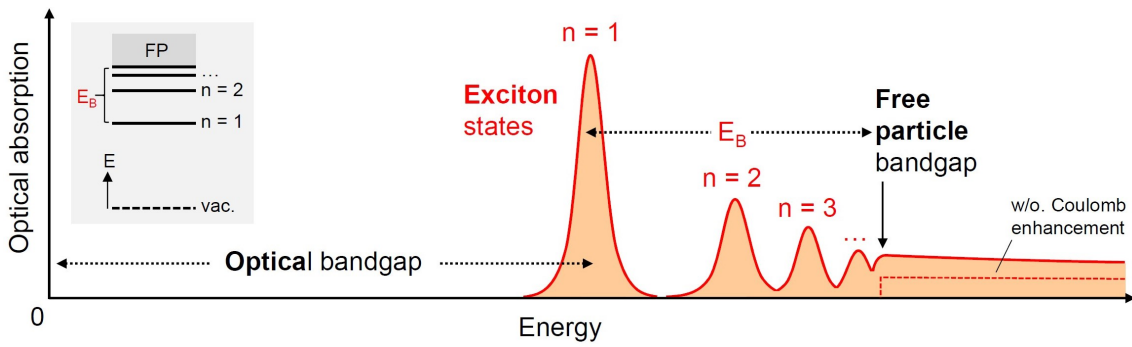


Figure 3: **TMD optical absorption.** Schematic representation of the optical absorption of a TMD with the contribution of the excitonic response (resonances) and the interband transitions. Taken from Ref. [22]

(like the absorption spectrum of the Hydrogen atom), and preserve the properties of the underlying band structure, namely the energy splitting between spin states, and the circular dichroism. Besides the excitons that appear in conventional absorption experiments, other types of excitons exist, which, because they do not appear in this type of measurement, are termed dark. Excitons may be dark for several reasons, for example, they may have a finite center of mass momentum placing them outside the light cone. Alternatively, excitons with given angular properties may be impossible to excite in interband transitions due to angular momentum selection rules. Excitons where the electron and hole have opposite spins are also dark because the interaction with light is not capable of producing the required spin-flip of the carrier.

The vast number of 2D materials, combined with their rich optical properties and the possibility of stacking them to create van-der-Waals heterostructures makes the field of nanodevices and layered materials a very intriguing one, with a plethora of possible systems to explore. Our goal with this dissertation is to study the main optical properties of TMDs due to their excitonic response. To that end, we will consider a series of problems, that we will solve using different techniques, casting light on the main properties of these systems. The text is organized as follows: In Section 2 we study the problem of a monolayer

of MoS₂ near a magnetic material, and compute its conductivity in the single particle picture; afterwards excitons are accounted for. In Section 3 we focus on a pump-probe type of experiment and compute the optical response associated with transitions between exciton states. Sections 4 and 5 are dedicated to the exciton-phonon interaction, where the former deals with the induced homogenous linewidth and the latter treats the polaron shift and the formation of phonon sidebands. Since every section covers a distinct topic, we close each of them with a brief summary of what was developed there. Nonetheless, in Section 6 we present a final overview of the entire work and future prospects. In Appendixes A to F we present some of the calculations given in the main text in a more detailed manner.

Published papers in peer-reviewed journals

During the course of the Master's degree the following works were published in peer-reviewed journals:

1. *Analytical description of the 1s exciton linewidth temperature dependence in transition metal dichalcogenides*, **J. C. G. Henriques**, N. A. Mortensen, and N. M. R. Peres Phys. Rev. B **103**, 235402 (2021)
2. *Calculation of the nonlinear response functions of intra-exciton transitions in two-dimensional transition metal dichalcogenides*, **J. C. G. Henriques**, Høgni C. Kamban, Thomas G. Pedersen, and N. M. R. Peres, Phys. Rev. B **103**, 235412 (2021)
3. *A theoretical model of the polarizability due to transitions between exciton states in transition metal dichalcogenides: Application to WSe₂*, **J. C. G. Henriques**, M. F. C. M. Quintela, and N. M. R. Peres, JOSA B **38**, 7 (2021)
4. *Exciton-polariton mediated interaction between two nitrogen-vacancy color centers in diamond using two-dimensional transition metal dichalcogenides*, **J. C. G. Henriques**, B. Amorim, and N. M. R. Peres, Phys. Rev. B **103**, 085407 (2021)
5. *Analytical quantitative semiclassical approach to the Lo Surdo–Stark effect and ionization in two-dimensional excitons*, **J. C. G. Henriques**, Høgni C. Kamban, Thomas G. Pedersen, and N. M. R. Peres, Phys. Rev. B **102**, 035402 (2020)
6. *Topological photonic Tamm states and the Su-Schrieffer-Heeger model*, **J. C. G. Henriques**, T. G. Rappoport, Y. V. Bludov, M. I. Vasilevskiy, and N. M. R. Peres, Phys. Rev. A **101** 043811 (2020)
7. *Excitons in phosphorene: A semi-analytical perturbative approach*, **J. C. G. Henriques**, and N. M. R. Peres, Phys. Rev. B **101** 035406 (2020)
8. *Excitonic magneto-optical Kerr effect in two-dimensional transition metal dichalcogenides induced by spin proximity*, **J. C. G. Henriques**, G. Catarina, A. T. Costa, J. Fernández-Rossier, and N. M. R. Peres, Phys. Rev. B **101** 045408 (2020)

Excitonic magneto-optical Kerr effect due to proximity effects

In this section, as a first study of the properties of transition metal dichalcogenides (TMDs), we will compute the optical conductivity of a MoS_2 based heterostructure (see Fig. 4). With this system as a concrete motivation, we will discuss the most important aspects of the optical properties of TMDs, laying the foundations for the topics treated in the remaining sections.

Proximity effects were first found in the beginning of the 20th century during the study of superconductors [29]. At the time, it was observed that when placed near a superconductor, a non-superconducting material would acquire superconductive properties. Although proximity effects have been known for decades, it was the rise of 2D materials [30] that unlocked their true potential. When dealing with bulk materials, proximity effects are nothing more than a residual phenomena restricted to a nanometric region near the surface of the system, and as a result their role is often neglected [31]. In 2D materials, however, the situation is strikingly different. Due to their reduced thickness (they are known as two dimensional after all) the influence of proximity effects is not restricted to a small fraction of the sample, and affects the system in its entirety [32], drastically modifying its properties. These effects are responsible for inducing new features in the adjacent regions, such as turning a nonmagnetic material into a magnetic one, or giving rise to topologically nontrivial properties where otherwise there were none [31–34].

As was discussed in the previous section, spin-orbit coupling plays a significant role in the optical and electronic properties of TMDs. One of the consequences of the spin-orbit interaction is the coupling of the spin and valley degrees of freedom, which leads to valley-dependent helicity of interband optical transitions [35, 36]. A key aspect to control the valley degrees of freedom is to break the time-reversal symmetry between the Dirac valleys, which can be achieved with the application of an external magnetic field. Unfortunately, this proves to be an extremely hard task, since fields as large as ~ 10 T are necessary to produce a minute splitting of ~ 1 meV [37–41].

It is in this context that the combination of proximity effects and TMDs appears. It has been shown

both theoretically and experimentally that proximity to a magnetic material produces large valley splitting magnitudes [40–47], thus avoiding the use of huge external magnetic fields. This effect is the result of a proximity induced exchange interaction and orbital hybridization between the TMD and the magnetic material, leading to modifications in the band structure and giant valley splittings, ranging from a few to hundreds of meV [48] (far superior to what can be achieved with external magnetic fields). With the ability to control the valley degrees of freedom by choosing an adequate substrate, magneto-optical effects, such as the Kerr effect, can be explored in the absence of magnetic fields. Succinctly, the Kerr effect refers to the phenomenon where linearly polarized light reflected off a magnetized interface experiences a rotation of its plane of polarization. The Kerr angle quantifies the rotation of the plane of polarization between the incident and reflected beams (the latter being, in general, elliptically polarized). As we will see, when the time-reversal symmetry is broken due to proximity with a magnetic material the Hall conductivity becomes finite leading to a nonzero Kerr rotation angle.

In this section we will consider the heterostructure depicted in Fig. 4 composed of MoS_2 /hBN single layer/cobalt thin film/quartz, a system for which a giant magnetic exchange was found recently [48]. Following that work, the cobalt thin film is composed of three layers. The monolayer of hBN is used as a buffer and the cobalt provides the proximity-induced exchange. Since both the cobalt and the hBN are extremely thin, we assume that most of the dielectric screening is provided by the quartz substrate.

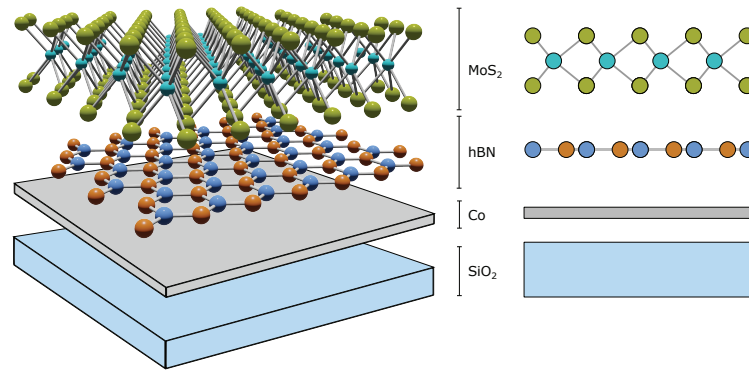


Figure 4: **Schematic representation of the heterostructure of MoS_2 /hBN/Co/ SiO_2 .** Representation of the system considered in this section: a heterostructure composed of MoS_2 / hBN/ cobalt thin film/ quartz; both a three-dimensional perspective and a transverse cut view of the heterostructure are shown. The hBN monolayer and acts as a buffer to protect MoS_2 from direct contact with the metallic cobalt thin film (three layers).

2.1 Model Hamiltonian and band structure

In order to study the optical properties of TMDs (or any other material for the same matter) one must first study the electronic properties of the desired system, in particular its band structure. To obtain the electronic energy dispersion of these systems, i.e. the structure of their valence and conduction bands, different approaches can be applied. The more sophisticated one, but also the most computationally demanding, is the calculation through density functional theory (DFT). This *ab-initio* technique allows the computation of the complete band structure of the desired material from its geometric configuration, atomic composition, and surrounding environment. Although the results obtained this way are indeed excellent, the computational cost reduces their appeal. Another possible approach to describe the band structure of TMDs, and complement the DFT study, is the introduction of model Hamiltonians. These Hamiltonians are usually constructed to describe a specific region of the Brillouin zone (BZ) in a narrow energy window, capturing only a small number of valence and conduction bands; this is in stark contrast with DFT calculations where the complete band structure is obtained. This, however, is not a significant problem, since the main properties we wish to describe are usually well captured by the low energy physics in the vicinity of a few high symmetry points in the BZ. Moreover, the model Hamiltonians depend on a small set of parameters whose value is determined by fitting its eigenenergies to the results found from DFT calculations. With this approach it is possible to describe the desired physical properties while dealing with an analytical framework gaining insight into the underlying physics. The model Hamiltonians used throughout this work are derived in Appendix A.

The simplest model Hamiltonian to describe TMDs in the vicinity of the K and K' valleys starts with the usual Dirac Hamiltonian, H_{Dirac} , found from tight binding models in, for example, hexagonal boron nitride (hBN). Contrary to hBN where the Hamiltonian is written in the sub-lattice basis, in TMDs the Dirac Hamiltonian is constructed in the basis of the atomic orbitals, namely $|\psi_c\rangle = |d_{z^2}\rangle$ and $|\psi_v^\tau\rangle = (|d_{x^2-y^2}\rangle + i\tau|d_{xy}\rangle)/\sqrt{2}$. Nonetheless, its form is identical to the one found for hBN, and reads:

$$H_{\text{Dirac}} = \hbar v_F (\tau k_x \sigma_x + k_y \sigma_y) + \frac{\Delta}{2} \sigma_z.$$

Here, $\tau = \pm 1$ is the valley index referring to the K or K', valley respectively, $\mathbf{k} = (k_x, k_y)$ is the electronic momentum measured relatively to the Dirac point in question, σ_x , σ_y and σ_z are Pauli matrices, v_F is the Fermi velocity, and Δ is the so called mass term, in analogy to the Dirac Hamiltonian found in relativistic quantum mechanics. This term appears as the result of the different on site energies of the two types of atomic orbitals in the Hamiltonian basis. The diagonalization of this Hamiltonian yields identical approximately parabolic bands in the K and K' valleys, all of which spin degenerate.

Due to the broken inversion symmetry and the heavy metal atoms, hosting d -orbitals, spin-orbit coupling plays a significant role in TMDs, breaking the aforementioned spin degeneracy. As a consequence, in addition to H_{Dirac} , a spin orbit coupling contribution, H_{SOC} , must be included in the Hamiltonian:

$$H_{\text{SOC}} = \tau s_z \left(\lambda_c \frac{1 + \sigma_z}{2} + \lambda_v \frac{1 - \sigma_z}{2} \right),$$

where $s_z = \pm 1$ is the spin index labeling spin up and down states, and λ_c and λ_v describe the spin orbit coupling induced splitting in the conduction and valence bands, respectively. Diagonalizing $H_{\text{Dirac}} + H_{\text{SOC}}$ one finds four non-degenerate bands in each valley (two conduction and two valence bands), reflecting the loss of spin degeneracy. However, the time-reversal symmetry between the K and K' valleys remains, and the band structure in the vicinity of these two symmetry points is identical, with the roles of spin up and spin down interchanged. This spin-valley locking is one of the main features of TMDs, and is intimately related with the fields of spintronics and valleytronics [49–51].

For most situations the Dirac and spin-orbit Hamiltonians are enough to characterize the electronic properties of TMDs near the Dirac points. However, in the present discussion, where we consider the TMD to be placed near a magnetic material, an additional term is required, which describes the exchange interaction between the two systems, similarly to a Zeeman effect. Crucially, this term breaks the time reversal-symmetry between the Dirac valleys, and it reads:

$$H_{\text{ex}} = -s_z \left(B_c \frac{1 + \sigma_z}{2} + B_v \frac{1 - \sigma_z}{2} \right),$$

with B_c and B_v the effective exchange splitting for the conduction and valence band, respectively. In the present study we are considering the simpler case of an out of plane magnetization, which breaks the valley symmetry but keeps spin as a good quantum number. In the cases where the magnetization has an in-plane component, the spin states are mixed, and new phenomena appear both in the single particle and in the excitonic response. This, however, will not be considered here. Besides these three contributions, one could also include a term describing Rashba spin-orbit coupling, which would also contribute to mixing spin-states. However, for simplicity, we opt to neglect this effect, which is not expected to produce significant modifications in the final result [36]. Hence, the total Hamiltonian describing the electronic properties near the Dirac points in the presence of a proximity induced exchange interaction, reads

$$H = H_{\text{Dirac}} + H_{\text{SOC}} + H_{\text{ex}}. \quad (2.1)$$

The values of v_F , Δ , $\lambda_{c/v}$ and $B_{c/v}$ are obtained from fitting the eigenvalues of Eq. (2.1) to DFT calculations. This process is beyond the scope of the present work, and we take these values from the literature (see Table 1).

In order to explicitly obtain the energy spectrum of Eq. (2.1), one must solve the eigenproblem $H|u_{c/v,\mathbf{k}}^{\tau,s_z}\rangle = E_{c/v,\mathbf{k}}^{\tau,s_z}|u_{c/v,\mathbf{k}}^{\tau,s_z}\rangle$ (see Appendix A). Although tedious, this is a straightforward calculation, which yields for the dispersion relation:

$$E_{c/v,\mathbf{k}}^{\tau,s_z} = \frac{s_z}{2} [\tau (\lambda_c + \lambda_v) - (B_c + B_v)] \pm \sqrt{\left(\frac{E_g^{\tau,s_z}}{2}\right)^2 + \hbar^2 v_F^2 \mathbf{k}^2}, \quad (2.2)$$

where $+$ ($-$) stands for the conduction (valence) band dispersion, and

$$E_g^{\tau,s_z} = \Delta + \tau s_z \Delta \lambda - s_z \Delta B$$

is the valley and spin dependent energy band gap, with $\Delta \lambda = \lambda_c - \lambda_v$ and $\Delta B = B_c - B_v$. Depending on the values of the different parameters the order of the bands may differ. This band ordering plays a crucial role in the excitonic problem, as will be discussed in sections to come. The eigenvectors of Eq. (2.1) read:

$$|u_{c,\mathbf{k}}^{\tau,s_z}\rangle = \frac{1}{\sqrt{(\mathcal{M}_{\mathbf{k}}^{\tau,s_z})^2 + v_F^2 \hbar^2 k^2}} \begin{pmatrix} \mathcal{M}_{\mathbf{k}}^{\tau,s_z} \\ \tau \hbar k v_F e^{i\tau\theta} \end{pmatrix} \quad (2.3)$$

$$|u_{v,\mathbf{k}}^{\tau,s_z}\rangle = \frac{1}{\sqrt{(\mathcal{M}_{\mathbf{k}}^{\tau,s_z})^2 + v_F^2 \hbar^2 k^2}} \begin{pmatrix} \tau \hbar k v_F e^{-i\tau\theta} \\ -\mathcal{M}_{\mathbf{k}}^{\tau,s_z} \end{pmatrix}, \quad (2.4)$$

with $\tan \theta = k_y/k_x$, and $\mathcal{M}_{\mathbf{k}}^{\tau,s_z} = \Delta/2 + B_v s_z - \lambda_v s_z \tau + E_{c,\mathbf{k}}^{\tau,s_z}$, or $\mathcal{M}_{\mathbf{k}}^{\tau,s_z} = \Delta/2 - B_c s_z + \lambda_c s_z \tau - E_{v,\mathbf{k}}^{\tau,s_z}$. Note that if the parameters Δ , $\lambda_{v/c}$ and $B_{v/c}$ approach zero, we recover a graphene-like system, as expected.

To apply these expressions, let us focus on the specific case of the system depicted in Fig. 4. As we have already mentioned, in this heterostructure the hBN serves as a buffer layer to protect the MoS₂, while the Cobalt thin film is responsible for the proximity induced exchange interaction. We consider these two materials to be thin enough to not contribute to the dielectric screening, which is entirely due to the SiO₂ substrate. The parameters to model the valence and conduction bands of this heterostructure were obtained from DFT calculations in Ref. [48], and are displayed in Table 1.

Variable	Value	Variable	Value	Variable	Value
Δ	1.759 eV	B_c	1.964 meV	r_0	41.4 Å
λ_c	-1.361 meV	B_v	6.365 meV	κ	2.45
λ_v	72.96 meV	$\hbar v_F$	3.52 eV·Å		

Table 1: **Model parameters for MoS₂ heterostructure.** Parameters used throughout the section for the Hamiltonian of MoS₂ near a cobalt thin film (three layers). The parameters were taken from Refs. [48, 52].

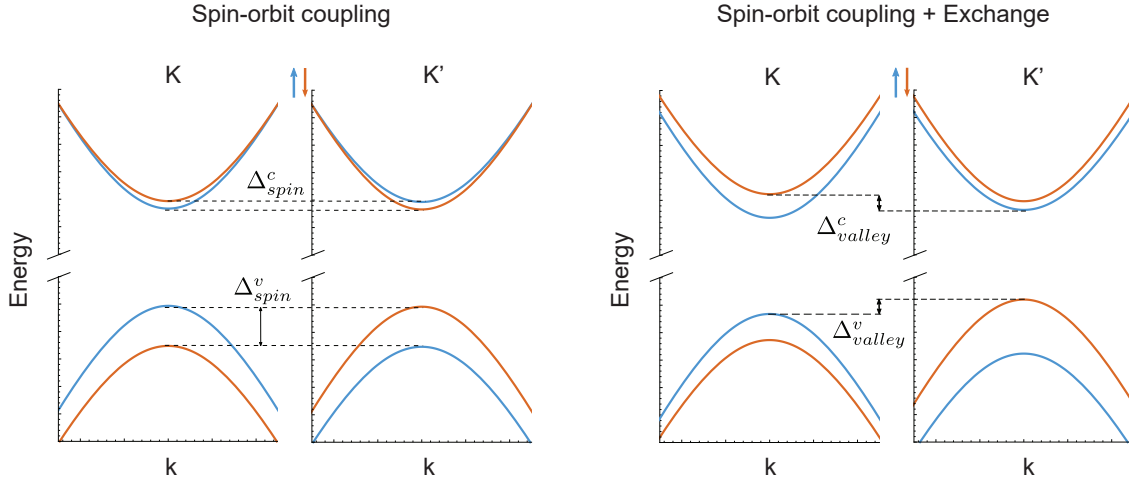


Figure 5: **Schematic representation of the band structure of MoS₂**. Valence and conduction bands near the Dirac points (K and K') with (Right) and without (Left) the exchange interaction. The parameters of Ref. [48], given in Table 1, were considered.

In Fig. 5 we depict the valence and conduction bands, for spin up and spin down states, with and without the exchange interaction, in the vicinity of the K and K' points. Starting by analyzing the case where only spin-orbit coupling is considered, we see that, as expected, we no longer have the two degenerate spin bands characteristic of a Dirac Hamiltonian, since the presence of spin-orbit coupling breaks the symmetry between the two spin states, lifts the spin degeneracy and unfolds each band in two. The energy difference between the two spin states, lifts the spin degeneracy and unfolds each band in two. The energy difference between spin-up and spin-down states is $\Delta_{\text{spin}}^c = 2\lambda_c$ for the conduction band, and $\Delta_{\text{spin}}^v = 2\lambda_v$ for the valence band. Comparing the bands at the K and K' valleys, we observe a symmetric band structure, with an inversion of roles between the spin states. Although in this material the two closest valence and conduction bands refer to the same spin state, this is not the case in other TMDs, such as WSe₂ and WS₂, where the spin-orbit coupling induced shift in the conduction band has the opposite direction. Also, even though in MoS₂ the shift in the conduction band is rather small, it can take values of a few tens of meV in other TMDs. Focusing now on the cases where the exchange interaction is present, we realize that bands that were once aligned are now shifted relative to each other due to the magnetic proximity effect. The relative shifts are $\Delta_{\text{valley}}^c = 2B_c$ for the conduction band, and $\Delta_{\text{valley}}^v = 2B_v$ for the valence band. The presence of this proximity effect is thus responsible for breaking the time-reversal symmetry. In the presence of the exchange interaction the system presents four non-degenerate pairs of approximately parabolic bands at each Dirac valley. Each pair of bands is associated with a different energy threshold to excite an electron from the valence to the conduction band. This lack of degeneracy is what allows us to exploit some material properties that were otherwise inaccessible in the absence of an external magnetic field, such as a finite optical Hall conductivity. In Table 2 the gaps associated with every allowed interband transition are shown; these values will be useful future analysis.

$(\tau, s_z, v) \rightarrow (\tau, s_z, c)$	E_g^{τ, s_z}	Value (eV)
$\tau = 1, s_z = 1$	$\Delta + \Delta\lambda - \Delta B$	1.689
$\tau = 1, s_z = -1$	$\Delta - \Delta\lambda + \Delta B$	1.829
$\tau = -1, s_z = 1$	$\Delta - \Delta\lambda - \Delta B$	1.838
$\tau = -1, s_z = -1$	$\Delta + \Delta\lambda + \Delta B$	1.680

Table 2: **Energy gaps.** Analytical expressions and numerical values for the gaps of the transitions $(\tau, s_z, v) \rightarrow (\tau, s_z, c)$, that is, the transition between the valence and conduction band, for a state of spin projection s_z in the valley τ for MoS₂. The numerical values were obtained with the parameters shown in Table 1.

2.2 Absorbed power from Fermi's golden rule

In order to obtain the optical conductivity of the heterostructure depicted in Fig. 4, we start by computing the absorbed power using Fermi's golden rule. Consider the applied time-dependent electric field given by

$$\mathbf{E}(t) = \frac{1}{2} (\mathbf{E}_0 e^{i\omega t} + \mathbf{E}_0^* e^{-i\omega t}),$$

with ω its angular frequency, and $\mathbf{E}_0$ the amplitude of the electric field with a given polarization. To describe the carrier-light interaction we work in the dipole approximation, such that the interaction Hamiltonian reads

$$H_{\text{int}} = -e\mathbf{E}(t) \cdot \mathbf{r}, \quad (2.5)$$

where e is the electron charge, and $\mathbf{r}$ the position operator.

The direct application of Fermi's golden rule gives the transition rate between a given initial and final state, induced by the dipole interaction. In order to obtain the absorbed power we must multiply Fermi's golden rule by the energy of the transition and sum over all the initial and final states, that is

$$P = \frac{2\pi}{\hbar} \sum_{i,f} |\hbar\omega| |\langle f | H_{\text{int}} | i \rangle|^2 [\delta(E_i - E_f + \hbar\omega) + \delta(E_i - E_f - \hbar\omega)],$$

where P denotes the absorbed power, $|i\rangle$ and $|f\rangle$ refer to the initial and final states, with energies E_i and E_f respectively. This expression was obtained considering that in the unperturbed system we have a fully occupied valence band and an empty conduction band. When this condition is not verified, which may be the case in doped systems, the occupation of the valence and conduction bands must be explicitly included. Also, in the following calculations we will only be interested in the response at positive frequencies, rendering one of the δ -functions redundant, which leads to its omission.

Now, let us consider two distinct scenarios regarding the polarization of the electric field: i) the light is linearly polarized, for example along the x direction such that $\mathbf{E}_0 = E_0 \hat{\mathbf{u}}_x$, with $\hat{\mathbf{u}}_x$ the unit vector along

the x axis. Due to the in-plane symmetry of our system the choice of the polarization direction is irrelevant (this would not be the case in anisotropic 2D materials such as phosphorene [14, 53]). The absorbed power when linearly polarized light is used reads:

$$P_x = \frac{\pi}{2\hbar} e^2 E_0^2 \sum_{i,f} \hbar\omega |\langle f|x|i \rangle|^2 \delta(E_i - E_f + \hbar\omega), \quad (2.6)$$

where the redundant δ -function was already dropped; ii) the light is circularly polarized, with $\mathbf{E}_0 = E_0 (\hat{\mathbf{u}}_x \pm i\hat{\mathbf{u}}_y) / \sqrt{2}$, where $+$ ($-$) refers to positive (negative) circular polarization, and $\hat{\mathbf{u}}_y$ is the unit vector along the y axis. Contrary to linearly polarized light, these two polarization possibilities are not equivalent due to the circular dichroism present in TMDs, resulting in the selective interaction of each of the two polarizations with a single Dirac valley. The absorbed power associated with these orthogonal polarizations reads:

$$P_{\pm} = \frac{\pi}{4\hbar} e^2 E_0^2 \sum_{i,f} \hbar\omega |\langle f|x \pm iy|i \rangle|^2 \delta(E_i - E_f + \hbar\omega). \quad (2.7)$$

To establish the relation between the power obtained from Fermi's golden rule and the optical conductivity we introduce the current density vector

$$\mathbf{J} = \frac{1}{2} (\mathbf{J}_0 e^{i\omega t} + \mathbf{J}_0^* e^{-i\omega t}),$$

where the amplitude $\mathbf{J}_0$ obeys Ohm's law $\mathbf{J}_0 = \bar{\bar{\sigma}} \mathbf{E}_0$, with $\bar{\bar{\sigma}}$ the conductivity tensor, which in general reads

$$\bar{\bar{\sigma}} = \begin{pmatrix} \sigma_{xx,1} + i\sigma_{xx,2} & \sigma_{xy,1} + i\sigma_{xy,2} \\ \sigma_{yx,1} + i\sigma_{yx,2} & \sigma_{yy,1} + i\sigma_{yy,2} \end{pmatrix},$$

but can be simplified for the current system as

$$\bar{\bar{\sigma}} = \begin{pmatrix} \sigma_{xx,1} + i\sigma_{xx,2} & \sigma_{xy,1} + i\sigma_{xy,2} \\ -\sigma_{xy,1} - i\sigma_{xy,2} & \sigma_{xx,1} + i\sigma_{xx,2} \end{pmatrix}, \quad (2.8)$$

where we set $\sigma_{yy} = \sigma_{xx}$ and $\sigma_{xy} = -\sigma_{yx}$. Here σ_{xx} and σ_{xy} are the longitudinal and Hall conductivities, respectively, and the indexes 1 and 2 refer to their real and imaginary parts, i.e. $\sigma_{xx,1} \equiv \text{Re}\sigma_{xx}$ and $\sigma_{xx,2} \equiv \text{Im}\sigma_{xx}$. We now note that the power can be written in terms of the current density vector as

$$P = \langle P(t) \rangle_T = \left\langle \int_A \mathbf{J}(t) \cdot \mathbf{E}(t) dA \right\rangle_T \\ = \frac{A}{2} \text{Re} (\mathbf{J}_0 \cdot \mathbf{E}_0^*)$$

where $\langle \dots \rangle_T$ indicates that a mean over the period $T = 2\pi/\omega$ should be taken, and the integral is performed over the area of the sample, A . Using Ohm's law to write $\mathbf{J}_0$ in terms of $\mathbf{E}_0$ we obtain

$$P_x = \frac{A}{2} E_0^2 \sigma_{xx,1}, \quad P_{\pm} = \frac{A}{2} E_0^2 (\sigma_{xx,1} \mp \sigma_{xy,2}). \quad (2.9)$$

Solving for the conductivities one finds

$$\sigma_{xx,1} = \frac{2P_x}{AE_0^2} = \frac{P_+ + P_-}{AE_0^2}, \quad \sigma_{xy,2} = \frac{P_- - P_+}{AE_0^2}, \quad (2.10)$$

with P_x , P_+ and P_- given by Eqs. (2.6) and (2.7). For convenience let us introduce two new conductivities, defined as

$$\sigma_{+,1} = \frac{2P_+}{AE_0^2}, \quad \sigma_{-,1} = \frac{2P_-}{AE_0^2}, \quad (2.11)$$

which correspond to the optical conductivity associated with the polarizations $(\hat{\mathbf{u}}_x \pm i\hat{\mathbf{u}}_y) / \sqrt{2}$. Using these definitions we can also write

$$\sigma_{xx,1} = \frac{\sigma_{+,1} + \sigma_{-,1}}{2}, \quad \sigma_{xy,2} = \frac{\sigma_{-,1} - \sigma_{+,1}}{2} \quad (2.12)$$

Since we have only found expressions for $\sigma_{xx,1}$ and $\sigma_{xy,2}$, in order to obtain $\sigma_{xx,2}$ and $\sigma_{xy,1}$ the Kramers-Kronig relations must be used. These relations establish the connection between the real and imaginary part of any response function (that is, a function analytical in the upper half part of the complex plane). For a function $\chi(\omega) = \chi_1(\omega) + i\chi_2(\omega)$ we have:

$$\chi_1(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_2(\nu)}{\nu - \omega} d\nu, \quad \chi_2(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_1(\nu)}{\nu - \omega} d\nu,$$

where $\mathcal{P}$ denotes the Cauchy principal value of the integral.

2.3 Single-particle picture

Now that expressions defining the optical conductivity have been obtained, and before we move on to the excitonic problem, let us compute the single particle response, starting with the case of linearly polarized light. Since we are concerned with interband optical transition we consider the initial state, $|i\rangle$, to correspond to an electron with spin s_z in the valence band of the τ valley, with a given momentum $\mathbf{k}$, i.e. the state $|u_{v,\mathbf{k}}^{\tau,s_z}\rangle$ with energy $E_{v,\mathbf{k}}^{\tau,s_z}$. As a result of the negligible momentum photons carry we restrict ourselves to vertical transitions, such that the momentum of the initial and final states coincides. Neglecting processes involving flipping the spin of the electron, the final state, $|f\rangle$, corresponds to $|u_{c,\mathbf{k}}^{\tau,s_z}\rangle$ with energy $E_{c,\mathbf{k}}^{\tau,s_z}$. In the end, summing over the required degrees of freedom, the longitudinal conductivity from Fermi's golden rule reads

$$\sigma_{xx,1} = \frac{e^2\pi}{A\hbar} \sum_{\mathbf{k},\tau,s_z} \hbar\omega \left| \langle u_{c,\mathbf{k}}^{\tau,s_z} | x | u_{v,\mathbf{k}}^{\tau,s_z} \rangle \right|^2 \delta(E_{v,\mathbf{k}}^{\tau,s_z} - E_{c,\mathbf{k}}^{\tau,s_z} + \hbar\omega). \quad (2.13)$$

To compute the matrix element it is useful to first compute $\langle u_{c,\mathbf{k}}^{\tau,s_z} | [H, x] | u_{v,\mathbf{k}}^{\tau,s_z} \rangle$. This can be done by expanding the commutator, i.e. $[A, B] = AB - BA$, and making use of the Hamiltonian eigenvalue

relation, or by first computing the commutator, followed by the evaluation of the matrix element. Equating both results, an expression for $\langle u_{c,\mathbf{k}}^{\tau,s_z} | x | u_{v,\mathbf{k}}^{\tau,s_z} \rangle$ is found. Explicitly:

$$\begin{aligned} \langle u_{c,\mathbf{k}}^{\tau,s_z} | [H, x] | u_{v,\mathbf{k}}^{\tau,s_z} \rangle &= \langle u_{c,\mathbf{k}}^{\tau,s_z} | Hx - xH | u_{v,\mathbf{k}}^{\tau,s_z} \rangle \\ &= \langle u_{c,\mathbf{k}}^{\tau,s_z} | x | u_{v,\mathbf{k}}^{\tau,s_z} \rangle (E_{c,\mathbf{k}}^{\tau,s_z} - E_{v,\mathbf{k}}^{\tau,s_z}), \end{aligned}$$

as well as

$$\langle u_{c,\mathbf{k}}^{\tau,s_z} | [H, x] | u_{v,\mathbf{k}}^{\tau,s_z} \rangle = -i\tau\hbar v_F \langle u_{c,\mathbf{k}}^{\tau,s_z} | \sigma_x | u_{v,\mathbf{k}}^{\tau,s_z} \rangle,$$

thus:

$$\langle u_{c,\mathbf{k}}^{\tau,s_z} | x | u_{v,\mathbf{k}}^{\tau,s_z} \rangle = -i\tau\hbar v_F \frac{\langle u_{c,\mathbf{k}}^{\tau,s_z} | \sigma_x | u_{v,\mathbf{k}}^{\tau,s_z} \rangle}{E_{c,\mathbf{k}}^{\tau,s_z} - E_{v,\mathbf{k}}^{\tau,s_z}}, \quad (2.14)$$

where $\tau = \pm 1$ appears from the commutator $[H, x]$. Although in the present case the appearance of τ is quite irrelevant, since we will be taking the square modulus of the matrix element, its existence is crucial in the study of circularly polarized light. Inserting Eq. (2.14) into Eq. (2.13), and converting the sum over $\mathbf{k}$ into an integral, we obtain:

$$\sigma_{xx,1} = \frac{e^2 \pi \hbar^2 v_F^2}{(2\pi)^2 \hbar} \sum_{\tau,s_z} \int \hbar\omega \frac{|\langle u_{c,\mathbf{k}}^{\tau,s_z} | \sigma_x | u_{v,\mathbf{k}}^{\tau,s_z} \rangle|^2}{(E_{c,\mathbf{k}}^{\tau,s_z} - E_{v,\mathbf{k}}^{\tau,s_z})^2} \delta(E_{v,\mathbf{k}}^{\tau,s_z} - E_{c,\mathbf{k}}^{\tau,s_z} + \hbar\omega) d\mathbf{k}, \quad (2.15)$$

To evaluate the integral over $d\mathbf{k}$ we start by computing the angular contribution. Since the δ -function depends only on the modulus of $\mathbf{k}$, this will cancel the terms proportional to $e^{i\theta}$, while the remaining ones will be multiplied by 2π . The integral over dk is computed with the help of the following relation

$$\delta(f(k)) = \frac{\delta(k - k_0)}{|\nabla f(k)|}, \quad f(k_0) = 0.$$

After both integrals have been performed, one finds

$$\frac{\sigma_{xx,1}}{\sigma_0} = \sum_{\tau,s_z} \frac{(E_g^{\tau,s_z})^2 + \hbar^2 \omega^2}{4\hbar^2 \omega^2} \Theta(\hbar\omega - E_g^{\tau,s_z}), \quad (2.16)$$

with $\sigma_0 = e^2/4\hbar$ graphene's universal conductivity, and $\Theta(x)$ the Heaviside function, which sets the threshold for allowed interband optical transitions. In the high energy limit, $\hbar\omega \gg E_g^{\tau,s_z}$, one finds $\sigma_{xx,1} \rightarrow \sigma_0$, in agreement with our analysis following Eq. (2.4). This is a sensible result, since for high excitation energies all the other energy scales become irrelevant, and a graphene-like system is recovered (the same would be true if $E_g^{\tau,s_z} \rightarrow 0$). In panel (a) of Fig. 6 we depict $\sigma_{xx,1}$ as a function of the photon energy, $\hbar\omega$, and observe that, as expected, the real part of the longitudinal conductivity is composed of four different contributions, associated with transitions involving the four non-degenerate band gaps given in Table 2. In order to study the effect of a finite linewidth in the optical conductivity we approximate the δ -function in

Fermi's golden rule by a lorentzian with a finite width; the dependence of the conductivity on the broadening of the lorentzian is depicted in Fig. 6b. There, we observe that as the linewidth grows, the sharp increases in $\sigma_{xx,1}$ become less pronounced. In fact, due to the small exchange splitting, linewidths of 5 meV already obscure some of the features of the conductivity.

Now, let us focus on the case of circularly polarized light, by evaluating $\sigma_{\pm,1}$. From Fermi's golden rule one finds

$$\sigma_{\pm,1} = \frac{\pi e^2}{2A\hbar} \sum_{\mathbf{k}, \tau, s_z} \hbar\omega |\langle u_{c,\mathbf{k}}^{\tau, s_z} | x \pm iy | u_{v,\mathbf{k}}^{\tau, s_z} \rangle|^2 \delta(E_{v,\mathbf{k}}^{\tau, s_z} - E_{c,\mathbf{k}}^{\tau, s_z} + \hbar\omega). \quad (2.17)$$

To evaluate the matrix element, the same strategy as before is employed. Carrying out the necessary calculations, we arrive at:

$$\frac{\sigma_{\pm,1}}{\sigma_0} = \sum_{\tau, s_z} \frac{(E_g^{\tau, s_z} \pm \tau \hbar\omega)^2}{4\hbar^2\omega^2} \Theta(\hbar\omega - E_g^{\tau, s_z}). \quad (2.18)$$

From this expression we clearly see that light with positive circular polarization interacts predominantly with the K valley ($\tau = 1$), while light with negative circular polarization interacts mainly with the K' valley ($\tau = -1$). In reality, for the least energetic interband transitions, that is, $\hbar\omega = E_g^{\tau, s_z}$, the excitation is exactly valley selective. Due to the lack of spin degeneracy, this can be exploited to selectively pump carriers with a specific spin into the conduction band, even in the absence of the proximity induced exchange splitting. Also, we note that, as expected according to Eq. (2.12), when we take the arithmetic mean of $\sigma_{+,1}$ and $\sigma_{-,1}$ we recover $\sigma_{xx,1}$; this is also depicted in panel (a) of Fig. 6. Looking at panel (c) of the same figure we observe that in the low energy region both $\sigma_{+,1}$ and $\sigma_{-,1}$ vanish, since the photon energy is not yet sufficient to produce optical excitations. Then, at $\hbar\omega = 1.68$ eV, $\sigma_{-,1}$ increases sharply due to the optical transitions between spin down bands in the K' valley that become energetically available (cf. Table 2). Afterwards, at $\hbar\omega = 1.689$ eV, $\sigma_{+,1}$ suffers a sudden increase as a result of the transitions involving spin up electrons in the K valley. The 9 meV energy separation is as consequence of the exchange interaction. At higher energies we again observe sharp increases in $\sigma_{+,1}/\sigma_{-,1}$, due to the coupling to spin down/up electrons in the K/K' valley. This analysis is in line with what was previously stated regarding the selective coupling of circularly polarized light with carriers in the Dirac valleys.

In order to obtain the imaginary part of the Hall conductivity, $\sigma_{xy,2}$, we can once again use $\sigma_{+,1}$ and $\sigma_{-,1}$. Taking the difference between $\sigma_{+,1}$ and $\sigma_{-,1}$, and dividing it by 2, one obtains

$$\frac{\sigma_{xy,2}}{\sigma_0} = - \sum_{\tau, s_z} \tau \frac{E_g^{\tau, s_z}}{2\hbar\omega} \Theta(\hbar\omega - E_g^{\tau, s_z}). \quad (2.19)$$

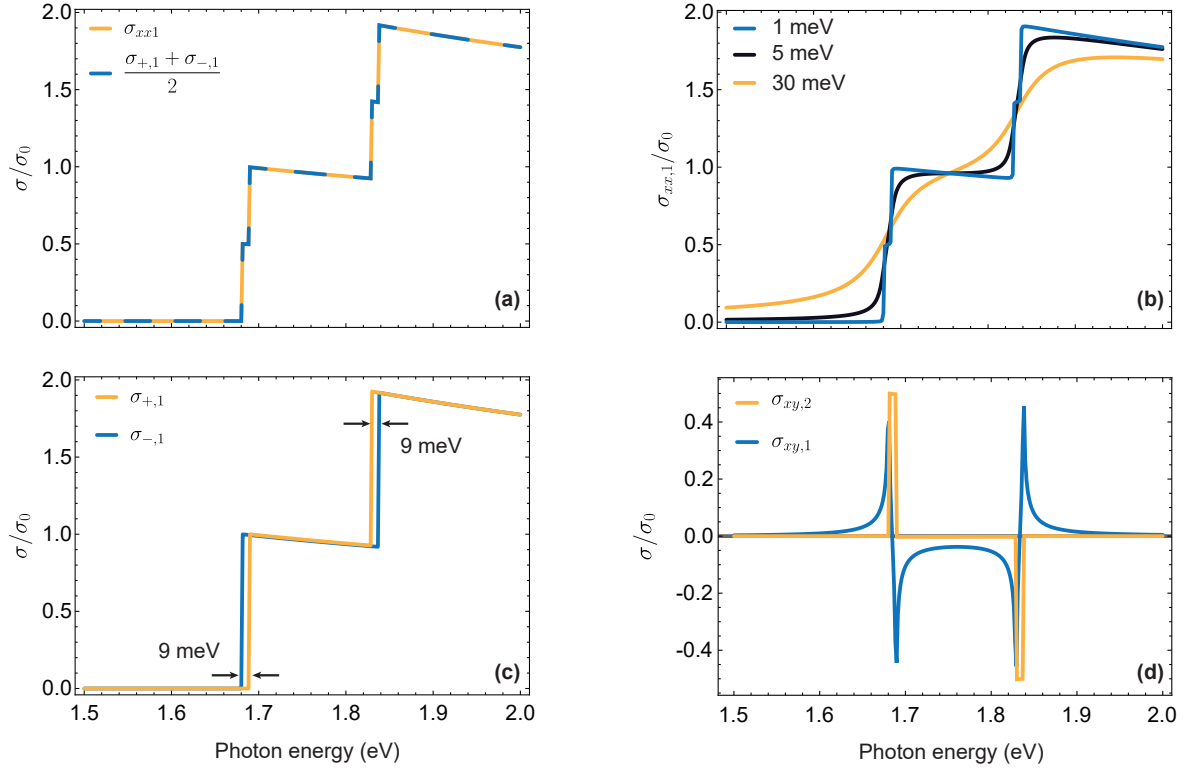


Figure 6: **Single particle longitudinal and Hall conductivities.** (a) Real part of the longitudinal conductivity obtained with Eqs. (2.10) and (2.12); (b) Effect of the linewidth, η , when the δ -function in Fermi's golden rule is modeled by a lorentzian with a total linewidth of $\eta = 1, 5$ and 30 meV; (c) Real part of the conductivities associated with positive and negative circular polarization, as defined in Eq. (2.11). The 9 meV separation corresponds to $2\Delta B$ and it is the energy difference between band gaps that are degenerate in the absence of the exchange interaction; (d) Real and Imaginary parts of the Hall conductivity defined in Eqs. (2.19) and (2.21).

For the gaps given in Table 2, we can express this as

$$\frac{\sigma_{xy,2}}{\sigma_0} = \begin{cases} 0 & \hbar\omega < E_g^{-1,-1} \\ \frac{E_g^{-1,-1}}{2\hbar\omega} & E_g^{-1,-1} < \hbar\omega < E_g^{1,1} \\ \frac{B_c - B_v}{\hbar\omega} & E_g^{1,1} < \hbar\omega < E_g^{1,-1} \\ -\frac{E_g^{-1,1}}{2\hbar\omega} & E_g^{1,-1} < \hbar\omega < E_g^{-1,1} \\ 0 & \hbar\omega > E_g^{-1,1} \end{cases} \quad (2.20)$$

It is important to note that this expression is only valid for the parameters used in this work, since the order of the various gaps depends on the values of Δ , B_c , B_v , λ_c , and λ_v . If other values had been considered for these parameters, it would be necessary to put the domain restrictions in the correct order and sum the different contributions to $\sigma_{xy,2}$ accordingly. Another important aspect to emphasize is that in the limit $\Delta B = 0$, the imaginary part of Hall conductivity, $\sigma_{xy,2}$, vanishes. This is easily understood since the middle branch of Eq. (2.20) becomes identically zero, and the intervals where the second and fourth

branch are defined tend to zero in this limit. This behavior was verified to exist for all possible ordering of the different E_g^{τ,s_z} . The plot of $\sigma_{xy,2}$ is given in Fig. 6d, where we see that, in agreement with Eq. (2.20), $\sigma_{xy,2}$ vanishes both at low and high energies; in the intermediate region two peaks are clearly visible, with a region of negligible intensity between them, as a result of the small value of $B_c - B_v$ when compared to $\hbar\omega$. Comparing panels (c) and (d), one clearly understands that as $\Delta B \rightarrow 0$ the separation between the two lines in panel (c) vanishes, and consequently the peaks in panel (d) are quenched. The real part of the Hall conductivity, $\sigma_{xy,1}$, is obtained by applying the Kramers-Kronig transformation to Eq. (2.20), and it reads

$$\frac{\sigma_{xy,1}}{\sigma_0} = \sum_{\tau,s_z} \tau \frac{E_g^{\tau,s_z}}{2\pi\hbar\omega} \ln \left(\frac{\hbar\omega - E_g^{\tau,s_z}}{\hbar\omega + E_g^{\tau,s_z}} \right). \quad (2.21)$$

The plot of $\sigma_{xy,1}$ as a function of the photon energy is depicted in Fig. 6d, where we observe the expected two dispersive resonances aligned with the peaks of $\sigma_{xy,2}$. Considering again the effect of a finite linewidth, as depicted in Fig. 6b, both the real and imaginary parts of σ_{xy} would be progressively attenuated with increasing broadening.

2.4 Excitonic response and the Kerr angle

Having studied the electronic band structure and the single particle response, we are ready to move on to the calculation of the excitonic effects. To do so, we will divide our study in three stages: first, the equation governing the excitonic problem will be discussed; then, we will briefly describe how this equation can be solved in a gaussian basis in order to obtain the exciton binding energies and wave functions; in the end, we will use these results to evaluate the excitonic optical response, and compute the Kerr rotation angle.

2.4.1 Wannier equation

2.4.1.1 Derivation

The starting point of our discussion is the derivation of the Wannier equation, which we briefly outline here, and whose detailed calculation is given in Appendix B. Consider the following bosonic operator describing the creation of an exciton composed of an electron and a hole with a spin projection s_z , both in the vicinity of the K or K' valleys (labeled by τ), with center of mass momentum $\mathbf{Q}$ (measured relatively to the valley of interest) and quantum numbers labeled by ν (containing the principal and angular quantum numbers, e.g. $\nu = 1s$)[54]:

$$b_{\nu,\mathbf{Q}}^\dagger = \frac{1}{\sqrt{A}} \sum_{\mathbf{k}} \psi_{\nu,\mathbf{k}}^* c_{\mathbf{k}+\alpha\mathbf{Q},c}^\dagger c_{\mathbf{k}-\beta\mathbf{Q},v} \quad (2.22)$$

where A is the area of the monolayer, $\mathbf{k}$ is the relative momentum of the electron and hole, $\psi_{v,\mathbf{k}}^*$ is the Fourier transform of the exciton wave function, and $c_{\mathbf{k}+\alpha\mathbf{Q},c}^\dagger$ is the creation operator of an electron in the conduction band near the K or K' valleys, with momentum $\mathbf{k} + \alpha\mathbf{Q}$, where $\alpha = m_e/(m_e + m_h)$ with $m_{e/h}$ the effective mass of the electron/hole; a similar definition applies to the other electron operator with $\beta = 1 - \alpha$. When this operator acts on the excitonic ground state $|GS\rangle$, corresponding to a full valence band and an empty conduction band, one finds

$$b_{\mathbf{Q},v}^\dagger |GS\rangle = |\tau, s_z, v, \mathbf{Q}\rangle \quad (2.23)$$

The energy of such a state reads

$$E_{\mathbf{Q},v}^{\tau,s_z} = E_g^{\tau,s_z} + E_v^{\tau,s_z} + \frac{\hbar^2 \mathbf{Q}^2}{2M^{\tau,s_z}}, \quad (2.24)$$

with E_g^{τ,s_z} the electronic band gap between the valence and conduction bands with spin s_z in the τ valley, E_v^{τ,s_z} the exciton binding energy and $\hbar^2 \mathbf{Q}^2 / 2M^{\tau,s_z}$ its center of mass kinetic energy with $M^{\tau,s_z} = m_e^{\tau,s_z} + m_h^{\tau,s_z}$. In the following we will omit the indexes τ and s_z to simplify the notation, only displaying them when strictly necessary. This should not rise any confusion if one keeps present that in order to approach the excitonic problem the spin projection and the valley of the carriers must be known, since this information is needed to obtain the band gap and the effective masses. We note in passing that in future sections different notations will be used, according to what is best suited for the problem in question.

The electronic Hamiltonian describing the electron-electron interaction is composed of a kinetic and a potential term, which can be quantized in terms of electron operators as

$$\hat{H}_0 = \sum_{\mathbf{k},\lambda} E_{\mathbf{k},\lambda} c_{\mathbf{k},\lambda}^\dagger c_{\mathbf{k},\lambda}, \quad (2.25)$$

where the sum in λ runs over the conduction and valence bands, and $E_{\mathbf{k},\lambda}$ corresponds to the energy dispersion we found in Eq. (2.2). The potential term reads

$$\hat{H}_{\text{int}} = \frac{1}{2A} \sum_{\lambda} \sum_{\mathbf{q},\mathbf{k},\mathbf{p}} V(\mathbf{q}) F_{\lambda_1,\lambda_2,\lambda_3,\lambda_4}(\mathbf{k}, \mathbf{p}, \mathbf{q}) c_{\mathbf{p}+\mathbf{q},\lambda_1}^\dagger c_{\mathbf{k}-\mathbf{q},\lambda_2}^\dagger c_{\mathbf{k},\lambda_3} c_{\mathbf{p},\lambda_4} \quad (2.26)$$

where $V(\mathbf{q})$ is the Fourier transform of the interaction potential, and

$$F_{\lambda_1,\lambda_2,\lambda_3,\lambda_4}(\mathbf{k}, \mathbf{p}, \mathbf{q}) = u_{\mathbf{p}+\mathbf{q},\lambda_1}^\dagger u_{\mathbf{k}-\mathbf{q},\lambda_2}^\dagger u_{\mathbf{k},\lambda_3} u_{\mathbf{p},\lambda_4} \quad (2.27)$$

with $u_{\mathbf{k},\lambda}$ the spinor describing the band λ evaluated at $\mathbf{k}$, obtained previously in Eq. (2.4). Note that the sum over the transferred momentum in Eq. (2.26) excludes the term $\mathbf{q} = 0$, since this term cancels with the background contribution in the jellium model.

To arrive at the equation that defines the wave functions $\psi_{v,\mathbf{k}}$ and the associated binding energies, we begin by stating that the total Hamiltonian is diagonal in the exciton operator representation, that is

$$\hat{H} = \sum_{\mathbf{Q},\nu} E_{\mathbf{Q},\nu} b_{\mathbf{Q},\nu}^\dagger b_{\mathbf{Q},\nu}. \quad (2.28)$$

This imposition is in principle always possible, given that the wavefunction $\psi_{v,\mathbf{k}}$ is chosen appropriately. Then, we compute the commutator $[\hat{H}, b_{\mathbf{Q},\nu}^\dagger]$ using the exciton representation, Eq. (2.28), and the electron representation, Eqs. (2.25) and (2.26), of the Hamiltonian. In the end, we demand both results to be equal. Although we may keep the center of mass momentum $\mathbf{Q}$ finite throughout the calculation, in the end we set it equal to zero, due to the negligible momentum photon's carry. Computing the necessary commutators (see Appendix B), we arrive at an integral equation in momentum space, termed Bethe–Salpeter equation (BSE) [55]. Reintroducing the spin and valley indexes, we find:

$$E_{0,\nu}^{\tau,s_z} \psi_{v,\mathbf{k}}^{\tau,s_z} = \psi_{v,\mathbf{k}}^{\tau,s_z} \left(E_{\mathbf{k},c}^{\tau,s_z} - E_{\mathbf{k},v}^{\tau,s_z} \right) - \frac{1}{A} \sum_{\mathbf{p}} \psi_{v,\mathbf{p}}^{\tau,s_z} V(\mathbf{k} - \mathbf{p}) F_{c,v,v,c}^{\tau,s_z}(\mathbf{k}, \mathbf{p}, \mathbf{k} - \mathbf{p}). \quad (2.29)$$

The term on the left hand side corresponds to the product of exciton energy with its wave function. The first term on the right hand side gives the energy difference of the electron and hole in the non interacting limit, while the second term describes the electron-hole attractive interaction. An additional term that appears in the BSE (see Appendix B) was left out on the basis that it is not expected to significantly contribute to the exciton binding energy, although it contributes to the renormalization of the band gap in the interacting limit. At this point, two approximations are introduced: i) the term $(E_{\mathbf{k},c}^{\tau,s_z} - E_{\mathbf{k},v}^{\tau,s_z})$ is expanded to second order in $\mathbf{k}$, yielding

$$E_{\mathbf{k},c}^{\tau,s_z} - E_{\mathbf{k},v}^{\tau,s_z} \approx E_g^{\tau,s_z} + \frac{\hbar^2 \mathbf{k}^2}{2\mu^{\tau,s_z}},$$

with μ^{τ,s_z} the electron-hole reduced mass

$$\mu^{\tau,s_z} = \frac{E_g^{\tau,s_z}}{4v_F^2}.$$

The term E_g^{τ,s_z} does not contribute to the binding energy since it is independent of $\mathbf{k}$ and can be combined with the term on the left hand side of Eq. (2.29); ii) the form factor $F_{c,v,v,c}^{\tau,s_z}(\mathbf{k}, \mathbf{p}, \mathbf{k} - \mathbf{p})$ is approximated to one, that is

$$F_{c,v,v,c}^{\tau,s_z}(\mathbf{k}, \mathbf{p}, \mathbf{k} - \mathbf{p}) \rightarrow 1 + O(1/E_g^{\tau,s_z}).$$

This is a good approximation near the Dirac points due to the large energy gap between the valence and conduction band. With these two approximations, Eq. (2.29) can be transformed into a differential equation in real space. Performing the Fourier transform we arrive at the Wannier equation:

$$-\frac{\hbar^2}{2\mu^{\tau,s_z}} \nabla^2 \psi_v^{\tau,s_z}(\mathbf{r}) + V(\mathbf{r}) \psi_v^{\tau,s_z}(\mathbf{r}) = E_v^{\tau,s_z} \psi_v^{\tau,s_z}(\mathbf{r}), \quad (2.30)$$

with ∇^2 the Laplace operator and $V(\mathbf{r})$ the interaction potential in real space. Formally, this equation is identical to the Schrodinger equation applied in many quantum mechanics problems, such as the 2D Hydrogen atom. The main difference between Eq. (2.30) and that of the Hydrogen atom lies in the potential term, where we consider the Rytova–Keldysh [56, 57] instead of the usual Coulomb potential. The Rytova–Keldysh potential, known to accurately reproduce the results found from *ab-initio* calculations [58], allows for the description of non-local screening, which is essential in these 2D systems. This potential is found from the solution of the Poisson equation for a point charge embedded in a thin dielectric medium (see Appendix C), and it reads

$$V_{\text{RK}}(\mathbf{r}) = \frac{\hbar c \alpha \pi}{2r_0} \left[\mathbf{H}_0 \left(\frac{\kappa r}{r_0} \right) - Y_0 \left(\frac{\kappa r}{r_0} \right) \right], \quad (2.31)$$

where c is the speed of light, $\alpha \sim 1/137$ the fine structure constant, r_0 a screening length microscopically related to the polarizability of the monolayer, and κ the mean dielectric constant of the media above and below the monolayer; $\mathbf{H}_0$ is the Struve function of order zero, and Y_0 the Bessel function of the second kind, also of order zero. For large distances the Rytova–Keldysh potential presents a Coulomb $1/r$ tail, but diverges logarithmically near the origin. The comparison between the Coulomb and the Rytova–Keldysh potentials is depicted in Fig. 7. Although in real space this potential presents an involved form defined in

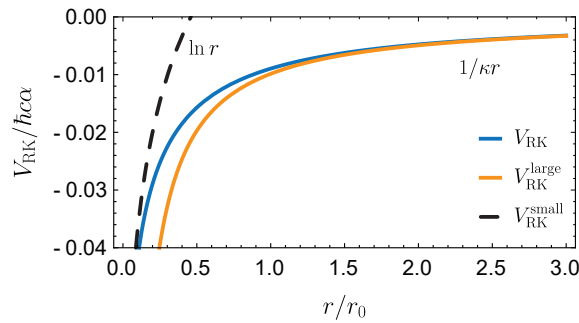


Figure 7: **Comparison between the Coulomb and Rytova–Keldysh potentials**, taking $\kappa = 2.45$, and $r_0 = 41.4 \text{ \AA}$ corresponding to the case of MoS₂ on a substrate of quartz. As discussed in the text, the Rytova–Keldysh potential approaches the Coulomb potential asymptotically at large distances.

terms of special functions, its representation in momentum space is rather illuminating

$$V_{\text{RK}}(\mathbf{q}) = \hbar c \alpha \frac{2\pi}{q(\kappa + r_0 q)}. \quad (2.32)$$

This expression clearly resembles the potential found in the random phase approximation (RPA) when a many-body theory of the interacting electron gas is formulated. Moreover, we see that when $r_0 q \ll \kappa$, that is for long wave length interactions, Eq. (2.32) approaches the Fourier transform of the 2D Coulomb potential, and the thickness of the thin layer becomes irrelevant. In the opposite limit, for short range interactions, where $r_0 q \gg \kappa$, we recover the Fourier transform of the 3D Coulomb potential. The Rytova–Keldysh potential thus represents an interpolation between these two different regimes.

2.4.1.2 Solution

In order to obtain the binding energies and wave functions of the excitonic problem Eq. (2.30) must be solved. To extract the solutions of the Wannier equation different techniques, with different degrees of numerical complexity, may be employed. Throughout this dissertation different paths to solve the exciton problem will be explored; in the current section we will follow a semi-analytical framework, like the one developed in Ref. [13], based on the expansion of the wave functions in a given basis, followed by a numerical diagonalization of the Hamiltonian. Drawing inspiration from the 2D Hydrogen atom, we expand the exciton wave function in a gaussian basis as

$$\psi_v^{\tau, s_z}(\mathbf{r}) = \mathcal{N}_v^{\tau, s_z} \sum_{j=1}^N c^{\tau, s_z}(j; v) e^{im\theta} r^{|m|} e^{-\zeta_j r^2}, \quad (2.33)$$

where

$$\mathcal{N}_v^{\tau, s_z} = \left(\pi \sum_{j=1}^N \sum_{p=1}^N c^{\tau, s_z}(j; v) c^{\tau, s_z}(p; v) \frac{\Gamma(1 + |m|)}{(\zeta_j + \zeta_p)^{1+|m|}} \right)^{-1/2}$$

is a normalization constant, N is the number of functions in the gaussian basis, $c^{\tau, s_z}(j; v)$ are the expansion coefficients (yet to be determined) and m is the angular quantum number. The term $e^{im\theta} r^{|m|}$ follows from the solution of the 2D Hydrogen atom, where the complex exponential gives the angular dependence of the wave function, and $r^{|m|}$ describes its behavior near the origin; the long distance decay is modeled by the gaussian term $e^{-\zeta_j r^2}$. The coefficients ζ_j are defined according to the rule [59]:

$$\Omega_j = \frac{\ln \zeta_j}{B},$$

where Ω_j belongs to a linearly spaced interval $[\Omega_{\min}, \Omega_{\max}]$ containing N entries, and B is a parameter typically chosen between 6 and 8. Using this trial wave function the Wannier equation can be recast in the form of the discretized Griffin-Hill-Wheeler (GHW) equation [60], see Appendix B, that is

$$\sum_{j=1}^N [H^{\tau, s_z}(\zeta_i, \zeta_j) - S^{\tau, s_z}(\zeta_i, \zeta_j) E_v^{\tau, s_z}] c^{\tau, s_z}(j; v) = 0, \quad (2.34)$$

with $H^{\tau, s_z}(\zeta_i, \zeta_j)$ and $S^{\tau, s_z}(\zeta_i, \zeta_j)$ the Hamiltonian and the overlap kernels, whose analytical expressions are given in Appendix B. This equation corresponds to a generalized eigenvalue problem, that when diagonalized yields the binding energies, E_v^{τ, s_z} , and the expansion coefficients, $c^{\tau, s_z}(j; v)$. We note that this problem is diagonal in the sub-space of the angular quantum number, since the entries of $H^{\tau, s_z}(\zeta_i, \zeta_j)$ and $S^{\tau, s_z}(\zeta_i, \zeta_j)$ do not mix different m . As a result, to solve the GHW equation one starts by choosing the desired value of m , and after the diagonalization has been performed the solutions correspond to states with different principal quantum numbers, n . For example, if $m = 0$ is chosen, the eigenproblem retrieves the wave functions and binding energies of the states with $n = 1, 2, 3, \dots$ corresponding to

Valley	Spin	$\mu^{\tau,s_z}/m_0$	E_g^{τ,s_z} (eV)	E_{1s}^{τ,s_z} (eV)
$\tau = 1$	$s_z = 1$	0.422	1.689	-0.381
	$s_z = -1$	0.457	1.829	-0.391
$\tau = -1$	$s_z = 1$	0.459	1.838	-0.392
	$s_z = -1$	0.420	1.680	-0.380

Table 3: **Binding energies of the 1s exciton.** Reduced masses, μ^{τ,s_z} , band gaps, E_g^{τ,s_z} , and binding energies of the 1s exciton, E_{1s}^{τ,s_z} , for the four possible spin and valley configurations. The reduced mass is given in units of the bare electron mass, m_0 . The binding energies were obtained using $N = 70$ gaussians, $\Omega_{\min} = -1$, $\Omega_{\max} = 5$ and $B = 6$. The parameters of Table 1 were used.

$\nu = 1s, 2s, 3s, \dots$, respectively; for $m = \pm 1$ one obtains the information regarding the states $n = 2, 3, 4, \dots$ that is $\nu = 2p, 3p, 4p, \dots$ and so on.

In Table 3 we display the reduced masses, energy band gaps and binding energies for the 1s exciton state in the considered physical system (cf. Fig. 4), for different spin and valley combinations. We focus solely on the 1s state since it corresponds to the most tightly bound exciton, that is, farther away from the conduction band edge, and is the most relevant one in the excitonic optical response. From the values in Table 3 we observe that the reduced masses are similar for all spin and valley combinations, with the maximum relative difference being inferior to 10%. This is to be expected since $\mu^{\tau,s_z} \propto E_g^{\tau,s_z}$, which does not differ greatly between the four distinct spin and valley configurations. As a result of the homogeneity in the reduced masses, the exciton binding energy is also similar in all cases. Nonetheless, it is already possible to note that as the reduced mass increases, the exciton becomes more tightly bound. The absolute value of the binding energy is larger than what is found in typical 3D semiconductors (such as GaAs), and exceeds the thermal energy at room temperature (26 meV) by more than 10 times.

One of the main advantages of this semi-analytical approach, is that it also allows for an analytical representation of the wave function in momentum space, which reads

$$\begin{aligned} \psi_v^{\tau,s_z}(\mathbf{k}) &= \int e^{i\mathbf{r}\cdot\mathbf{k}} \psi_v^{\tau,s_z}(\mathbf{r}) d\mathbf{r} \\ &= \mathcal{N}_v^{\tau,s_z} \sum_{j=1}^N c^{\tau,s_z}(j; \nu) \int e^{ikr \cos(\theta - \theta_k)} e^{im\theta} r^{|m|+1} e^{-\zeta_j r^2} dr d\theta. \end{aligned}$$

Using the integral definition of the Bessel function of the first kind

$$J_n(z) = \frac{1}{2\pi i^n} \int_0^{2\pi} e^{iz \cos \phi} e^{in\phi} d\phi$$

one finds

$$\begin{aligned}\psi_v^{\tau,s_z}(\mathbf{k}) &= \mathcal{N}_v^{\tau,s_z} \sum_{j=1}^N 2\pi i^m c^{\tau,s_z}(j;v) e^{im\theta_k} \int J_m(kr) r^{|m|+1} e^{-\zeta_j r^2} dr \\ &= \mathcal{N}_v^{\tau,s_z} \pi \left(\frac{i}{2}\right)^{|m|} k^{|m|} e^{im\theta_k} \sum_{j=1}^N c^{\tau,s_z}(j;v) \frac{e^{-k^2/4\zeta_j}}{\zeta_j^{1+m}}.\end{aligned}\quad (2.35)$$

This result is useful to define the exciton operator.

2.4.2 Optical conductivity and Kerr angle

In a similar fashion to what was done in the single particle picture, to compute the conductivity due to excitonic effects we will employ Fermi's golden rule. This time, we will consider the initial state to be the excitonic vacuum, $|GS\rangle$, corresponding to a full valence band and an empty conduction band, and the final state to be $|\tau, s_z, v, \mathbf{Q}\rangle$, that is, an exciton composed of an electron and hole in the τ valley and spin s_z , with quantum numbers v and with a center of mass momentum $\mathbf{Q}$. Working once more in the limit of vertical transitions one should expect that $\mathbf{Q} \rightarrow 0$ from momentum conservation.

Let us start with the study of linearly polarized light, once more assuming the polarization direction to be along the x -axis. The longitudinal conductivity reads:

$$\sigma_{xx} = \frac{ie^2}{A\hbar} \sum_{\tau,s_z} \sum_{\mathbf{Q},v} (E_g^{\tau,s_z} + E_v^{\tau,s_z}) \frac{|\langle \tau, s_z, v, \mathbf{Q} | \hat{x} | GS \rangle|^2}{\hbar\omega - E_g^{\tau,s_z} - E_v^{\tau,s_z} + i0^+}. \quad (2.36)$$

Note that this expression refers to the complete σ_{xx} and not only to its real part. This compact expression is found from Fermi's golden rule using the Sokhotski–Plemelj relation

$$\frac{1}{x \pm i0^+} = \mathcal{P} \frac{1}{x} \mp i\pi\delta(x).$$

Although in the present form we have a vanishingly small imaginary part in the denominator, $i0^+$, later we will introduce a finite linewidth, η , encompassing all possible decay channels. Furthermore, let us again emphasize that the binding energy depends on the valley and spin indexes through the effective mass of the carriers, which vary slightly between valleys and spin states (cf. Table 3).

Now, to compute the matrix element, we express the operator x in second quantization using electron operators. Doing so:

$$\begin{aligned}\hat{x} &= \sum_{\mathbf{k}} \langle u_{\mathbf{k},c}^{\tau,s_z} | x | u_{\mathbf{k},v}^{\tau,s_z} \rangle c_{\mathbf{k},c}^\dagger c_{\mathbf{k},v} + \text{h.c.} \\ &= \sum_{\mathbf{k}} -i\tau\hbar v_F \frac{\langle u_{\mathbf{k},c}^{\tau,s_z} | \sigma_x | u_{\mathbf{k},v}^{\tau,s_z} \rangle}{E_{c,\mathbf{k}}^{\tau,s_z} - E_{v,\mathbf{k}}^{\tau,s_z}} c_{\mathbf{k},c}^\dagger c_{\mathbf{k},v} + \text{h.c.}\end{aligned}\quad (2.37)$$

where we used the result previously found in Eq. (2.14). The matrix element in Eq. (2.36) is evaluated with the help of Wick's theorem, explicitly:

$$\begin{aligned}\langle \tau, s_z, \nu, \mathbf{Q} | \hat{x} | GS \rangle &= -i \frac{\tau \hbar v_F}{\sqrt{A}} \sum_{\mathbf{k}, \mathbf{p}} \frac{\langle u_{c, \mathbf{p}}^{\tau, s_z} | \sigma_x | u_{v, \mathbf{p}}^{\tau, s_z} \rangle}{E_{c, \mathbf{p}}^{\tau, s_z} - E_{v, \mathbf{p}}^{\tau, s_z}} \psi_{v, \mathbf{k}}^{\tau, s_z} \langle GS | c_{\mathbf{k}-\beta \mathbf{Q}, v}^\dagger c_{\mathbf{k}+\alpha \mathbf{Q}, c} c_{\mathbf{p}, c}^\dagger c_{\mathbf{p}, v} | GS \rangle \\ &= -i \frac{\tau \hbar v_F}{\sqrt{A}} \sum_{\mathbf{k}, \mathbf{p}} \frac{\langle u_{c, \mathbf{p}}^{\tau, s_z} | \sigma_x | u_{v, \mathbf{p}}^{\tau, s_z} \rangle}{E_{c, \mathbf{p}}^{\tau, s_z} - E_{v, \mathbf{p}}^{\tau, s_z}} \psi_{v, \mathbf{k}}^{\tau, s_z} \langle GS | c_{\mathbf{k}-\beta \mathbf{Q}, v}^\dagger c_{\mathbf{p}, v} | GS \rangle \langle GS | c_{\mathbf{k}+\alpha \mathbf{Q}, c} c_{\mathbf{p}, c}^\dagger | GS \rangle,\end{aligned}$$

where from the first to the second line Wick's theorem was used, and only the term which gives a finite contribution was kept; the others vanish due to the orthogonality of the states in the Fock space. From the two matrix elements in the previous equation two Kronecker- δ appear, allowing us to write

$$\langle \tau, s_z, \nu, \mathbf{Q} | \hat{x} | GS \rangle = -i \frac{\tau \hbar v_F}{\sqrt{A}} \sum_{\mathbf{k}} \frac{\langle u_{c, \mathbf{k}}^{\tau, s_z} | \sigma_x | u_{v, \mathbf{k}}^{\tau, s_z} \rangle}{E_{c, \mathbf{k}}^{\tau, s_z} - E_{v, \mathbf{k}}^{\tau, s_z}} \psi_v^{\tau, s_z}(\mathbf{k}) \delta_{\mathbf{Q}, 0},$$

where, as predicted, a restriction imposing $\mathbf{Q} = 0$ appears. Using the analytical expression given in Eq. (2.35) for $\psi_v^{\tau, s_z}(\mathbf{k})$ and transforming the sum over $\mathbf{k}$ into an integral in momentum space, one finds:

$$\begin{aligned}\langle \tau, s_z, \nu, \mathbf{Q} | \hat{x} | GS \rangle &= -i \tau \delta_{\mathbf{Q}, 0} \mathcal{N}_v^{\tau, s_z} \sum_{j=1}^N c^{\tau, s_z}(j; \nu) \frac{\sqrt{A}}{8} \times \\ &\quad \left[\frac{\delta_{m, 0}}{\zeta_j^{1/2}} \mathcal{F} \left(\frac{E_g^{\tau, s_z}}{4 \sqrt{\zeta_j} \hbar v_F} \right) + \frac{\delta_{m, 2\tau}}{\zeta_j^{3/2}} \mathcal{G} \left(\frac{E_g^{\tau, s_z}}{4 \sqrt{\zeta_j} \hbar v_F} \right) \right]\end{aligned}\quad (2.38)$$

with

$$\begin{aligned}\mathcal{F}(x) &= \exp(x^2) \left[\sqrt{\pi} \text{Erfc}(x) - x \text{Ei}(-x^2) \right], \\ \mathcal{G}(x) &= \exp(x^2) \left[-\sqrt{\pi} \left(x^2 - \frac{1}{2} \right) \text{Erfc}(x) - x^3 \text{Ei}(-x^2) \right],\end{aligned}$$

where $\text{Erfc}(x)$ and $\text{Ei}(x)$ are the complementary error function and the exponential integral function, respectively. Note that initially we defined $\mathbf{k}$ as a momentum in the vicinity of the Dirac points, and thus the sum over $\mathbf{k}$ should be truncated at small values. However, due to the fast convergence of the integrals, allowing the integration domain to cover the entirety of the reciprocal space does not introduce significant errors in the final result. For convenience let us also present the result found for the matrix element $\langle \tau, s_z, \nu, \mathbf{Q} | \hat{y} | GS \rangle$, which is computed in an analogous way to the matrix element of $\hat{x}$, and will be useful later in the text

$$\begin{aligned}\langle \tau, s_z, \nu, \mathbf{Q} | \hat{y} | GS \rangle &= -\delta_{\mathbf{Q}, 0} \mathcal{N}_v^{\tau, s_z} \sum_{j=1}^N c^{\tau, s_z}(j; \nu) \frac{\sqrt{A}}{8} \times \\ &\quad \left[\frac{\delta_{m, 0}}{\zeta_j^{1/2}} \mathcal{F} \left(\frac{E_g^{\tau, s_z}}{4 \sqrt{\zeta_j} \hbar v_F} \right) + \frac{\delta_{m, 2\tau}}{\zeta_j^{3/2}} \mathcal{G} \left(\frac{E_g^{\tau, s_z}}{4 \sqrt{\zeta_j} \hbar v_F} \right) \right]\end{aligned}\quad (2.39)$$

Analyzing Eqs. (2.38) and (2.39), it is clear that a selection rule emerges regarding the symmetry of the exciton states: the only states which are optically active, that is, with a finite optical matrix element, are those with $m = 0$ and $m = \pm 2$ (the later being true in the K/K' valleys respectively). This restriction on the angular quantum number appears from angular integrals such as $\exp [im\theta]$ and $\exp [i(m \pm \tau)\theta]$. Furthermore, note that $\mathcal{F}(x) > \mathcal{G}(x) \forall x$, which leads to a more intense optical response of the states with vanishing angular quantum number. For convenience we write

$$\langle \nu, \mathbf{Q} | \hat{x} | GS \rangle = \delta_{\mathbf{Q},0} \sqrt{A} \Lambda_{x,\nu}^{\tau,s_z}, \quad (2.40)$$

where the form of $\Lambda_{x,\nu}^{\tau,s_z}$ follows directly from Eq. (2.38). A similar definitions applies to the matrix element of $\hat{y}$.

Returning to Eq. (2.36), and making use of the result we have just derived, one finds

$$\frac{\sigma_{xx}}{\sigma_0} = 4i \sum_{\tau,s_z} \sum_{\nu} (E_g^{\tau,s_z} + E_{\nu}^{\tau,s_z}) \frac{|\Lambda_{\nu}^{\tau,s_z}|^2}{\hbar\omega - E_g^{\tau,s_z} - E_{\nu}^{\tau,s_z} + i0^+}, \quad (2.41)$$

where we once more introduced graphene's conductivity σ_0 . The sum over ν , which accounts for the different exciton states, corresponds to a sum over the angular quantum numbers, $m = 0, \pm 2$, and a sum over the associated principal quantum numbers. We thus expect to see different resonances with decreasing intensity, associated with the different principal quantum numbers for each m , when $\sigma_{xx,1}$ is depicted as a function of the photon energy. Due to the existence of four non-degenerate band gaps, each of which associated with an exciton spectrum, we expect $\sigma_{xx}(\hbar\omega)$ to be composed of groups of four resonances for each state ν .

The response to circularly polarized light is once again characterized by the conductivities $\sigma_{\pm}$, which we write as:

$$\sigma_{\pm} = \frac{ie^2}{2A\hbar} \sum_{\tau,s_z} \sum_{\mathbf{Q},\nu} (E_g^{\tau,s_z} + E_{\nu}^{\tau,s_z}) \frac{|\langle \tau, s_z, \nu, \mathbf{Q} | \hat{x} \pm i\hat{y} | GS \rangle|^2}{\hbar\omega - E_g^{\tau,s_z} - E_{\nu}^{\tau,s_z} + i0^+}. \quad (2.42)$$

To evaluate this matrix element we recall the results given in Eqs. (2.38) and (2.39). Combining the two equations we find

$$\begin{aligned} \langle \tau, s_z, \nu, \mathbf{Q} | \hat{x} \pm i\hat{y} | GS \rangle = & -i(1 \pm \tau) \delta_{\mathbf{Q},0} \mathcal{N}_{\nu}^{\tau,s_z} \sum_{j=1}^N c^{\tau,s_z}(j; \nu) \frac{\sqrt{A}}{8} \times \\ & \left[\frac{\delta_{m,0}}{\zeta_j^{1/2}} \mathcal{F} \left(\frac{E_g^{\tau,s_z}}{4\sqrt{\zeta_j} \hbar v_F} \right) + \frac{\delta_{m,2\tau}}{\zeta_j^{3/2}} \mathcal{G} \left(\frac{E_g^{\tau,s_z}}{4\sqrt{\zeta_j} \hbar v_F} \right) \right] \end{aligned} \quad (2.43)$$

This expression clearly shows that when positive circular polarization is used, the optical matrix element is only finite for $\tau = 1$ while the $\tau = -1$ valley is only excited when negative circular polarization is applied. Here, we once again find the circular dichroism of TMDs in the vicinity of the Dirac valleys. The

fact that in the excitonic problem the valley selectivity appears to be always exact is a consequence of the approximations made when passing from the BSE to the Wannier equation. As in the case of linear polarization, we introduce the definition $\langle \tau, s_z, \nu, \mathbf{Q} | \hat{x} \pm i\hat{y} | GS \rangle = \delta_{\mathbf{Q},0} \sqrt{A} \Lambda_{\pm, \nu}^{\tau, s_z}$.

In a rather compact form, we can write a general conductivity as

$$\frac{\sigma_\gamma}{\sigma_0} = 4i \sum_{\tau, s_z} \sum_{\nu} \frac{(E_g^{\tau, s_z} + E_\nu^{\tau, s_z}) |\Lambda_\gamma^{\tau, s_z}|^2}{\hbar\omega - E_g^{\tau, s_z} - E_\nu^{\tau, s_z} + i\eta}, \quad (2.44)$$

where $\gamma = \{xx, +, -\}$ and η is a finite linewidth, which can be used to fit this expression to experimental data. Although in principle η could also be spin and valley dependent, we treat it as a constant value to simplify our analysis. Now that all the required equations have been derived let us plot and analyze the

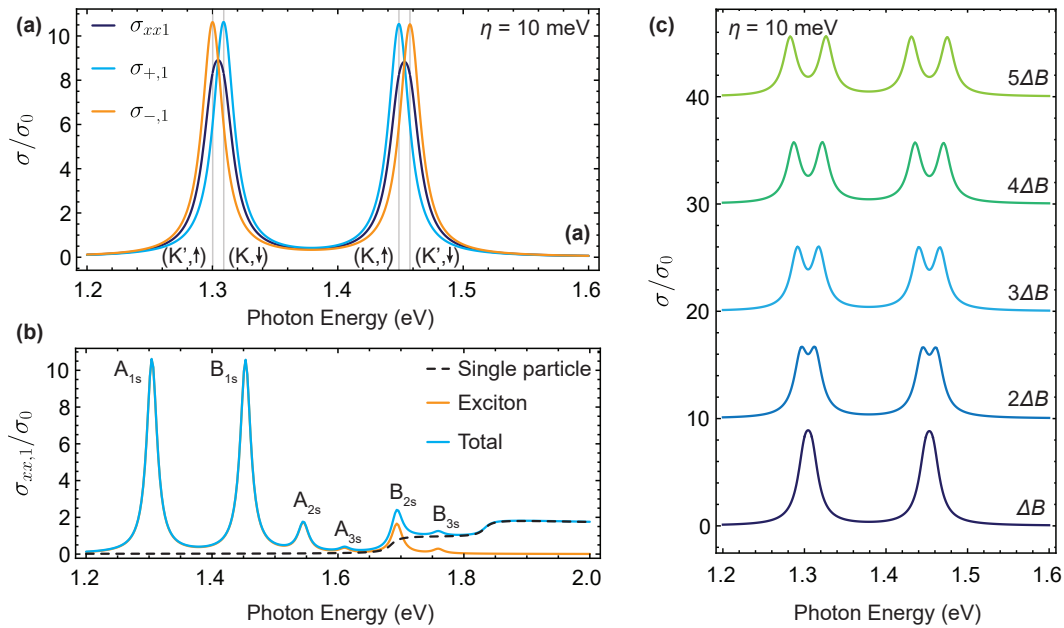


Figure 8: **Excitonic longitudinal conductivity.** (a) Real part of the conductivities $\sigma_{xx,1}$, $\sigma_{+,1}$ and $\sigma_{-,1}$ as a function of the photon energy $\hbar\omega$ due to the 1s exciton. As expected $\sigma_{-,1}$ interacts with the $\tau = -1$ valley while $\sigma_{+,1}$ interacts with the $\tau = 1$ (cf. Table 3); (b) Longitudinal conductivity, $\sigma_{xx,1}$, accounting for different exciton states and the single particle contribution; (c) Plot of $\sigma_{xx,1}$ as a function of the photon energy for different values of ΔB (starting with 9 meV up to 45 meV). The different plots are vertically shifted for clarity.

different conductivities as a function of the photon energy. In panel (a) of Fig. 8 we depict the real part of σ_{xx} , σ_+ and σ_- as a function of the photon energy. For simplicity, we take only into consideration the contribution from the 1s exciton. These plots show an interesting behavior, as the presence of excitons produces major changes in the line shape of the conductivities relatively to the single particle picture (cf. Fig. 6). The spectrum can be divided in two sets of resonances separated by approximately 140 meV. This large splitting between the two sets of peaks is a direct consequence of spin-orbit coupling, and gives rise to the well known *A*– and *B*–series in the optical spectrum of TMDs. The small splitting within each

set of resonances is due to the breaking of time-reversal symmetry induced by proximity effects; once again we observe the selective coupling of σ_+ with the K valley and σ_- with the K' valley. Due to the small value considered for the exchange splitting, $\Delta B = 9$ meV, the two peaks in the $A-$ and $B-$ series are hardly resolved if the system is excited with linearly polarized light (characterized by the conductivity σ_{xx}); for smaller linewidths the distinction would be easier. For completeness, in panel (b) we depict $\sigma_{xx,1}$ taking into account multiple exciton states, combined with the single-particle response. As predicted, the resonances associated with the $1s$ exciton are by far the dominant ones. To understand the role of ΔB on the optical conductivity we turn to Fig. 8c where $\sigma_{xx,1}$ is depicted as a function of the photon energy for different values of exchange splitting (the conductivities are vertically separated for clarity). At the bottom of the figure, the conductivity already shown in panel (a), with $\Delta B = 9$ meV, is depicted. Above that, and in ascending order, we depict $\sigma_{xx,1}$ when the exchange splitting is of 18, 27, 36 and 45 meV, that is, the multiples of $\Delta B = 9$ meV. As the splitting increases the energy difference between the four band gaps also increases and the resonances become more resolved. Here, to facilitate the analysis, we considered the exciton binding energy to be independent of ΔB , which although not strictly true (since $\mu^{\tau, s_z} \propto \Delta B$), is a reasonable approximation. Recalculating the binding energy for each value of ΔB , would only lead to minor shifts in the position and strength of the resonances, without significantly changing the general behavior of the conductivity.

Similarly to the single particle picture, we can use $\sigma_{\pm}$ to obtain the Hall conductivity, σ_{xy} . We have already seen that the imaginary part of the Hall conductivity can be obtained from the real parts of $\sigma_{\pm}$ by taking their difference and dividing by two. This relation can be extended to the real part of the Hall conductivity using the Kramers-Kronig relations. The general expression reads

$$\sigma_{xy} = \left(\frac{\sigma_{+,2} - \sigma_{-,2}}{2} \right) + i \left(\frac{\sigma_{-,1} - \sigma_{+,1}}{2} \right). \quad (2.45)$$

Both the real and imaginary parts of the Hall conductivity are plotted in Fig. 9. The analysis of the depicted data shows that, curiously enough, when passing from the non-interacting case to the one where excitonic effects are taken into account, an (approximated) inversion of behavior occurs between the real and imaginary parts of σ_{xy} . If we compare $\sigma_{xy,1}$ with excitons, with $\sigma_{xy,2}$ in the non-interacting case, the former appears to be a smoothed out version of the latter. The same goes for $\sigma_{xy,2}$ with excitons, and $\sigma_{xy,1}$ without them. The difference between the optical conductivities computed with and without excitonic effects can be understood by taking a closer look at Fig. 8a. Looking at the difference between $\sigma_{-,1}$ and $\sigma_{+,1}$, we see that, at lower energies, both conductivities are close to zero. Then, $\sigma_{-,1}$ starts to outgrow $\sigma_{+,1}$ until the former reaches a maximum, which means that $\sigma_{xy,2}$ also reaches a maximum. Next, $\sigma_{-,1}$ decreases, and $\sigma_{+,1}$ increases, which leads to $\sigma_{xy,2} = 0$ when the lines intercept, and afterwards to a

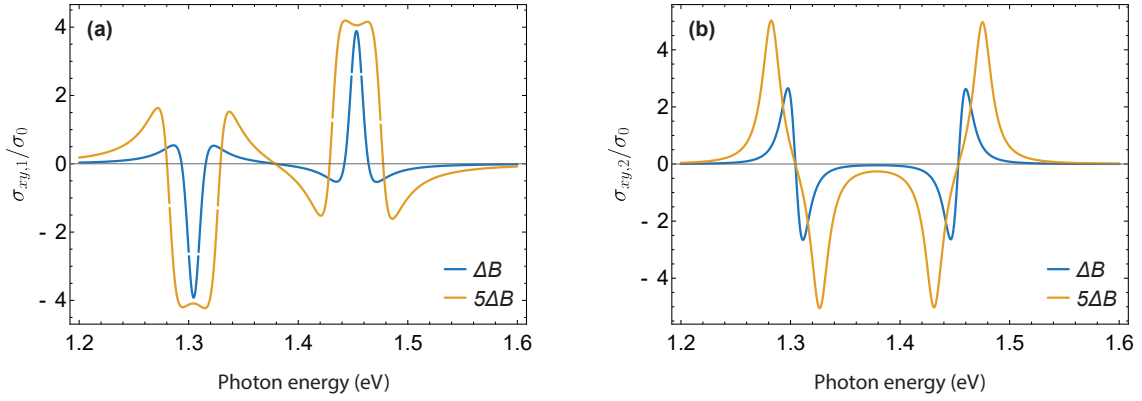


Figure 9: **Excitonic Hall conductivity**. Real (a) and imaginary (b) parts of the Hall conductivity, σ_{xy} , defined as in Eq. (2.45). The parameters are the same as the ones used in Fig. 8. In both panels we depict the conductivity for two values of ΔB , namely 9 and 45 meV.

minimum of $\sigma_{xy,2}$, when $\sigma_{+,1}$ reaches its maximum. Subsequently, $\sigma_{-,1}$ decreases, and both conductivities are, again, close to zero. From this point onward the process happens in reverse order. Comparing this description with Fig. 9, we realize that this is precisely the behavior presented by $\sigma_{xy,2}$. Although interesting, we believe that this inversion of behavior is nothing more than fortuitous, since the physical processes underlying the two responses (single particle, and excitonic) are drastically different. In the same figure the role of ΔB is also studied, where we observe that as ΔB increases the line shape is modified as a result of the shift of the resonances in Fig. 8, leading to an increased magnitude of the Hall conductivity.

Now that the Hall conductivity has been determined we can move on to the computation of the Kerr angle. In Appendix B of Ref. [61] it was shown that, in the limit of small angles, the Kerr angle is related to the linear and Hall conductivities according to the relation:

$$\theta_K = \text{Re} \left(\frac{2\pi\alpha\sigma_{xy}/\sigma_0}{(\epsilon_{\text{sub}} - 1) + \Sigma} \right)$$

with $\alpha \sim 1/137$ the fine structure constant, ϵ_{sub} the dielectric constant of the substrate and

$$\Sigma = 2\pi\alpha\sqrt{\epsilon_{\text{sub}}}\frac{\sigma_{xx}}{\sigma_0} + \pi^2\alpha^2 \left(\frac{\sigma_{xx}^2 + \sigma_{xy}^2}{\sigma_0^2} \right) + 2\pi\alpha i \frac{\sigma_{xy}}{\sigma_0}. \quad (2.46)$$

Due to the complexity of the considered system, it is no easy task to fully describe the effects of the hBN layer, the cobalt thin film, and the SiO_2 substrate on the TMD. As an approximation, we consider the effect of the substrate to dominate over all others, and thus only consider its contribution to the problem, such that $\epsilon_{\text{sub}} = \epsilon_{\text{SiO}_2}$. The Kerr angle is depicted as a function of the photon energy in Fig. 10. Since $\epsilon_{\text{SiO}_2} - 1 \gg \Sigma$ the Kerr angle approximately takes its shape from the real part of σ_{xy} . If $\epsilon_{\text{sub}} \sim 1$ this is no longer true, due to the more complex structure of the denominator. This, however, corresponds to an unrealistic scenario, since even if the SiO_2 was removed, dielectric screening from the magnetic material

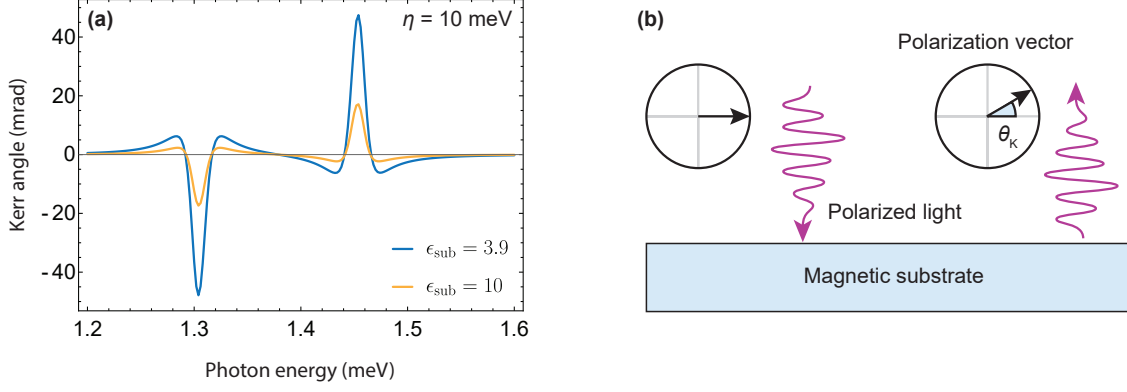


Figure 10: **Excitonic Kerr angle.** (a) Kerr angle due to the excitonic optical response, considering a linewidth of 10 meV, for two distinct substrates: SiO₂ ($\epsilon_{\text{sub}} = 3.9$) and sapphire ($\epsilon_{\text{sub}} = 10$). (b) Pictorial representation of the Kerr effect. When polarized light is reflected of a magnetic substrate its plane of polarization is rotated by an angle θ_K .

would still be present. Furthermore, we see that as expected from the definition of θ_K , the magnitude of the Kerr angle decreases with increasing dielectric screening from the environment. Also, we obtain a Kerr angle orders of magnitude larger than the ones from Refs. [62, 63], where a 2D electron gas was studied. For a smaller line width the magnitude of the Kerr angle would be even larger. The 10 meV we considered for the broadening can be seen as a conservative value, since line widths as low as 2 meV have been reported for TMDs encapsulated in hBN [64]. Advanced experimental apparatus have reported Kerr rotation measurements with a resolution of 10 nrad [65, 66], which is clearly sufficient to measure the effect depicted in Fig. 10 where the maximum angle is in excess of 40 mrad. We further note that in Ref. [67] the Kerr angle for a 4 nm thick cobalt film was measured, presenting a magnitude one order of magnitude smaller when compared to the values of Fig. 10. This is a good indicator that an experiment made in the system we are considering should essentially probe the Kerr effect due to the TMD. In Ref. [68] a spatial map of the Kerr angle for bilayer MoS₂ was constructed, with results qualitatively identical to ours.

2.5 Overview

In this section we have studied a MoS₂ heterostructure near a magnetic material, which is responsible for a proximity induced exchange interaction. In the beginning, we started by introducing the model Hamiltonian that describes the electronic band structure in the vicinity of the Dirac points, emphasizing the role played by spin-orbit coupling and the exchange interaction. With this Hamiltonian, and using Fermi's golden rule, we computed the optical absorption in the single-particle picture, and found the well known valley-selective interband optical response when circularly polarized light is used.

Afterwards, we investigated the role of excitons in the optical response of TMDs. To describe the excitonic problem we introduced the Wannier equation, whose solution determines the exciton binding energies and wave functions. Although many techniques can be used to find the solutions of the Wannier equation, we presented a semi-analytical method based on the expansion of the wave functions in a gaussian basis followed by the numerical diagonalization of the Hamiltonian. In future sections, other methods to solve this problem will be introduced. Knowing the exciton wave functions and binding energies, we computed the excitonic contribution to the optical conductivity using Fermi's golden rule. The obtained result presented the expected features in this type of spectrum with the $A-$ and $B-$ series clearly resolved. Once again, circular dichroism marked the optical response. Due to the proximity induced exchange interaction the time-reversal symmetry was broken, and the resonances of the $A-$ and $B-$ series were split into two sets of peaks. As a result of this loss of symmetry a finite Hall response emerged, even in the absence of an external magnetic field. In the end, we computed the Kerr rotation angle, which was readily obtained from the real part of the Hall conductivity.

The main goal of this section was to introduce the most important concepts and techniques used in the study of the optical properties of TMDs. Much of what was discussed up to this point will be useful in the sections to come.

Optical transitions between exciton states

In the previous section we studied the optical properties of TMDs, computing the excitonic contribution to the optical conductivity. There, we observed that the s -states were at the origin of the main features of the conductivity as a function of the photon energy [69]. These exciton states are indeed responsible for most of the optical properties of TMDs, however, as we have already noted in Section 1, other excitonic states exist, for example the p -states, which can not be probed directly due to interband optical selection rules. In the current section, our goal is to study the existence of such states, and how they can be optically accessed.

The dielectric response of TMDs due to excitons can be separated in two different regimes. The first is the one we considered in the previous section, which we term as the interband one, and occurs when an electron in the valence band is promoted to the conduction band, leading to the formation of excitonic states [70, 71]. From those, the s -states are optically active and can be seen in absorption measurements [72], in agreement with what we found when the optical conductivity was computed in the previous section. The other possible regime, which we call the intra-exciton one, consists of transitions between exciton states, such as the $1s$ and the $2p$ states [73, 74]. Each of the $1s \rightarrow np$ transitions [70, 75–77] is characterized by an in-plane polarizability, which in turn determines the dielectric response of the system in a pump-probe experiment. In this type of experiment a pump laser is responsible for populating the $1s$ state, while the probe is tuned to induce the $1s \rightarrow np$ transitions (see Fig. 11).

In this section, we will compute the polarizability associated with the intra-exciton transitions using two different techniques, one that follows directly from perturbation theory and requires the evaluation of a sum over states, and another which bypasses this sum. To be specific, we will consider the case of WSe_2 with which experiments similar to the one just mentioned have been performed. In Ref. [78], a 90 fs laser pulse centered at $\lambda = 742$ nm was shined on a WSe_2 monolayer populating the $1s$ excitonic state. At a certain variable time delay, the low-energy dielectric response was probed by a mid-infrared pulse. A schematic representation of this experiment is depicted in Fig. 11. The field-resolved time-domain

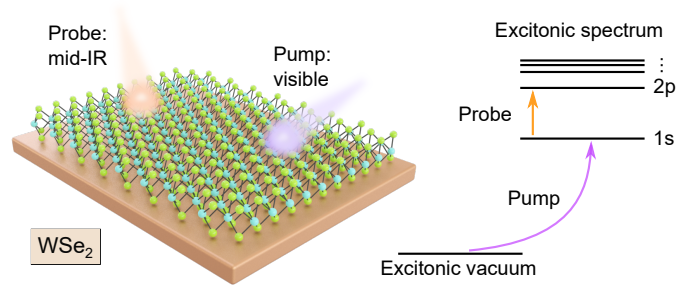


Figure 11: **Pump-probe experiment on WSe_2 .** Schematic representation of the pump-probe experiment which allows the study of the $1s \rightarrow np$ intra-exciton transitions.

data allowed the retrieving of the full dielectric response of the excited sample. The dielectric response is characterized by the real and imaginary parts of dielectric function, $\Delta\epsilon = \Delta\epsilon_1 + i\Delta\epsilon_2$, the latter being related with the conductivity. Here, both the real part of the dielectric function as well as the real part of the conductivity will be computed from the dynamical polarizability.

3.1 Dynamical Polarizability

We shall start our discussion with the introduction of the dynamical polarizability tensor, $\alpha_{ij}(\omega)$. First, we will present the commonly used expression for the polarizability, obtained from time dependent perturbation theory. Then, we will modify the resulting expression in order to obtain an alternative definition for the polarizability. We note that throughout this section atomic units (a.u.) will be used, unless otherwise stated.

3.1.1 Polarizability from perturbation theory

As derived from time dependent perturbation theory [79] the dynamical polarizability tensor can be generally written as (see Appendix D)

$$\alpha_{ij}(\omega) = \sum_{v \neq 0} \frac{\langle \psi_0 | x_i | \psi_v \rangle \langle \psi_v | x_j | \psi_0 \rangle}{E_v - E_0 - \omega} + \frac{\langle \psi_0 | x_j | \psi_v \rangle \langle \psi_v | x_i | \psi_0 \rangle}{E_v - E_0 + \omega}, \quad (3.1)$$

where x_i refers to either x or y , $|\psi_v\rangle$ are the unperturbed eigenstates of the system with energy E_v ; the sum runs over all possible states with the exception of the ground state, $|\psi_0\rangle$. Note that v is a general index, which can be used to label any desired state. If one allows the photon frequency to be a complex quantity with a small imaginary part, $\omega \rightarrow \omega + i0^+$, then it is clear by inspecting Eq. (3.1) that the plot of the imaginary part of the polarizability as a function of the photon energy, should present multiple resonances,

corresponding to the energies $\omega = E_v - E_0$, while the imaginary part should follow a dispersive shape with a zero crossing at $\omega = E_v - E_0$.

Our present goal is to compute the polarizability associated with optical transitions starting from the $1s$ state to the excited states of the exciton. Since the Rytova-Keldysh potential is a central potential, the radial and angular degrees of freedom in the Wannier equation can be easily decoupled. As a result, it is possible to show that the solutions of the Wannier equation have the angular dependence $e^{im\theta}$ with $m = 0, \pm 1, \pm 2, \dots$, like what we proposed in the previous section when the expansion of the wave functions on a gaussian basis was introduced. Since the $1s$ state has a vanishing angular quantum number, $m = 0$, and the dipole operator contributes either with $\cos \theta$ or $\sin \theta$, it is clear that the matrix elements in Eq. (3.1) are only finite if $|\psi_v\rangle$ belongs to the p -series ($m = \pm 1$).

In order to evaluate the dynamical polarizability we will follow two distinct approaches. The more traditional one passes by finding the wave functions of the $1s$ and np states, followed by the evaluation of the matrix elements in Eq. (3.1), and the computation of the sum over states where the different contributions are added. As an alternative, we will also present a way of computing $\alpha_{ij}(\omega)$, which requires only the $1s$ wave function and avoids the sum over states. This technique is similar to the Dalgarno-Lewis' method [80], which is sometimes used to remove the sums over states found from perturbation theory (an example of this is the exact computation of the static polarizability of the 3D Hydrogen atom [81]). The description of this alternative method will now be presented.

3.1.2 Dalgarno-Lewis approach

The first step in our calculation is to consider the carrier-light interaction, once again treated within the dipole approximation. The total Hamiltonian of the system consist of the sum of the unperturbed Hamiltonian, H_0 , and the interaction term, $H_{\text{int}} = -\mathbf{r} \cdot \mathcal{E}(t)$, that is

$$\begin{aligned} H &= H_0 - \mathbf{r} \cdot \mathcal{E}(t) \\ &= -\frac{1}{2\mu} \nabla^2 + V_{\text{RK}}(\mathbf{r}) - \mathbf{r} \cdot \mathcal{E}(t), \end{aligned} \quad (3.2)$$

where once again μ is the reduced mass of the exciton, $V_{\text{RK}}(\mathbf{r})$ is the Rytova-Keldysh potential, $\mathbf{r}$ is the position operator, and $\mathcal{E}(t)$ is the external time dependent electric field

$$\mathcal{E}(t) = \mathcal{E}_0 (e^{-i\omega t} + e^{i\omega t}),$$

with ω the field's frequency and $\mathcal{E}_0$ its amplitude with a given polarization. Note that this Hamiltonian is already present when $\alpha_{ij}(\omega)$ is derived from time-dependent perturbation theory.

To be specific, let us consider the electric field to be aligned along the x direction, such that the associated time-dependent Schrödinger equation reads

$$[H_0 - x\mathcal{E}(t)] |\psi(t)\rangle = i\frac{\partial}{\partial t} |\psi(t)\rangle, \quad (3.3)$$

with $|\psi(t)\rangle$ the state vector describing the system when the electric field is applied. In the absence of the external field this corresponds to the eigenvalue problem whose solutions are the binding energies and wave functions of the unperturbed system. Now, in order to find the state vector $|\psi(t)\rangle$ we expand it in powers of the electric field amplitude [82–84], that is

$$|\psi(t)\rangle = e^{-iE_0 t} |\psi_{1s}\rangle + \mathcal{E}_0 e^{-i(E_0 - \omega)t} |\phi(\omega)\rangle + \mathcal{E}_0 e^{-i(E_0 + \omega)t} |\phi(-\omega)\rangle + \mathcal{O}(\mathcal{E}_0^2),$$

where only terms up to first order in the electric field were kept. Here, $|\phi(\omega)\rangle$ is the first order correction to the state vector $|\psi_0\rangle$. Inserting this expansion in the Schrödinger equation, and grouping the terms with the same power of $\mathcal{E}_0$, and same temporal dependence, one finds

$$H_0 |\psi_{1s}\rangle = E_{1s} |\psi_{1s}\rangle \quad (3.4)$$

$$x |\psi_{1s}\rangle = (E_{1s} \mp \omega - H_0) |\phi(\pm\omega)\rangle, \quad (3.5)$$

where the first equation simply states the eigenvalue relation of the unperturbed system, while the second one defines the first order corrections as the solution of a differential equation. Inserting Eq. (3.5) into the definition of the polarizability tensor, Eq. (3.1), one finds

$$\begin{aligned} \alpha_{xx}(\omega) &= \sum_{v \neq 0} \sum_{\pm} \frac{\langle \psi_{1s} | x | \psi_v \rangle \langle \psi_v | (E_0 \pm \omega) - H_0 | \phi(\mp\omega) \rangle}{E_v - E_0 \mp \omega} \\ &= - \sum_{v \neq 0} \langle \psi_{1s} | x | \psi_v \rangle \langle \psi_v | \phi(-\omega) \rangle + \langle \psi_{1s} | x | \psi_v \rangle \langle \psi_v | \phi(\omega) \rangle, \end{aligned} \quad (3.6)$$

where we can now use the fact that $\langle \psi_{1s} | x | \psi_{1s} \rangle = 0$, which holds due to the lack of angular dependence of the $1s$ state, to apply the completeness relation $\sum_v |\psi_v\rangle \langle \psi_v| = \mathbb{I}$. Doing so, we arrive at the following expression for the dynamical polarizability:

$$\alpha_{xx}(\omega) = -\langle \psi_{1s} | x | \phi(-\omega) \rangle - \langle \psi_{1s} | x | \phi(\omega) \rangle, \quad (3.7)$$

which, as opposed to Eq. (3.1), requires the computation of only two matrix elements to automatically obtain all the contributions to the polarizability. Note that to be able to evaluate the two matrix elements, $\psi_{1s}(\omega)$ and $\phi(\omega)$ must be known. The former can be described, for example, with a variational *ansatz* (which we will do later in the text), while the latter is found from the solution of Eq. (3.5).

In the following we present a numerical algorithm to obtain the $1s$ and np wave functions and binding energies in order to evaluate the polarizability through Eq. (3.1). Then, we will discuss how to solve Eq. (3.5) to obtain $\phi(\omega)$ and compute the polarizability using Eq. (3.7). In the end both results will be compared and discussed.

3.2 Shooting algorithm

Let us now explore a method to obtain the wave function of the $1s$ as well as the p -states, in order to compute the polarizability using the definition with the sum over states. To obtain these wave functions one could make use of the expansion in a gaussian basis given in the previous section, which allows the treatment of both s - and p -states. However, to present different alternatives to solve the Wannier equation, let us follow instead a numerical path, implementing a so called shooting algorithm [85–88].

The basic premise of this method lies in the fact that the Wannier equation (see previous section) only yields continuous wave functions with a continuous derivative for specific energy values, which correspond to the binding energies of the excitonic states. Our task is thus to find what energy values produce smooth wave functions. The shooting method is generally implemented in the following manner: i) first, an initial guess for the binding energy is chosen; ii) using this energy the Wannier equation is integrated from left to right, and from right to left, matching the two results somewhere far away from the edges of the domain. This can be done explicitly by discretizing the differential equation, or by using an appropriate numerical package. Also, one can choose to match the wave functions themselves, or their logarithmic derivative; iii) next, the wave functions are scaled in the matching point, forcing the continuity of the complete wave function (this step is not necessary if one works with the logarithmic derivatives); iv) afterwards, the continuity of the derivative of the resulting function must be verified; if it is a smooth function, then the initial guess for the binding energy was correct, if not the process must be repeated with a new guess for the binding energy until the continuity condition is satisfied.

In a more detailed way, we start with the Wannier equation, and, as usual, write the wave function as $\psi(\mathbf{r}) = R(r)\Phi(\theta)$, with $\Phi(\theta) \propto e^{im\theta}$ where $m = 0, \pm 1, \pm 2, \dots$ is the angular quantum number. Using this, the Wannier equation is transformed into a differential equation defining the radial function $R(r)$. Performing the substitution $u(r) = R(r)\sqrt{r}$, one finds

$$-\frac{1}{2\mu} \frac{d^2 u}{dr^2} + \left[\frac{m^2}{2\mu r^2} - \frac{1}{8\mu r^2} + V_{\text{RK}}(r) \right] u(r) = Eu(r), \quad (3.8)$$

where the term proportional to m^2 is the well known centrifugal potential, and the boundary conditions are $u(r = 0) = 0$ and $u(r \rightarrow \infty) = 0$. To facilitate numerical calculations it is convenient to instead consider the boundary conditions $u(r = \epsilon) = \epsilon$ and $u(r = R) = \epsilon$, where ϵ is a small, yet finite, quantity and R is chosen sufficiently deep into the region where $u(r)$ decays monotonically to zero, such that $u(R) \sim 0$. Working with $u(r)$ instead of $R(r)$ has the advantage of eliminating terms with a first derivative in the radial coordinate. Note that transforming the problem from $R(r)$ to $u(r)$ is a natural modification since $|u(r)|^2 = |R(r)|^2 r$ corresponds to the radial probability density. The shooting algorithm can be directly applied to Eq. (3.8), however, to improve the efficiency of the calculation we can introduce the change of

variable $x = \ln r$, and the new function $u(x) = f(x)e^{x/2}$, leading to the differential equation

$$-\frac{1}{2\mu} \frac{d^2}{dx^2} f(x) + \left[\frac{m^2}{2\mu} + e^{2x} V_{\text{RK}}(e^x) \right] f(x) = e^{2x} f(x) E. \quad (3.9)$$

The advantage of working with a logarithmic grid (considering that when numerically evaluated the differential equation is discretized) lies in the improved description of the region near $r = 0$, which is critical when the differential equation is integrated from left to right. Note that it is more important to have a detailed description near $r = 0$ than in the region $r \rightarrow \infty$, since in the former the wave function and its derivative vary abruptly, while in the latter the changes are more gradual due to the slow decaying behaviour of the wave functions at large distances.

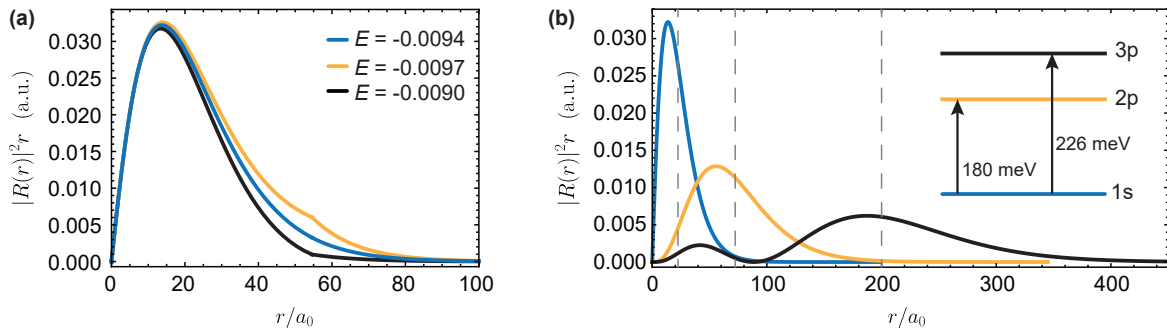


Figure 12: **Shooting method wave functions.** (a) Wave function of the $1s$ state using three different energy guesses (whose values are presented in atomic units). The correct binding energy is $E = -0.0094$ since it leads to a smooth wave function. (b) Radial probability density ($|R(r)|^2 r$) of the the $1s$ state and the first excited states with $|m| = 1$, obtained using the shooting method. The dashed lines mark the exciton Bohr radius of the three considered states. In both panels the radius is given in units of the Bohr radius a_0 . The parameters of Table 4 were used.

In Fig. 12a we depict the wave functions obtained with the shooting method for the $1s$ state ($m = 0$), using three distinct guesses for the binding energy. Comparing the three results it is clear that $E = -0.0094$ a.u (255 meV). corresponds to the correct binding energy, since it produces a smooth wave function, as opposed to the other two guesses, whose wave functions present a sharp kink in the matching point (implying that the used energy is not physically meaningful). The binding energy of other s -states can be obtained by changing the initial guess for the binding energy. To obtain the solutions of other exciton states, e.g. the $2p$ state, we modify the centrifugal potential (which now becomes finite), and introduce new guesses for the binding energy. The plot of the radial probability density of the $1s$, $2p$ and $3p$ states is depicted in Fig. 12b. There, we observe that the wave functions follow the same qualitative traits as their counterpart for the 2D Hydrogen atom, with the difference of being more spread out in space as a consequence of the reduced interaction strength. The dashed lines mark the exciton Bohr radius of each state, corresponding to $23a_0$, $72a_0$ and $200a_0$, with $a_0 = 0.53\text{\AA}$ the Bohr radius, for the $1s$, $2p$ and $3p$ states, respectively. At last, the inset in Fig. 12b, schematically shows some of the $1s \rightarrow np$ transitions,

with the associated energy given in meV. The energy of each transition was obtained by subtracting the binding energies found using the shooting method of the involved states. Using these wave functions the matrix elements of the dipole operator between the $1s$ and the np states can be numerically evaluated, and using them the polarizability as defined in Eq. (3.1) is obtained.

3.3 Variational method

In this sub-section we will discuss how the dynamical polarizability can be computed using Eq. (3.7). To this end we start by discussing how the $1s$ wave function can be described with a variational *ansatz*, and how to obtain $|\phi(\omega)\rangle$ from Eq. (3.5). Note that, once again, we could use the method of the previous section, or even the shooting method we have just described, to obtain the wave function of the $1s$ state, but, as mentioned before, with the goal of showcasing different possible techniques to solve the Wannier equation we opt to follow a variational approach.

Let us consider the following double exponential variational *ansatz* proposed in Ref. [89] to describe the $1s$ exciton state:

$$\psi_{1s}(r) = C (e^{-ar} + be^{-\gamma r}), \quad (3.10)$$

where C is a normalization constant determined such that $\langle \psi_{1s} | \psi_{1s} \rangle = 1$, and a , b and γ are variational parameters determined from minimizing the expectation value of the Hamiltonian of the unperturbed system. As we have already seen, although not identical, the Rytova-Keldysh potential bears some similarities with the Coulomb potential, leading to the proposal of a wave function like the one of the ground state of the Hydrogen atom, e^{-ar} . To account for the differences between the two potentials a second exponential, $e^{-\gamma r}$, is added to the trial wave function. In Ref. [89] it was shown that this variational *ansatz* is capable of describing the exact results to a very high precision. In Fig. 13 we compare the radial probability density obtained using the shooting method and the variational *ansatz*, and observe that the variational approach indeed produces an outstanding description of the numerically exact results.

Now that a description of the $1s$ wave function has been found, let us move on to the problem of finding $|\phi(\omega)\rangle$. Due to the complexity of Eq. (3.5), which corresponds to a non-homogeneous differential equation containing special functions, the first order correction to the state vector, $|\phi(\omega)\rangle$, can not be found analytically, and Eq. (3.5) must be solved numerically. This can be achieved either directly by numerically integrating the differential equation, or by transforming it into a linear system. The latter option is the one we will explore.

Like in the case of the shooting method, where the boundary conditions were applied at an arbitrary large number R , here it is also convenient to follow a similar procedure. To that end, we enclose the

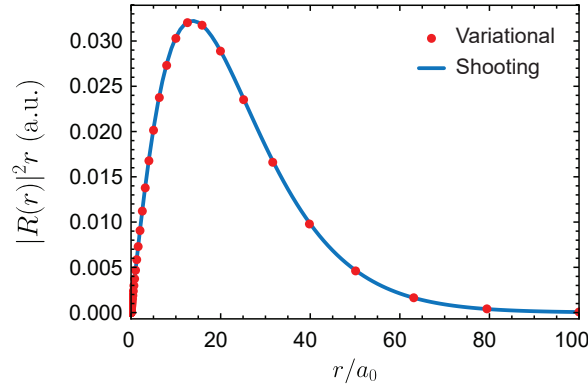


Figure 13: **1s wave function.** Comparison between the 1s wave function obtained from the shooting method and using the variational *ansatz* given in Eq. (3.10). The agreement between the two approaches is clear. The variational parameters are $a = 0.05$, $b = -0.41$ and $\gamma = 2.13$. In both cases a binding energy of $E = -0.0094$ a.u (255 meV) was found.

system in a disk of radius R , modifying the 1s wave function as

$$\psi_{1s}^{\text{fin.}}(r) = C (e^{-ar} + be^{-ar}) \left(1 - \frac{r}{R}\right). \quad (3.11)$$

For a large enough R this modification should not impact the quality of the results, since $\lim_{R \rightarrow \infty} \psi_{1s}^{\text{fin.}}(r) = \psi_{1s}(r)$; this should be interpreted only as a technique to improve the stability of the numerical solution. If, however, R is not chosen sufficiently large, then we will be in fact describing a confined system such as, for example, a quantum dot. In that case, as a result of the confinement, besides the bound states, states with positive energies would also appear [90–92], modifying the optical properties of the system. In Fig. 12b we saw that the probability density of $3p$ state is already close to zero for $r = 400a_0$. Choosing, for example, $R = 900a_0$ is enough to obtain accurate results, since that far way from the origin the wave functions of the low energy p -state have effectively reached zero, and the more energetic p -states, even if not accurately described, play a negligible role in the final result.

The first step to solve the differential equation, Eq. (3.5), is to note that this task can be transformed in the problem of minimizing the following functional [83, 84]:

$$\mathcal{J} = \langle \phi(\omega) | H_0 - E_0 + \hbar\omega | \phi(\omega) \rangle + \langle \phi(\omega) | x_\alpha | \psi_{1s} \rangle + \langle \psi_{1s} | x_\alpha | \phi(\omega) \rangle. \quad (3.12)$$

This functional is defined in this particular way in order to recover Eq. (3.5) when $\mathcal{J}$ is differentiated with respect to $\langle \phi(\omega) |$. To give general expressions we introduced $x_\alpha = \{x, y\}$, however in the end, we will focus on the case where $x_\alpha = x$. Now, to obtain $|\phi(\omega)\rangle$ we expand it in a Bessel-Fourier basis as:

$$\begin{aligned} \phi(\omega; \mathbf{r}) &= \sum_{n=1}^N \sum_{l=\pm 1} c_{ln}^\alpha(\omega) J_l \left(\frac{z_{ln} r}{R} \right) e^{il\theta} \\ &= \sum_{n=1}^N \left[c_{+n}^\alpha(\omega) e^{i\theta} - c_{-n}^\alpha(\omega) e^{-i\theta} \right] J_1 \left(\frac{z_{1n} r}{R} \right), \end{aligned} \quad (3.13)$$

where N is the number of functions in the basis, $c_{ln}^\alpha(\omega)$ are the expansion coefficients which are determined from the minimization of the functional $\mathcal{J}$, $J_l(x)$ is the Bessel function of the first kind of l -th order and z_{ln} corresponds to the n -th zero of $J_l(x)$. One important aspect of this expansion is that as R increases, the number of functions in the basis, N , should also increase to find accurate results. In this expansion we are only considering the terms with angular quantum number $m = \pm 1$ since from our experience, we know that only terms with this angular dependence will couple with the ground state wave function via a dipole induced transition. Although we chose to work in a Bessel-Fourier basis other choices could have been made, for example, a gaussian basis, or Sturmian functions. Also, we note that if the external electric field is aligned along the x direction then one should expect to find $c_{+n} = -c_{-n}$, (in order to recover a $\cos \theta$) and if it is aligned along y direction then $c_{+n} = c_{-n}$ (to find a $\sin \theta$); these two observations can be used as a consistency check in the end of the calculation. Considering H_0 to be given by the sum of a kinetic term with the Rytova-Keldysh potential, one finds

$$\begin{aligned} \mathcal{J} = & \pi \sum_{n=1}^N \sum_{l=\pm 1} c_{ln}^\alpha (c_{ln}^\alpha)^* R^2 [J_{|l|+1}(z_{ln})]^2 \left[\frac{1}{2\mu} \frac{z_{ln}^2}{R^2} - E_0 + \omega \right] + 2\pi \sum_{n=1}^N \sum_{k=1}^N \sum_{l=\pm 1} c_{ln}^\alpha (c_{lk}^\alpha)^* \mathcal{V}_{kn}^{(l)} \\ & + \pi \sum_{n=1}^N \sum_{l=\pm 1} (\delta_{\alpha,x} - il\delta_{\alpha,y}) (c_{ln}^\alpha)^* \mathcal{S}_n^{(l)} + \pi \sum_{n=1}^N \sum_{l=\pm 1} (\delta_{\alpha,x} + il\delta_{\alpha,y}) c_{ln}^\alpha \mathcal{S}_n^{(l)} \end{aligned}$$

where we introduced the definitions

$$\mathcal{V}_{kn}^{(l)} = \int_0^R J_l\left(\frac{z_{lk}r}{R}\right) V_{RK}(r) J_l\left(\frac{z_{ln}r}{R}\right) r dr, \quad (3.14)$$

$$\mathcal{S}_n^{(l)} = \int_0^R J_l\left(\frac{z_{ln}r}{R}\right) r^2 \psi_0^{\text{fin.}}(r) dr, \quad (3.15)$$

which correspond to the matrix element of the Rytova-Keldysh potential between two basis functions, and the probability amplitude of the dipole induced transition between the $1s$ state and the basis functions, respectively. To obtain this expression the orthogonality relation of Bessel functions on a disk

$$\int_0^a J_\nu\left(z_{vm}\frac{\rho}{a}\right) J_\nu\left(z_{vn}\frac{\rho}{a}\right) \rho d\rho = \frac{a^2}{2} J_{\nu+1}^2(z_{vm}) \delta_{m,n},$$

as well as the property $J_{-m} = (-1)^m J_m$ with $m > 0$ were used. The different coefficients are determined from the condition:

$$\frac{\partial \mathcal{J}}{\partial (c_{ij}^\alpha)^*} = 0, \quad j = 1, 2, \dots, N_{\text{max}},$$

which defines a linear system whose solution determines the expansion coefficients. Explicitly one finds:

$$\mathbb{M}^{(l)}(\omega) \mathbf{c}_l^\alpha(\omega) = -\frac{1}{2} (\delta_{\alpha,x} - il\delta_{\alpha,y}) \mathbf{S}^{(l)} \quad (3.16)$$

where

$$\left[\mathbb{M}^{(l)}(\omega) \right]_{ij} = \frac{R^2}{2} \left[J_{|l|+1}(z_{li}) \right]^2 \left[\frac{1}{2\mu R^2} z_{li}^2 - E_0 + \omega \right] \delta_{ij} + \mathcal{V}_{ij}^{(l)} \quad (3.17)$$

and

$$\mathbf{S}^{(l)} = \begin{pmatrix} S_1^{(l)} \\ S_2^{(l)} \\ \vdots \\ S_N^{(l)} \end{pmatrix}, \quad \mathbf{c}_l^\alpha(\omega) = \begin{pmatrix} c_{l1}^\alpha(\omega) \\ c_{l2}^\alpha(\omega) \\ \vdots \\ c_{lN}^\alpha(\omega) \end{pmatrix}.$$

It is now easy to verify what we stated at the beginning: when we are dealing with a field along the x direction, we have $c_{+n} = -c_{-n}$, because $\mathbb{M}^{(+)} = \mathbb{M}^{(-)}$ and $\mathbf{S}^{(+)} = -\mathbf{S}^{(-)}$. Following the same reasoning, when dealing with the y direction we have $c_{+n} = c_{-n}$, since the term $il\delta_{\alpha,y}$ changes sign when l changes sign. Moreover, we note that the most computationally demanding part of the calculation is the evaluation of the matrix elements containing the Rytova-Keldysh potential, $\mathcal{V}_{ij}^{(l)}$. Fortunately, the burden of this task is greatly reduced because i) $\mathcal{V}_{ij}^{(l)}$ is symmetric, that is $\mathcal{V}_{ij}^{(l)} = \mathcal{V}_{ji}^{(l)}$, reducing the number of independent entries from N^2 to $N(N+1)/2$, and ii) $\mathcal{V}_{ij}^{(l)}$ is independent of the photon energy, and as a result only needs to be computed once. From Eq. (3.7), one easily shows that the dynamical polarizability can be expressed as

$$\begin{aligned} \alpha_{xx}(\omega) &= -[\langle \psi_{1s} | x | \phi(-\omega) \rangle + \langle \psi_{1s} | x | \phi(\omega) \rangle] \\ &= -2\pi \left[\mathbf{c}_+^x(-\omega) \cdot \mathbf{S}^{(+)} + \mathbf{c}_+^x(\omega) \cdot \mathbf{S}^{(+)} \right] \end{aligned} \quad (3.18)$$

3.4 Relation between polarizability, dielectric function, and optical conductivity

Now, before moving on to the comparison and analysis of the dynamical polarizability obtained with the two presented methods, let us try to establish the relation between the polarizability and the dielectric function, which in turn can be related to the optical conductivity. Determining how these quantities are related is of crucial importance, since experimentally it is the dielectric function or the conductivity that are measured, not the dynamical polarizability.

Let us consider that our problem can be described as a two dimensional gas of excitons, with an exciton density N_X , subject to an external electric field $\mathcal{E}_{\text{ext}}$. Furthermore, let us introduce the dipole moment of a single exciton, $\mathbf{p}$, which is related to the exciton local field, $\mathcal{E}_X$, through the polarizability tensor, $\bar{\bar{\alpha}}$, as

$$\mathbf{p} = \bar{\bar{\alpha}} \cdot \mathcal{E}_X. \quad (3.19)$$

From the individual dipole moment, the polarization of the monolayer, $\mathbf{P}$, may be written as

$$\mathbf{P} = N_X \mathbf{p}. \quad (3.20)$$

Assuming the local electric field, $\mathcal{E}_X$, to be approximately the same as the external field, which should be valid in a diluted exciton gas, that is, with a small exciton density, we write the susceptibility of the exciton gas as

$$\chi = \frac{\mathbf{P}}{\epsilon_0 \mathcal{E}_X} = \frac{N_X \alpha}{\epsilon_0}, \quad (3.21)$$

where ϵ_0 is the permittivity of vacuum, and we are considering the vectors to be colinear. From the susceptibility, the dielectric function can be extracted as

$$\Delta\epsilon(\omega) = \frac{\chi}{d} = \frac{N_X}{d\epsilon_0} \alpha(\omega), \quad (3.22)$$

where d is the effective thickness of the monolayer [58]. From the dielectric function, the conductivity is readily obtained [93]

$$\sigma(\omega) = -i\epsilon_0\omega\Delta\epsilon(\omega). \quad (3.23)$$

In the end of the section both $\Delta\epsilon(\omega)$ and $\sigma(\omega)$ will be computed and compared with the experimentally obtained results of Ref. [78].

We stress once again that there are other terms contributing to the total susceptibility of the system besides the intra-exciton response, namely: transition from the exciton vacuum to the ns -levels and to other even parity states, the background susceptibility accounting for transitions to higher-energy bands, among other[94, 95].

3.5 Results

At last, let us explicitly compute the dynamical polarizability, $\alpha(\omega)$, obtained with the two methods we have described in this section. The system we consider is the one depicted in Fig. 11; the parameters to model it are presented in Table 4.

κ	μ (m_0)	r_0 (a_0)	d (a_0)	N_X (cm^{-2})	R (a_0)	N
3.32	0.167	52	12	1.8×10^{12}	900	20

Table 4: **WSe₂ parameters.** Parameters to model excitons in WSe₂ on a diamond window. The values of κ , r_0 , d and N_X were taken from [78]; the reduced mass was obtained from the data presented in [52]. The values of R and N enter in the Fourier-Bessel expansion. Lengths are given in terms of the Bohr radius a_0 , and m_0 the bare electron mass.

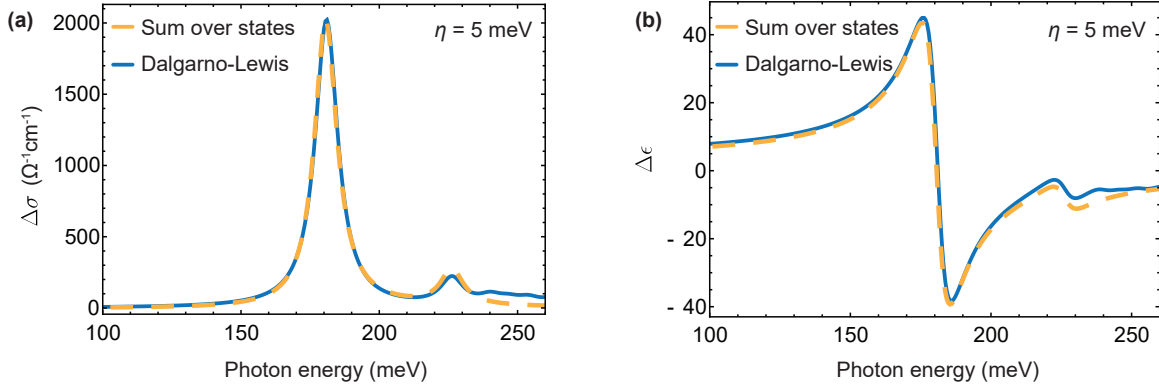


Figure 14: **Optical response of intra-exciton transitions.** Depiction of the optical conductivity (a) and dielectric function (b) as a function of the photon energy for intra-exciton transitions, obtained using the sum over states and the Dalgarno-Lewis approaches. In the sum over states only the transitions to the $2p$ and $3p$ state were considered. The parameters of Table 4 were used.

In Fig. 14 we depict the real part of the conductivity and the real part of the dielectric function in terms of the photon energy. These two quantities are obtained from the imaginary and real parts of the polarizability $\alpha(\omega)$ through Eqs. (3.22) and (3.23). In order to extract the real and imaginary parts of $\alpha(\omega)$ we shifted the photon energy by a small imaginary part, η , such that $\omega \rightarrow \omega + i\eta$. The microscopic determination of η is by no means a simple task, since it depends on the individual broadenings of the $1s$ and np states, which in turn depend on radiative and non-radiative decay channels. Here, for simplicity, we set $\eta = 5$ meV, since a small value of η allows different resonances to be resolved. In realistic samples at room temperature one should expect η to be in the range of 50 meV, while at cryogenic temperatures its value should be significantly smaller.

The results of Fig. 14 were obtained using the two described approaches to obtain the conductivity: i) using the sum over states definition of $\alpha(\omega)$; ii) employing the Dalgarno-Lewis approach which does not require the sum over states. Comparing the two methods we observe that, as expected, they are in good agreement with each other, the main difference being in the number of resonances described. In the sum over states approach we considered the contributions of the $1s \rightarrow 2p$ and $1s \rightarrow 3p$ transitions, leading to the two visible resonances. With the Dalgarno-Lewis approach, however, all the contributions are automatically accounted for, which leads to the appearance of other resonances beyond the $1s \rightarrow 3p$, resulting in the formation of a plateau-like structure near 250 meV. Although this behavior is absent in the sum over states result, it could be reproduced if we had considered transitions to higher p -states. These higher energy transition are less relevant than the two main ones due to their reduced oscillator strength, rendering them almost invisible for $\eta \gtrsim 10$ meV.

Although the p -states are optically dark in interband transitions, it is clear from Fig. 14 that they leave an optical fingerprint in pump-probe experiments, as can be seen from the resonances that appear

in the dielectric function and the conductivity. As we have already mentioned, in this type of experiment the pump laser induces interband transitions which populate the s -series. By adjusting the energy of the laser one can selectively pump the $1s$ state alone (the large energy spacing between s -states, which is in excess of 100 meV, makes this an easy enough task). Then, with the introduction of another laser, the probe, transitions between the populated $1s$ state and the p -series can be induced, originating the resonances in Fig. 14. One important aspect to consider is that the population of the $1s$ state is not constant in time. When the pulse of the pump laser is applied, excitons quickly start to populate the $1s$ state in a sub picosecond time scale until a maximum exciton density is obtained. After this point, the exciton population starts to decay, first through radiative recombination, followed by Auger recombination (a non-radiative recombination mechanism where the excess energy is transferred to other particles, exciting them) [96]. The evolution of the exciton density with time can be described with two coupled rate equations [78]. Let us consider that the excitons (N_X) can be divided into two groups, the bright (N_{BX}) and the dark (N_{DX}) ones, where bright excitons are those which can recombine radiatively. The population of bright excitons increases when the pump laser populates the $1s$ state; afterwards it decreases due to radiative recombination, Auger recombination, and exciton-phonon interactions which may result in the scattering of excitons beyond the light cone, i.e. the excitons acquire a large center of mass momentum, rendering them dark. For the dark excitons, its population only increases as a result of scattering of bright excitons, and decreases due to Auger recombination. Based on these considerations, we describe the time evolution of each population as:

$$\begin{aligned}\frac{d}{dt}N_{BX} &= G(t) - \frac{1}{\tau_R}N_{BX} - \frac{\gamma_{\text{Auger}}}{2}(N_{BX} + N_{DX})^2 - \Gamma N_{DX} \\ \frac{d}{dt}N_{DX} &= \Gamma N_{BX} - \frac{\gamma_{\text{Auger}}}{2}(N_{BX} + N_{DX})^2,\end{aligned}$$

where τ_R is the radiative lifetime, γ_{Auger} quantifies Auger recombination (which we treat with a bi-molecular model [78]) and Γ controls exciton-phonon scattering; the function $G(t)$ characterizes the creation of excitons by the pump laser. The total exciton density $N_X = N_{BX} + N_{DX}$ is obtained from the numerical solution of the two rate equations, and its result as a function of time is depicted in Fig. 15, where we considered the pump laser to take a gaussian shape with a linewidth of 90 fs (the values of τ_R , γ_{Auger} and Γ were taken from [78]). The analysis of Fig. 15a is in agreement with what we mentioned before: initially the population increases sharply, followed by a period of accelerated decay mainly due to radiative recombination, which in turn is followed by a region with reduced decay rate as a result of Auger recombination. From Fig. 15a it is clear that one should expect that depending on the instance the probe laser induces the $1s \rightarrow np$ transition, the magnitude of the optical response should vary; the longer the interval of time between the application of the pump and the probe lasers, the more attenuated are the

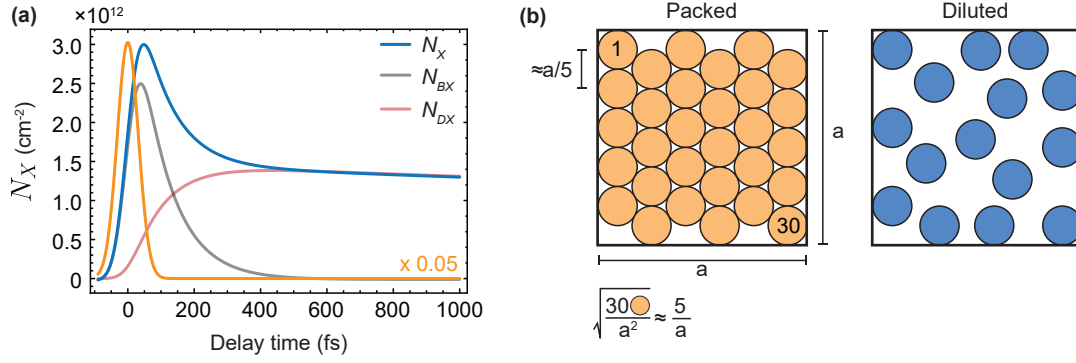


Figure 15: **Exciton density.** (a) Depiction of the exciton density (blue) as a function of time, obtained from the numerical solution of the rate equations. The pump pulse (orange) was modeled as a gaussian pulse with a linewidth of 90 fs. The parameters $\tau = 0.15$ ps, $\gamma = 0.13$ cm²/s and $\Gamma = 3.7$ ps⁻¹ [78]. (b) Pictorial representation of an exciton gas where the exciton wave functions (represented by the circles) do not overlap (blue), and in the critical density where overlap becomes significant (orange). The critical density is related with the exciton Bohr radius approximately according to $(N_X^{\text{crit}})^{-1/2} \sim a_X$.

features in the conductivity and dielectric response (this is clear from Eqs. (3.22) and (3.23) where we see that $\Delta\epsilon$ and σ are proportional to N_X).

Another important aspect one should consider is the effect of exciton-exciton interactions. This interaction is not included in our model, and its treatment is not trivial, yet, we should discuss it and assess if it is expected to play a significant role in the considered system. As the exciton density increases, the mean distance between excitons decreases, and new effects may appear as a result of the overlap of the wave functions. One way to estimate the critical exciton density is to compare its inverse square root to the exciton Bohr radius (similarly to the Mott criterion for the metal-insulator transition); if the two values are comparable, then exciton-exciton interactions may be of importance (see Fig. 15b). For an exciton density of $N_X = 1.8 \times 10^{12}$ cm⁻² (the value used in Fig. 14) one finds

$$\frac{1}{\sqrt{N_X}} \approx 140a_0,$$

while for $N_X = 3 \times 10^{12}$ cm⁻², we obtain

$$\frac{1}{\sqrt{N_X}} \approx 108a_0.$$

Comparing these value with the ones found for the exciton Bohr radius of the $1s$, $2p$ and $3p$ states ($23a_0$, $72a_0$ and $200a_0$, respectively) it is plausible to assume that for $N_X = 1.8 \times 10^{12}$ cm⁻² exciton-exciton interactions should not be significant for the $1s$ and $2p$ states, but may be relevant for the $3p$ state (which is less important in the optical response due to the smaller oscillator strength of the $1s \rightarrow 3p$ transition). For $N_X = 3 \times 10^{12}$ cm⁻², one can expect the exciton-exciton interaction to be negligible for the $1s$ state but it may be significant in the $2p$ and (even more so) in the $3p$ states. As a consequence of this interaction,

the $1s \rightarrow np$ resonances may be renormalized and its location may vary slightly as a function of the exciton density. The linewidth can also be affected by this interaction.

Finally, in Fig. 16, we depict fits to the experimental data obtained in [78]. To perform the fit we started

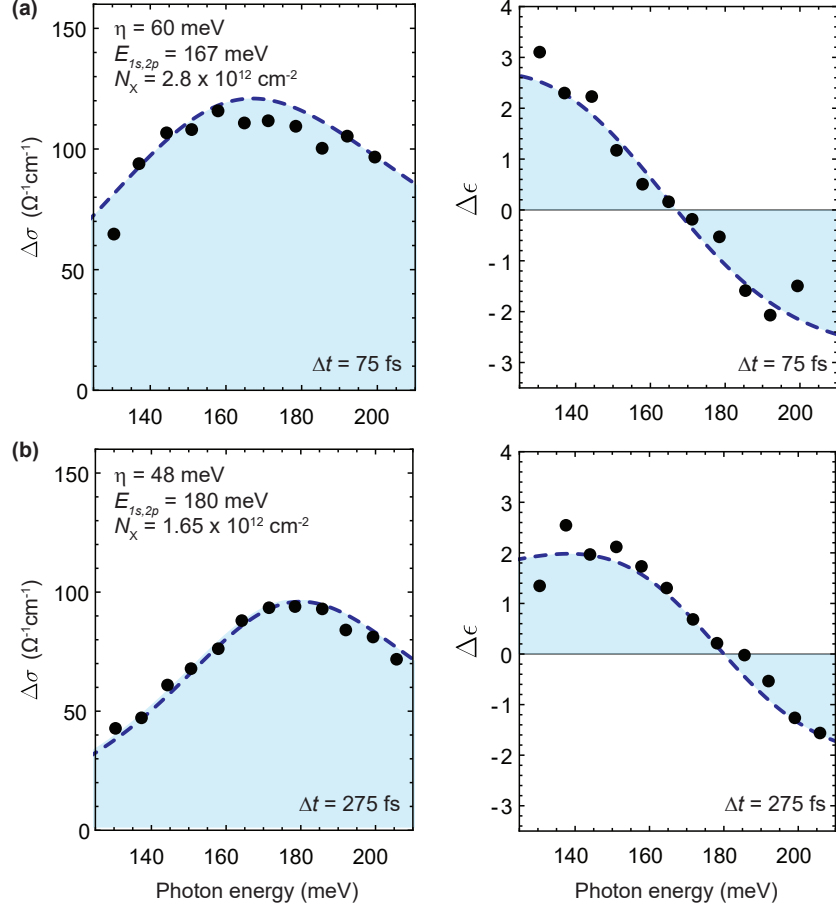


Figure 16: **Fit to experimental data** modeling the $1s \rightarrow 2p$ transition with a Lorentz oscillator. The experimental points were taken from [78]. The values found for the fitting parameters are in good agreement with the ones found by the authors of [78].

by computing the $1s$ and $2p$ wave function and binding energies with the shooting method, followed by the evaluation of the $1s \rightarrow 2p$ oscillator strength. Afterwards we considered a single term in the sum over states definition of $\alpha(\omega)$, that is,

$$\alpha_{xx}^{\text{fit}}(\omega) = \frac{2|\langle\psi_{1s}|x|\psi_{2p}\rangle|^2 E_{1s,2p}}{E_{1s,2p}^2 - \omega^2 - 2i\omega\eta}$$

and defined the dielectric function and conductivity with Eqs. (3.22) and (3.23). To allow a better description of the experimental data we considered $E_{1s,2p} = E_{1s} - E_{2p}$ to be a fitting parameter, while keeping the oscillator strength fixed. Although this is not strictly correct, since modifying the binding energies implies modifications in the wave functions, we do not expect $E_{1s,2p}$ to deviate significantly from the value we found with the shooting method, and as a result the oscillator strength should be approximately constant. The

linewidth η and the exciton density N_X were also considered as fitting parameters. The results depicted in Fig. 16 agree with what was found in [78], and are in line with our previous discussion. Comparing panels (a) and (b) we observe that as the delay time between the pump and probe laser increases, the exciton density decreases, as we predicted earlier. Moreover, we observe that while in panel (b) the energy $E_{1s,2p}$ perfectly matches the value found in Fig. 12b, in panel (a) this value is slightly different; this may be related to exciton-exciton interactions as a result of the higher exciton density. Regarding the linewidths we note that they are too large to allow more than one resonance to be resolved, as expected. The different values found for η between the two panels may also be associated with the different intensity of the exciton-exciton interaction between the two panels.

3.6 Overview

In this section we have studied excitons with angular quantum number $m = \pm 1$ which form the so called p -series. Although these excitons can not be excited in interband transitions due to optical selection rules, their existence can still be studied in intra-exciton transitions.

To study this type of transitions we introduced the expression for the dynamical polarizability as derived from time-dependent perturbation theory. In this format, the polarizability is given by a sum over state of different Lorentz oscillators each weighted with a given oscillator strength. To evaluate the polarizability two approaches were employed: i) Numerically solving the Wannier equation with a shooting method, we obtained the wave functions and binding energies of the $1s$ and p -states, which allowed us to compute the oscillator strengths of different transitions. Then, the sum over states definition of $\alpha(\omega)$ was used to compute the polarizability. ii) Expanding the state vector in powers of the applied electric field, we defined a new state vector (given by the solution of a differential equation) which allowed us to bypass the sum over states, and lead to a definition of $\alpha(\omega)$ which required only the computation of two matrix elements to account for all the resonances automatically. To obtain this new state vector we converted the differential equation into a linear system. These two approaches produced results in good agreement with each other, with the Dalgarno-Lewis method having the advantage of avoiding the sum over states, and accounting directly for all the possible $1s \rightarrow np$ transitions. This, however, is only a slight advantage, since in a realistic scenario only a few resonances (or even just one) are experimentally resolved.

The Dalgarno-Lewis approach can also be compared with the method we presented in the previous section. There the excitonic wave function were expanded in a gaussian basis, and the expansion coefficients as well as the binding energies were found from a generalized eigenvalue problem. These wave functions could then be used to compute the oscillators strengths and obtain $\alpha(\omega)$ from its sum over

states definition. The approach we presented in this section is somewhat similar to this procedure, only this time it is not the exciton wave function that is expanded in a basis, but rather its first order correction in the presence of the electric field. The advantage of this modification is that a single diagonalization is required to automatically obtain the complete spectrum.

After the study of the polarizability we discussed how it can be related with the dielectric function and the conductivity, presenting plots of these two quantities as a function of the photon energy. The results showed resonances associated with the internal exciton transitions $1s \rightarrow np$, which can be experimentally studied in pump-probe experiments. The role of the exciton density (and thus of the delay time between the pump and probe pulses) was studied through a system of coupled rate equations, where we observed that for large delay times, the optical response should become less pronounced due to the decreasing exciton density. Although exciton-exciton interactions were not considered in our description, we studied if they were expected to be relevant in the studied system. We concluded that this type of interaction should be negligible for the $1s$ state, but it may play a significant role in the p -states as a result of their larger exciton Bohr radius.

Temperature dependence of the homogeneous linewidth in transition metal dichalcogenides

In this section we aim to explore the role of the exciton-phonon interaction in the optical properties of transition metal dichalcogenides (TMDs), in particular, how this interaction affects the life time of the lowest lying optically accessible exciton, the $1s$ state of the A -series [22, 69, 97–99].

As we have seen in the previous sections, the optical response of TMDs is dominated by excitonic resonances associated with the optically bright states, that is, those which can be accessed in interband spectroscopy measurements. Furthermore, we have also explored a class of dark excitons, the p -states. Although these states can not be excited in interband transitions due to optical selection rules, they can be studied in pump-probe experiments where first the $1s$ state is populated, and then a laser induces transitions between the $1s$ and the p -states. In the current section we will study another class of dark excitons, which we briefly mentioned in the previous section: momentum dark excitons [54, 72, 100].

Excitons with a finite center of mass momentum are called dark in the sense that they are located outside of the light cone, i.e. photons do not carry sufficient momentum to reach them, and, as a result, interband optical transitions can not probe these states directly. These excitons, composed of an electron and hole in different points of the Brillouin zone (BZ), can only be reached with the absorption or emission of phonons, the quanta of the lattice vibration, which transfer the necessary momentum to transport the carriers between different points of the BZ. In Fig. 17a we schematically depict a bright exciton, with the two carriers in the same point of the BZ, and two examples of dark excitons: one where the electron and hole are in the same valley but with different momenta, and another where the carriers are in two different valleys of the BZ. In Fig. 17b, for reference, we depict the principal high symmetry points of the BZ. Although excitons with finite center of mass momentum do not appear as resonances in spectroscopy measurements, they play a significant role in determining the linewidth of the resonance, something we have so far treated phenomenologically. Moreover, momentum dark excitons also affect the population dynamics of the different states (like we saw in the previous section) and the quantum yield of the system

[54].

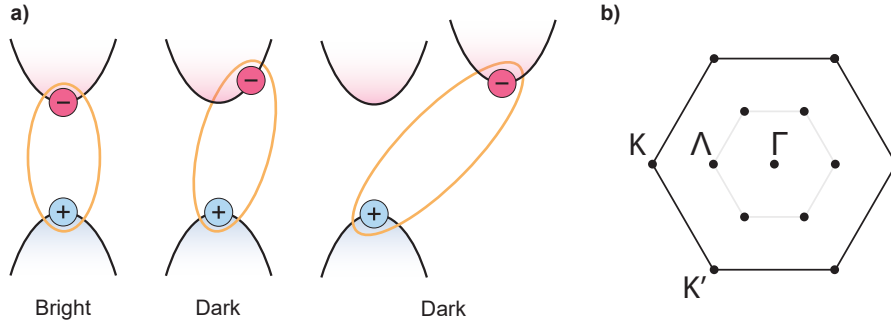


Figure 17: **Momentum bright and dark excitons.** a) Schematic representation of an optically bright exciton, created from the vertical excitation of an electron from the conduction to the valence band, and momentum forbidden dark excitons, which can not be optically excited; they can, however, be obtained from optically bright ones after a scattering event with phonons, which can transport the carrier to another region in the same valley, or to a different valley altogether. b) Representation of the first BZ with the labels of the most important high symmetry points

Our goal in this section is to analytically describe the linewidth of the lowest lying bright exciton in different TMDs at finite temperature. To do so, three different contributions must be accounted for, namely: i) the radiative linewidth, which is temperature independent; ii) the contribution from intravalley exciton-phonon scattering, that is, scattering events with small momentum transfer; iii) the linewidth from intervalley scattering, where the transferred momentum is large enough to link different valleys of the BZ.

The first part of this section will be dedicated to the Wannier equation, and how it can be used to describe momentum dark excitons. Although we have previously introduced this topic, we will briefly discuss it once again to emphasize some key points, and clarify the notation, which differs slightly from what was previously used. Afterwards, we will compute the exciton energy spectrum near the principal high symmetry points of the Brillouin zone for some of the most common TMDs, comparing the features that differentiate them. Then, we will derive analytical expressions for the radiative linewidth, followed by the intra and intervalley scattering contributions. In the end, we compare our theoretical prediction with the experimental results of Ref. [101].

4.1 Wannier equation and exciton spectrum

4.1.1 Wannier equation revisited

As before, the starting point to obtain the Wannier equation is to define the exciton creation operator. Since this time we consider the possibility of having excitons with a finite center of mass momentum some

modifications must be introduced in its definition, when compared to what was presented in Section 2. For the creation of an exciton composed of an electron in the ξ_e valley and a hole in the ξ_h valley, with center of mass momentum $\mathbf{Q} = \mathbf{k}_e^{\xi_e} - \mathbf{k}_h^{\xi_h}$ (where the electron and hole momenta are measured relatively to ξ_e and ξ_h , respectively) and quantum numbers labeled by v , we introduce:

$$b_{v,\mathbf{Q}}^\dagger = \frac{1}{\sqrt{A}} \sum_{\mathbf{k}} \psi_{v,\mathbf{k}}^{*,\xi_e,\xi_h} c_{\mathbf{k}+\alpha\mathbf{Q},c}^{\dagger,\xi_e} c_{\mathbf{k}-\beta\mathbf{Q},v}^{\xi_h} \quad (4.1)$$

where A is the area of the monolayer, $\mathbf{k}$ is the relative momentum of the electron and hole, $\psi_{v,\mathbf{k}}^{*,\xi_e,\xi_h}$ is the Fourier transform of the exciton wave function, $c_{\mathbf{k}+\alpha\mathbf{Q},c}^{\dagger,\xi_e}$ is the creation operator of an electron in the conduction band of the ξ_e valley, with momentum $\mathbf{k} + \alpha\mathbf{Q}$, where $\alpha = m_e^{\xi_e} / (m_e^{\xi_e} + m_h^{\xi_h})$ with $m_e^{\xi_e}/m_h^{\xi_h}$ the effective mass of the electron/hole in the ξ_e/ξ_h valley, and $c_{\mathbf{k}-\beta\mathbf{Q},v}^{\xi_h}$ is an annihilation operator defined in a similar manner with $\beta = m_h^{\xi_h} / (m_e^{\xi_e} + m_h^{\xi_h})$. The information about the spin of the carriers can be included in the valley indexes ξ_e and ξ_h . Note that indexes such as ξ_e refer to points in the BZ, and can be interpreted as momenta measured relatively to its center. The total momentum of the exciton reads $\mathbf{Q}_{total} = \xi_e - \xi_h + \mathbf{Q}$. If the electron and hole sit in the same valley, the two $\mathbf{Q}$ are identical and the valley indexes are redundant. This was the case in the previous sections, where we did not need to keep track of the valley of both carriers, and a valley index indicating if we were dealing with the K or K' valley was sufficient. When this operator acts on the excitonic ground state (a full valence band and an empty conduction band) we find

$$b_{\mathbf{Q},v}^{\dagger,\xi_e,\xi_h} |GS\rangle = |\xi_e, \xi_h, v, \mathbf{Q}\rangle \quad (4.2)$$

The energy of such a state reads

$$E_{\mathbf{Q},v}^{\xi_e,\xi_h} = E_g^{\xi_e,\xi_h} + E_v^{\xi_e,\xi_h} + \frac{\hbar^2 \mathbf{Q}^2}{2M_{\xi_e,\xi_h}}, \quad (4.3)$$

with $E_g^{\xi_e,\xi_h}$ the electronic band gap between the conduction band edge at ξ_e and the valence band maximum at ξ_h , $E_v^{\xi_e,\xi_h}$ is the exciton binding energy and $\hbar^2 \mathbf{Q}^2 / 2M_{\xi_e,\xi_h}$ its center of mass kinetic energy. This last term originates the parabolic dispersion near the high symmetry point $\xi_e - \xi_h$ in the exciton BZ.

Now, to obtain the Wannier equation from the exciton operator a similar procedure to the one previously presented is followed, only this time a new set of indexes referring to the valley information of the carriers appears. The detailed derivation of the Beth-Salpeter equation, and its transformation to the Wannier equation is given in B. The end result reads

$$-\frac{\hbar^2}{2\mu_{\xi_e,\xi_h}} \nabla^2 \psi_v^{\xi_e,\xi_h}(\mathbf{r}) + V_{\text{RK}}(\mathbf{r}) \psi_v^{\xi_e,\xi_h}(\mathbf{r}) = E_v^{\xi_e,\xi_h} \psi_v^{\xi_e,\xi_h}(\mathbf{r}). \quad (4.4)$$

This equation is almost identical to the one we obtained in Section 2, the only difference being in the indexes referring to the configuration of the two carriers, which may now be located in different points of

the BZ. Hence, the Wannier equation can be used to compute the binding energies of both bright and momentum dark excitons. The only difference between these two cases is in the reduced mass $\mu_{\xi_e \xi_h}$ which should be determined from the effective masses of the carriers in the appropriate valleys. Once more, the interaction potential is treated in the Rytova-Keldysh formalism [56–58]

$$V_{\text{RK}}(r) = -\hbar c \alpha \frac{\pi}{2r_0} \left[\mathbf{H}_0 \left(\frac{\kappa r}{r_0} \right) - Y_0 \left(\frac{\kappa r}{r_0} \right) \right].$$

With this, we see that the Wannier equation can be used to model any type of exciton (within the considered approximations), no matter the spin and valley configuration of the carriers, as long as the reduced mass is correctly chosen.

4.1.2 Variational solution

Up to this point we have presented different techniques to solve the Wannier equation, namely: i) expanding the wave function in a given basis followed by the numerical diagonalization of the Hamiltonian; ii) numerically solving the differential equation with a shooting algorithm; iii) obtaining the wave functions and binding energies from a variational *ansatz*. In this section, we will once again follow a variational approach to solve the Wannier equation [102], which, due to its simplicity, certainly is the most appealing choice to develop an analytical framework. However, contrarily to the previous section, we will not use the double exponential variational *ansatz*, and will use instead a trial wave function inspired by the solution of the 2D Hydrogen atom :

$$\psi(r) = \sqrt{\frac{2}{\pi a^2}} e^{-r/a}, \quad (4.5)$$

where a is a variational parameter determined from minimizing the energy in Eq. (4.4). In Fig. 18a we compare the binding energies obtained using this *ansatz*, with the ones found from the numerical diagonalization of the Hamiltonian; comparing the two results it is clear that this trial wave function is already capable of reproducing the numerical results with great accuracy. To obtain even better results we could return to the double exponential *ansatz* [89],

$$\psi(r) = \mathcal{N} (e^{-ar} + b e^{-a\gamma r}),$$

however, the use of this trial wave function would lead to a more involved analytical treatment, which we deem as unnecessary given the already sufficient quality of the results produced by Eq. (4.5).

In order to study the dependence of the variational parameter a with the μ , κ and r_0 that enter in the Wannier equation, it is useful to consider the scaling procedure given in [89]. Working in atomic units, we perform two rescaling operations: we modify the lengths according to $r \rightarrow r\kappa/\mu$ while the energies

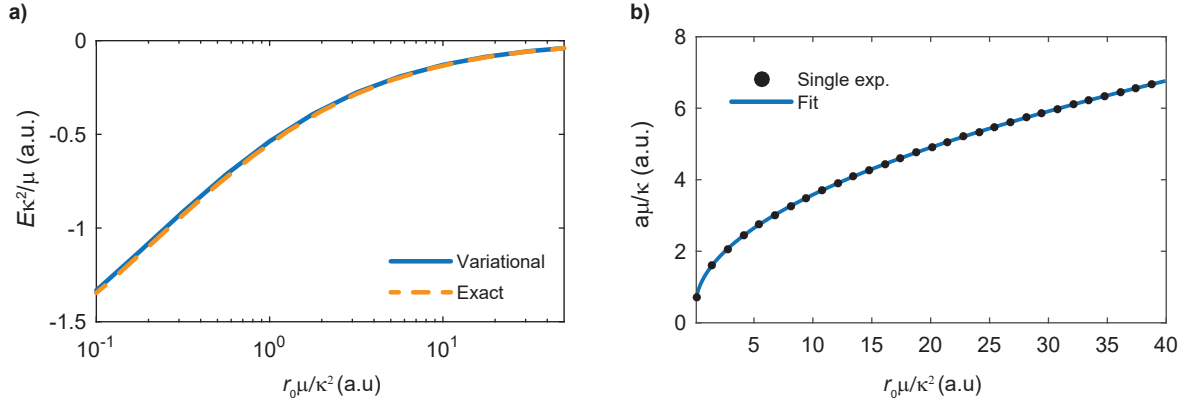


Figure 18: **Variational solution.** a) Comparison between the binding energies obtained using the variational *ansatz* of Eq. (4.5) and the numerical diagonalization of the Hamiltonian using a gaussian basis. b) Comparison between the values of the variational parameter a obtained from the minimization of the expectation value of the Hamiltonian, and the fit with Eq. (4.6). All quantities are given in atomic units (a.u.).

are scaled as $E \rightarrow E\mu/\kappa^2$. With this technique, the excitonic problem can be described using a single effective parameter (as opposed to the current three) defined as

$$\tilde{r}_0 = \frac{r_0\mu}{\kappa^2}.$$

Studying the dependence of a with $\tilde{r}_0$, we observe that in the relevant region of the parameters space, i.e. $r_0\mu = 30 - 40$ atomic units [89, 103], the variational parameter is accurately described by the model (written in S.I. units)

$$\frac{a}{a_0} = \frac{\kappa\chi_0}{(\mu/m_0)} + \sqrt{\frac{r_0/a_0}{\mu/m_0}}, \quad (4.6)$$

where $\chi_0 = 0.4$ is determined by fitting Eq. (4.6) to the values of a obtained from the extremization of the binding energy. Here, once again, a_0 is the Bohr radius and m_0 the electron bare mass. In Fig. 18b we compare the fit with the values of a obtained directly from the variational procedure, and observe an excellent agreement. If the region over which the fit is performed was chosen closer to $\tilde{r}_0 = 0$ the value of χ_0 would approach 0.5 and an Hydrogen-like behavior would be recovered. This is in agreement with the limit

$$\lim_{r_0 \rightarrow 0} V_{\text{RK}} = V_{\text{Coulomb}}.$$

The fact that in the relevant region of parameters for TMDs the value of χ_0 differs from 0.5 reflects the non-Hydrogenic nature of excitons in these 2D systems; the term $\sqrt{r_0/\mu}$ further enhances this difference.

Note that having an analytical description of the variational parameter a is a rather useful achievement. In fact, Eq. (4.6) allows us to obtain an analytical expression for the binding energy of the 1s state. Using

the variational *ansatz* to evaluate the energy that appears in the Wannier equation, one quickly finds

$$E_{1s} = \frac{\hbar^2}{2\mu a^2} + \frac{e^2}{4\pi\epsilon_0 r_0} \left[\frac{1-x}{1+x^2} - \frac{\text{ArcCsch}(x) + \text{ArcSinh}(x)}{(1+x^2)^{3/2}} \right], \quad (4.7)$$

where e is the electron charge, ϵ_0 is the vacuum permittivity, $x = a\kappa/(2r_0)$ and a is given by Eq. (4.6).

4.1.3 Exciton spectrum

In this part of the section we use the Wannier equation, Eq. (4.4), to obtain the exciton spectrum of both bright and momentum dark excitons, in different TMDs. We denote the excitons by the location of the hole and electron, respectively, e.g. the $K\Lambda$ exciton is composed of a hole in the K valley and an electron in the Λ valley. Moreover, we only consider excitons with the hole in the K valley, since these are the most relevant ones for the computation of the non-radiative linewidths (discussed further ahead).

In order to compute the exciton spectrum, information about different material parameters is required, in particular the effective masses and the energy of the band edges in different points of the BZ. We take these parameters from Ref. [52] where they were obtained from density functional theory (DFT) calculations using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation. The effective masses used for the Λ valley were taken as the square root of the product of the effective masses along the x and y directions.

In Fig. 19a we show a schematic representation of the valence and conduction band in different points of the BZ for molybdenum and tungsten based TMDs. As we already know, and are once again faced with, due to spin-orbit coupling the spin degeneracy is broken in TMDs and consequently the spin down (dashed) and spin up (solid) bands are separated in energy (except in the Γ point, where they remain overlapped).

Depicted in Fig. 19b is the energy spectrum for the KK , $K\Lambda$ and KK' excitons in MoS_2 , MoSe_2 , WS_2 and WSe_2 on a substrate of SiO_2 . Our results are in good agreement with those of Ref. [54], where the energy spectrum was obtained from a fully numerical solution of the BSE. The similarity between the two results strengthens the idea that the approximations we introduce in order to go from the BSE to the Wannier equation are reasonable. Our results are also in line with the ones reported in Ref. [104] using *ab initio* calculations.

As we have seen in previous sections, in TMDs, contrary to, for example, hBN, spin-orbit coupling plays a significant role in the electronic (and excitonic) properties of these materials. This effect is particularly noticeable in the valence band where in the K valley the spin up band is pushed below the spin down band by a few hundreds of meV in the four considered TMDs. In the conduction band the effect of spin-orbit coupling is significantly smaller, especially in MoS_2 , and the ordering of the spin up and spin down bands varies depending on the transition metal atom; in tungsten based TMDs the spin down band sits above the

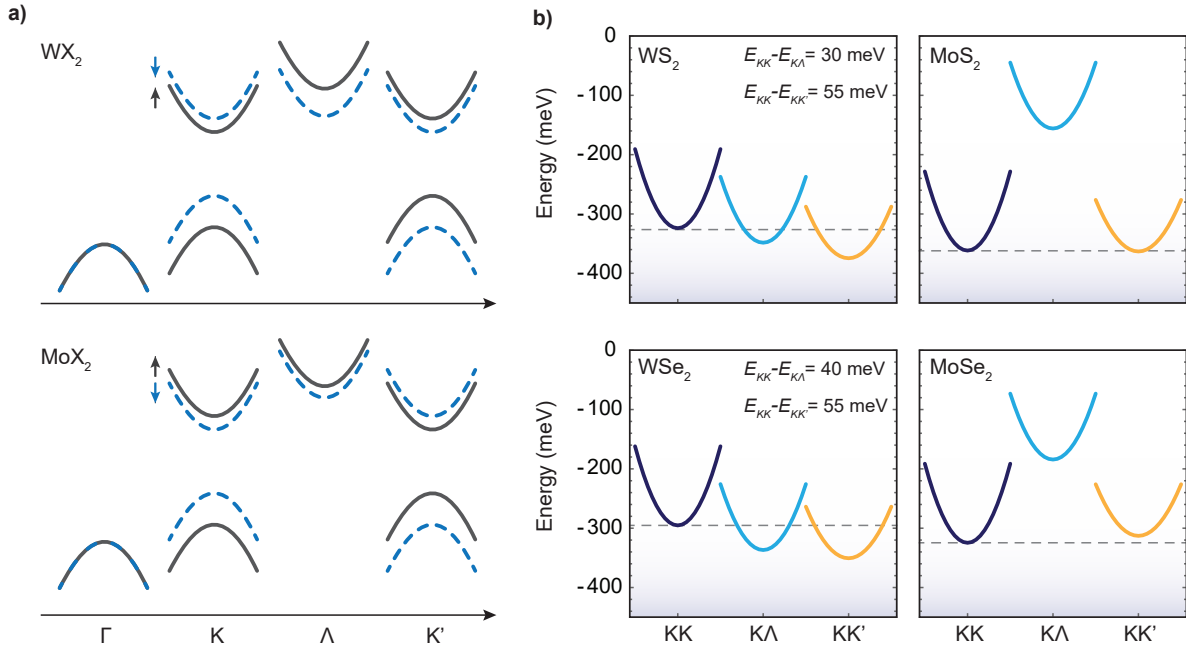


Figure 19: **Exciton spectrum.** a) Schematic representation of the valence and conduction band near the principal high symmetry points of the BZ for molybdenum and tungsten based TMDs (MoX_2 and WX_2 , respectively). Solid lines and dashed lines refer to spin up and spin down bands respectively. In the Γ point these are overlapped. b) Representation of the exciton dispersion relation for the most relevant momentum dark excitons in MoS_2 , $MoSe_2$, WS_2 and WSe_2 on a substrate of SiO_2 . The energies are given relatively to the conduction band edge in the K valley. In all depicted cases both the hole and the electron have spin down. The parameters of Ref. [52] were used.

spin up band (approximately 30 meV), while the opposite occurs in molybdenum based TMDs (a splitting of 3 and 20 meV is found for MoS_2 and $MoSe_2$, respectively). Since in these materials the spin and valley degrees of freedom are coupled [35], a similar analysis holds in the K' valley if the roles of spin up and spin down are inverted. As a consequence of the band ordering, and the larger spin-orbit splitting in the valence band, in the K valley the lowest lying bright exciton is composed of an electron and a hole with spin down. Since we are not taking into consideration processes involving spin flips, hereinafter we consider only spin down carriers, unless otherwise stated.

These observations regarding the electronic band structure are helpful to understand the results shown in Fig. 19b. For WS_2 and WSe_2 , in the K valley, the spin down conduction band appears above the spin up band; on the other hand, and as a result of the spin-valley coupling, in the K' valley the spin down band is the one that appears at lower energies. As a consequence, this leads to the appearance of the KK' exciton below the optically active one (in other words, both excitons have the same valence band, but the conduction band of the KK' exciton appears below the conduction band of the KK exciton). For MoS_2 and $MoSe_2$ the ordering of the conduction bands is different, and so are the relative positions of the KK and KK' excitons. It is important to note that besides the relative position of the bands, the effective

masses also play a role in the ordering of the exciton states, since larger effective masses lead to more tightly bound excitons. In the K valley the spin up conduction band has a larger effective mass than the spin down band; the opposite being true in the K' valley.

Another noteworthy aspect of the band structure of TMDs is the existence of a satellite minimum in the conduction band halfway along the path from the K/K' valley to the BZ center, that is, in the Λ valley. The energy difference between the conduction band edge at the K and Λ valleys is significantly different for tungsten and molybdenum based TMDs. While for the former the band edge at the Λ valley lies just 27 meV above the band edge of the K valley in WS_2 and 5 meV below it in WSe_2 , for the latter, the band edge at Λ sits approximately 163 and 246 meV above the band edge at the K valley for MoSe_2 and MoS_2 , respectively. Since in the Λ valley the effective masses are larger than in the K valley (by approximately a factor of 2), the $K\Lambda$ excitons are more tightly bound than the KK or KK' ones. This larger binding energy, combined with the small energy separation between the conduction band edges in tungsten based TMDs, leads to the appearance of the $K\Lambda$ exciton below the optically active one in WS_2 and WSe_2 . In MoS_2 and MoSe_2 the band edge at Λ is located too far up relatively to the band edge at K , and as a consequence the $K\Lambda$ exciton appears above the optically bright exciton. These considerations are in agreement with the results depicted in Fig. 19b. The position of the $K\Lambda$ exciton plays a crucial role in the optical properties of TMDs, especially in the efficiency of intervalley phonon scattering, which is directly linked to the linewidth of the resonances.

4.2 Homogeneous linewidth

Having dealt with the problem of finding the exciton binding energies and wave functions, we move on to the computation of the homogeneous linewidth of the $1s$ exciton of the A -series. In what follows, employing Fermi's golden rule, we will compute the contributions originating from the radiative recombination of excitons, and the intra and intervalley scattering with phonons.

4.2.1 Radiative linewidth

Starting with the radiative contribution to the linewidth, we describe the carrier-photon interaction in the dipole approximation, that is

$$H_{X\text{-light}} = -e\mathbf{r} \cdot \mathbf{E}(t) \quad (4.8)$$

with e the electron charge and $\mathbf{E}(t)$ the time-dependent electric field. In the dipole approximation we assume the electric field to be constant over the size of the exciton, a condition that is easily verified for

TMDs. To obtain the radiative linewidth, we use Fermi's golden rule to evaluate the transition rate between the exciton state given in Eq. (4.2), and the exciton vacuum with an extra photon in the light field, that is

$$\gamma_{\text{rad},\nu} = \frac{\hbar}{\tau_\nu} = 2\pi \sum_{\mathbf{q}} |\langle GS; 1_{\mathbf{q}} | \mathbf{e} \cdot \mathbf{r} | \nu, \mathbf{Q} = 0 \rangle|^2 \delta(E_{0,\nu} - \hbar\omega_{\mathbf{q}}), \quad (4.9)$$

where the sum runs over the photon momentum and $\hbar\omega_{\mathbf{q}} = \hbar c q$ is the dispersion relation of light. For simplicity we omitted the indexes referring to the electron and hole valleys since in this case we consider both to be in the K valley. Moreover, we set $\mathbf{Q} = 0$ since only states that verify this condition are optically active and may recombine radiatively (if we started with an arbitrary value of $\mathbf{Q}$, momentum conservation in Fermi's golden rule would retrieve the condition $\mathbf{Q} = 0$; this is something we have found before when working in the limit of vertical transitions). Although we wrote Eq. (4.9) for an exciton with arbitrary quantum numbers ν , in the end we will only be interested in the contribution of the $1s$ state.

To evaluate the optical matrix element in Eq. (4.9) it is useful to quantize the interaction Hamiltonian. The electric field can be quantized in the usual way, and in the dipole approximation it reads

$$\mathbf{E}(t) \approx i \sum_{\mathbf{q},\lambda} \sqrt{\frac{\hbar\omega_{\mathbf{q}}}{2V\epsilon_0}} \left[\mathbf{e}_\lambda a_{\mathbf{q},\lambda}(t) - (\mathbf{e}_\lambda)^* a_{\mathbf{q},\lambda}^\dagger(t) \right], \quad (4.10)$$

with V the volume of the system, ϵ_0 the permittivity of vacuum, $\mathbf{e}_\lambda$ a polarization vector and $a_{\mathbf{q},\lambda}^{(\dagger)}$ the annihilation (creation) operator of a photon with momentum $\mathbf{q}$ and polarization λ . In terms of electron operators the position operator $\mathbf{r}$ reads

$$\begin{aligned} \hat{\mathbf{r}} &= \sum_{\mathbf{k}} \langle u_{\mathbf{k},c} | i \nabla_{\mathbf{k}} | u_{\mathbf{k},v} \rangle c_{\mathbf{k},c}^\dagger c_{\mathbf{k},v} + h.c. \\ &= i \sum_{\mathbf{k}} \xi_{\mathbf{k}cv} c_{\mathbf{k},c}^\dagger c_{\mathbf{k},v} + h.c., \end{aligned} \quad (4.11)$$

where $h.c.$ stands for hermitian conjugate, $\nabla_{\mathbf{k}}$ is the gradient operator in $\mathbf{k}$ -space, $u_{\mathbf{k},\lambda}$ is the periodic part of the Bloch function of the band λ , near the K valley, and the $c^{(\dagger)}$ are electronic annihilation (creation) operators; the quantity $\xi_{\mathbf{k}cv} = \langle u_{\mathbf{k},c} | \nabla_{\mathbf{k}} | u_{\mathbf{k},v} \rangle$ is termed Berry connection. Note that in general other terms could appear in the definition of $\hat{\mathbf{r}}$, e.g. terms with $c_{\mathbf{k},c}^\dagger c_{\mathbf{k},c}$, however their contribution to the present calculation vanishes, and as a consequence we chose to omit them. This way of computing the excitonic part of the matrix element is equivalent to what was used in Section 2, when the matrix element of the position operator was transformed into the matrix element of Pauli matrices.

Introducing the representation of $|\nu, \mathbf{Q} = 0\rangle$ in terms of electron operators, Eq. (4.2), and using Wick's theorem to evaluate the excitonic part of the optical matrix element, we find

$$\gamma_{\text{rad},\nu} = 2\pi \frac{e^2}{2\epsilon_0} \frac{A}{V} \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} \left| \frac{1}{A} \sum_{\lambda,\mathbf{k}} \psi_{\nu,\mathbf{k}} \xi_{\mathbf{k}cv}^* \cdot \mathbf{e}_\lambda^* \right|^2 \delta(E_{0,\nu} - \hbar\omega_{\mathbf{q}}) \delta_{0,\mathbf{q}||} \quad (4.12)$$

where A is the area of the monolayer and $\delta_{0,\mathbf{q}_{||}}$ describes the in-plane momentum conservation. Using the Kronecker- δ , converting the sum into an integral, writing $E_{0,\nu} = E_g + E_\nu$ and $\hbar\omega_{\mathbf{q}} = \hbar c q$ we obtain

$$\gamma_{\text{rad},\nu} = \frac{4\pi}{\hbar} \alpha (E_g + E_\nu) \left| \frac{1}{A} \sum_{\lambda,\mathbf{k}} \psi_{\nu,\mathbf{k}} \xi_{\mathbf{k}c\nu}^* \cdot \mathbf{e}_\lambda^* \right|^2, \quad (4.13)$$

with $\alpha \sim 1/137$ the fine structure constant.

Now, in order to continue with the calculation the Berry connection must be evaluated. The first step is to find the $|u_{\mathbf{k},\nu}\rangle$ and $|u_{\mathbf{k},c}\rangle$. These quantities were previously found in Eq. (2.4) as the eigenvectors of the low energy Hamiltonian near the Dirac points, which reads

$$H = \hbar v_F (\tau k_x \sigma_x + k_y \sigma_y) + \frac{\Delta}{2} \sigma_z + \tau s_z \left(\lambda_c \frac{1 + \sigma_z}{2} + \lambda_v \frac{1 - \sigma_z}{2} \right), \quad (4.14)$$

where the first two terms form the usual Dirac Hamiltonian, and the third one describes the spin-orbit coupling (SOC) which breaks spin degeneracy; v_F is the Fermi velocity, σ_i is the i -Pauli matrix, Δ is the band gap in the absence of SOC, $\lambda_{c/v}$ describes the SOC splitting in the conduction/valence band, and $\tau = \pm 1$ and $s_z = \pm 1$ are the valley (K/K') and spin (up/down) indexes. The diagonalization of this Hamiltonian yields the following energy dispersion relation

$$E_{\pm}(\mathbf{k}) = \frac{\tau s_z (\lambda_c + \lambda_v)}{2} \pm \sqrt{\left(\frac{E_g^{\tau,s_z}}{2} \right)^2 + \hbar^2 v_F^2 k^2},$$

with $E_g^{\tau,s_z} = \Delta + \tau s_z (\lambda_c - \lambda_v)$ the *ab-initio* band gap, which depends on the valley-spin configuration. Near the band edges the spinors $|u_{\mathbf{k},\nu}\rangle$ and $|u_{\mathbf{k},c}\rangle$ take the simple form:

$$|u_\nu(|\mathbf{k}| \ll 1)\rangle \approx \begin{bmatrix} \frac{-\hbar v_F \tau k e^{-i\tau\theta}}{E_g^{\tau,s_z}} \\ 1 \end{bmatrix}, \quad |u_c(|\mathbf{k}| \ll 1)\rangle \approx \begin{bmatrix} 1 \\ \frac{\hbar v_F \tau k e^{i\tau\theta}}{E_g^{\tau,s_z}} \end{bmatrix} \quad (4.15)$$

Using the approximate expressions near the band edge for the Bloch factors, Eq. (4.15), we compute the Berry connection, followed by its dot product with the polarization vectors. In the end, for a TMD in a medium with dielectric constant κ , we find the following expression for the radiative linewidth

$$\begin{aligned} \gamma_{\text{rad},\nu} &= \frac{8\pi}{\hbar\kappa} \alpha (E_g + E_\nu) \left(\frac{\hbar v_F}{E_g^{\tau,s_z}} \right)^2 \left| \frac{1}{A} \sum_{\mathbf{k}} \psi_{\nu,\mathbf{k}} \right|^2 \\ &= \frac{8\pi}{\hbar\kappa} \alpha (E_g + E_\nu) \left(\frac{\hbar v_F}{E_g^{\tau,s_z}} \right)^2 \psi_\nu^2(\mathbf{r} = 0), \end{aligned} \quad (4.16)$$

where $\psi_\nu^2(\mathbf{r} = 0)$ can be found using Eqs. (4.5) and (4.6) when $\nu = 1s$. Note that this expression features two distinct energy gaps; while E_g^{τ,s_z} is the *ab-initio* energy gap found from DFT calculations, E_g is the real (i.e. experimentally measurable) energy gap containing exchange corrections, and can be found from e.g.

GW calculations. As we mentioned before, although we derived an expression for an arbitrary ν , we are only interested in the $1s$ state; nonetheless, it is interesting to note that, as expected, γ_{rad} vanishes for p -states, since $\psi_{p\text{-state}}(\mathbf{r} = 0) = 0$ (see Fig. 12). This is in agreement with the optical selection rules that forbid the direct optical excitation (or radiative recombination) of these states.

From the analysis of Eq. (4.16) we expect the radiative linewidth to increase as the band gap widens, and to decrease, approximately following a power law, as the dielectric screening from the environment increases. When we compute the value of γ_{rad} for the lowest bright exciton in the K valley in MoS₂, MoSe₂, WS₂ and WSe₂ on quartz we obtain linewidths of approximately 5 meV, in agreement with other theoretical predictions [105] and experimental measurements [106].

4.2.2 Carrier-phonon scattering

In order to evaluate the linewidth stemming from exciton-phonon scattering, we start by discussing the interaction Hamiltonian that mediates the processes of carrier-phonon scattering. In general, the Hamiltonian reads [107]

$$H_{\text{carrier-ph}} = \sum_{\mathbf{q}, \mathbf{k}, \alpha} g_{\mathbf{k}, \mathbf{q}}^{(e), \alpha} c_{\mathbf{k}+\mathbf{q}, c}^{\dagger} c_{\mathbf{k}, c} \left(a_{-\mathbf{q}, \alpha}^{\dagger} + a_{\mathbf{q}, \alpha} \right) + g_{\mathbf{k}, \mathbf{q}}^{(h), \alpha} c_{\mathbf{k}+\mathbf{q}, v}^{\dagger} c_{\mathbf{k}, v} \left(a_{-\mathbf{q}, \alpha}^{\dagger} + a_{\mathbf{q}, \alpha} \right), \quad (4.17)$$

where the first and second terms describe the scattering of phonons with electrons in the conduction and valence bands, respectively; $g_{\mathbf{k}, \mathbf{q}}^{(e), \alpha}$ and $g_{\mathbf{k}, \mathbf{q}}^{(h), \alpha}$ are the carrier-phonon couplings, $c/c^{\dagger}$ and $a/a^{\dagger}$ are annihilation/creation operators of electrons and phonons, respectively; the sums are over the transferred momentum $\mathbf{q}$, the carrier momentum $\mathbf{k}$ and the phonon mode α . The momenta are measured relatively to the center of the BZ. The mode α corresponds to one of the 9 different branches of the phonon dispersion relation; 3 of which are acoustic, and 6 are optical. The most relevant modes in carrier-phonon coupling are the longitudinal acoustic, LA, transverse acoustic, TA, longitudinal optical, LO, transverse optical, TO, and out-of-plane optical, A₁, modes [108].

Since we will be interested in studying both intra and intervalley scattering processes, it is convenient to write this Hamiltonian in a slightly different form. Instead of having sums over the momenta measured relatively to the center of the BZ, we introduce sums over the high symmetry points of the BZ combined with sums over small momenta which cover the vicinity of each symmetry point. Hence

$$H_{\text{carrier-ph}} = \sum_{\mathbf{q}, \mathbf{k}, \alpha} \sum_{i, j \in \text{BZ}} \left(g_{\mathbf{k}, \mathbf{q}}^{(e), i, j, \alpha} c_{\mathbf{k}+\mathbf{q}, c}^{\dagger, i+j} c_{\mathbf{k}, c}^i + g_{\mathbf{k}, \mathbf{q}}^{(h), i, j, \alpha} c_{\mathbf{k}+\mathbf{q}, v}^{\dagger, i+j} c_{\mathbf{k}, v}^i \right) \left(a_{-\mathbf{q}, \alpha}^{\dagger, -j} + a_{\mathbf{q}, \alpha}^j \right). \quad (4.18)$$

In this new notation, the index in superscript indicates the high symmetry point with respect to which the momentum in subscript is measured. Note that i and j refer to points in the BZ, and thus can also be

interpreted as momenta. For intravalley scattering, where the total transferred momentum is small, we have $j = \Gamma$, and the index i may be dropped if we are interested in processes where the initial state is associated with specific valley, e.g. the K valley. For intervalley scattering we use $j \neq \Gamma$, and the index i must be kept in order to keep track of the valley where the carrier is located.

The form of the couplings $g_{\mathbf{k},\mathbf{q}}^{(e),i,j,\alpha}$ and $g_{\mathbf{k},\mathbf{q}}^{(h),i,j,\alpha}$ depends on the physical mechanism underlying the scattering events. In TMDs three different mechanisms are particularly relevant in the carrier-phonon interaction: the deformation potential, the Fröhlich mechanism and the piezoelectric mechanism. Each of these coupling mechanisms has a distinct physical origin [109]. The deformation potential, associated with both acoustic and optical phonons, stems from the changes induced on the electronic band structure due to the deformation of the crystal lattice. The Fröhlich interaction, which essentially promotes coupling with LO phonons, has its origin on the interaction of carriers with the electric field created by the uniform displacement of the charged atoms. Finally, the piezoelectric mechanism, mainly associated with acoustic phonons, is due to the interaction of the carriers with a strain induced macroscopic electrical polarization field. Of the three, we will focus on the deformation potential, since this is expected to give the dominant contribution in TMDs [108]. The other two mechanisms are less relevant because the contribution from scattering in the conduction band approximately cancels the contribution from scattering in the valence band.

In the deformation potential framework the carrier-phonon coupling is assumed to be approximately independent of the carrier momentum and it reads [110–113]

$$g_{\mathbf{k},\mathbf{q}}^{(\lambda),i,j,\alpha} \rightarrow g_{\mathbf{q}}^{(\lambda),j,\alpha} = \sqrt{\frac{\hbar}{2A\rho\omega_{\mathbf{q}}^{j,\alpha}}} M_{\mathbf{q}}^{j,\alpha}, \quad (4.19)$$

with A the area of the monolayer, ρ its mass density, $\hbar\omega_{\mathbf{q}}^{j,\alpha}$ the energy dispersion of a phonon with momentum $\mathbf{q}$ measured relatively to j , belonging to branch α , and $M_{\mathbf{q}}^{j,\alpha}$ is termed the coupling matrix element. In what follows we will use a first order deformation potential (Ξ) for intravalley scattering with acoustic phonons, that is,

$$M_{\mathbf{q}} = \Xi q,$$

and consider the phonon dispersion to be linear (that is, the Debye model). To describe intravalley scattering assisted by optical phonons, and all intervalley processes, we will consider the phonon's dispersion relations to be constant (the Einstein model), and will use a zero order deformation potential (D^0), that is

$$M_{\mathbf{q}} = D^0.$$

The values of the deformation potentials (Ξ and D^0), as well as the phonon energies, are taken from Ref. [112] where these quantities were obtained from DFT calculations. Note that the deformation potentials

are effective parameters chosen to reproduce the transport properties predicted from *ab-initio* calculations. Moreover, the value of the deformation potentials depends on the phonon branch (acoustic or optical) and the nature of the scattering event, e.g. the electron scattering events $K \rightarrow K$, $K \rightarrow K'$ and $K \rightarrow \Lambda$ all have different deformation potentials.

4.2.3 Exciton-phonon scattering

To obtain the exciton-phonon interaction Hamiltonian H_{X-ph} , Eq. (4.18) must be written in terms of exciton operators, like the one in Eq. (4.1). To do so we write

$$H_{X-ph} = \sum_{\mathbf{Q}', \mathbf{Q}} \sum_{\mu\nu} \sum_{\zeta_e, \zeta_h} \sum_{\xi_e, \xi_h} \langle \mu, \zeta_h, \zeta_e, \mathbf{Q}' | H_{\text{carrier-ph}} | \nu, \zeta_h, \xi_e, \mathbf{Q} \rangle b_{\mu, \mathbf{Q}'}^{\dagger \zeta_h \zeta_e} b_{\nu, \mathbf{Q}}^{\xi_h \xi_e}, \quad (4.20)$$

where the sums are over the initial and final exciton quantum numbers, ν and μ , high symmetry points, ξ and ζ , and center of mass momenta, $\mathbf{Q}$ and $\mathbf{Q}'$. As before, we use the convention that the momentum in subscript are measured relatively to the high symmetry points in superscript. In order to find H_{X-ph} , we express the exciton states in terms of electron operators and use Wick's theorem to evaluate the matrix element. Carrying out the calculation, given in detail in Appendix E, we find

$$\begin{aligned} \hat{H}_{X-ph} = & \sum_{\mathbf{q}, \alpha} \sum_{\mathbf{Q}, \xi_e, \xi_h} \sum_{\nu, \mu} \sum_{j \in \text{BZ}} g_{\nu, \mu, \mathbf{q}}^{(e), \alpha, \xi_h, \xi_e, j} b_{\mu, \mathbf{q}+\mathbf{Q}}^{\dagger \zeta_h, (\xi_e+j)} b_{\nu, \mathbf{Q}}^{\xi_h, \xi_e} \left(a_{-\mathbf{q}, \alpha}^{\dagger, -j} + a_{\mathbf{q}, \alpha}^j \right) \\ & - \sum_{\mathbf{q}, \alpha} \sum_{\mathbf{Q}, \xi_e, \xi_h} \sum_{\nu, \mu} \sum_{j \in \text{BZ}} g_{\nu, \mu, \mathbf{q}}^{(h), \alpha, \xi_h, \xi_e, j} b_{\mu, \mathbf{q}+\mathbf{Q}}^{\dagger (\xi_h-j), \xi_e} b_{\nu, \mathbf{Q}}^{\xi_h, \xi_e} \left(a_{-\mathbf{q}, \alpha}^{\dagger, -j} + a_{\mathbf{q}, \alpha}^j \right), \end{aligned} \quad (4.21)$$

with the exciton-phonon couplings given by

$$g_{\nu, \mu, \mathbf{q}}^{(e), \alpha, \xi_h, \xi_e, j} = \frac{g_{\mathbf{q}}^{(e), j, \alpha}}{A} \sum_{\mathbf{k}} \psi_{\mu, \mathbf{k}+\beta_{\xi_h}(\xi_e+j)\mathbf{q}}^{\xi_h, (\xi_e+j)} \psi_{\nu, \mathbf{k}}^{\xi_h, \xi_e}, \quad \beta_{\xi_h, (\xi_e+j)} = \frac{m_h^{\xi_h}}{m_h^{\xi_h} + m_e^{\xi_e+j}} \quad (4.22)$$

$$g_{\nu, \mu, \mathbf{q}}^{(h), \alpha, \xi_h, \xi_e, j} = \frac{g_{\mathbf{q}}^{(h), j, \alpha}}{A} \sum_{\mathbf{k}} \psi_{\mu, \mathbf{k}-\alpha_{(\xi_h-j), \xi_e}}^{(\xi_h-j), \xi_e} \psi_{\nu, \mathbf{k}}^{\xi_h, \xi_e}, \quad \alpha_{(\xi_h-j), \xi_e} = \frac{m_e^{\xi_e}}{m_h^{\xi_h-j} + m_e^{\xi_e}}, \quad (4.23)$$

where the first one is associated with the cases where the carrier in the conduction band is scattered, while the second describes scattering in the valence band. The form of $g_{\mathbf{q}}^{(e), j, \alpha}$ and $g_{\mathbf{q}}^{(h), j, \alpha}$ follows from Eq. (4.19).

The Hamiltonian of Eq. (4.21) may be used to describe both intra as well as intervalley scattering processes. For the case of intravalley scattering ($j = \Gamma$) it can be expressed in a simpler form as

$$\hat{H}_{X-ph}^{\text{intra}} = \sum_{\mathbf{q}, \alpha} \sum_{\mathbf{Q}, \xi_e, \xi_h} \sum_{\nu, \mu} \left(g_{\nu, \mu, \mathbf{q}}^{(e), \alpha, \xi_h, \xi_e} - g_{\nu, \mu, \mathbf{q}}^{(h), \alpha, \xi_h, \xi_e} \right) b_{\mu, \mathbf{q}+\mathbf{Q}}^{\dagger \zeta_h, \xi_e} b_{\nu, \mathbf{Q}}^{\xi_h, \xi_e} \left(a_{-\mathbf{q}, \alpha}^{\dagger} + a_{\mathbf{q}, \alpha} \right). \quad (4.24)$$

4.2.4 Intravalley scattering linewidth

To obtain the linewidth due to intravalley scattering we will once again use Fermi's golden rule. Since we are interested in the broadening of the lowest lying bright exciton in the K valley, we will consider both the electron and hole to remain in this valley after the scattering event takes place; as a result we will drop the indexes ξ_e and ξ_h to simplify the notation. Noting that the initial state corresponds to a $1s$ exciton with vanishing center of mass momentum, from Fermi's golden rule we find

$$\gamma_{\text{intra}} = 2\pi \sum_{\mu, \mathbf{Q}'} \sum_{\alpha, \mathbf{q}} \sum_{\pm} |\langle \mu, \mathbf{Q}'; \pm 1_{\alpha, \mathbf{q}} | H_{\chi\text{-ph}}^{\text{intra}} | 1s, \mathbf{Q} = 0; n_{\text{ph}}(T) \rangle|^2 \delta(E_{\mathbf{Q}', \mu} - E_{0,1s} \pm \hbar\omega_{\mathbf{q}}^{\alpha}), \quad (4.25)$$

where the sum is over the final state center of mass momentum, $\mathbf{Q}'$, and quantum numbers μ , as well as the transferred momentum $\mathbf{q}$, the phonon branch α and the emission (+) or absorption (−) of phonons; the matrix element assumes that the initial state has a given phonon distribution $n_{\text{ph}}(T)$, and the final state has one more or one less phonon in the mode α with momentum $\mathbf{q}$. The Hamiltonian $H_{\chi\text{-ph}}^{\text{intra}}$ is obtained from $H_{\chi\text{-ph}}$ by selecting the contributions with $j = \Gamma$ and setting $\xi_e = \xi_h = K$. Working the argument of the δ –function one realizes that $E_{\mathbf{Q}', \mu} - E_{0,1s} \geq 0$, and as a result only processes involving absorption of phonons are possible in order to satisfy energy conservation.

To compute the matrix element in the definition of γ_{intra} we have to determine $g_{v,\mu,\mathbf{q}}^{(e),\alpha}$ as well as $g_{v,\mu,\mathbf{q}}^{(h),\alpha}$. From Eq. (4.22), we find

$$\begin{aligned} g_{v,\mu,\mathbf{q}}^{(e),\alpha} &= \frac{g_{\mathbf{q}}^{(e),\alpha}}{A} \sum_{\mathbf{k}} \psi_{\mu,\mathbf{k}+\beta_{KK}\mathbf{q}}^* \psi_{v,\mathbf{k}} \\ &= g_{\mathbf{q}}^{(e),\alpha} \int \psi_{\mu}^*(\mathbf{r}) \psi_v(\mathbf{r}) e^{-i\beta_{KK}\mathbf{r}\cdot\mathbf{q}} d\mathbf{r} \approx g_{\mathbf{q}}^{(e),\alpha} \delta_{\mu v}, \end{aligned} \quad (4.26)$$

where in the last step we used the fact that the transferred momentum in intravalley processes is small to approximate the complex exponential to one; the Kronecker– δ follows from the orthogonality relation of the exciton wave functions. A similar procedure can be applied to $g_{v,\mu,\mathbf{q}}^{(h),\alpha}$, yielding

$$g_{v,\mu,\mathbf{q}}^{(h),\alpha} \approx g_{\mathbf{q}}^{(h),\alpha} \delta_{\mu v}.$$

From these results we see that when the transferred momentum is small, the coupling with phonons does not change the exciton quantum numbers. This is to be expected, since the the $1s$ state is separated from the other exciton states ($2s$, $2p$, $3s$, etc.) by hundreds of meV, while the energy of intravalley phonons is only of a few tens of meV.

For intravalley scattering with acoustic phonons, using a first order deformation potential, and considering a linear dispersion relation, we obtain from Fermi's golden rule

$$\gamma_{\text{intra,ac}} = \frac{|\Xi^{(e)} - \Xi^{(h)}|^2}{2\rho v_{\text{ac}}^2} \left(\frac{2M_{KK}v_{\text{ac}}}{\hbar} \right)^2 n_{\text{BE}}(2M_{KK}v_{\text{ac}}/\hbar) \quad (4.27)$$

$$\approx \frac{|\Xi^{(e)} - \Xi^{(h)}|^2}{\rho v_{\text{ac}}^2} \frac{M_{KK}}{\hbar^2} k_B T \quad (4.28)$$

where v_{ac} is the sound velocity of the material (determined by the slope of the phonon dispersion relation), $M_{KK} = m_e^K + m_h^K$, n_{BE} is the Bose-Einstein distribution, T the temperature of the system and k_B the Boltzmann constant. Note that the Bose-Einstein distribution function comes from the matrix element of the phonon operators that enter in the Hamiltonian. In the last step we considered $2M_{KK}v_{\text{ac}}^2 \ll k_B T$, which is easily satisfied for realistic parameters, to linearize the Bose-Einstein distribution. The values of the different parameters can be found in [108] and [112]. The values used for the deformation potential account simultaneously for coupling with LA and TA phonons. For intravalley scattering with optical phonons, we consider a zero order deformation potential and a constant energy dispersion. In the end we find

$$\gamma_{\text{intra,op}} = \frac{|D_0^{(e)} - D_0^{(h)}|^2}{2\rho\hbar\omega_{\text{op}}} \frac{M_{KK}}{\exp\left(\frac{\hbar\omega_{\text{op}}}{k_B T}\right) - 1}, \quad (4.29)$$

where $\hbar\omega_{\text{op}}$ is the energy of the optical phonons. Once more, the values of the different parameters may be found in [108] and [112]. The values used for the deformation potential simultaneously account for coupling with the LO, TO and A_1 phonon branches. Let us note that, within the considered approximations, both the acoustic and optical contributions are insensitive to dielectric screening from the environment.

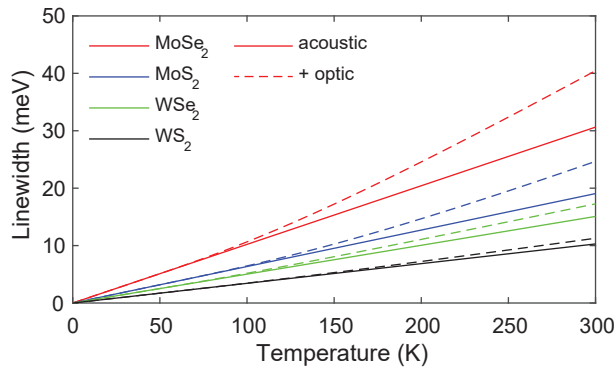


Figure 20: **Intravalley scattering linewidth.** Intravalley linewidth as a function of temperature in four different TMDs. The solid lines represent the contribution from scattering with acoustic phonons, and the dashed lines give the total contribution (acoustic plus optical phonons).

In Fig. 20 we depict the intravalley linewidth as a function of temperature for different TMDs. Due to the values of the deformation potentials obtained from DFT calculations, one finds that scattering with

acoustic phonons is significantly more efficient than scattering with optical phonons [112], and as a consequence the total intravalley scattering linewidth increases linearly with temperature with a small exponential correction. Furthermore, we observe that the linewidth takes larger values for molybdenum based TMDs than for tungsten based ones, as a consequence of the higher effective masses and deformation potentials of the former. Moreover, TMDs with the selenium produce larger broadenings than the ones with sulfur; this is due to the higher values of ρv_{ac} and $\hbar\omega_{op}$ in TMDs with sulfur, which suppresses the contribution from $\gamma_{intra,ac}$ and $\gamma_{intra,op}$, respectively.

4.2.5 Intervalley scattering linewidth

The linewidth originating from intervalley exciton-phonon scattering can be computed following a similar procedure to the one used for the intravalley case. Here, we consider that in the initial state (a bright exciton) both the electron and hole are located in the K valley, and that after the scattering event the electron is taken to another point of the BZ. We consider only the contribution from electron scattering since this should be the dominant process (more on this later). Moreover, we assume that the quantum numbers of the exciton are unchanged by the scattering event. As in the intravalley case this is a reasonable assumption considering, for example, the large energy separation between the 1s and 2s states, when compared to the energies of the involved phonons. Once more employing Fermi's golden rule, the intervalley linewidth associated with scattering of the electron in the conduction band to a specific valley reads

$$\gamma_{inter,j} = 2\pi \sum_{\mu, Q', \zeta_e, \zeta_h} \sum_{\alpha, q} \sum_{\pm} |\langle 1s, \zeta_h, \zeta_e, Q'; \pm 1_{\alpha, j, q} | H_{X-ph}^{inter,j} | 1s, K, K, Q = 0, n_{ph}(T) \rangle|^2 \times \delta \left(E_{Q', 1s}^{\zeta_h, \zeta_e} - E_{0, 1s}^{KK} \pm \hbar\omega_q^{j, \alpha} \right), \quad (4.30)$$

where this time the valley indexes can not be suppressed, and $\hat{H}_{X-ph}^{inter,j}$ is obtained from $\hat{H}_{X-ph}$ by ignoring the term referring to scattering in the valence band, and selecting the contribution of scattering in the conduction band to a single valley (assuming $j \neq \Gamma$), that is

$$\hat{H}_{X-ph}^{inter,j} = \sum_{q, \alpha} \sum_{Q, \zeta_e, \zeta_h} \sum_{v, \mu} g_{v, \mu, q}^{(e), \alpha, \zeta_h, \zeta_e, j} b_{\mu, q+Q}^{\dagger \zeta_h, (\zeta_e+j)} b_{v, Q}^{\zeta_h, \zeta_e} \left(a_{-q, \alpha}^{\dagger, -j} + a_{q, \alpha}^j \right) \quad (4.31)$$

Contrarily to the intravalley case, in the present scenario the coupling element $g_{v, \mu, q}^{(e), \alpha, \zeta_h, \zeta_e, j}$ can not be written as the product of the electron-phonon coupling with a Kronecker- δ , since what allowed us to obtain that result in the first place was an approximation based on the small transferred momentum during the scattering event, which certainly does not hold in intervalley processes. Nonetheless, since we consider the exciton to be in the 1s state before and after the scattering event takes place, we can

use the variational *ansatz* presented in the beginning of the section to obtain an analytical expression for $g_{v,\mu,\mathbf{q}}^{(e),\alpha,\xi_h,\xi_e,j}$. Thus

$$\begin{aligned} g_{1s,1s,\mathbf{q}}^{(e),\alpha,\xi_h,(\xi_e+j)} &= g_{\mathbf{q}}^{(e),\alpha} \int \psi_{\xi_h,(\xi_e+j),1s}^*(\mathbf{r}) \psi_{\xi_h,\xi_e,1s}(\mathbf{r}) e^{i\beta_{\xi_h,(\xi_e+j)}\mathbf{r}\cdot(\mathbf{j}+\mathbf{q})} d\mathbf{r} \\ &\approx g_{\mathbf{q}}^{(e),\alpha} \int \psi_{\xi_h,(\xi_e+j),1s}^*(\mathbf{r}) \psi_{\xi_h,\xi_e,1s}(\mathbf{r}) e^{i\beta_{\xi_h,(\xi_e+j)}\mathbf{r}\cdot\mathbf{j}} d\mathbf{r} \\ &= g_{\mathbf{q}}^{(e),\alpha} \frac{4a_1a_2(a_1+a_2)}{[(a_1+a_2)^2 + (a_1a_2\beta_2|j|)^2]^{3/2}}, \end{aligned} \quad (4.32)$$

where to simplify the notation we introduced the indexes $1 = \{\xi_h, \xi_e\}$ and $2 = \{\xi_h, \xi_e + j\}$; from the first to the second line we used $j \gg |\mathbf{q}|$ to approximate $\mathbf{j} + \mathbf{q} \approx \mathbf{j}$.

To obtain an explicit expression for $\gamma_{\text{inter},j}$ we start by combining Eq. (4.32) with Eq. (4.31) and insert the result in Fermi's golden rule. Afterwards, we compute the matrix element, transform the sum over the transferred momentum into an integral and in the end obtain

$$\gamma_{\text{inter},j} = \sum_{\alpha,\pm} w_{\xi} \frac{|D_{K \rightarrow \xi}^{0,\alpha,(e)}|^2}{\rho \hbar \omega_{j,\alpha}} \frac{8M_{\xi} a_K^2 a_{\xi}^2 (a_K + a_{\xi})^2}{[(a_K + a_{\xi})^2 + \beta_{\xi}^2 a_K^2 a_{\xi}^2 j^2]^3} \left[\frac{1}{2} \pm \frac{1}{2} + n_{\text{BE}}(\hbar \omega_{j,\alpha}) \right] \Theta(-\Delta_{K\xi} \mp \hbar \omega_{j,\alpha}) \quad (4.33)$$

where the sums are over the phonon modes α (acoustic and optical), and the emission (+) or absorption (−) of phonons; ξ is defined as $\xi = K + j$, and w_{ξ} is the degeneracy factor of the $K \rightarrow \xi$ scattering event; $M_{\xi} = m_{e,\xi} + m_{h,K}$, is the translational mass of the $K\xi$ exciton, and $\beta_{\xi} = m_{h,K}/M_{\xi}$. The Heaviside function $\Theta(x)$ sets the threshold for energetically allowed scattering processes, and $\Delta_{K\xi} = \Delta_{K\xi}^{\text{CB}} + \Delta_{K\xi}^{\text{binding}}$ is the energy difference of the conduction band edge at the K and ξ valleys ($\Delta_{K\xi}^{\text{CB}}$) plus the difference of the binding energy of the KK and $K\xi$ excitons ($\Delta_{K\xi}^{\text{binding}}$). The variational parameter $a_{\xi}(a_K)$ is associated with the wave function of the $K\xi$ (KK) exciton, whose dependence with μ , κ and r_0 is given by Eq. (4.6). Note that we chose to label different quantities solely with the electron valley, since we consider the hole to always be in the K valley, thus allowing for a simpler notation.

One of the most important elements of Eq. (4.33) is the Heaviside function, which determines the available scattering channels. From Fig. 19 we observe that in molybdenum based TMDs we have $\Delta_{K\Lambda} \sim 100$ meV, while for the tungsten based ones $\Delta_{K\Lambda} \sim -30$ meV. Since the energy of the phonons that mediate intervalley processes does not exceed 50 meV, intervalley scattering should play a negligible role in MoX_2 TMDs, since these events are not energetically favorable. However, for WX_2 TMDs the position of the $K\Lambda$ exciton relatively to the bright one makes intervalley scattering an energetically favorable process, and it is expected to give a significant contribution to the linewidth. Furthermore, in tungsten based TMDs, scattering to the K' valley is also energetically favorable, but requires twice the momentum than what is required in the scattering to the Λ valley. Since in Eq. (4.33) the transferred momentum (j) appears in the

denominator, the contribution of scattering to the K' valley is suppressed relatively to the contribution from scattering to the Λ valley; this effect is further enhanced by the difference in the deformation potential magnitude, which is approximately five times larger for $K \rightarrow \Lambda$ than for $K \rightarrow K'$ scattering events. Finally, we note that, contrary to the intravalley contribution, Eq. (4.33) depends on the dielectric screening from the environment, and can in principle be tuned this way. The dielectric screening not only affects the value of a_K and a_ξ , but also changes the exciton binding energies and, as a consequence, the relative position of the different exciton states. As the dielectric screening increases, the binding energies decrease, and intervalley scattering channels may become unavailable. This effect is depicted on the top panel of Fig. 21, where we observe that the intervalley linewidth decreases as a power law with the dielectric screening, up to a critical value where the scattering channels requiring phonon emission become energetically unfavorable leading to a sharp decrease of the linewidth.

4.3 Results

Now that analytical expressions describing both the radiative and non-radiative linewidths have been derived, let us study the specific case of the $1s$ exciton in WS_2 on a substrate of quartz as a function of temperature. Our theoretical prediction as well as the experimental data measured in Ref. [101] are depicted in the bottom panel of Fig. 21, where a good quantitative agreement between theory and experiment is seen. In Ref. [101] a theoretical model based on a self-consistent numerical solution of the optical Bloch equations was also presented to describe the experimental data. Although their theoretical formulation is far more complex than our own, the theoretical results of Ref. [101] give as good a description of the experimental data as the analytical model we presented here.

We observe that the total linewidth is composed of a constant radiative term of approximately 5 meV, combined with the almost linear contribution from intravalley scattering (cf. Fig. 20), and an exponentially increasing intervalley term. These contributions amount to a total linewidth of approximately 25 meV at room temperature. Furthermore, we observe that, as expected, the intervalley contribution stems almost entirely from $K \rightarrow \Lambda$ events, as a consequence of the low efficiency of the $K \rightarrow K'$ scattering events (something similar would happen with the $K \rightarrow \Gamma$ hole scattering, which is why we chose to neglect it). In the $K \rightarrow \Lambda$ scattering, acoustic phonons yield a more significant contribution than the optical ones. In the low temperature region we observe that contrarily to the intravalley linewidth the intervalley term is finite due to the efficient process of scattering through phonon emission. As the temperature increases so do the intra and intervalley contributions, presenting similar magnitudes at room temperature.

A similar calculation for WSe_2 would yield an identical result, with a slightly larger total linewidth, as

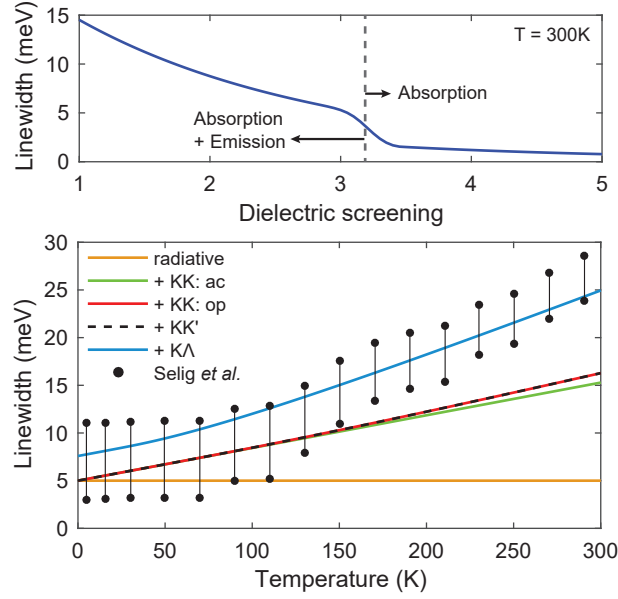


Figure 21: **Total linewidth.** (Top) Intervalley linewidth of the 1s resonance as a function of the environment dielectric screening for WS_2 on quartz. As the dielectric screening increases the excitons become less bound and the separation between the $K\Lambda$ and KK exciton decreases, which originates the suppression of scattering channels. (Bottom) Different contributions to the total linewidth as a function of temperature. Contributions labeled by KK refer to intravalley scattering, while $K\Lambda$ and KK' refer to intervalley scattering. The parameters of [72, 108, 112] were used. The experimental data was taken from the work of Selig *et al.* [101].

a consequence of the more favorable intravalley scattering processes (cf. Fig. 20). For MoS_2 and MoSe_2 , where intervalley processes are energetically inefficient the total linewidth is basically given by the radiative and intravalley contributions.

4.4 Overview

In the beginning of this section we revisited the Wannier equation, this time considering the possibility of having excitons with finite center of mass momentum. From our calculation it follows that the Wannier equation is suited to describe any type of exciton in the most common TMDs (where our approximations hold), regardless of the spin and valley configuration of the carriers, as long as the value of the reduced mass is correctly chosen.

Afterwards, we solved the Wannier equation using a variational *ansatz*, this time using a trial wave function with a single exponential (similar to the ground state of the 2D Hydrogen atom). The simplicity of the trial function allowed us to find an analytical model which accurately described the value of the variational parameter in terms of the system's parameters. Using this result we were able to find an analytical expression for the binding energy of the 1s exciton state, which in turn allowed us to obtain the

energy spectrum of both bright and momentum dark excitons.

Then, employing Fermi's golden rule, we computed the radiative and non-radiative contributions to the linewidth of the $1s$ resonance in different TMDs. A value of approximately 5 meV was found for the radiative linewidth of the four considered systems. For the linewidth stemming from intravalley scattering we observed that interaction with acoustic phonons dominates over optical ones, leading to an almost linear increase of the linewidth with temperature, with a superlinear correction at high temperatures. Also, TMDs with Mo instead of W presented significantly larger intravalley linewidths. Regarding the intervalley contribution to the linewidth, we found that it is negligible in molybdenum based TMDs, but is crucial for those containing tungsten. This difference between the two types of TMDs is a direct consequence of the electronic band structure, in particular the position of the satellite minimum in the conduction band relatively to the Dirac valleys.

At last, let us emphasize the usefulness of the results we have derived. One of the principal application of excitons in TMDs is in optoelectronic nanodevices [114–117], which may be required to operate at finite temperature. The behavior of such devices at finite temperature is limited by the broadening of the $1s$ -excitonic line [64], and is thus useful to have a simple model with high predictive power to describe it. This is exactly what we have achieved in this section, where the derived analytical expressions combined with parameters known from DFT calculations allow for a quick estimate of the linewidth at any temperature in different systems. Compared with more sophisticated approaches based on the direct solution of the BSE and the computation of the linewidths through self-consistent iterative methods [101], our approach avoids the computational cost, while giving more insight into the underlying physics.

Polaron shift and phonon sidebands

In this part of the text we wish to extend the study of the exciton-phonon interaction. While in the previous section we dealt with the phonon induced homogeneous linewidth in TMDs using Fermi's golden rule, here we shall discuss the effect of the exciton-phonon coupling in the position and lineshape of the excitonic resonance. As before, we restrict ourselves to the lowest lying exciton state (the 1s state of the *A*-series), and consider four different materials as our test subjects, MoS₂, MoSe₂, WS₂ and WSe₂. Other materials as well as other resonances in the optical spectrum may be addressed using similar ideas to the ones we will present. To obtain the absorption spectrum in the presence of exciton-phonon coupling we will use the formalism of Green's functions.

5.1 Exciton Green function

As a first step to obtain the excitonic Green's function we must introduce the Hamiltonian of the system. As discussed in the previous section, this Hamiltonian is composed of three distinct terms: i) the excitonic Hamiltonian, ii) the Hamiltonian of the lattice phonons (which was not explicitly treated in the previous section) and iii) the exciton-phonon interaction term. Hence, we write

$$H_{X-ph} = \sum_{\mathbf{Q}} E_{\mathbf{Q},1s} b_{\mathbf{Q},1s}^\dagger b_{\mathbf{Q},1s} + \sum_{\mathbf{q},\lambda} \hbar\omega_{\mathbf{q}}^\lambda \left(a_{\mathbf{q},\lambda}^\dagger a_{\mathbf{q},\lambda} + \frac{1}{2} \right) + \sum_{\mathbf{q},\lambda} \sum_{\mathbf{Q}} g_{\mathbf{q}}^\lambda b_{\mathbf{Q}+\mathbf{q},1s}^\dagger b_{\mathbf{Q},1s} \left(a_{-\mathbf{q},\lambda}^\dagger + a_{\mathbf{q},\lambda} \right),$$

where $E_{\mathbf{Q},1s}$ is the energy dispersion of the 1s exciton, $\hbar\omega_{\mathbf{q}}^\lambda$ is the energy of a phonon with momentum $\mathbf{q}$ belonging to the λ branch and $g_{\mathbf{q}}^\lambda$ is the exciton-phonon coupling associated with the scattering of an exciton with momentum $\mathbf{Q}$ to a state with momentum $\mathbf{Q} + \mathbf{q}$ with the emission/absorption of a phonon with momentum $\pm\mathbf{q}$. In agreement with the previous section the explicit form of $g_{\mathbf{q}}^\lambda$ reads

$$g_{\mathbf{q}}^\lambda = g_{1s,1s,\mathbf{q}}^{(e),\lambda} - g_{1s,1s,\mathbf{q}}^{(h),\lambda}.$$

Here, as before, we neglect the contribution from other exciton states besides the 1s, which should be a reasonable approximation considering that the exciton states are separated by energies far larger than the ones phonons carry. Also, note that following the notation of the previous section this Hamiltonian is written for the case of intravalley processes only. This was done to simplify the notation in what follows; the extension to the intervalley terms, which are relevant for WS₂ and WSe₂, is easily attained from the intravalley results.

Having introduced the Hamiltonian of the system, we now define the retarded Green's function of the 1s exciton in the time domain as

$$G_{Q,1s}^R(t, t') = -\frac{i}{\hbar} \Theta(t - t') \left\langle \left[b_{Q,1s}(t), b_{Q,1s}^\dagger(t') \right] \right\rangle, \quad (5.1)$$

with $\langle \dots \rangle$ a thermodynamic average and $\Theta(x)$ the Heaviside function which guarantees the causal behavior of the response function. In its present form the Green's function is not particularly useful since it contains the commutator of two bosonic operators evaluated at different times; something which may not be trivially known. To obtain a more insightful expression for the retarded Green's function we will employ the so called equation of motion approach [118, 119].

5.1.1 Equation of motion

The equation of motion technique is based on differentiating Eq. (5.1) with respect to t , followed by solving the resulting differential equation, which is usually achieved in the frequency representation. In Appendix F we present an equivalent approach using imaginary time Green's functions and diagrammatic techniques.

5.1.1.1 Bare Green's function

As a first application of this method let us explicitly determine the form of $G_{Q,1s}^R$ from Eq. (5.1) in the absence of phonons, such that the Hamiltonian contains only the excitonic contribution. Following the equation of motion approach, we differentiate Eq. (5.1) with respect to t and find

$$\begin{aligned} \frac{\partial}{\partial t} G_{Q,1s}^R(t, t') &= -\frac{i}{\hbar} \delta(t - t') \left\langle \left[b_{Q,1s}(t), b_{Q,1s}^\dagger(t') \right] \right\rangle \\ &\quad - \frac{i}{\hbar} \Theta(t - t') \left\langle \left[\frac{\partial}{\partial t} b_{Q,1s}(t), b_{Q,1s}^\dagger(t') \right] \right\rangle, \end{aligned}$$

where the Dirac- δ appears from the derivative of the Heaviside function. This allows us to readily evaluate the commutator in the first term, since the two operators must now be taken at the same instant t ; we thus write $\left[b_{Q,1s}(t), b_{Q,1s}^\dagger(t) \right] = 1$. To evaluate the time derivative of $b_{Q,1s}$ in the second term we apply the Heisenberg equation of motion (see Appendix D for a brief overview of the different representations of

quantum mechanics)

$$\frac{\partial}{\partial t} b_{\mathbf{Q},1s}(t) = -\frac{i}{\hbar} [b_{\mathbf{Q},1s}(t), H].$$

Since in this first example we are considering the exciton on its own, that is, with no phonons present, the commutator is easily evaluated, and one obtains

$$\frac{\partial}{\partial t} b_{\mathbf{Q},1s}(t) = -\frac{i}{\hbar} E_{\mathbf{Q},1s} b_{\mathbf{Q},1s}(t). \quad (5.2)$$

Using this, the derivative of the Green's function may be expressed as

$$i\hbar \frac{\partial}{\partial t} G_{\mathbf{Q},1s}^R(t, t') = \delta(t - t') - E_{\mathbf{Q},1s} \frac{i}{\hbar} \Theta(t - t') \left\langle [b_{\mathbf{Q},1s}(t), b_{\mathbf{Q},1s}^\dagger(t')] \right\rangle,$$

where we identify the second term as the retarded Green's function itself, multiplied by $E_{\mathbf{Q},1s}$. Thus:

$$\left[i\hbar \frac{\partial}{\partial t} - E_{\mathbf{Q},1s} \right] G_{\mathbf{Q},1s}^R(t, t') = \delta(t - t').$$

This differential equation can be readily solved in the frequency domain. Considering $G_{\mathbf{Q},1s}^R(t, t') \equiv G_{\mathbf{Q},1s}^R(t - t')$ and introducing the Fourier representations of $G_{\mathbf{Q},1s}^R$ and $\delta(t - t')$, we find

$$G_{\mathbf{Q},1s}^R(\omega) = \frac{1}{\hbar\omega - E_{\mathbf{Q},1s} + i\frac{\eta}{2}}, \quad (5.3)$$

where the small imaginary term $i\eta \rightarrow i0^+$ was introduced to guarantee that the function is causal (analytical in the upper half part of the complex plane). We term this expression the bare Green's function of the exciton, and from it one can obtain the optical response of the system due to the 1s exciton. In fact, this should come as no surprise, since this expression is identical to what we found using Fermi's golden rule in Section 2, the only difference being that here we do not have the optical matrix element in the numerator. This, however, only scales the response of the system, keeping its qualitative features intact, and demands the center of mass momentum $\mathbf{Q}$ to vanish (since we are considering only vertical interband transitions). Using the Sokhotski–Plemelj relation we write

$$-\text{Im} G_{\mathbf{Q},1s}^R(\omega) = \pi \delta(\hbar\omega - E_{\mathbf{Q},1s}) = \lim_{\eta \rightarrow 0^+} \frac{\frac{\eta}{2}}{(\hbar\omega - E_{\mathbf{Q},1s})^2 + \left(\frac{\eta}{2}\right)^2}. \quad (5.4)$$

Where we modeled the δ -function using a Lorentzian centered at the exciton energy $E_{\mathbf{Q},1s}$ with a full width at half maximum of η . In the limit of vanishing η the δ -function behavior is recovered. It should now be clear that the imaginary part of the retarded Green's function may be used to describe the excitonic resonances that appear in the optical spectra of TMDs. For the case without phonons, we may intuitively write

$$\alpha(\hbar\omega) \propto -\text{Im} \frac{\delta_{\mathbf{Q},0}}{\hbar\omega - E_{0,1s} + i\frac{\eta}{2}}. \quad (5.5)$$

where $\alpha(\omega)$ stands for the absorption as a function of the photon energy [108, 120].

5.1.1.2 Full Green's function

Now that the simple case of the bare exciton Green's function was studied, we move on to the more complex situation where phonons are present in the system, and coupling with excitons is possible. Using once again the equation of motion approach, the retarded Green's function is defined as the solution of:

$$\frac{\partial}{\partial t} G_{Q,1s}^R(t, t') = -\frac{i}{\hbar} \delta(t - t') - \frac{i}{\hbar} \Theta(t - t') \left\langle \left[\frac{\partial}{\partial t} b_{Q,1s}(t), b_{Q,1s}^\dagger(t') \right] \right\rangle,$$

with

$$\frac{\partial}{\partial t} b_{Q,1s}(t) = -\frac{i}{\hbar} [b_{Q,1s}(t), H].$$

The difference relatively to what we found before is that this time the Hamiltonian entering in the commutator contains the contribution of the excitons, the phonons, and their interaction. The commutator of $b_{Q,1s}(t)$ with the excitonic part of the Hamiltonian follows directly from Eq. (5.2). Furthermore, we note that the commutator of $b_{Q,1s}(t)$ with the phonon Hamiltonian vanishes, since the exciton and phonon operators act on different sub-spaces and as a result their commutator is identically zero. Finally, the commutator of $b_{Q,1s}(t)$ with the exciton-phonon interaction Hamiltonian has to be explicitly evaluated; this is easily done if one notes that $[b_{Q,1s}(t), b_{K+q,1s}^\dagger(t) b_{K,1s}(t)] = b_{K,1s}(t) \delta_{Q-q,K}$. Performing the necessary calculations one finds

$$\begin{aligned} \frac{\partial}{\partial t} b_{Q,1s}(t) = & -\frac{i}{\hbar} E_{Q,1s} b_{Q,1s}(t) \\ & -\frac{i}{\hbar} \sum_{q,\lambda} g_q^\lambda b_{Q-q,1s}(t) [a(t)_{-q,\lambda}^\dagger + a(t)_{q,\lambda}]. \end{aligned}$$

Using this result we write

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} G_{Q,1s}^R(t, t') = & \delta(t - t') - \frac{i}{\hbar} E_{Q,1s} \Theta(t - t') \langle [b_{Q,1s}(t), b_{Q,1s}^\dagger(t')] \rangle \\ & -\frac{i}{\hbar} \Theta(t - t') \sum_{q,\lambda} g_q^\lambda \langle [b_{Q-q,1s}(t) a_{-q,\lambda}^\dagger(t), b_{Q,1s}^\dagger(t')] \rangle \\ & -\frac{i}{\hbar} \Theta(t - t') \sum_{q,\lambda} g_q^\lambda \langle [b_{Q-q,1s}(t) a_{q,\lambda}(t), b_{Q,1s}^\dagger(t')] \rangle. \end{aligned}$$

Now, once more, we can identify the second term as the exciton Green's function itself. The third and forth terms, however, correspond to new Green's functions, which are yet to be determined. Defining

$$\Gamma_{Q,q,1s}^+(t, t') = -\frac{i}{\hbar} \Theta(t - t') \langle [b_{Q+q,1s}(t) a_{q,\lambda}^\dagger(t), b_{Q,1s}^\dagger(t')] \rangle \quad (5.6)$$

$$\Gamma_{Q,-q,1s}^-(t, t') = -\frac{i}{\hbar} \Theta(t - t') \langle [b_{Q+q,1s}(t) a_{-q,\lambda}(t), b_{Q,1s}^\dagger(t')] \rangle, \quad (5.7)$$

we obtain

$$i\hbar \frac{\partial}{\partial t} G_{Q,1s}^R(t, t') = \delta(t - t') + E_{Q,1s} G_{Q,1s}^R(t, t') + \sum_{\mathbf{q}, \lambda} g_{-\mathbf{q}}^\lambda \left[\Gamma_{Q, \mathbf{q}, 1s}^+(t, t') + \Gamma_{Q, -\mathbf{q}, 1s}^-(t, t') \right].$$

Contrarily to the case where phonons were not accounted for, a single application of the equation of motion approach did not allow us to obtain a compact expression for $G_{Q,1s}^R$. To progress with the calculation we are now required to determine $\Gamma_{Q, \mathbf{q}, 1s}^+(t, t')$ and $\Gamma_{Q, -\mathbf{q}, 1s}^-(t, t')$. To do so, we will apply once again the equation of motion approach to each of these new functions. Starting with $\Gamma_{Q, \mathbf{q}, 1s}^+(t, t')$, and differentiating it with respect to t , we find

$$\frac{\partial}{\partial t} \Gamma_{Q, \mathbf{q}, 1s}^+(t, t') = -\frac{i}{\hbar} \Theta(t - t') \left\langle \left[\frac{\partial}{\partial t} (b_{Q+\mathbf{q}, 1s}(t) a_{\mathbf{q}, \lambda}^\dagger(t)), b_{Q, 1s}^\dagger(t') \right] \right\rangle, \quad (5.8)$$

where this time no δ -function appears. When we differentiate $\Gamma_{Q, \mathbf{q}, 1s}^+(t, t')$ with respect to t , the derivative of the Heaviside function yields a Dirac- δ , $\delta(t - t')$, multiplied by

$$\left\langle \left[b_{Q+\mathbf{q}, 1s}(t) a_{\mathbf{q}, \lambda}^\dagger(t), b_{Q, 1s}^\dagger(t') \right] \right\rangle.$$

Since the δ -function forces the operators to be evaluated at the same instant t , we write this as

$$\left\langle \left[b_{Q+\mathbf{q}, 1s}(t) a_{\mathbf{q}, \lambda}^\dagger(t), b_{Q, 1s}^\dagger(t) \right] \right\rangle = \left\langle a_{\mathbf{q}, \lambda}^\dagger(t) \right\rangle.$$

Because the expectation value of $a_{\mathbf{q}, \lambda}^\dagger(t)$ vanishes, the Dirac- δ is suppressed. To evaluate the time derivative of $b_{Q+\mathbf{q}, 1s}(t) a_{\mathbf{q}, \lambda}^\dagger(t)$ the Heisenberg equation is once again used:

$$\frac{\partial}{\partial t} b_{Q+\mathbf{q}, 1s}(t) a_{\mathbf{q}, \lambda}^\dagger(t) = -\frac{i}{\hbar} \left[b_{Q+\mathbf{q}, 1s}(t) a_{\mathbf{q}, \lambda}^\dagger(t), H \right].$$

Evaluating all the necessary terms in the commutator we arrive at

$$\begin{aligned} \frac{\partial}{\partial t} b_{Q+\mathbf{q}, 1s}(t) a_{\mathbf{q}, \lambda}^\dagger(t) = & -\frac{i}{\hbar} E_{Q+\mathbf{q}, 1s} b_{Q+\mathbf{q}, 1s}(t) a_{\mathbf{q}, \lambda}^\dagger(t) \\ & + \frac{i}{\hbar} \hbar \omega_{\mathbf{q}}^\lambda b_{Q+\mathbf{q}, 1s}(t) a_{\mathbf{q}, \lambda}^\dagger(t) \\ & + \frac{i}{\hbar} \sum_{\mathbf{K}} g_{\mathbf{q}}^\lambda b_{Q+\mathbf{q}, 1s}(t) b_{\mathbf{K}+\mathbf{q}, 1s}^\dagger(t) b_{\mathbf{K}, 1s}(t) \\ & - \frac{i}{\hbar} \sum_{\mathbf{p}, \nu} g_{\mathbf{p}}^\nu b_{Q+\mathbf{q}-\mathbf{p}, 1s}(t) a_{\mathbf{p}, \nu}(t) a_{\mathbf{q}, \lambda}^\dagger(t) \end{aligned}$$

where the first and second terms come from the commutator with the exciton and phonon contributions to the Hamiltonian, respectively, while the last two terms are due to the commutator with the exciton-phonon

interaction Hamiltonian. Inserting this result in Eq. (5.8) one obtains

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Gamma_{Q,q,1s}^+(t, t') &= (E_{Q+q,1s} - \hbar\omega_q^\lambda) \Gamma_{Q,q,1s}^+(t, t') \\ &+ \frac{i}{\hbar} \sum_{\mathbf{K}} g_q^\lambda \Theta(t - t') \left\langle \left[b_{Q+q,1s}(t) b_{\mathbf{K}+q,1s}^\dagger(t) b_{\mathbf{K},1s}(t), b_{Q,1s}^\dagger(t') \right] \right\rangle \\ &- \frac{i}{\hbar} \sum_{\mathbf{p}, \nu} g_p^\nu \Theta(t - t') \left\langle \left[b_{Q+q-p,1s}(t) a_{\mathbf{p},\nu}(t) a_{\mathbf{q},\lambda}^\dagger(t), b_{Q,1s}^\dagger(t') \right] \right\rangle, \end{aligned}$$

where we were able to identify the definition of $\Gamma_{Q,q,1s}^+(t, t')$ in the terms multiplying $E_{Q+q,1s}$ and $\hbar\omega_q^\lambda$. Unfortunately, the application of the equation of motion approach to $\Gamma_{Q,q,1s}^+(t, t')$ lead us to an expression where additional Green's functions appear, this time containing products of three operators. As the number of operators increases so does the complexity of the commutators that must be evaluated if the equation of motion is to be applied once again. Since there is no guarantee that applying this approach to the new Green's functions would close the system of equations, leading to a rather tedious problem, we introduce a mean field approximation. This procedure allows us to approximately decouple the products of three operators by performing means over the non-interacting system, thus greatly simplifying the problem at hand. Explicitly, we perform the approximation

$$\begin{aligned} b_{Q+q,1s}(t) b_{\mathbf{K}+q,1s}^\dagger(t) b_{\mathbf{K},1s}(t) &\approx \left\langle b_{Q+q,1s}(t) b_{\mathbf{K}+q,1s}^\dagger(t) \right\rangle b_{\mathbf{K},1s}(t) + b_{Q+q,1s}(t) \left\langle b_{\mathbf{K}+q,1s}^\dagger(t) b_{\mathbf{K},1s}(t) \right\rangle \\ &= \delta_{Q,\mathbf{K}} b_{\mathbf{K},1s}(t), \end{aligned}$$

where we used the fact that the expectation value of the exciton number operator is approximately zero due to the large energy of the exciton. Furthermore, we also consider

$$\begin{aligned} b_{Q+q-p,1s}(t) a_{\mathbf{p},\nu}(t) a_{\mathbf{q},\lambda}^\dagger(t) &\approx b_{Q+q-p,1s}(t) \left\langle a_{\mathbf{p},\nu}(t) a_{\mathbf{q},\lambda}^\dagger(t) \right\rangle \\ &= \delta_{\mathbf{q},\mathbf{p}} \delta_{\nu,\lambda} b_{Q,1s}(t) \left[1 + n_{\text{BE}}(\hbar\omega_q^\lambda) \right], \end{aligned}$$

where $n_{\text{BE}}(\hbar\omega_q^\lambda)$ is the Bose-Einstein distribution function for phonons in the λ -mode with energy $\hbar\omega_q^\lambda$.

Using this mean field decoupling we find

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Gamma_{Q,q,1s}^+(t, t') &= (E_{Q+q,1s} - \hbar\omega_q^\lambda) \Gamma_{Q,q,1s}^+(t, t') \\ &+ \frac{i}{\hbar} g_q^\lambda \Theta(t - t') \left\langle \left[b_{Q,1s}(t), b_{Q,1s}^\dagger(t') \right] \right\rangle \\ &- \frac{i}{\hbar} g_q^\lambda \Theta(t - t') \left\langle \left[b_{Q,1s}(t), b_{Q,1s}^\dagger(t') \right] \right\rangle \left[1 + n_{\text{ph}}(\hbar\omega_q^\lambda) \right]. \end{aligned}$$

Recalling the definition of $G_{Q,1s}^R(t, t')$ this can be simplified as

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \Gamma_{Q,q,1s}^+(t, t') &= (E_{Q+q,1s} - \hbar\omega_q^\lambda) \Gamma_{Q,q,1s}^+(t, t') \\ &+ n_{\text{BE}}(\hbar\omega_q^\lambda) g_q^\lambda G_{Q,1s}^R(t, t'). \end{aligned} \tag{5.9}$$

With this we see that the mean field decoupling allowed us to close the system of equations, since $G_{Q,1s}^R(t, t')$ is defined in terms of $\Gamma_{Q,q,1s}^+(t, t')$ which is in turn defined in terms of $G_{Q,1s}^R(t, t')$. In order to find $\Gamma_{Q,-q,1s}^-(t, t')$ a completely analogous procedure to the one just presented can be followed; the final result reads

$$i\hbar \frac{\partial}{\partial t} \Gamma_{Q,-q,1s}^-(t, t') = \left(E_{Q+q,1s} + \hbar\omega_q^\lambda \right) \Gamma_{Q,-q,1s}^-(t, t') + \left[1 + n_{BE}(\hbar\omega_q^\lambda) \right] g_q^\lambda G_{Q,1s}^R(t, t'), \quad (5.10)$$

which differs from $\Gamma_{Q,-q,1s}^-$ in the sign of $\hbar\omega_q^\lambda$ and in the term with the phonon distribution function, which should hint at the distinct physical role these two functions will play further ahead.

5.1.2 Green's function and self energy

So far we have obtained three coupled differential equations which when solved define the excitonic Green's function, $G_{Q,1s}^R(t, t')$. Just like in the case of the bare Green's function, to solve the system of equations it is convenient to work in the frequency domain. Introducing the necessary Fourier representations one finds

$$\begin{aligned} [\hbar\omega - E_{Q,1s}] G_{Q,1s}^R(\omega) &= 1 + \sum_{q,\lambda} g_{-q}^\lambda \left[\Gamma_{Q,q,1s}^+(\omega) + \Gamma_{Q,-q,1s}^-(\omega) \right], \\ \Gamma_{Q,q,1s}^+(\omega) &= g_q^\lambda \frac{n_{BE}(\hbar\omega_q^\lambda)}{\hbar\omega - E_{Q+q,1s} + \hbar\omega_q^\lambda} G_{Q,1s}^R(\omega), \\ \Gamma_{Q,-q,1s}^-(\omega) &= g_q^\lambda \frac{1 + n_{BE}(\hbar\omega_q^\lambda)}{\hbar\omega - E_{Q+q,1s} - \hbar\omega_q^\lambda} G_{Q,1s}^R(\omega). \end{aligned}$$

Combining the three equations yields

$$G_{Q,1s}^R(\omega) = \frac{1}{\hbar\omega - E_{Q,1s} - \Sigma_Q(\hbar\omega) + i\frac{\eta}{2}}, \quad (5.11)$$

where

$$\Sigma_Q(\hbar\omega) = \sum_{q,\lambda} |g_q^\lambda|^2 \left[\frac{n_{BE}(\hbar\omega_q^\lambda)}{\hbar\omega - E_{Q+q,1s} + \hbar\omega_q^\lambda + i\frac{\eta}{2}} + \frac{1 + n_{BE}(\hbar\omega_q^\lambda)}{\hbar\omega - E_{Q+q,1s} - \hbar\omega_q^\lambda + i\frac{\eta}{2}} \right], \quad (5.12)$$

is the self-energy, and we recall that the sums are over the transferred momentum $\mathbf{q}$ and phonon mode λ . Similarly to the case where phonons were absent, we may write the absorption as a function of the photon energy as

$$\begin{aligned} \alpha(\hbar\omega) &\propto -\delta_{Q,0} \text{Im} G_{Q,1s}^R \\ &\propto -\text{Im} \frac{\delta_{Q,0}}{\hbar\omega - E_{Q,1s} - \Sigma_Q(\hbar\omega) + i\frac{\eta}{2}}. \end{aligned} \quad (5.13)$$

An identical result to this one was obtained in Ref. [120] where the optical Bloch equations were solved including non-Markovian processes.

Comparing Eqs. (5.5) and (5.13) we note that the self-energy is the main difference between the cases where phonons are or are not included, and it is solely due to the exciton-phonon interaction; if the coupling constant vanishes, so does the self energy. Moreover, we emphasize that the self-energy is composed of two terms with distinct physical meanings. The term with $n_{\text{BE}}(\hbar\omega_{\mathbf{q}}^{\lambda})$ on the numerator is associated with processes involving absorption of phonons, while the other term is linked to processes with phonon emission, clearly seen from the +1 in the numerator indicating spontaneous emission of phonons. The effect of the self-energy (and thus of the exciton-phonon coupling) is two fold: on the one hand, the real part of $\Sigma_{\mathbf{Q}}$ shifts the location of the absorption peak, which is no longer centred at the exciton energy $E_{\mathbf{Q},1s}$; on the other hand, the imaginary part of $\Sigma_{\mathbf{Q}}$ contributes to the broadening of the resonance. Lastly, we note that we consider the small imaginary term η to be the same for both the Green's function and the self-energy (regardless of the phonon mode λ). At first this may seem an odd thing to consider, since in the previous section we observed that different phonon modes give rise to different contributions to the total linewidth. However, if we were to consider mode-dependent linewidths in the self energy, somewhat nonphysical results would appear. Take for example the case of MoS_2 , where we found that due to the more efficient coupling with acoustic phonons the induced linewidth at room temperature was approximately 20 meV, while coupling with optical phonons contributed only with 5 meV. If these mode dependent linewidths were introduced in the self energy the obtained spectrum would contain much sharper features due to coupling with optical phonons, resulting in odd-looking absorption spikes, while the features associated with acoustic phonons would be much broader. Our choice of a single broadening η , simultaneously encompassing all the decay channels (radiative as well as phonon induced), assumes that all the decay mechanism are coupled and leads to more realistic smooth results. This is in line with Matthiessen's rule [121] and is a consequence of the approximations we introduced, which lead to a not fully self consistent treatment of the problem. In the language of Appendix F, this lack of self consistency results from neglecting higher order Feynman diagrams in the self energy series expansion. Hence, in what follows, we take the broadening η as a temperature dependent quantity, whose value can be obtained from the results of the previous section.

Let us now briefly clarify how the self-energy can be evaluated. First, we recall the definition of the exciton energy (which for the moment we consider to be composed of an electron and a hole in the K valley), and write $E_{\mathbf{Q}+\mathbf{q},1s} = E_g + E_{1s} + \hbar^2 (\mathbf{Q} + \mathbf{q})^2 / 2M$, with E_g the band gap, E_{1s} the exciton binding energy and $M = m_e + m_h$ its mass. Then, we take the thermodynamic limit and transform the sum over $\mathbf{q}$ into an integral over the momentum. At last, we look back on the definition of the exciton-phonon coupling

given before Eq. (4.26) and, using the single exponential variational *ansatz* $\psi_{1s}(r) \propto e^{-r/a}$, we write:

$$g_{\mathbf{q}}^{\lambda} = g_{\mathbf{q}}^{(e),\lambda} \frac{8}{[4 + q^2 a^2 \beta^2]^{3/2}} - g_{\mathbf{q}}^{(h),\lambda} \frac{8}{[4 + q^2 a^2 (1 - \beta)^2]^{3/2}}, \quad (5.14)$$

where a is the variational parameters of the $1s$ state trial wave function, and $\beta = m_h/M$. Contrarily to the previous section, here the Kronecker- δ approximation can no longer be applied, since it would lead to a diverging integral as a result of the slow decay of the integrand at large momenta. The asymptotic $1/q^3$ behavior of $g_{\mathbf{q}}^{\lambda}$ guarantees the fast convergence of the integral.

As we discussed when the Hamiltonian of the system was introduced in the beginning of the section, the results so far derived are only valid for the case of intravalley scattering. However, the extension to the intervalley case is easily obtained from here. To do so we need only to modify the energy of the exciton, $E_{\mathbf{Q}+\mathbf{q},1s}$, which should now refer to intervalley excitons, and the exciton-phonon coupling element, $g_{\mathbf{q}}^{\lambda}$, which can be obtained from Eq. (4.32) without the approximation of small $\mathbf{q}$.

5.2 Results

In this part of the section we will apply the expressions so far derived to study the absorption peak due to the $1s$ exciton at finite temperature in four TMDs. As in the previous section we will work within the deformation potential framework, considering the coupling to acoustic and optical phonons; the parameters of Refs. [52] are used to characterize the TMDs, while those of Refs. [108, 112] are used to obtain the exciton-phonon couplings, and the phonon energies.

In Fig. 22a we depict the absorption spectrum of MoSe_2 due to the $1s$ exciton at $T = 300$ K; the energy is measured relatively to the position of the absorption peak in the absence of exciton-phonon coupling, and the absorption is given in arbitrary units. Since in this material intervalley processes are not efficient, we consider only coupling with phonons from the center of the BZ to carriers in the conduction and valence bands. In Fig. 22a the black line corresponds to the result obtained with the bare Green's function, the solid line shaded in blue corresponds to the absorption peak obtained with the full Green's function (taking into consideration the intravalley coupling of excitons with acoustic and optical phonons) and the dashed blue line is a Lorentzian whose peak was shifted to be aligned with the solid blue line (cf. Eq.(5.4)). Comparing the resonances obtained with and without accounting for the presence of phonons in the system (blue and black solid lines, respectively), we observe that, as expected, when phonons are included in the calculation the position of the resonance is shifted, and its broadening increases. The coupling with phonons originates a red-shift of the central position of the resonance of approximately 21 meV; this is the so called polaron shift. Moreover, when we compare the solid and dashed blue lines,

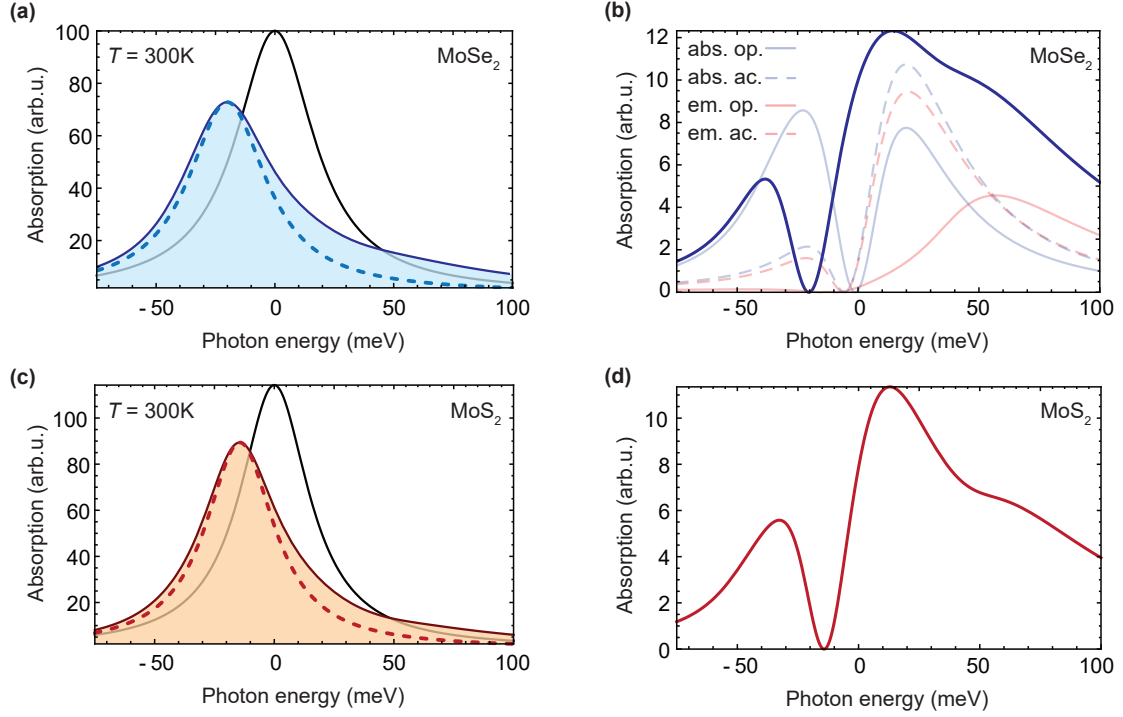


Figure 22: **MoX₂ absorption spectra.** Panels (a) and (c) depict the absorption peak due to the 1s exciton in MoSe₂ and MoS₂, respectively. The solid black line represents the absorption when phonons are not accounted for, the shaded region describes the absorption peak in the presence of phonons, and the dashed line is a Lorentzian function scaled and shifted to coincide with the peak when phonons are present. Panels (b) and (d) show the phonon side bands obtained by subtracting the Lorentzian function to the shaded region. In addition, in panel (b) we present as faint lines the individual contributions to the sidebands of emission (em.) or absorption (abs.) of acoustic (ac.) or optical (op.) phonons.

we observe that the absorption peak does not present the same lineshape as a Lorentzian, in fact, its linewidth is not homogeneous, being significantly larger in the high energy side of the resonance.

To better understand the inhomogeneity of the absorption spectrum, we depict in Fig. 22b the difference between the solid and dashed blue lines of Fig. 22a, which should allow us to gain insight on how the absorption peak deviates from a Lorentzian lineshape. Inspecting this figure, three distinct structures, called phonon sidebands, are clearly resolved: one below the exciton peak, and two above it. We thus see that the effect of the exciton-phonon coupling is significantly more intense in the high energy side of the resonance leading to the formation of two broad phonon sidebands, increasing the inhomogeneity of the lineshape at higher energies. At lower energies a single less intense side band is resolved. To uncover the physical processes underlying each of the sidebands we artificially select a single coupling channel, e.g. absorption of optical phonons, and then compute the resulting absorption spectrum, and the associated sidebands. The contributions of each of the four considered coupling processes, i.e. absorption or emission of optical or acoustic phonons, are depicted as faint lines in Fig. 22b. Using these results, one can easily assign the sideband at approximately 50 meV to the emission of optical phonons, while

the sideband at approximately -40 meV is mainly due to the absorption of optical phonons. The role of acoustic phonons is more noticeable in the structure at approximately 10 meV which is mainly due to processes involving their emission and absorption; scattering with the absorption of optical phonons also contribute to this sideband. Furthermore, since the sidebands due to the absorption of optical phonons are nearly symmetric relatively to the peak position in the absence of phonons, we conclude that this coupling channel primarily contributes to an increased homogeneous linewidth, while emission of optical phonons and processes involving acoustic phonons are the ones responsible for the inhomogeneity of the resonance's linewidth. At last, we note that the position of the sidebands can not be directly determined from the energy of the involved phonons; in fact, this is determined in a non-trivial manner by the phonon energy, the exciton-phonon coupling strength and the phonon population, as can be seen by setting the denominator of the Green's function to zero.

As a comparison with the results we have just discussed, in Fig. 22c we showcase the absorption spectrum of MoS_2 at room temperature. As expected, these results are similar to the ones we found for MoSe_2 with only a few key differences which are worth mentioning. First, we note that the absorption peak is slightly narrower, as a result of the smaller value of η we used, in agreement with what was found in the previous section. Furthermore, as a consequence of the slightly less efficient coupling with phonons, in MoS_2 we find a smaller polaron shift, which is now of approximately 15 meV. Compared to the results of MoSe_2 we also note the smaller asymmetry of the linewidth at higher energies. To better understand the character of the inhomogeneous linewidth we look at the phonon sidebands depicted in Fig. 22d. Once more we find three clearly resolved sidebands, whose underlying physical processes are similar to those of MoSe_2 . The fact that in MoS_2 the optical phonons are more energetic (approximately 50 meV compared with the 40 meV found in MoSe_2) results in a smaller optical phonon population, reducing the intensity of the sidebands at higher energies.

In Fig. 23a and 23c we depict the absorption spectrum of WSe_2 and WS_2 at $T = 300$ K. Since in these materials scattering of electrons in the conduction band to the Λ valley is favorable we include this process in the self-energy (scattering of holes to the Γ valley is neglected). Comparing these results to the ones we found for MoSe_2 and MoS_2 , we observe that in the present scenario the absorption peaks are narrower, less inhomogeneous, and present a smaller polaron shift, which now amounts to 11 meV and 8 meV for WSe_2 and WS_2 , respectively. These differences are a consequence of the less efficient exciton-phonon coupling in tungsten based TMDs, where the deformation potentials that enter in the exciton-phonon coupling are significantly smaller than the ones of TMDs with molybdenum. Analyzing the sidebands depicted in Fig. 23b and 23d we observe that only two sidebands are resolved, as opposed to the three we found in Fig. 22. The quenching of the sideband that appears at around 50 meV in MoSe_2 and MoS_2 , is a

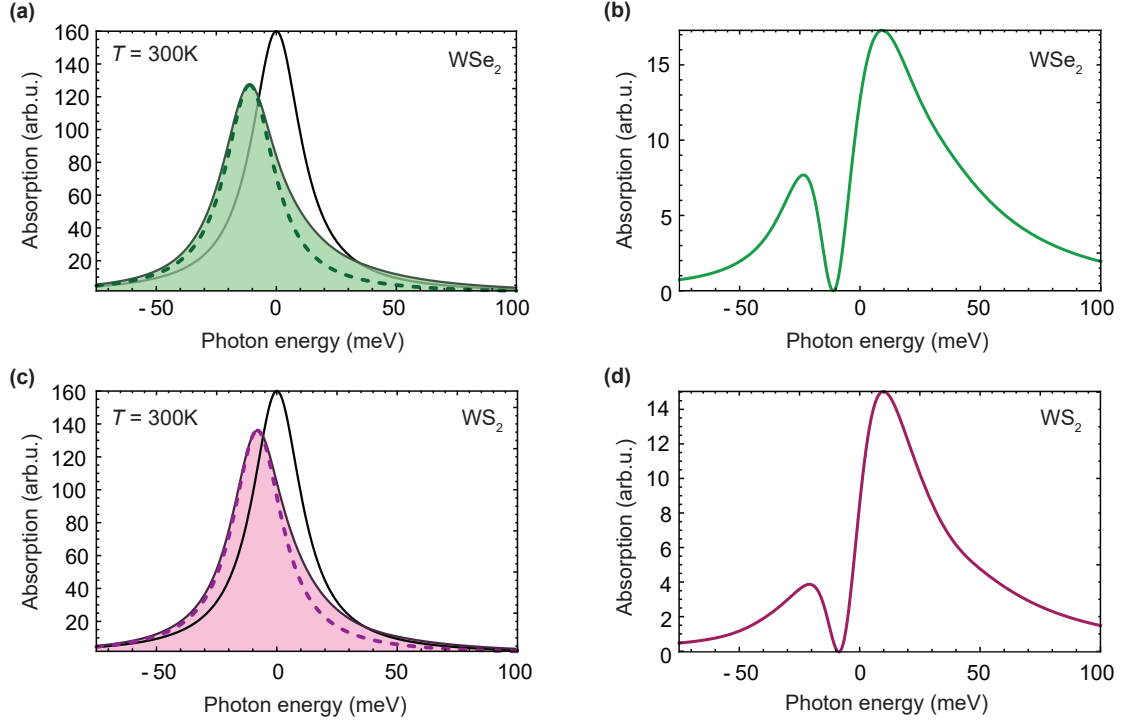


Figure 23: **WX_2 absorption spectra.** The four panels depict analogous results to the ones of Fig. 22 only this time for WSe_2 and WS_2 .

consequence of a less efficient coupling to optical phonons and is responsible for the less asymmetric absorption spectrum in TMDs with tungsten. Moreover, we once again find higher phonon energies in materials with sulfur, resulting in smaller phonon population, and reduced sidebands. The contribution of intervalley processes is mainly due to acoustic phonons, as a consequence of the smaller deformation potentials of processes involving optical phonons. Since in intervalley scattering acoustic and optical phonons are treated in a similar manner to intravalley processes involving optical phonons, we find that the contribution to the absorption spectrum from intervalley acoustic phonons resembles the contribution of optical phonons depicted in Fig. 22b. Also, we found that although intervalley scattering is of great importance in determining the homogeneous linewidth in these materials (cf. Fig. 21), its role is less significant in the polaron shift and phonon sidebands.

So far we have compared the absorption spectra of different TMDs at a temperature of $T = 300\text{K}$. It should be clear, however, that the polaron shift and the formation of phonon sidebands are temperature dependent phenomena, after all the phonon occupation number enters directly in the definition of the self-energy. In what follows we study how the absorption spectra of the studied TMDs changes with temperature. In Fig. 24a we depict the absorption spectrum of MoSe_2 normalized to its maximum for different temperatures ranging from 1 K to 300 K; once again the energy is measured relatively to the position of the absorption peak in the absence of phonons. Starting at $T = 1\text{K}$, we note that at such a low

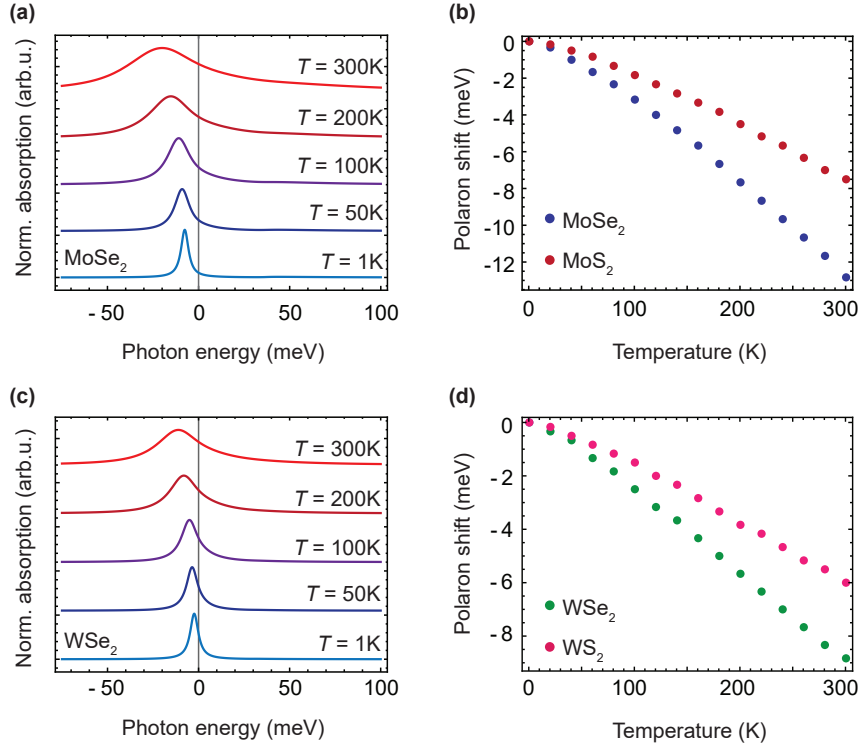


Figure 24: **Polaron shift.** Panel (a) shows the dependence of the absorption resonance due to the $1s$ exciton in MoSe_2 as a function of temperature. In panel (b), the polaron shift, defined as the difference in the position of the absorption peak at a given temperature and at $T = 0$ K, is depicted as a function of temperature for MoSe_2 and MoS_2 . Panels (c) and (d) present analogous results for WSe_2 and WS_2 .

temperature the phonon occupation number is effectively zero, however, processes involving spontaneous emission of phonons still produce a significant polaron shift. As the temperature grows and the phonon population increases, the absorption peak becomes progressively more red shifted, the lineshape of the resonance becomes more asymmetric and the overall linewidth increases. In Fig. 24b the shift of the resonance relative to its position at $T = 0$ K (the polaron shift) is depicted as a function of temperature for the two considered molybdenum based TMDs. Due to the more efficient coupling with phonons in MoSe_2 it presents a larger polaron shift than MoS_2 .

Displayed in Fig. 24c is the absorption spectrum of WSe_2 at different temperatures. At $T = 1$ K we observe that, like in the previous case, the resonance is already shifted relative to its position when phonons are not accounted for, due to processes involving spontaneous phonon emission; yet, the red shift is significantly smaller than the one found in MoSe_2 . At first this may seem surprising, since in WSe_2 intervalley scattering with emission of phonons is efficient even at small temperatures, which could give an extra contribution to the polaron shift. However, by artificially selecting only intervalley scattering channels we observed that these processes have a greater impact on the linewidth of the resonance than on its position. As the temperature grows we once again observe an increased linewidth and red shift of the absorption peak. In Fig. 24d we present the polaron shift as a function of the temperature for WSe_2 and

WS₂. As expected, and in line with the results found for molybdenum based TMDs, the specimen with sulfur presents a smaller polaron shift due to the smaller phonon populations.

5.3 Comparison with experimental data

As an application of the results we have obtained we will try to describe the experimental data presented in Ref. [122], where the shift of the 1s excitonic resonance of WS₂ was measured as a function of temperature. To accurately describe this effect we must consider something so far ignored: the temperature dependence of the band gap. As the temperature increases two distinct effects take place: i) on the one hand, as we have just seen, the exciton-phonon interaction modifies the position of the resonance, red shifting the excitonic peak; ii) on the other hand, the band gap decreases as the temperature increases, also contributing to the excitonic resonance shift. A microscopic description of the dependence of the band gap with temperature is by no means a simple task, and is beyond the scope of this work; as a consequence, we will describe this effect in a phenomenological way. One of the most common ways of describing the temperature evolution of the band gap in semiconductors is through the Varshni empirical model [123]. Due to the lack of physical meaning of the parameters in this model, other more satisfactory options have been developed [124]. One of those alternatives, capable of producing better descriptions than the Varshni relation, is the semiempirical vibronic model of Huang and Rhys [125], which takes into account the effect of phonons and changes in the bonding length [126]:

$$E_g(T) = E_g(0) - S\langle\hbar\omega_A\rangle \left[\coth \frac{\langle\hbar\omega_A\rangle}{2k_B T} - 1 \right]. \quad (5.15)$$

Here, $E_g(T)$ is the magnitude of the band gap at a temperature T , $\langle\hbar\omega\rangle$ is a parameter related with the average acoustic phonon energy (about 10 meV [126]), k_B is the Boltzmann constant, and S is a fitting parameter which describes the electron-phonon coupling. The expression for the 1s resonance position as a function of T , relatively to its position at $T = 0$ K, which we label as $\Delta E_X^{\text{Total}}$, reads:

$$\begin{aligned} \Delta E_X^{\text{Total}}(T) &= \Delta E_X(T) + \Delta E_g(T) \\ &= \Delta E_X(T) - S\langle\hbar\omega_A\rangle \left[\coth \frac{\langle\hbar\omega_A\rangle}{2k_B T} - 1 \right] \end{aligned} \quad (5.16)$$

where $\Delta E_X(T)$ is the red shift of the exciton line due to exciton-phonon coupling that we computed above.

Using Eq. (5.16) and the results of Fig. 24d, we performed a fit to the experimental data of Ref. [122]. The comparison between our theoretical description and the experimental results is depicted in Figure 25; the resulting values of the fit parameters are $S = 1.63$ and $\langle\hbar\omega_A\rangle = 15.9$ meV. Inspecting Figure 25 we note that the experimental points are well fitted by a combination of the Huang-Rhys model with the

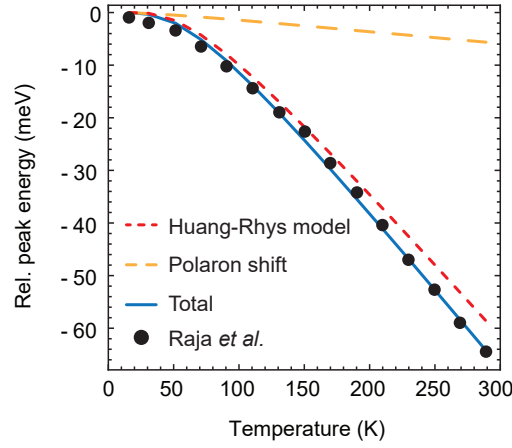


Figure 25: **Polaron shift.** Comparison between the fit obtained with Eq. (5.16) and the experimental data of Ref. [122] for WS_2 . An excellent agreement between the theoretical description and the experimental points is evident. Also depicted are the isolated contributions of the polaron shift, and the gap renormalization described with the Huang-Rhys model. The values of the fitting parameters are $S = 1.63$ and $\langle \hbar\omega_A \rangle = 15.9$ meV.

polaron shift. At room temperature the gap renormalization is responsible for a shift of approximately 60 meV while the polaron shift contributes with approximately 10 meV. Although the evolution of the band gap clearly gives the main contribution to the red shift of the exciton resonance, the shift due to exciton-phonon coupling is still relevant. We note that we considered the contribution of coupling through the deformation potential mechanism only, yet the piezoelectric and Fröhlich mechanisms, although less relevant, could still yield an additional red shift. The values of the fitting parameters, which we recall to be $S = 1.63$ and $\langle \hbar\omega_A \rangle = 15.9$ meV, are in line with results previously found in the literature for other TMDs. In Refs. [126, 127], where MoSe_2 was studied, a value of $\langle \hbar\omega_A \rangle = 11.6$ meV was found. Noting that WS_2 presents higher phonon energies than MoSe_2 , we consider our value of 15.9 meV to be a reasonable one. In Ref. [126] a value of $S = 1.93$ was found for MoSe_2 , but values between 3 and 4 have also been reported [127]; thus our value of $S = 1.63$ roughly agrees with the ones found in previous works.

5.4 Overview

In this section we have studied the effect of the exciton-phonon interaction in the position and lineshape of the lowest lying excitonic absorption peak, referring to the $1s$ state of the A -series. To study these phenomena, we used the formalism of Green's functions. First we introduce the exciton Green's function and computed it in the absence of the exciton-phonon interaction using the equation of motion approach. Afterwards, the case where phonons are accounted for was considered. Once again the equation of motion approach was used, only this time a mean field decoupling was required. In the end we found that

the presence of the exciton-phonon interaction lead to the appearance of a self energy, whose real part produces a red shift of the exciton resonance, while the imaginary part gives rise to phonon side bands, that is, an inhomogeneous broadening of the resonance.

Due to the considered approximations, i.e. the mean field decoupling in the equation of motion approach, our theoretical model is not entirely self consistent, and a phenomenological broadening needs to be introduced in the Green's function and in the self energy (which we assume to be equal in both cases). This broadening is a temperature dependent quantity, whose value we considered to be given by the results of the previous section. When the specific case of four TMDs was considered we found an excellent agreement with Ref. [120] where the same problem was treated with optical Bloch equations solved in a self-consistent Born approximation including non-Markovian processes. To improve our theoretical description it would be required to take the used approximations to higher orders.

In the final part of this section we compared our theoretical findings with the experimentally retrieved data of Ref. [122] for WS_2 . By doing so we observed that two distinct factors contribute to the shift of the absorption peak: i) the exciton-phonon coupling; ii) the temperature dependence of the band gap. As it turns out, the latter is significantly larger than the former, approximately by a factor of 6. In order to describe the temperature dependence of the band gap we used the semi-empirical model of Huang and Rhys, which is a more physically meaningful alternative to the well known Varshni formula. When the temperature dependence of the gap was combined with the exciton-phonon coupling induced shift, a good description of the experimental data was obtained.

Finally, we stress that the description of the absorption spectrum including interaction with phonons is crucial if one wishes to interpret experimental results, especially if these are not obtained at cryogenic temperatures. Even if the position of the absorption peak could be adjusted to match experimental results, the inhomogeneous broadening due to the formation of phonon side bands (especially in the high energy side of the resonance) can only be well described if the interaction with phonons is accounted for.

Final Remarks

In this dissertation, as the title suggested, we explored some optical properties of excitons in 2D materials, with a primary focus on TMDs. Throughout the four main sections of the text different topics were discussed, ranging from the computation of the optical conductivity of a TMD subject to excitonic effects, to the details of exciton-phonon interactions, employing different techniques along the way.

In Section 2 we studied a TMD near a magnetic material and observed that the magnetic proximity effect breaks the time-reversal symmetry, unlocking a finite Hall response even in the absence of an external magnetic field. Moreover, when the conductivity was computed, we observed the well known valley selectivity in the absorption of circularly polarized light, and how the absorption spectrum is essentially due to the excitation of s -states of the excitonic series. In Section 3 we focused on the p -states, which, although absent in interband spectroscopy measurements, can still be studied in pump-probe experiments. Starting from a microscopic definition of the polarizability due to transitions from the $1s$ state to the p -states, we computed the associated dielectric function and conductivity and compared it with experimental data; the role of the $1s$ exciton density and the relevance of exciton-exciton interactions was also discussed. The effect of exciton-phonon coupling, which is crucial to describe optical properties at finite temperature, was the subject of Sections 4 and 5. There, we observed that in TMDs with molybdenum the $1s$ excitonic resonance presents a homogeneous linewidth which increases approximately linearly with temperature, with an exponential correction at high temperatures, while for TMDs with tungsten the linewidth deviates from a linear dependence even at low temperatures. Moreover, we also studied how the resonance of the $1s$ state becomes increasingly more inhomogeneous and increasingly more red shifted as the temperature increases. One of the main takeaway messages of these two sections was the different interaction of excitons with phonons in Mo and W based TMDs, as a result of the formation of momentum dark excitons below the optically bright one in TMDs containing tungsten.

Regarding the technical aspects of the text, we described the exciton problem with the Wannier equation, which we obtained from the BSE. To obtain the binding energies and wave functions of the desired

exciton states we solved the Wannier equation by i) diagonalizing the Hamiltonian in a gaussian basis, ii) numerically solving the differential equation using a shooting algorithm and iii) employing a variational approach using two different *ansätze*, one with the combination of two exponentials, and another using a single exponential; the latter allowed us to obtain an analytical expression for the binding energy of the 1s state since an analytical formula for the associated variational parameter was also found. To compute the optical response of the studied systems we used Fermi's golden rule as well as the formalism of Green's functions.

As future lines of research, it would be interesting to expand the ideas presented in this dissertation to the case of bilayers, and even twisted bilayers. How would the optical spectra change? What would be the role of interlayer excitons? How would the twist angle and the temperature influence the properties of the system? Further studying how these systems and their optical properties can be introduced in novel research areas, be it quantum information, nanodevices, etc. would also be intriguing.

Bibliography

- [1] J. M. Lourenço. *The NOVAthesis L^AT_EX Template User's Manual*. NOVA University Lisbon. 2021. url: <https://github.com/joaomlourenco/novathesis/raw/master/template.pdf> (cit. on p. iii).
- [2] R. G. Dickinson and L. Pauling. "The crystal structure of molybdenite". In: *Journal of the American Chemical Society* 45.6 (1923), pp. 1466–1471 (cit. on p. 1).
- [3] J. A. Wilson and A. Yoffe. "The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties". In: *Advances in Physics* 18.73 (1969), pp. 193–335 (cit. on pp. 1, 2).
- [4] S. Manzeli et al. "2D transition metal dichalcogenides". In: *Nature Reviews Materials* 2.8 (2017), pp. 1–15 (cit. on pp. 1–3).
- [5] R. Frindt and A. Yoffe. "Physical properties of layer structures: optical properties and photoconductivity of thin crystals of molybdenum disulphide". In: *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 273.1352 (1963), pp. 69–83 (cit. on p. 1).
- [6] P. Joensen, R. Frindt, and S. R. Morrison. "Single-layer MoS₂". In: *Materials research bulletin* 21.4 (1986), pp. 457–461 (cit. on p. 1).
- [7] K. S. Novoselov et al. "Electric field effect in atomically thin carbon films". In: *science* 306.5696 (2004), pp. 666–669 (cit. on p. 1).
- [8] F. Xia et al. "Two-dimensional material nanophotonics". In: *Nature Photonics* 8.12 (2014), pp. 899–907 (cit. on pp. 1, 2).
- [9] J. D. Caldwell et al. "Photonics with hexagonal boron nitride". In: *Nature Reviews Materials* 4.8 (2019), pp. 552–567 (cit. on p. 1).

- [10] C. R. Dean et al. "Boron nitride substrates for high-quality graphene electronics". In: *Nature nanotechnology* 5.10 (2010), pp. 722–726 (cit. on p. 1).
- [11] S. Dai et al. "Tunable phonon polaritons in atomically thin van der Waals crystals of boron nitride". In: *Science* 343.6175 (2014), pp. 1125–1129 (cit. on p. 1).
- [12] K. Watanabe, T. Taniguchi, and H. Kanda. "Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal". In: *Nature materials* 3.6 (2004), pp. 404–409 (cit. on p. 1).
- [13] J. Henriques et al. "Optical absorption of single-layer hexagonal boron nitride in the ultraviolet". In: *Journal of Physics: Condensed Matter* 32.2 (2019), p. 025304 (cit. on pp. 1, 23).
- [14] A. Carvalho et al. "Phosphorene: from theory to applications". In: *Nature Reviews Materials* 1.11 (2016), pp. 1–16 (cit. on pp. 1, 14).
- [15] A. Rodin, A. Carvalho, and A. C. Neto. "Strain-induced gap modification in black phosphorus". In: *Physical review letters* 112.17 (2014), p. 176801 (cit. on p. 1).
- [16] J.-W. Jiang and H. S. Park. "Negative poisson's ratio in single-layer black phosphorus". In: *Nature communications* 5.1 (2014), pp. 1–7 (cit. on p. 1).
- [17] H. Yuan et al. "Polarization-sensitive broadband photodetector using a black phosphorus vertical p–n junction". In: *Nature nanotechnology* 10.8 (2015), pp. 707–713 (cit. on p. 1).
- [18] J. Ribeiro-Soares et al. "Group theory analysis of phonons in two-dimensional transition metal dichalcogenides". In: *Physical Review B* 90.11 (2014), p. 115438 (cit. on p. 2).
- [19] R. Bromley, R. Murray, and A. Yoffe. "The band structures of some transition metal dichalcogenides. III. Group VIA: trigonal prism materials". In: *Journal of Physics C: Solid State Physics* 5.7 (1972), p. 759 (cit. on p. 2).
- [20] O. Lopez-Sanchez et al. "Ultrasensitive photodetectors based on monolayer MoS₂". In: *Nature nanotechnology* 8.7 (2013), pp. 497–501 (cit. on p. 3).
- [21] F. K. Perkins et al. "Chemical vapor sensing with monolayer MoS₂". In: *Nano letters* 13.2 (2013), pp. 668–673 (cit. on p. 3).
- [22] G. Wang et al. "Colloquium: Excitons in atomically thin transition metal dichalcogenides". In: *Rev. Mod. Phys.* 90.2 (2018), p. 021001 (cit. on pp. 3, 4, 50).
- [23] G. Sallen et al. "Robust optical emission polarization in MoS₂ monolayers through selective valley excitation". In: *Physical Review B* 86.8 (2012), p. 081301 (cit. on p. 3).

- [24] A. Molina-Sánchez et al. “Effect of spin-orbit interaction on the optical spectra of single-layer, double-layer, and bulk MoS₂”. In: *Physical Review B* 88.4 (2013), p. 045412 (cit. on p. 3).
- [25] K. Kosmider, J. W. González, and J. Fernández-Rossier. “Large spin splitting in the conduction band of transition metal dichalcogenide monolayers”. In: *Physical Review B* 88.24 (2013), p. 245436 (cit. on p. 3).
- [26] T. Cao et al. “Valley-selective circular dichroism of monolayer molybdenum disulphide”. In: *Nature communications* 3.1 (2012), pp. 1–5 (cit. on p. 3).
- [27] K. Behnia. “Polarized light boosts valleytronics”. In: *Nature nanotechnology* 7.8 (2012), pp. 488–489 (cit. on p. 3).
- [28] T. Cheiwchanchamnangij and W. R. Lambrecht. “Quasiparticle band structure calculation of monolayer, bilayer, and bulk MoS₂”. In: *Physical Review B* 85.20 (2012), p. 205302 (cit. on pp. 3, 4).
- [29] R. Holm and W. Meissner. “Messungen mit Hilfe von flüssigem Helium. XIII”. In: *Zeitschrift für Physik* 74.11-12 (1932), pp. 715–735 (cit. on p. 7).
- [30] K. Novoselov et al. “2D materials and van der Waals heterostructures”. In: *Science* 353.6298 (2016), p. 1164 (cit. on p. 7).
- [31] A. I. Buzdin. “Proximity effects in superconductor-ferromagnet heterostructures”. In: *Rev. Mod. Phys.* 77.3 (2005), p. 935 (cit. on p. 7).
- [32] I. Žutić et al. “Proximitized materials”. In: *Materials Today* 22 (2019), pp. 85–107 (cit. on p. 7).
- [33] Z. Wang et al. “Proximity-induced ferromagnetism in graphene revealed by the anomalous Hall effect”. In: *Phys. Rev. Lett.* 114.1 (2015), p. 016603 (cit. on p. 7).
- [34] L. Fu and C. L. Kane. “Superconducting proximity effect and Majorana fermions at the surface of a topological insulator”. In: *Phys. Rev. Lett.* 100.9 (2008), p. 096407 (cit. on p. 7).
- [35] D. Xiao et al. “Coupled spin and valley physics in monolayers of MoS₂ and other group-VI dichalcogenides”. In: *Physical review letters* 108.19 (2012), p. 196802 (cit. on pp. 7, 56, 99, 103, 105).
- [36] B. Scharf et al. “Magnetic proximity effects in transition-metal dichalcogenides: converting excitons”. In: *Phys. Rev. Lett.* 119.12 (2017), p. 127403 (cit. on pp. 7, 10).
- [37] D. MacNeill et al. “Breaking of valley degeneracy by magnetic field in monolayer MoSe₂”. In: *Phys. Rev. Lett.* 114.3 (2015), p. 037401 (cit. on p. 7).

- [38] A. V. Stier et al. “Exciton diamagnetic shifts and valley Zeeman effects in monolayer WS₂ and MoS₂ to 65 Tesla”. In: *Nat. Comm.* 7 (2016), p. 10643 (cit. on p. 7).
- [39] A. Arora et al. “Valley Zeeman splitting and valley polarization of neutral and charged excitons in monolayer MoTe₂ at high magnetic fields”. In: *Nano Letters* 16.6 (2016), pp. 3624–3629 (cit. on p. 7).
- [40] C. Zhao et al. “Enhanced valley splitting in monolayer WSe₂ due to magnetic exchange field”. In: *Nat. Nano.* 12 (2017), p. 757 (cit. on pp. 7, 8).
- [41] D. Zhong et al. “Van der Waals engineering of ferromagnetic semiconductor heterostructures for spin and valleytronics”. In: *Science Advances* 3 (2017), e1603113 (cit. on pp. 7, 8).
- [42] K. L. Seyler et al. “Valley manipulation by optically tuning the magnetic proximity effect in WSe₂/CrI₃ heterostructures”. In: *Nano Lett.* 18 (2018), p. 3823 (cit. on p. 8).
- [43] J. Qi et al. “Giant and tunable valley degeneracy splitting in MoTe₂”. In: *Phys. Rev. B* 92.12 (2015), p. 121403 (cit. on p. 8).
- [44] L. Xu et al. “Large valley splitting in monolayer WS₂ by proximity coupling to an insulating antiferromagnetic substrate”. In: *Phys. Rev. B* 97.4 (2018), p. 041405 (cit. on p. 8).
- [45] N. Li et al. “Large valley polarization in monolayer MoTe₂ on a magnetic substrate”. In: *Phys. Chem. Chem. Phys.* 20.5 (2018), pp. 3805–3812 (cit. on p. 8).
- [46] Q. Zhang et al. “Large Spin-Valley Polarization in Monolayer MoTe₂ on Top of EuO (111)”. In: *Advanced Materials* 28.5 (2016), pp. 959–966 (cit. on p. 8).
- [47] K. Zollner, P. E. F. Junior, and J. Fabian. “Proximity exchange effects in MoSe₂ and WSe₂ heterostructures with CrI₃: Twist angle, layer, and gate dependence”. In: *Phys. Rev. B* 100 (2019), p. 085128 (cit. on p. 8).
- [48] K. Zollner, P. E. F. Junior, and J. Fabian. “Giant proximity exchange and valley splitting in transition metal dichalcogenide/hBN/(Co, Ni) heterostructures”. In: *Phys. Rev. B* 101 (8 2020), p. 085112 (cit. on pp. 8, 11, 12).
- [49] F. Langer et al. “Lightwave valleytronics in a monolayer of tungsten diselenide”. In: *Nature* 557.7703 (2018), pp. 76–80 (cit. on p. 10).
- [50] Y. Ye et al. “Electrical generation and control of the valley carriers in a monolayer transition metal dichalcogenide”. In: *Nature nanotechnology* 11.7 (2016), pp. 598–602 (cit. on p. 10).

- [51] J. R. Schaibley et al. “Valleytronics in 2D materials”. In: *Nature Reviews Materials* 1.11 (2016), pp. 1–15 (cit. on p. 10).
- [52] A. Kormányos et al. “k.p theory for two-dimensional transition metal dichalcogenide semiconductors”. In: *2D Materials* 2 (2015), p. 022001 (cit. on pp. 11, 43, 55, 56, 78).
- [53] J. C. G. Henriques and N. M. R. Peres. “Excitons in phosphorene: A semi-analytical perturbative approach”. In: *Phys. Rev. B* 101 (3 2020), p. 035406 (cit. on p. 14).
- [54] E. Malic et al. “Dark excitons in transition metal dichalcogenides”. In: *Physical Review Materials* 2.1 (2018), p. 014002 (cit. on pp. 19, 50, 51, 55).
- [55] H. Haug and S. W. Koch. *Quantum theory of the optical and electronic properties of semiconductors*. World Scientific Publishing Company, 2009 (cit. on p. 21).
- [56] S. Rytova. “The Screened Potential of a Point Charge in a Thin Film”. In: *Moscow University Physics Bulletin* 22.30 (1967) (cit. on pp. 22, 53, 114).
- [57] L. Keldysh. “Coulomb interaction in thin semiconductor and semimetal films”. In: *Sov. J. of Exp. and Theor. Phys. Lett.* 29 (1979), p. 658 (cit. on pp. 22, 53).
- [58] P. Cudazzo, I. V. Tokatly, and A. Rubio. “Dielectric screening in two-dimensional insulators: Implications for excitonic and impurity states in graphane”. In: *Physical Review B* 84.8 (2011), p. 085406 (cit. on pp. 22, 43, 53, 117).
- [59] J. R. Mohallem. “A further study on the discretisation of the Griffin-Hill-Wheeler equation”. In: *Zeitschrift für Physik D Atoms, Molecules and Clusters* 3.4 (1986), pp. 339–344 (cit. on p. 23).
- [60] J. J. Griffin and J. A. Wheeler. “Collective motions in nuclei by the method of generator coordinates”. In: *Physical Review* 108.2 (1957), p. 311 (cit. on p. 23).
- [61] G. Catarina, N. M. Peres, and J. Fernández-Rossier. “Magneto-optical Kerr effect in spin split two-dimensional massive Dirac materials”. In: *2D Materials* 7.2 (2020), p. 025011 (cit. on p. 30).
- [62] A. Perov, L. Solnyshkova, and D. Khomitsky. “Terahertz radiation-induced conductivity, Kerr and Faraday angles, and spin textures in a two-dimensional electron gas with spin-orbit coupling subjected to a high magnetic field and periodic potential”. In: *Phys. Rev. B* 82 (2010), p. 165328 (cit. on p. 31).
- [63] C. Yang et al. “Spectral dependence of spin photocurrent and current-induced spin polarization in an InGaAs/InAlAs two-dimensional electron gas”. In: *Phys. Rev. Lett.* 96.18 (2006), p. 186605 (cit. on p. 31).

- [64] F. Cadiz et al. “Excitonic linewidth approaching the homogeneous limit in MoS₂-based van der Waals heterostructures”. In: *Physical Review X* 7.2 (2017), p. 021026 (cit. on pp. 31, 69).
- [65] C. Gong et al. “Discovery of intrinsic ferromagnetism in two-dimensional van der Waals crystals”. In: *Nature* 546.7657 (2017), pp. 265–269 (cit. on p. 31).
- [66] A. Kapitulnik et al. “Polar Kerr effect as probe for time-reversal symmetry breaking in unconventional superconductors”. In: *New Journal of Physics* 11.5 (2009), p. 055060 (cit. on p. 31).
- [67] S. M. Hamidi et al. “Enhanced Polar Magneto-optical Kerr Rotation in Cobalt Thin Film Incorporating Ag Nanoparticles”. In: *J. Supercond. Nov. Magn.* 27 (2014), p. 867 (cit. on p. 31).
- [68] J. Lee, K. F. Mak, and J. Shan. “Electrical control of the valley Hall effect in bilayer MoS₂ transistors”. In: *Nat. Nano.* 11.5 (2016), p. 421 (cit. on p. 31).
- [69] G. Berghäuser and E. Malic. “Analytical approach to excitonic properties of MoS₂”. In: *Physical Review B* 89.12 (2014), p. 125309 (cit. on pp. 33, 50).
- [70] W.-T. Hsu et al. “Dielectric impact on exciton binding energy and quasiparticle bandgap in monolayer WS₂ and WSe₂”. In: *2D Materials* 6.2 (2019) (cit. on p. 33).
- [71] P. Steinleitner et al. “Direct Observation of Ultrafast Exciton Formation in a Monolayer of WSe₂”. In: *Nano Letters* 17.3 (2017) (cit. on p. 33).
- [72] M. Koperski et al. “Optical properties of atomically thin transition metal dichalcogenides: observations and puzzles”. In: *Nanophotonics* 6.6 (2017) (cit. on pp. 33, 50, 68).
- [73] K. Miyajima, K. Sakaniwa, and M. Sugawara. “Optical transitions from the lowest to higher exciton and biexciton Rydberg states in CuCl”. In: *Physical Review B* 94.19 (2016) (cit. on p. 33).
- [74] G. Berghäuser, A. Knorr, and E. Malic. “Optical fingerprint of dark 2p-states in transition metal dichalcogenides”. In: *2D Materials* 4.1 (2016) (cit. on p. 33).
- [75] C.-K. Yong et al. “Valley-dependent exciton fine structure and Autler–Townes doublets from Berry phases in monolayer MoSe₂”. In: *Nature Materials* 18.10 (2019) (cit. on p. 33).
- [76] G. Berghäuser et al. “Mapping of the dark exciton landscape in transition metal dichalcogenides”. In: *Physical Review B* 98.2 (2018) (cit. on p. 33).
- [77] P. Merkl et al. “Ultrafast transition between exciton phases in van der Waals heterostructures”. In: *Nature Materials* 18.7 (2019) (cit. on p. 33).
- [78] C. Poellmann et al. “Resonant internal quantum transitions and femtosecond radiative decay of excitons in monolayer WSe₂”. In: *Nature Materials* 14.9 (2015) (cit. on pp. 33, 43, 45–48).

- [79] R. Dick. *Advanced Quantum Mechanics*. Springer, 2012 (cit. on pp. 34, 118).
- [80] A. Dalgarno, J. T. Lewis, and D. R. Bates. “The exact calculation of long-range forces between atoms by perturbation theory”. In: *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* 233.1192 (1955) (cit. on p. 35).
- [81] B. R. Desai. *Quantum Mechanics with Basic Field Theory*. Cambridge: Cambridge University Press, 2009. doi: 10.1017/CB09780511813979 (cit. on p. 35).
- [82] P. W. Fowler. “Energy, polarizability and size of confined one-electron systems”. In: *Molecular Physics* 53.4 (1984) (cit. on p. 36).
- [83] M. Karplus. “Variation-Perturbation Approach to the Interaction of Radiation with Matter”. In: *The Journal of Chemical Physics* 37.11 (1962), pp. 2723–2724 (cit. on pp. 36, 40).
- [84] M. Karplus and H. J. Kolker. “A Variation-Perturbation Approach to the Interaction of Radiation with Atoms and Molecules”. In: *The Journal of Chemical Physics* 39.6 (1963) (cit. on pp. 36, 40).
- [85] J. Izaac and J. Wang. *Computational Quantum Mechanics*. Undergraduate Lecture Notes in Physics. Springer International Publishing, 2018 (cit. on p. 37).
- [86] G. V. Berghe, V. Fack, and H. E. D. Meyer. “Numerical methods for solving radial Schrödinger equations”. In: *Journal of Computational and Applied Mathematics* 28 (1989) (cit. on p. 37).
- [87] B. R. Johnson. “New numerical methods applied to solving the one-dimensional eigenvalue problem”. In: *The Journal of Chemical Physics* 67.9 (1977) (cit. on p. 37).
- [88] B. R. Johnson. “The renormalized Numerov method applied to calculating bound states of the coupled-channel Schrödinger equation”. In: *The Journal of Chemical Physics* 69.10 (1978) (cit. on p. 37).
- [89] T. G. Pedersen. “Exciton Stark shift and electroabsorption in monolayer transition-metal dichalcogenides”. In: *Physical Review B* 94.12 (2016), p. 125424 (cit. on pp. 39, 53, 54).
- [90] L. Chao-Cador and E. Ley-Koo. “Two-dimensional hydrogen atom confined in circles, angles, and circular sectors”. In: *International Journal of Quantum Chemistry* 103.4 (2005) (cit. on p. 40).
- [91] B. Munkhbat et al. “Transition metal dichalcogenide metamaterials with atomic precision”. In: *Nature Communications* 11.1 (2020), p. 4604 (cit. on p. 40).
- [92] N. Aquino, G. Campoy, and A. Flores-Riveros. “Accurate energy eigenvalues and eigenfunctions for the two-dimensional confined hydrogen atom”. In: *International Journal of Quantum Chemistry* 103.3 (2005) (cit. on p. 40).

-
- [93] R. A. Kaindl et al. “Transient terahertz spectroscopy of excitons and unbound carriers in quasi-two-dimensional electron-hole gases”. In: *Physical Review B* 79 (4 2009) (cit. on p. 43).
 - [94] H. Gu et al. “Layer-dependent dielectric and optical properties of centimeter-scale 2D WSe₂: evolution from a single layer to few layers”. In: *Nanoscale* 11 (47 2019) (cit. on p. 43).
 - [95] I. Epstein et al. “Near-Unity Light Absorption in a Monolayer WS₂ Van der Waals Heterostructure Cavity”. In: *Nano Letters* 20.5 (2020) (cit. on p. 43).
 - [96] N. Kumar et al. “Exciton-exciton annihilation in MoSe₂ monolayers”. In: *Physical Review B* 89.12 (2014), p. 125427 (cit. on p. 45).
 - [97] K. F. Mak, D. Xiao, and J. Shan. “Light–valley interactions in 2D semiconductors”. In: *Nature Photonics* 12.8 (2018), pp. 451–460 (cit. on p. 50).
 - [98] G. Berghäuser et al. “Mapping of the dark exciton landscape in transition metal dichalcogenides”. In: *Physical Review B* 98.2 (2018), p. 020301 (cit. on p. 50).
 - [99] X.-X. Zhang et al. “Experimental evidence for dark excitons in monolayer WSe₂”. In: *Physical review letters* 115.25 (2015), p. 257403 (cit. on p. 50).
 - [100] H. Yu et al. “Exploration of the bright and dark exciton landscape and fine structure of MoS₂ using G₀W₀-BSE”. In: *Physical Review B* 100.12 (2019), p. 125413 (cit. on p. 50).
 - [101] M. Selig et al. “Excitonic linewidth and coherence lifetime in monolayer transition metal dichalcogenides”. In: *Nature communications* 7.1 (2016), pp. 1–6 (cit. on pp. 51, 67–69).
 - [102] M. F. M. Quintela and N. M. Peres. “A colloquium on the variational method applied to excitons in 2D materials”. In: *The European Physical Journal B* 93.12 (2020), pp. 1–16 (cit. on p. 53).
 - [103] T. Olsen et al. “Simple screened hydrogen model of excitons in two-dimensional materials”. In: *Physical review letters* 116.5 (2016), p. 056401 (cit. on p. 54).
 - [104] T. Deilmann and K. S. Thygesen. “Finite-momentum exciton landscape in mono- and bilayer transition metal dichalcogenides”. In: *2D Materials* 6.3 (2019), p. 035003 (cit. on p. 55).
 - [105] M. Palummo, M. Bernardi, and J. C. Grossman. “Exciton radiative lifetimes in two-dimensional transition metal dichalcogenides”. In: *Nano letters* 15.5 (2015), pp. 2794–2800 (cit. on p. 60).
 - [106] G. Scuri et al. “Large excitonic reflectivity of monolayer MoSe₂ encapsulated in hexagonal boron nitride”. In: *Physical review letters* 120.3 (2018), p. 037402 (cit. on p. 60).
 - [107] M. Selig. PhD thesis. Technische Universität Berlin (Germany), 2018 (cit. on p. 60).

- [108] S Shree et al. "Observation of exciton-phonon coupling in MoSe 2 monolayers". In: *Physical Review B* 98.3 (2018), p. 035302 (cit. on pp. 60, 61, 64, 68, 72, 78).
- [109] M. Cardona and Y. Y. Peter. *Fundamentals of semiconductors*. Springer, 2005 (cit. on p. 61).
- [110] K. Kaasbjerg, K. S. Thygesen, and K. W. Jacobsen. "Phonon-limited mobility in n-type single-layer MoS 2 from first principles". In: *Physical Review B* 85.11 (2012), p. 115317 (cit. on p. 61).
- [111] K. Kaasbjerg, K. S. Thygesen, and A.-P. Jauho. "Acoustic phonon limited mobility in two-dimensional semiconductors: Deformation potential and piezoelectric scattering in monolayer MoS 2 from first principles". In: *Physical Review B* 87.23 (2013), p. 235312 (cit. on p. 61).
- [112] Z. Jin et al. "Intrinsic transport properties of electrons and holes in monolayer transition-metal dichalcogenides". In: *Physical Review B* 90.4 (2014), p. 045422 (cit. on pp. 61, 64, 65, 68, 78).
- [113] X. Li et al. "Intrinsic electrical transport properties of monolayer silicene and MoS 2 from first principles". In: *Physical Review B* 87.11 (2013), p. 115418 (cit. on p. 61).
- [114] M. Feierabend et al. "Proposal for dark exciton based chemical sensors". In: *Nature communications* 8.1 (2017), pp. 1–6 (cit. on p. 69).
- [115] Q. Ma et al. "Tunable Optical Properties of 2D Materials and Their Applications". In: *Advanced Optical Materials* 9.2 (2021), p. 2001313 (cit. on p. 69).
- [116] R. Lv et al. "Transition metal dichalcogenides and beyond: synthesis, properties, and applications of single-and few-layer nanosheets". In: *Accounts of chemical research* 48.1 (2015), pp. 56–64 (cit. on p. 69).
- [117] T. Mueller and E. Malic. "Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors". In: *npj 2D Materials and Applications* 2.1 (2018), pp. 1–12 (cit. on p. 69).
- [118] R. A. Jishi. *Feynman diagram techniques in condensed matter physics*. Cambridge University Press, 2013 (cit. on pp. 71, 127, 130, 134).
- [119] H. Bruus and K. Flensberg. *Many-body quantum theory in condensed matter physics: an introduction*. Oxford university press, 2004 (cit. on pp. 71, 130, 134).
- [120] D. Christiansen et al. "Phonon sidebands in monolayer transition metal dichalcogenides". In: *Physical review letters* 119.18 (2017), p. 187402 (cit. on pp. 72, 77, 85).

-
- [121] Y Takeda and T. Pearsall. "Failure of Matthiessen's rule in the calculation of carrier mobility and alloy scattering effects in GaO. 47InO. 53As". In: *Electronics Letters* 17.16 (1981), pp. 573–574 (cit. on p. 77).
 - [122] A. Raja et al. "Enhancement of exciton–phonon scattering from monolayer to bilayer WS₂". In: *Nano letters* 18.10 (2018), pp. 6135–6143 (cit. on pp. 83–85).
 - [123] Y. P. Varshni. "Temperature dependence of the energy gap in semiconductors". In: *physica* 34.1 (1967), pp. 149–154 (cit. on p. 83).
 - [124] K. O'donnell and X Chen. "Temperature dependence of semiconductor band gaps". In: *Applied physics letters* 58.25 (1991), pp. 2924–2926 (cit. on p. 83).
 - [125] K. Huang and A. Rhys. *Theory of light absorption and non-radiative transitions in F-centres*. World Scientific, 2000, pp. 74–92 (cit. on p. 83).
 - [126] S. Tongay et al. "Thermally driven crossover from indirect toward direct bandgap in 2D semiconductors: MoSe₂ versus MoS₂". In: *Nano letters* 12.11 (2012), pp. 5576–5580 (cit. on pp. 83, 84).
 - [127] B. K. Choi et al. "Temperature dependence of band gap in MoSe₂ grown by molecular beam epitaxy". In: *Nanoscale research letters* 12.1 (2017), pp. 1–7 (cit. on p. 84).
 - [128] G.-B. Liu et al. "Three-band tight-binding model for monolayers of group-VIB transition metal dichalcogenides". In: *Physical Review B* 88.8 (2013), p. 085433 (cit. on pp. 99, 100, 102–104).
 - [129] J. Á. Silva-Guillén, P. San-Jose, and R. Roldán. "Electronic band structure of transition metal dichalcogenides from ab initio and slater–koster tight-binding model". In: *Applied Sciences* 6.10 (2016), p. 284 (cit. on pp. 99, 100).
 - [130] G.-B. Liu et al. "Electronic structures and theoretical modelling of two-dimensional group-VIB transition metal dichalcogenides". In: *Chemical Society Reviews* 44.9 (2015), pp. 2643–2663 (cit. on pp. 100, 103).
 - [131] S. Konschuh. "Spin-orbit coupling effects: from graphene to graphite". PhD thesis. 2011 (cit. on p. 102).
 - [132] E Cappelluti et al. "Tight-binding model and direct-gap/indirect-gap transition in single-layer and multilayer MoS₂". In: *Physical Review B* 88.7 (2013), p. 075409 (cit. on p. 102).
 - [133] H. Ochoa and R. Roldán. "Spin-orbit-mediated spin relaxation in monolayer MoS₂". In: *Physical Review B* 87.24 (2013), p. 245421 (cit. on p. 103).

- [134] P.-O. Löwdin. “A note on the quantum-mechanical perturbation theory”. In: *The Journal of Chemical Physics* 19.11 (1951), pp. 1396–1401 (cit. on pp. 103, 105).
- [135] R Winkler et al. *Spin-Orbit Coupling in Two-Dimensional Electron and Hole Systems*. Vol. 41. Springer, 2003 (cit. on pp. 103, 105).
- [136] A. Kormányos et al. “Monolayer MoS 2: Trigonal warping, the Γ valley, and spin-orbit coupling effects”. In: *Physical review b* 88.4 (2013), p. 045416 (cit. on p. 104).
- [137] A. Migdal. “Interaction between electrons and lattice vibrations in a normal metal”. In: *Sov. Phys. JETP* 7.6 (1958), pp. 996–1001 (cit. on p. 133).

Details on the model Hamiltonian

In this appendix we will study in more detail the model Hamiltonian used to describe the physics in the vicinity of the Dirac valleys in TMDs. Our study will be divided into two different instances: first, we will derive an effective Hamiltonian from a three band tight-binding model; then we will explicitly compute the eigenvalues and eigenvectors of the Hamiltonian.

A.1 Tight-binding model

A.1.1 Structure and orbitals

Before we introduce the tight-binding Hamiltonian let us consider the lattice of a general group-VI dichalcogenides MX_2 , with $M = \{\text{Mo, W}\}$ and $X = \{\text{S, Se}\}$. As can be seen in Fig. 26, in the monolayer form, this type of material presents a trigonal prismatic geometry, with two layers of X atoms, separated by a single layer of M atoms [35]. The crystal symmetry of this structure is described by the D_{3h} point group, as opposed to the D_{6h}^4 of the bulk [35, 128]. The most noticeable difference between these two cases is the loss of inversion symmetry in the monolayer limit (although it is recovered when an even number of layer is stacked). When seen from above, the lattice presents a honeycomb structure similar to that of graphene.

Contrary to graphene or hBN, where the band structure is mainly due to s and p orbitals, it is known from first principles calculations that TMDs present a more complex orbital configuration. In these materials, the valence and conduction bands are originated almost entirely by the hybridization of d orbitals of the transition metal with the p orbitals of the chalcogen [129]. In the Dirac valleys, near the top of the valence band, the orbital configuration is dominated by the combinations of the $d_{x^2-y^2}$ and d_{xy} orbitals which hybridize with p_x and p_y orbitals. For the conduction band, the d_{z^2} (also called $d_{3z^2-r^2}$) and p orbitals are the most relevant ones. The role of s orbitals is negligible throughout the entire Brillouin zone.

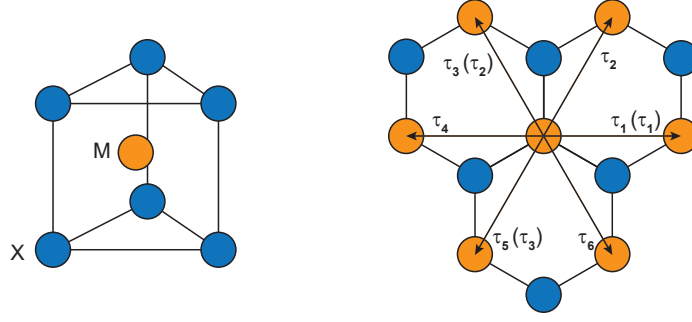


Figure 26: **TMD lattice.** Side and top views of the crystal lattice of a MX_2 TMD. Also represented are the six τ_i vectors which connect the M atom to its closed M neighbors.

As a consequence of the presence of the d orbitals, TMDs experience strong spin-orbit coupling effects.

A.1.2 Tight-binding model

To describe the band structure of the TMD we will first construct a tight-binding Hamiltonian without considering spin-orbit effects. This interaction will be accounted for in a later part of the calculation. The basic premise of a tight-binding model is that an electron in a given orbital is located in the vicinity of its parent ion, but may experience a transition, or hopping, to a an orbital of a nearby ion. The likelihood of these transitions is characterized by the hopping integrals. In order for us to construct the tight-binding Hamiltonian of the TMD we must first choose which orbitals and which hoppings we wish to consider; obviously, increasing the number of orbitals and the number of hoppings yields a more accurate model, but also a more complex one.

Over the years many tight binding Hamiltonians have been developed, containing different numbers of orbitals, and hoppings ranging from the nearest-neighbor to third-nearest-neighbor approximations [130]. These models give descriptions with varying degree of accuracy when they are fitted to *ab initio* calculations. Since in this appendix we are not interested in fitting the dispersion of the tight-binding Hamiltonian to first principles calculations, we will construct the simplest tight-binding description which already allows us to obtain the model Hamiltonian given in the main text. To that end we will account for three orbitals alone; these are the d_{z^2} , the d_{xy} and the $d_{x^2-y^2}$ of the transition metal atoms [128]. Also, we will only consider the contribution from hoppings between metal atoms in a nearest-neighbor approximation. With these approximations, we will obtain a model capable of describing the energy landscape only in the close vicinity of the Dirac valleys. If besides these orbitals we considered the d_{xz} and d_{yz} orbitals of the metal atom, as well as the p_x , p_y and p_z orbitals of the chalcogen, and if we included hoppings between the metal and chalcogen atoms, then the dispersion relation of such a model would be well fitted to *ab initio* results in most of the Brillouin zone [128–130].

Taking into account the aforementioned approximations, we directly write the tight binding Hamiltonian in real space as:

$$H_{\text{TB}} = \sum_{\mathbf{R}} \sum_{i=1}^6 \sum_{\mu, \nu} \langle d_{\mu}, \mathbf{R} | H | d_{\nu}, \mathbf{R} + \boldsymbol{\tau}_i \rangle | d_{\mu}, \mathbf{R} \rangle \langle d_{\nu}, \mathbf{R} + \boldsymbol{\tau}_i | \\ + \sum_{\mathbf{R}} \sum_{\nu} \langle d_{\nu}, \mathbf{R} | H | d_{\nu}, \mathbf{R} \rangle | d_{\nu}, \mathbf{R} \rangle \langle d_{\nu}, \mathbf{R} | + \text{h.c.}, \quad (\text{A.1})$$

where the sum over $\mathbf{R}$ covers the entire lattice, and the vectors $\boldsymbol{\tau}_i$ connect the nearest metal atoms and are depicted in Fig. 26; the indexes μ and ν refer to the different d orbitals that compose our basis, $\{d_{z^2}, d_{xy}, d_{x^2-y^2}\}$. Since this is an orthogonal set of orbitals no overlap terms have to be considered. The first line in the definition of H_{TB} describes the hopping of an electron in the orbital d_{μ} in the metal atom located at $\mathbf{R}$, to the orbital d_{ν} in one of the six closest metal atoms, located at $\mathbf{R} + \boldsymbol{\tau}_i$. The matrix element of the Hamiltonian between these two states is termed the hopping integral, and we compute it in the Slater-Koster two center approximation. For the moment, to simplify the notation, let us relabel the matrix element as $\langle d_{\mu}, \mathbf{R} | H | d_{\nu}, \mathbf{R} + \boldsymbol{\tau}_i \rangle \equiv t_{\mu\nu}^i$. The second term of H_{TB} corresponds to an on-site energy term of the d_{ν} orbital. The matrix element is termed the crystal field, and we set it equal to Δ_{ν} , with $\nu = \{z^2, xy, x^2 - y^2\}$.

To obtain the energy landscape of the tight binding model it is convenient to consider the Hamiltonian in momentum space. To achieve that, we introduce the Fourier representation of the state vectors, that is

$$|\mathbf{R}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} |\mathbf{k}\rangle.$$

Introducing this into Eq. (A.1), and using the orthogonality of plane waves, that is, $\sum_{\mathbf{R}} e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{R}} = N\delta_{\mathbf{k},\mathbf{q}}$, we find

$$H_{\text{TB}} = \sum_{\mathbf{k}} \sum_{i=1}^6 \sum_{\mu, \nu} e^{-i\mathbf{k}\cdot\boldsymbol{\tau}_i} t_{\mu\nu}^i | d_{\mu}, \mathbf{k} \rangle \langle d_{\nu}, \mathbf{k} | \\ + \sum_{\mathbf{k}} \sum_{\nu} \Delta_{\nu} | d_{\nu}, \mathbf{k} \rangle \langle d_{\nu}, \mathbf{k} | + \text{h.c.} \quad (\text{A.2})$$

where the complex exponentials appear from the introduction of the Fourier representation of the state vectors. Note that due the symmetry of the lattice the sum over the six $\boldsymbol{\tau}_i$ can be transformed into a sum over just three of these vectors if one writes $\sum_{i=1}^6 e^{-i\mathbf{k}\cdot\boldsymbol{\tau}_i} = \sum_{i=1}^3 2 \cos \mathbf{k} \cdot \boldsymbol{\tau}_i$ (these three $\boldsymbol{\tau}_i$ are the ones inside parenthesis in Fig. 26). This Hamiltonian can be expressed as $H_{\text{TB}} = \sum_{\mathbf{k}} \Phi_{\mathbf{k}}^{\dagger} H_{\text{TB},\mathbf{k}} \Phi_{\mathbf{k}}$, where

$$\Phi_{\mathbf{k}}^{\dagger} = [|d_{z^2}\rangle, |d_{xy}\rangle, |d_{x^2-y^2}\rangle] \otimes |\mathbf{k}\rangle$$

and

$$H_{\text{TB},\mathbf{k}} = \sum_{i=1}^3 2 \cos \mathbf{k} \cdot \boldsymbol{\tau}_i \begin{pmatrix} t_{z^2,z^2}^i & t_{z^2,xy}^i & t_{z^2,x^2-y^2}^i \\ t_{xy,z^2}^i & t_{xy,xy}^i & t_{xy,x^2-y^2}^i \\ t_{x^2-y^2,z^2}^i & t_{x^2-y^2,xy}^i & t_{x^2-y^2,x^2-y^2}^i \end{pmatrix} + \begin{pmatrix} \Delta_{z^2} & 0 & 0 \\ 0 & \Delta_{xy} & 0 \\ 0 & 0 & \Delta_{x^2-y^2} \end{pmatrix}.$$

At first glance one could consider that in order to obtain $H_{\text{TB},\mathbf{k}}$ a total of 30 parameters are required (9 for each i , and the three crystal fields). However, since $H_{\text{TB},\mathbf{k}}$ has to be hermitian, it is clear that $t_{\mu\nu}^i = (t_{\nu\mu}^i)^*$, reducing the number of independent parameters. Moreover, the symmetry of the problem imposes further restrictions on the hopping parameters; a clear examples of this is the case of t_{z^2,z^2}^i . Since this hopping integral involves in-plane symmetric orbitals aligned along the z -axis it should be clear that its value is the same for the three hopping directions. Although we could determine all the $t_{\mu\nu}^i$ from the $t_{\mu\nu}^1$ based solely on the symmetry operations of the D_{3h} point group [128], similarly to what we just discussed about $t_{z^2,z^2}^1 = t_{z^2,z^2}^2 = t_{z^2,z^2}^3$, we will instead compute the hoppings using Slater-Koster parameters [131, 132]. Denoting the matrix with the hoppings along the i direction by T_i we find:

$$T_1 = \frac{1}{4} \begin{pmatrix} 3V_{dd\delta} + V_{dd\sigma} & 0 & \sqrt{3}(V_{dd\delta} - V_{dd\sigma}) \\ 0 & 4V_{dd\pi} & 0 \\ \sqrt{3}(V_{dd\delta} - V_{dd\sigma}) & 0 & 3V_{dd\sigma} + V_{dd\delta} \end{pmatrix}, \quad (\text{A.3})$$

$$T_2 = \frac{1}{4} \begin{pmatrix} 3V_{dd\delta} + V_{dd\sigma} & \frac{3}{2}(V_{dd\delta} - V_{dd\sigma}) & \frac{\sqrt{3}}{2}(V_{dd\sigma} - V_{dd\delta}) \\ \frac{3}{2}(V_{dd\delta} - V_{dd\sigma}) & V_{dd\pi} + \frac{3}{4}(V_{dd\delta} + 3V_{dd\sigma}) & -\frac{\sqrt{3}}{4}(V_{dd\delta} + 3V_{dd\sigma} - 4V_{dd\pi}) \\ \frac{\sqrt{3}}{2}(V_{dd\sigma} - V_{dd\delta}) & -\frac{\sqrt{3}}{4}(V_{dd\delta} + 3V_{dd\sigma} - 4V_{dd\pi}) & 3V_{dd\pi} + \frac{1}{4}(V_{dd\delta} + 3V_{dd\sigma}) \end{pmatrix}, \quad (\text{A.4})$$

and

$$T_3 = \frac{1}{4} \begin{pmatrix} 3V_{dd\delta} + V_{dd\sigma} & -\frac{3}{2}(V_{dd\delta} - V_{dd\sigma}) & \frac{\sqrt{3}}{2}(V_{dd\sigma} - V_{dd\delta}) \\ -\frac{3}{2}(V_{dd\delta} - V_{dd\sigma}) & V_{dd\pi} + \frac{3}{4}(V_{dd\delta} + 3V_{dd\sigma}) & \frac{\sqrt{3}}{4}(V_{dd\delta} + 3V_{dd\sigma} - 4V_{dd\pi}) \\ \frac{\sqrt{3}}{2}(V_{dd\sigma} - V_{dd\delta}) & \frac{\sqrt{3}}{4}(V_{dd\delta} + 3V_{dd\sigma} - 4V_{dd\pi}) & 3V_{dd\pi} + \frac{1}{4}(V_{dd\delta} + 3V_{dd\sigma}) \end{pmatrix}. \quad (\text{A.5})$$

The matrix with the crystal fields (labeled by H_{Δ}) can be expressed as

$$H_{\Delta} = \begin{pmatrix} \Delta_0 & 0 & 0 \\ 0 & \Delta_2 & 0 \\ 0 & 0 & \Delta_2 \end{pmatrix}. \quad (\text{A.6})$$

Hence, in the Slater-Koster two center framework, we have 5 independent parameters, which are $V_{dd\delta}$, $V_{dd\sigma}$ and $V_{dd\pi}$ from the hoppings and the crystal fields Δ_0 and Δ_2 . Fitting to the spectrum of this Hamiltonian to first principles calculations sets the values of the different parameters. Our next task is to transform this three band Hamiltonian, into an effective two band one.

A.1.3 Low energy effective Hamiltonian

The first step to obtain an effective Hamiltonian in the Dirac valleys is to expand Eq. (A.2) in a Taylor series about the $\mathbf{k} = \mathbf{K}$ or $\mathbf{K}'$ valleys, that is near $\mathbf{k} = (\pm 4\pi/3a, 0)$ with a the lattice constant. Afterwards, one should note that at the Dirac points the wave-vector group is C_{3h} , and the Bloch states have to be eigenstates of C_3 ; that is achieved by chirally combining the orbitals [35, 128, 130]

$$|\psi_c\rangle = |d_{z^2}\rangle, \quad |\psi_v^\tau\rangle = \frac{1}{\sqrt{2}} \left(|d_{x^2-y^2}\rangle + i\tau |d_{xy}\rangle \right),$$

with $\tau = \pm 1$ for the K/K' valleys. The different orbital composition between the two valleys is responsible for the circular dichroism [130, 133] found repeatedly in the main text. In order to rewrite the Hamiltonian with these new state vectors in its basis, we introduce the following unitary transformation

$$U_\tau = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{-\tau i}{\sqrt{2}} & 1 \\ 0 & \frac{\tau i}{\sqrt{2}} & 1 \end{pmatrix}.$$

Applying this transformation to our tight binding Hamiltonian results in the following change of basis

$$\{|d_{z^2}\rangle, |d_{xy}\rangle, |d_{x^2-y^2}\rangle\} \xrightarrow{U_\tau} \{|\psi_c^\tau\rangle, |\psi_v^\tau\rangle, |\psi_v^{-\tau}\rangle\}. \quad (\text{A.7})$$

Explicitly, we write

$$H_{\text{TB},\mathbf{k}}^{\text{new},\tau} = U_\tau H_{\text{TB},\mathbf{k}} U_\tau^{-1}.$$

To transform $H_{\text{TB},\mathbf{k}}^{\text{new}}$ into a 2×2 effective Hamiltonian we use the Löwdin partitioning method [134, 135].

Writing $H_{\text{TB},\mathbf{k}}^{\text{new}}$ as

$$H_{\text{TB},\mathbf{k}}^{\text{new},\tau} = \left(\begin{array}{c|c} H_0 & M \\ \hline M^\dagger & \Delta \end{array} \right),$$

with H_0 a 2×2 matrix, and Δ a 1×1 matrix (a scalar). The effective 2×2 Hamiltonian is obtained from

$$H_{\mathbf{k}}^{\text{eff},\tau} \approx H_0 - M\Delta^{-1}M^\dagger.$$

Examining the four entries of $H_{\mathbf{k}}^{\text{eff},\tau}$ we observe that the diagonal is independent of $\mathbf{k}$, while the off-diagonal terms have the form $(\tau k_x - ik_y)\gamma$. Thus, the low-energy effective Hamiltonian, written in the $\{|\psi_c\rangle, |\psi_v^\tau\rangle\}$ basis, has the form of a massive Dirac Hamiltonian

$$H_{\mathbf{k}}^{\text{eff},\tau} = \begin{pmatrix} \Delta/2 & \gamma(\tau k_x - ik_y) \\ \gamma(\tau k_x + ik_y) & -\Delta/2 \end{pmatrix}, \quad (\text{A.8})$$

where Δ and γ are determined from the Slater-Koster parameters (their explicit relation is of no interest for our purposes). To include spin in this Hamiltonian we simply write

$$H_{\mathbf{k}}^{\text{eff}, \tau, s_z} = \begin{pmatrix} \Delta/2 & \gamma(\tau k_x - i k_y) \\ \gamma(\tau k_x + i k_y) & -\Delta/2 \end{pmatrix} \otimes I, \quad (\text{A.9})$$

where the basis is now $\{|\psi_c, \uparrow\rangle, |\psi_v^\tau, \uparrow\rangle, |\psi_c, \downarrow\rangle, |\psi_v^\tau, \downarrow\rangle\}$, and I is the 2×2 identity matrix.

A.1.4 Spin-orbit coupling

So far we were able to derive an effective two band Hamiltonian which describes the valence and conduction bands near the Dirac valleys. The effect of spin-orbit coupling has not been considered yet, and will now be accounted for. As an approximation we will consider this effect to be intra atomic, and write its Hamiltonian as [128, 136]

$$H_{\text{SOC}} = \lambda \mathbf{L} \cdot \mathbf{s}, \quad (\text{A.10})$$

with $\mathbf{L}$ and $\mathbf{s}$ the angular momentum and spin operators, respectively, and λ the spin-orbit coupling strength. This Hamiltonian can be expressed more conveniently in terms of ladder operators as

$$H_{\text{SOC}} = \lambda \left(\frac{L_+ s_- + L_- s_+}{2} + L_z s_z \right). \quad (\text{A.11})$$

The effect L_+ , L_- and L_z in states with angular quantum number l and magnetic quantum number m , represented by $|l, m\rangle$, is summarized as follows

$$\begin{aligned} L_+ |l, m\rangle &= \hbar \sqrt{l(l+1) - m(m+1)} |l, m+1\rangle \\ L_- |l, m\rangle &= \hbar \sqrt{l(l+1) - m(m-1)} |l, m-1\rangle \\ L_z |l, m\rangle &= \hbar m |l, m\rangle. \end{aligned}$$

The spin operators follow identical relations but acting on the states $|s, s_z\rangle$, that is, spin s and spin projection along the z -axis s_z .

To capture the effect of spin-orbit coupling in a first order of approximation we consider the following basis

$$\{|d_{z^2}, \uparrow\rangle, |d_{xy}, \uparrow\rangle, |d_{x^2-y^2}, \uparrow\rangle, |d_{z^2}, \downarrow\rangle, |d_{xy}, \downarrow\rangle, |d_{x^2-y^2}, \downarrow\rangle\},$$

which is identical to the one we used before, but with the spin degree of freedom explicitly included. To obtain the representation of the spin-orbit coupling in this basis we must compute the matrix elements of H_{SOC} . Before doing so, we note that although d_{z^2} is an eigenstate of L_z , corresponding to the state

$|l = 2, m = 0\rangle$, the orbitals d_{xy} and $d_{x^2-y^2}$ do not have a well defined magnetic quantum number, since these are constructed from the superposition of the states $|l = 2, m = \pm 1\rangle$ as

$$\begin{aligned} |d_{xy}\rangle &= \frac{-i}{\sqrt{2}} (|l = 2, m = 2\rangle - |l = 2, m = -2\rangle) \\ |d_{x^2-y^2}\rangle &= \frac{1}{\sqrt{2}} (|l = 2, m = 2\rangle + |l = 2, m = -2\rangle) \\ |d_{z^2}\rangle &= |l = 2, m = 0\rangle \end{aligned}$$

Using these relations, and recalling the effect of the angular momentum ladder operators, we note that the matrix elements of L_+ and L_- vanish since we include only $m = 0$ and $m = \pm 2$ orbitals in our basis. As a result, the spin-orbit coupling Hamiltonian reads

$$H_{\text{SOC}} = \frac{\lambda}{2} \begin{pmatrix} L_z & 0 \\ 0 & -L_z \end{pmatrix}, \quad (\text{A.12})$$

with

$$L_z = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 2i \\ 0 & -2i & 0 \end{pmatrix}.$$

To obtain the low energy effective Hamiltonian near the Dirac valleys we apply the same procedure as before. First, we perform the change of basis using the operator U_τ , followed by the application of the Löwdin partitioning technique [134, 135]. In the end, we obtain

$$H_{\text{SOC}}^{\text{eff}, \tau, s_z} = \begin{pmatrix} 0 & 0 \\ 0 & \tau s_z \lambda \end{pmatrix}, \quad (\text{A.13})$$

written in the basis $\{|\psi_c, \uparrow\rangle, |\psi_v^\tau, \uparrow\rangle, |\psi_c, \downarrow\rangle, |\psi_v^\tau, \downarrow\rangle\}$. Due to the simplicity of our model, this effective Hamiltonian only describes the spin splitting in the valence band (which is known to be dominant one). In order to capture the spin splitting in the conduction band, two things would be required: i) the atomic orbitals $|d_{xz}\rangle$ and $|d_{yz}\rangle$ should be included in our model. Since these orbitals are superpositions of states with $m = \pm 1$, the matrix elements of L_+ and L_- would no longer vanish; ii) the Löwdin partitioning technique should be taken to higher order to include additional corrections. Here, for simplicity, we simply add a phenomenological term describing the spin splitting in the conduction band

$$H_{\text{SOC}}^{\text{eff}, \tau, s_z} = \begin{pmatrix} \tau s_z \lambda_c & 0 \\ 0 & \tau s_z \lambda_v \end{pmatrix}. \quad (\text{A.14})$$

Combining $H_{\text{SOC}}^{\text{eff}, \tau, s_z}$ with $H_{\mathbf{k}}^{\text{eff}, \tau, s_z}$ an effective Hamiltonian describing a freestanding TMD monolayer is found [35].

A.1.5 Effect of magnetic field

Finally, let us consider how the effect of an external magnetic field can be included in our model. To describe the interaction of the spins with the magnetic field we introduce the Hamiltonian

$$H_B = -\frac{\mu_B}{\hbar} g \mathbf{s} \cdot \mathbf{B}, \quad (\text{A.15})$$

with μ_B the Bohr magneton and g an effective Landé which depends on the atomic orbitals. For simplicity we set $\langle \psi_c | g | \psi_c \rangle = g_c$ and $\langle \psi_v^\tau | g | \psi_v^\tau \rangle = g_v$. If we consider the magnetic field to be applied along the z -axis, the Hamiltonian reads

$$H_B = -\frac{\mu_B}{\hbar} g s_z B_z.$$

From here, and following a procedure like the one used before, we obtain the effective Hamiltonian

$$H_{\text{ex}}^{\text{eff}} = -s_z \begin{pmatrix} B_c & 0 \\ 0 & B_v \end{pmatrix}, \quad (\text{A.16})$$

where $B_c = \mu_B B_z g_c / 2$ and $B_v = \mu_B B_z g_v / 2$.

A.2 Eigenvalues and eigenvectors

In the first part of this appendix we derived the model Hamiltonian for monolayer TMDs, which we found to be given by the 2×2 matrix

$$H = \begin{bmatrix} \frac{\Delta}{2} + \tau s_z \lambda_c - s_z B_c & \hbar v_F (\tau k_x - i k_y) \\ \hbar v_F (\tau k_x + i k_y) & -\frac{\Delta}{2} + \tau s_z \lambda_v - s_z B_v \end{bmatrix}. \quad (\text{A.17})$$

If τ and s_z were not good quantum numbers, which is the case for an exchange field with an in-plane component, then the Hamiltonian would be represented by an 8×8 matrix. Using a symbolic calculus software to compute the eigenvalues and eigenvectors of this Hamiltonian can lead to rather messy expressions. To avoid that, we will manually diagonalize this Hamiltonian. Obviously, there is nothing special about the procedure here presented, and any other method should yield analogous results.

First, we compute the eigenvalues of H , which is a fairly straightaway task. The energies $E_{\pm, \mathbf{k}}^{\tau, s_z}$ follow from the solution of the equation

$$\begin{vmatrix} \left(\frac{\Delta}{2} + \tau s_z \lambda_c - s_z B_c \right) - E_{\pm} & \hbar v_F (\tau k_x - i k_y) \\ \hbar v_F (\tau k_x + i k_y) & \left(-\frac{\Delta}{2} + \tau s_z \lambda_v - s_z B_v \right) - E_{\pm} \end{vmatrix} = 0.$$

Explicitly:

$$E_{\pm, \mathbf{k}}^{\tau, s_z} = \frac{s_z}{2} [\tau (\lambda_c + \lambda_v) - (B_c + B_v)] \pm \sqrt{\left(\frac{E_g^{\tau, s_z}}{2} \right)^2 + \hbar^2 v_F^2 \mathbf{k}^2}, \quad (\text{A.18})$$

with $E_g^{\tau,s_z} = \Delta + \tau s_z(\lambda_c - \lambda_v) - s_z(B_c - B_v)$, which corresponds to the result presented in the main text.

With the eigenvalues found we move on to the computation of the eigenvectors, $|u_{c,k}^{\tau,s_z}\rangle$. To find the eigenvector associated with the eigenvalue $E_{+,k}^{\tau,s_z}$, that is $|u_{c,k}^{\tau,s_z}\rangle$, we write

$$\begin{bmatrix} \frac{\Delta}{2} + \tau s_z \lambda_c - s_z B_c & \hbar v_F(\tau k_x - i k_y) \\ \hbar v_F(\tau k_x + i k_y) & -\frac{\Delta}{2} + \tau s_z \lambda_v - s_z B_v \end{bmatrix} \begin{bmatrix} 1 \\ A \end{bmatrix} = E_{+,k}^{\tau,s_z} \begin{bmatrix} 1 \\ A \end{bmatrix},$$

which leads to

$$\begin{aligned} \left(\frac{\Delta}{2} - \tau s_z \lambda_v + s_z B_v + E_{+,k}^{\tau,s_z} \right) A &= \hbar v_F(\tau k_x + i k_y) \\ A &= \frac{\hbar v_F(\tau k_x + i k_y)}{\left(\frac{\Delta}{2} - \tau s_z \lambda_v + s_z B_v + E_{+,k}^{\tau,s_z} \right)}. \end{aligned}$$

Introducing the definition $\mathcal{M}_k^{\tau,s_z} = \Delta/2 - \tau s_z \lambda_v + s_z B_v + E_{+,k}^{\tau,s_z}$, we write

$$A = \frac{\hbar v_F(\tau k_x + i k_y)}{\mathcal{M}_k^{\tau,s_z}}.$$

Now the eigenvector needs to be normalized. Computing the current norm we find

$$\langle u_{c,k}^{\tau,s_z} | u_{c,k}^{\tau,s_z} \rangle = \frac{\left(\mathcal{M}_k^{\tau,s_z} \right)^2 + \hbar^2 v_F^2 k^2}{\left(\mathcal{M}_k^{\tau,s_z} \right)^2},$$

with $k^2 = k_x^2 + k_y^2$. Using this result to normalize the eigenvector one obtains

$$|u_{c,k}^{\tau,s_z}\rangle = \frac{1}{\sqrt{\left(\mathcal{M}_k^{\tau,s_z} \right)^2 + \hbar^2 v_F^2 k^2}} \begin{bmatrix} \mathcal{M}_k^{\tau,s_z} \\ \hbar v_F(\tau k_x + i k_y) \end{bmatrix}. \quad (\text{A.19})$$

Noting that since $\tau = \pm 1$, we write $(\tau k_x + i k_y) = \tau(k_x + \tau i k_y)$, which in polar coordinates reads $\tau k e^{i\tau\theta}$, where $\theta = \arctan(k_y/k_x)$. Hence:

$$|u_{c,k}^{\tau,s_z}\rangle = \frac{1}{\sqrt{\left(\mathcal{M}_k^{\tau,s_z} \right)^2 + \hbar^2 v_F^2 k^2}} \begin{bmatrix} \mathcal{M}_k^{\tau,s_z} \\ \hbar v_F \tau k e^{i\tau\theta} \end{bmatrix}. \quad (\text{A.20})$$

The other eigenvector, $|u_{v,k}^{\tau,s_z}\rangle$, directly follows from this one by noting that they must be orthogonal, since they are eigenvectors of an hermitian operator. Thus, it is trivial to find

$$|u_{v,k}^{\tau,s_z}\rangle = \frac{1}{\sqrt{\left(\mathcal{M}_k^{\tau,s_z} \right)^2 + \hbar^2 v_F^2 k^2}} \begin{bmatrix} \hbar v_F \tau k e^{-i\tau\theta} \\ \mathcal{M}_k^{\tau,s_z} \end{bmatrix}. \quad (\text{A.21})$$

Wannier equation

In this appendix we study in detail the Wannier equation, which is mentioned throughout text. We shall begin by deriving this equation from the definition of the exciton operator. Afterwards, its solution using a gaussian basis will be discussed.

B.1 Derivation

Let us start by defining the exciton creation operator as

$$b_{\mathbf{Q},\nu}^{\dagger,\xi_e,\xi_h} = \frac{1}{\sqrt{A}} \sum_{\mathbf{k}} \psi_{\nu,\mathbf{k}}^{\xi_e,\xi_h} c_{\mathbf{k}+\alpha_{\xi_e,\xi_h}\mathbf{Q},c}^{\dagger,\xi_e} c_{\mathbf{k}-\beta_{\xi_e,\xi_h}\mathbf{Q},v}^{\xi_h}, \quad (\text{B.1})$$

where A is the area of the monolayer, $\psi_{\nu,\mathbf{k}}^{\xi_e,\xi_h}$ is the Fourier transform of an exciton with quantum numbers denoted by ν , whose electron is located in the ξ_e point of the Brillouin zone and the hole in the ξ_h point; the relative momentum $\mathbf{k}$ is defined with respect to the ξ_e and ξ_h points. Note that spin index of the carrier can be incorporated in $\xi_{e/h}$. The operator $c_{\mathbf{k}+\alpha_{\xi_e,\xi_h}\mathbf{Q},c}^{\dagger,\xi_e}$ creates an electron in the conduction band, in the point ξ_e of the Brillouin zone, with momentum $\mathbf{k} + \alpha_{\xi_e,\xi_h}\mathbf{Q}$ relatively to this point in momentum space (a similar definition applies to $c_{\mathbf{k}-\beta_{\xi_e,\xi_h}\mathbf{Q},v}^{\xi_h}$). Also, $\alpha_{\xi_e,\xi_h} = m_e^{\xi_e} / (m_e^{\xi_e} + m_h^{\xi_h})$ and $\beta_{\xi_e,\xi_h} = m_h^{\xi_h} / (m_e^{\xi_e} + m_h^{\xi_h})$. Hence, in summary, $b_{\mathbf{Q},\nu}^{\dagger,\xi_e,\xi_h}$ corresponds to the creation of an exciton with quantum numbers ν and center of mass momentum $\mathbf{Q}$ measured relatively to the high symmetry points ξ_e and ξ_h , i.e. $\mathbf{Q} = \mathbf{k}_e^{\xi_e} - \mathbf{k}_h^{\xi_h}$. The total moment of the exciton reads $\mathbf{Q}_{total} = \xi_e - \xi_h + \mathbf{Q}$. When this operator acts on the excitonic ground state we find

$$b_{\mathbf{Q},\nu}^{\dagger,\xi_e,\xi_h} |GS\rangle = |\xi_e, \xi_h, \nu, \mathbf{Q}\rangle \quad (\text{B.2})$$

The energy of such a state reads

$$E_{\mathbf{Q},\nu}^{\xi_e,\xi_h} = E_g^{\xi_e,\xi_h} + E_\nu^{\xi_e,\xi_h} + \frac{\hbar^2 \mathbf{Q}^2}{2M_{\xi_e,\xi_h}}, \quad (\text{B.3})$$

with $E_g^{\xi_e, \xi_h}$ the band gap between the ξ_e and ξ_h points, $E_v^{\xi_e, \xi_h}$ the exciton binding energy and $\hbar^2 Q^2 / 2M_{\xi_e, \xi_h}$ its center of mass kinetic energy. Note that indexes such as ξ_e refer to high symmetry points in the Brillouin zone, and can be interpreted as momentum measured relatively to the Γ point of the Brillouin zone.

The electronic Hamiltonian is composed of a kinetic and a potential contribution. The kinetic term can be readily quantized in terms of electron operators and reads

$$\hat{H}_0 = \sum_{\mathbf{k}, \lambda, \xi} E_{\mathbf{k}, \lambda}^{\xi} c_{\mathbf{k}, \lambda}^{\dagger, \xi} c_{\mathbf{k}, \lambda}^{\xi}. \quad (\text{B.4})$$

The potential term reads

$$\hat{H}_{int} = \frac{1}{2A} \sum_{\{\lambda, \xi\}} \sum_{\mathbf{q}, \mathbf{k}_3, \mathbf{k}_4} V(\mathbf{q}) F_{\lambda_1, \lambda_2, \lambda_3, \lambda_4}^{\xi_1, \xi_2, \xi_3, \xi_4}(\mathbf{k}_3, \mathbf{k}_4, \mathbf{q}) c_{\mathbf{k}_4 + \mathbf{q}, \lambda_1}^{\dagger, \xi_1} c_{\mathbf{k}_3 - \mathbf{q}, \lambda_2}^{\dagger, \xi_2} c_{\mathbf{k}_3, \lambda_3}^{\xi_3} c_{\mathbf{k}_4, \lambda_4}^{\xi_4} \quad (\text{B.5})$$

where $V(\mathbf{q})$ is the Fourier transform of the interaction potential and

$$\begin{aligned} F_{\lambda_1, \lambda_2, \lambda_3, \lambda_4}^{\xi_1, \xi_2, \xi_3, \xi_4}(\mathbf{k}_3, \mathbf{k}_4, \mathbf{q}) &= u_{\mathbf{k}_4 + \mathbf{q}, \lambda_1}^{\dagger, \xi_1} u_{\mathbf{k}_3 - \mathbf{q}, \lambda_2}^{\dagger, \xi_2} u_{\mathbf{k}_3, \lambda_3}^{\xi_3} u_{\mathbf{k}_4, \lambda_4}^{\xi_4} \\ &= u_{\mathbf{k}_3 - \mathbf{q}, \lambda_2}^{\dagger, \xi_2} u_{\mathbf{k}_3, \lambda_3}^{\xi_3} u_{\mathbf{k}_4 + \mathbf{q}, \lambda_1}^{\dagger, \xi_1} u_{\mathbf{k}_4, \lambda_4}^{\xi_4} \end{aligned}$$

with $u_{\mathbf{k}, \lambda}^{\xi}$ the λ -band spinor of the ξ point of the Brillouin zone evaluated at $\mathbf{k}$ (measured relatively to ξ). Note that the term $\mathbf{q} = 0$ is excluded of the sum over $\mathbf{q}$ since it cancels with the background contribution in the jellium model.

To obtain the equation that defines the exciton wave functions we will assume that the total Hamiltonian, $\hat{H} = \hat{H}_0 + \hat{H}_{int}$, is diagonal in the $b_{\mathbf{Q}, v}^{\dagger, \xi_e, \xi_h}$ basis, that is

$$\hat{H} = \sum_{\mathbf{Q}, v, \xi_e, \xi_h} E_{\mathbf{Q}, v}^{\xi_e, \xi_h} b_{\mathbf{Q}, v}^{\dagger, \xi_e, \xi_h} b_{\mathbf{Q}, v}^{\xi_e, \xi_h} \quad (\text{B.6})$$

In order to find the equation defining the exciton wave function we will compute the commutator $[\hat{H}, b_{\mathbf{Q}, v}^{\dagger, \xi_e, \xi_h}]$ using the excitonic representation of the operators, as well as using their fermionic representation. In the end we demand both results to be equal.

The computation of $[\hat{H}, b_{\mathbf{Q}, v}^{\dagger, \xi_e, \xi_h}]$ using the bosonic representation of the Hamiltonian is trivial, and its result reads:

$$\begin{aligned} [\hat{H}, b_{\mathbf{Q}, v}^{\dagger, \xi_e, \xi_h}] &= E_{\mathbf{Q}, v}^{\xi_e, \xi_h} b_{\mathbf{Q}, v}^{\dagger, \xi_e, \xi_h} \\ &= E_{\mathbf{Q}, v}^{\xi_e, \xi_h} \frac{1}{\sqrt{A}} \sum_{\mathbf{k}} \psi_{v, \mathbf{k}}^{\xi_e, \xi_h} c_{\mathbf{k} + \alpha_{\xi_e, \xi_h} \mathbf{Q}, c}^{\dagger, \xi_e} c_{\mathbf{k} - \beta_{\xi_e, \xi_h} \mathbf{Q}, c}^{\xi_h}. \end{aligned} \quad (\text{B.7})$$

Contrarily to this commutator, computing $[\hat{H}, b_{\mathbf{Q}, v}^{\dagger, \xi_e, \xi_h}]$ using the fermionic representation of the Hamiltonian and the exciton operator is a rather cumbersome process. In order to compute this, we will break

the commutator in two, separating the contribution from H_0 and H_{int} . To simplify the calculations let us note that since we are interested in finding the binding energies, that is, the bottom of the parabolic dispersion given in Eq. (B.3), we set $Q = 0$.

Starting with the evaluation of $\left[\hat{H}_0, b_{Q,v}^{\dagger,\xi_e,\xi_h}\right]$, and using the following relations regarding commutators and anticommutators

$$[AB, C] = A[B, C] + [A, C]B, \quad (B.8)$$

$$[AB, C] = A\{B, C\} - \{A, C\}B, \quad (B.9)$$

one finds:

$$\left[\hat{H}_0, b_{Q,v}^{\dagger,\xi_e,\xi_h}\right] = \sum_{\mathbf{k}} \frac{\psi_{v,\mathbf{k}}^{\xi_e\xi_h}}{\sqrt{A}} \left(E_{\mathbf{k},c}^{\xi_e} - E_{\mathbf{k},v}^{\xi_h}\right) c_{\mathbf{k},c}^{\dagger,\xi_e} c_{\mathbf{k},v}^{\xi_h} \quad (B.10)$$

To compute $\left[\hat{H}_{int}, b_{Q,v}^{\dagger,\xi_e,\xi_h}\right]$, we start by writing

$$\left[\hat{H}_{int}, b_{Q,v}^{\dagger,\xi_e,\xi_h}\right] = \sum_{\{\lambda,\xi\}} \sum_{\mathbf{q}, \mathbf{k}_3, \mathbf{k}_4, \mathbf{k}} \frac{\psi_{v,\mathbf{k}}^{\xi_e\xi_h}}{2A^{3/2}} V(\mathbf{q}) F_{\lambda_1, \lambda_2, \lambda_3, \lambda_4}^{\xi_1, \xi_2, \xi_3, \xi_4}(\mathbf{k}_3, \mathbf{k}_4, \mathbf{q}) \left[c_{\mathbf{k}_4+\mathbf{q}\lambda_1}^{\dagger,\xi_1} c_{\mathbf{k}_3-\mathbf{q}\lambda_2}^{\dagger,\xi_2} c_{\mathbf{k}_3\lambda_3}^{\xi_3} c_{\mathbf{k}_4\lambda_4}^{\xi_4}, c_{\mathbf{k},c}^{\dagger,\xi_e} c_{\mathbf{k},v}^{\xi_h} \right].$$

Using Eqs. (B.8) and (B.9), it is possible to show that the commutator can be transformed into:

$$\begin{aligned} \left[c_{\mathbf{k}_4+\mathbf{q}\lambda_1}^{\dagger,\xi_1} c_{\mathbf{k}_3-\mathbf{q}\lambda_2}^{\dagger,\xi_2} c_{\mathbf{k}_3\lambda_3}^{\xi_3} c_{\mathbf{k}_4\lambda_4}^{\xi_4}, c_{\mathbf{k},c}^{\dagger,\xi_e} c_{\mathbf{k},v}^{\xi_h} \right] &= c_{\mathbf{k}_4+\mathbf{q}\lambda_1}^{\dagger,\xi_1} c_{\mathbf{k}_3-\mathbf{q}\lambda_2}^{\dagger,\xi_2} c_{\mathbf{k}_3\lambda_3}^{\xi_3} c_{\mathbf{k},v}^{\xi_h} \delta_{\mathbf{k}_4,\mathbf{k}} \delta_{\lambda_4,c} \delta_{\xi_4,\xi_e} \\ &\quad - c_{\mathbf{k}_4+\mathbf{q}\lambda_1}^{\dagger,\xi_1} c_{\mathbf{k}_3-\mathbf{q}\lambda_2}^{\dagger,\xi_2} c_{\mathbf{k}_4\lambda_4}^{\xi_4} c_{\mathbf{k},v}^{\xi_h} \delta_{\mathbf{k}_3,\mathbf{k}} \delta_{\lambda_3,c} \delta_{\xi_3,\xi_e} \\ &\quad + c_{\mathbf{k},c}^{\dagger,\xi_e} c_{\mathbf{k}_4+\mathbf{q}\lambda_1}^{\dagger,\xi_1} c_{\mathbf{k}_3\lambda_3}^{\xi_3} c_{\mathbf{k}_4\lambda_4}^{\xi_4} \delta_{\mathbf{k}_3-\mathbf{q},\mathbf{k}} \delta_{\lambda_2,v} \delta_{\xi_2,\xi_h} \\ &\quad - c_{\mathbf{k},c}^{\dagger,\xi_e} c_{\mathbf{k}_3-\mathbf{q}\lambda_2}^{\dagger,\xi_2} c_{\mathbf{k}_3\lambda_3}^{\xi_3} c_{\mathbf{k}_4\lambda_4}^{\xi_4} \delta_{\mathbf{k}_4+\mathbf{q},\mathbf{k}} \delta_{\lambda_1,v} \delta_{\xi_1,\xi_h}. \end{aligned}$$

In order to transform these products of four operators into products of two operators only we perform a mean field decoupling, such that:

$$\begin{aligned} c_{\mathbf{k}_4+\mathbf{q}\lambda_1}^{\dagger,\xi_1} c_{\mathbf{k}_3-\mathbf{q}\lambda_2}^{\dagger,\xi_2} c_{\mathbf{k}_3\lambda_3}^{\xi_3} c_{\mathbf{k},v}^{\xi_h} &\approx \left\langle c_{\mathbf{k}_4+\mathbf{q}\lambda_1}^{\dagger,\xi_1} c_{\mathbf{k},v}^{\xi_h} \right\rangle c_{\mathbf{k}_3-\mathbf{q}\lambda_2}^{\dagger,\xi_2} c_{\mathbf{k}_3\lambda_3}^{\xi_3} + c_{\mathbf{k}_4+\mathbf{q}\lambda_1}^{\dagger,\xi_1} c_{\mathbf{k},v}^{\xi_h} \left\langle c_{\mathbf{k}_3-\mathbf{q}\lambda_2}^{\dagger,\xi_2} c_{\mathbf{k}_3\lambda_3}^{\xi_3} \right\rangle \\ &\quad - \left\langle c_{\mathbf{k}_4+\mathbf{q}\lambda_1}^{\dagger,\xi_1} c_{\mathbf{k}_3\lambda_3}^{\xi_3} \right\rangle c_{\mathbf{k}_3-\mathbf{q}\lambda_2}^{\dagger,\xi_2} c_{\mathbf{k},v}^{\xi_h} - c_{\mathbf{k}_4+\mathbf{q}\lambda_1}^{\dagger,\xi_1} c_{\mathbf{k}_3\lambda_3}^{\xi_3} \left\langle c_{\mathbf{k}_3-\mathbf{q}\lambda_2}^{\dagger,\xi_2} c_{\mathbf{k},v}^{\xi_h} \right\rangle, \end{aligned}$$

where $\langle \dots \rangle$ refers to the expectation value on the exciton ground state (full valence band and empty

conduction band). Applying this technique to all the contributions, we find:

$$\begin{aligned} \left[\hat{H}_{int}, b_{0,v}^{\dagger, \xi_e, \xi_h} \right] = & - \sum_{\mathbf{k}, \mathbf{p}} \frac{\psi_{v,\mathbf{p}}^{\xi_e \xi_h}}{A^{3/2}} V(\mathbf{k} - \mathbf{p}) F_{c,v,v,c}^{\xi_e, \xi_h, \xi_h, \xi_e}(\mathbf{k}, \mathbf{p}, \mathbf{k} - \mathbf{p}) c_{\mathbf{k},c}^{\dagger, \xi_e} c_{\mathbf{k},v}^{\xi_h} \\ & - \sum_{\xi_1} \sum_{\mathbf{k}, \mathbf{p}} \frac{\psi_{v,\mathbf{p}}^{\xi_e \xi_h}}{A^{3/2}} V(\mathbf{k} - \mathbf{p}) F_{v,c,v,c}^{\xi_1, \xi_e, \xi_1, \xi_e}(\mathbf{k}, \mathbf{p}, \mathbf{k} - \mathbf{p}) c_{\mathbf{p},c}^{\dagger, \xi_e} c_{\mathbf{p},v}^{\xi_h} \\ & + \sum_{\xi_1} \sum_{\mathbf{k}, \mathbf{p}} \frac{\psi_{v,\mathbf{k}}^{\xi_e \xi_h}}{A^{3/2}} V(\mathbf{p} - \mathbf{k}) F_{v,v,v,v}^{\xi_1, \xi_h, \xi_1, \xi_h}(\mathbf{p}, \mathbf{k}, \mathbf{p} - \mathbf{k}) c_{\mathbf{k},c}^{\dagger, \xi_e} c_{\mathbf{k},v}^{\xi_h}. \end{aligned}$$

Combining this expression with the result of the commutator with $\hat{H}_0$ and equating it to the result we obtained using bosonic commutation relations we find

$$\begin{aligned} E_{0,v}^{\xi_e, \xi_h} \psi_{v,\mathbf{k}}^{\xi_e \xi_h} = & \psi_{v,\mathbf{k}}^{\xi_e \xi_h} \left(E_{\mathbf{k},c}^{\xi_e} - E_{\mathbf{k},v}^{\xi_h} \right) - \frac{1}{A} \sum_{\mathbf{p}} \psi_{v,\mathbf{p}}^{\xi_e \xi_h} V(\mathbf{k} - \mathbf{p}) F_{c,v,v,c}^{\xi_e, \xi_h, \xi_h, \xi_e}(\mathbf{k}, \mathbf{p}, \mathbf{k} - \mathbf{p}) \\ & + \frac{1}{A} \psi_{v,\mathbf{k}}^{\xi_e \xi_h} \sum_{\xi_1 \mathbf{p}} V(\mathbf{p}) \left\{ F_{v,v,v,v}^{\xi_1, \xi_h, \xi_1, \xi_h}(\mathbf{p} + \mathbf{k}, \mathbf{k}, \mathbf{p}) - F_{v,c,v,c}^{\xi_1, \xi_e, \xi_1, \xi_e}(\mathbf{p} + \mathbf{k}, \mathbf{k}, \mathbf{p}) \right\}. \end{aligned} \quad (\text{B.11})$$

Now, we introduce the following approximations: i) the first term on the right hand side is expanded up to second order in $\mathbf{k}$:

$$E_{\mathbf{k},c}^{\xi_e} - E_{\mathbf{k},v}^{\xi_h} \approx E_g^{\xi_e, \xi_h} + \frac{\hbar^2 \mathbf{k}^2}{2\mu_{\xi_e, \xi_h}};$$

ii) the form factor on the second term on the right hand side is approximated to 1. This is a good approximation in the vicinity of the Dirac points due to the large energy gap, and identically true in the Λ valley (the other point of the Brillouin zone we consider in this dissertation); iii) the third term on the right hand side is assumed to not vary significantly with $\mathbf{k}$ and is incorporated on the left hand side of the equation. Although this term does not contribute significantly to the binding energy, it plays a significant role in determining the value of the band gap in the interacting limit (which is beyond the scope of this work). Using these approximations, one finds the Beth-Salpeter equation as displayed in the main text:

$$E_v^{\xi_e, \xi_h} \psi_{v,\mathbf{k}}^{\xi_e \xi_h} = \frac{\hbar^2 \mathbf{k}^2}{2\mu_{\xi_e, \xi_h}} \psi_{v,\mathbf{k}}^{\xi_e \xi_h} - \frac{1}{A} \sum_{\mathbf{p}} \psi_{v,\mathbf{p}}^{\xi_e \xi_h} V(\mathbf{k} - \mathbf{p}). \quad (\text{B.12})$$

In this form, the BSE can be readily transformed into a differential equation in real space, the Wannier equation.

B.2 Solution with a gaussian basis

In this part of the appendix let us start by discuss how to obtain the Griffin-Hill-Wheeler equation. Our goal is to find the wave functions and binding energies that solve the Wannier equation. To this end, we state

that the solution of such an equation is

$$\Psi(\mathbf{r}) = \int f(\alpha) \phi(\mathbf{r}, \alpha) d\alpha, \quad (\text{B.13})$$

where $\phi(\mathbf{r}, \alpha)$ is a trial wave function, and $f(\alpha)$ is the generating function, which depends on the deformation parameter α . The role of $f(\alpha)$ is to deform $\phi(\mathbf{r}, \alpha)$ forcing it to satisfy the Wannier equation, and it should be chosen to minimize the energy, which we define as the expectation value of the Hamiltonian ($\mathcal{H}(\mathbf{r})$):

$$E(f(\alpha), f(\beta)) = \frac{\int \Psi^*(\mathbf{r}) \mathcal{H}(\mathbf{r}) \Psi(\mathbf{r}) d\mathbf{r}}{\int \Psi^*(\mathbf{r}) \Psi(\mathbf{r}) d\mathbf{r}} = \frac{\int f^*(\alpha) H(\alpha, \beta) f(\beta) d\alpha d\beta}{\int f^*(\alpha) S(\alpha, \beta) f(\beta) d\alpha d\beta}, \quad (\text{B.14})$$

where the denominator guarantees normalization, and $H(\alpha, \beta)$ and $S(\alpha, \beta)$ are the Hamiltonian and overlap kernels, respectively, defined as

$$H(\alpha, \beta) = \int \phi^*(\mathbf{r}, \alpha) \mathcal{H}(\mathbf{r}) \phi(\mathbf{r}, \beta) d\mathbf{r}, \quad (\text{B.15})$$

$$S(\alpha, \beta) = \int \phi^*(\mathbf{r}, \alpha) \phi(\mathbf{r}, \beta) d\mathbf{r}, \quad (\text{B.16})$$

which correspond to the expectation value of the Hamiltonian between trial wave functions $\phi(\mathbf{r}, \alpha)$, and their overlap. The condition of energy extremization is $\delta E = 0$, which explicitly reads

$$E(f(\alpha) + \delta f(\alpha), f(\beta)) - E(f(\alpha), f(\beta)) = 0$$

or equivalently

$$\int [H(\alpha, \beta) - S(\alpha, \beta) E] f(\beta) d\beta = 0,$$

which is the Griffin-Hill-Wheeler equation. The discretized form can be obtained by transforming α and β in discrete parameters, rather than continuous ones, thus

$$\sum_{j=1}^N [H(\alpha_i, \beta_j) - S(\alpha_i, \beta_j) E] f(\beta_j) = 0. \quad (\text{B.17})$$

Inspired by this discussion, we try to solve the Wannier equation using the wave function:

$$\psi_\nu(\mathbf{r}) = \sum_{j=1}^N c(j; \nu) e^{im\theta} \mathbf{r}^{|m|} e^{-\zeta_j r^2}, \quad (\text{B.18})$$

where in analogy to the previous discussion, $c(j; \nu)$ is the generating function, and $e^{im\theta} \mathbf{r}^{|m|} e^{-\zeta_j r^2}$ is the trial wave function, with ζ_j playing the role of the deformation parameter α . Using this function, the overlap kernel can be computed analytically, yielding

$$S(\zeta_i, \zeta_j) = \pi \frac{\Gamma(|m| + 1)}{(\zeta_i + \zeta_j)^{1+|m|}},$$

for $m = 0$ this simplifies to

$$S(\zeta_i, \zeta_j) = \frac{\pi}{\zeta_i + \zeta_j}. \quad (\text{B.19})$$

Expressing the Hamiltonian as a sum of a kinetic term with a potential one, that is

$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\nabla^2 + V_{\text{RK}}(\mathbf{r}), \quad (\text{B.20})$$

with $V_{\text{RK}}(\mathbf{r})$ the Rytova-Keldysh potential given in the main text, the Hamiltonian kernel also has an analytical solution, albeit a more involved one

$$\begin{aligned} H(\zeta_i, \zeta_j) = & \frac{2\pi\hbar^2}{\mu} \frac{\zeta_i\zeta_j\Gamma(2+|m|)}{(\zeta_i + \zeta_j)^{2+|m|}} + \frac{\pi\alpha\hbar c}{2r_0^2 (\zeta_i + \zeta_j)^{\frac{3}{2}+|m|}} \times \\ & \left[-2\kappa\Gamma\left(\frac{3}{2} + |m|\right) {}_2F_2\left(\left\{1, \frac{3}{2} + |m|\right\}, \left\{\frac{3}{2}, \frac{3}{2}\right\}, -x\right) \right. \\ & \left. + \pi r_0 \sqrt{\zeta_i + \zeta_j} G_{23}^{21}\left(x \left| \begin{array}{cc} -|m| & -\frac{1}{2} \\ 0 & 0 & -\frac{1}{2} \end{array} \right. \right) \right] \end{aligned} \quad (\text{B.21})$$

where $x = \kappa^2 / [4r_0^2 (\zeta_i + \zeta_j)]$, G is the MeijerG function and ${}_2F_2$ an Hypergeometric function. The fact that both $H(\zeta_i, \zeta_j)$ and $S(\zeta_i, \zeta_j)$ are symmetrical simplifies the calculations.

Rytova-Keldysh potential

In this appendix we present the derivation of the Rytova-Keldysh potential, which is used in the main text to describe the electrostatic interaction in monolayer two-dimensional materials. Although different approaches can be used to obtain this potential we follow the procedure first presented by Rytova in Ref. [56].

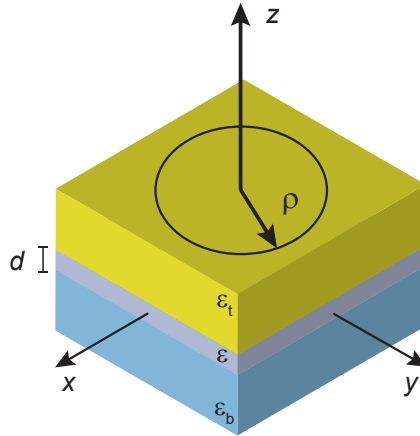


Figure 27: **Rytova-Keldysh system.** Schematic representation of a thin film, with thickness d and dielectric constant ϵ , placed between two dielectric media with dielectric constants ϵ_t and ϵ_b . The length ρ corresponds to the in-plane component of the position vector $\mathbf{r} = (\boldsymbol{\rho}, z)$.

The first step to obtain the Rytova-Keldysh potential is to consider a thin dielectric film, with a thickness d and dielectric constant ϵ , placed between two dielectric media with dielectric constants ϵ_t and ϵ_b for the top and bottom medium, respectively; a schematic representation of this system is depicted in Fig. 27. Let us also consider that a test charge is placed at $\mathbf{r}'$ somewhere inside the thin film. The electric potential in the three regions of the system follows from the solution of the Poisson equations

$$\nabla^2 \phi_1(\mathbf{r}, \mathbf{r}') = 0 \quad (\text{C.1})$$

$$\nabla^2 \phi_2(\mathbf{r}, \mathbf{r}') = -\frac{e}{\epsilon \epsilon_0} \delta(\mathbf{r} - \mathbf{r}') \quad (\text{C.2})$$

$$\nabla^2 \phi_3(\mathbf{r}, \mathbf{r}') = 0 \quad (\text{C.3})$$

subject to the boundary conditions

$$\begin{aligned}\phi_1(z=0) &= \phi_2(z=0), & \left. \frac{\partial \phi_1}{\partial z} \right|_{z=0} &= \frac{\epsilon_2}{\epsilon_1} \left. \frac{\partial \phi_2}{\partial z} \right|_{z=0} \\ \phi_2(z=d) &= \phi_3(z=d), & \left. \frac{\partial \phi_2}{\partial z} \right|_{z=d} &= \frac{\epsilon_3}{\epsilon_2} \left. \frac{\partial \phi_3}{\partial z} \right|_{z=d}\end{aligned}$$

To take advantage of the in-plane symmetry of the problem we perform a two-dimensional Fourier transform and work in the mixed representation $(\mathbf{q}, z)$, where $\mathbf{q}$ is the in-plane component of the three dimensional momentum $\mathbf{k} = (\mathbf{q}, k_z)$. Explicitly, we write the electric potential as

$$\phi_i(\mathbf{r}, \mathbf{r}') = \int \frac{d\mathbf{q}}{(2\pi)^2} \phi_i(\mathbf{q}, z, z') e^{i\mathbf{q} \cdot \boldsymbol{\rho}},$$

with $i = \{1, 2, 3\}$ and $\mathbf{r} = (\boldsymbol{\rho}, z)$. In this mixed representation, Eqs. (C.1) to (C.3) may be written as

$$\frac{\partial^2}{\partial z^2} \phi_1(\mathbf{q}, z, z') - q^2 \phi_1(\mathbf{q}, z, z') = 0 \quad (\text{C.4})$$

$$\frac{\partial^2}{\partial z^2} \phi_2(\mathbf{q}, z, z') - q^2 \phi_2(\mathbf{q}, z, z') = -\frac{e}{\epsilon \epsilon_0} \delta(z - z') \quad (\text{C.5})$$

$$\frac{\partial^2}{\partial z^2} \phi_3(\mathbf{q}, z, z') - q^2 \phi_3(\mathbf{q}, z, z') = 0. \quad (\text{C.6})$$

To solve these equations, and to ensure that the electric potential does not diverge in any region of the system, we propose the following solutions for ϕ_1 and ϕ_3 :

$$\phi_1(\mathbf{q}, z, z') = A_{\mathbf{q}} e^{qz} \quad (\text{C.7})$$

$$\phi_3(\mathbf{q}, z, z') = B_{\mathbf{q}} e^{-qz}, \quad (\text{C.8})$$

where ϕ_1 and ϕ_3 refer to the regions $z < 0$ and $z > d$, respectively. Since Eq. (C.5) contains a Dirac- δ , to find the form of ϕ_2 one must consider the case where $z > z'$ and $z < z'$ in separate. Hence we propose,

$$\phi_2^{z>z'}(\mathbf{q}, z, z') = C_{\mathbf{q}}^{z>z'} e^{-qz} + D_{\mathbf{q}}^{z>z'} e^{qz}. \quad (\text{C.9})$$

$$\phi_2^{z<z'}(\mathbf{q}, z, z') = C_{\mathbf{q}}^{z<z'} e^{-qz} + D_{\mathbf{q}}^{z<z'} e^{qz}, \quad (\text{C.10})$$

with $\phi_2^{z>z'} = \phi_2^{z<z'}$ for $z = z'$ and

$$\left. \frac{\partial \phi_2^{z<z'}}{\partial z} \right|_{z=z'} - \left. \frac{\partial \phi_2^{z>z'}}{\partial z} \right|_{z=z'} = \frac{e}{\epsilon \epsilon_0}. \quad (\text{C.11})$$

The discontinuity of the derivative is a direct consequence of the Dirac- δ . The coefficients $A_{\mathbf{q}}$, $B_{\mathbf{q}}$, $C_{\mathbf{q}}$ and $D_{\mathbf{q}}$ are determined from the boundary conditions of the electric potential plus the two restrictions from $\phi_2^{z>z'}$ and $\phi_2^{z<z'}$.

Solving the linear system of six equations, the coefficients are determined and an expression for $\phi_2^{z>z'}$ and $\phi_2^{z<z'}$ is found. Since our goal is to study monolayers, we will consider them to be a limiting case of an extremely thin film. Hence, we consider the limit $qd \ll 1$, which allows us to find

$$\phi_2(\mathbf{q}) = \frac{e}{2\epsilon_0 r_0 q \left(q + \frac{\kappa}{r_0}\right)}, \quad (\text{C.12})$$

with $r_0 = d\epsilon/2$ and $\kappa = (\epsilon_t + \epsilon_b)/2$ the mean dielectric constant of the media above and below the film. Note that this expression is independent of both z and z' because we considered the film to be infinitely thin, which also implies that $qz' \ll 1$, since $0 < z' < d$, and likewise for z . To obtain the representation of the electric potential in real space, a two-dimensional Fourier transform must be introduced. Explicitly, this reads:

$$\begin{aligned} \phi_2(\boldsymbol{\rho}) &= \int \frac{d^2\mathbf{q}}{(2\pi)^2} \phi_2(\mathbf{q}) e^{i\mathbf{q}\cdot\boldsymbol{\rho}} \\ &= \frac{e}{2\epsilon_0 r_0} \frac{1}{(2\pi)^2} \int \frac{e^{iq\rho \cos\theta}}{\frac{\kappa}{r_0} + q} dq d\theta. \end{aligned}$$

To solve this, one should start by noticing that the angular integral corresponds to nothing more than the integral definition of the Bessel function of the first kind of order zero, $J_0(x)$, such that

$$\begin{aligned} \phi_2(\boldsymbol{\rho}) &= \frac{e}{2\epsilon_0} \frac{1}{(2\pi)^2} \int \frac{J_0(\rho q)}{\kappa + r_0 q} dq \\ &= \frac{e}{4\pi\epsilon_0} \frac{\pi}{2r_0} \left[\mathbf{H}_0\left(\frac{\kappa\rho}{r_0}\right) - \mathbf{Y}_0\left(\frac{\kappa\rho}{r_0}\right) \right], \end{aligned} \quad (\text{C.13})$$

with $\mathbf{H}_0$ and $\mathbf{Y}_0$ the Struve and Bessel function of the second kind, respectively, both of order zero. This expression corresponds to the Rytova-Keldysh potential commonly used to describe the electrostatic interaction in 2D materials. In this context κ is the mean dielectric constant of the media above and below the monolayer; the parameter r_0 which was previously defined as $r_0 = d\epsilon/2$ is considered as an effective in-plane screening length which should be chosen to correctly reproduce first principles calculations. Clearly r_0 can not have the same interpretation as in the case of a thin film since the thickness and dielectric constant of the monolayer are not well defined quantities.

Since Eq. (C.13) presents a somewhat complicated form, defined in term of special functions, it is convenient to study how it behaves in some limiting cases. In the limit of small distances, that is $\rho \rightarrow 0$, the Rytova-Keldysh potential presents a logarithmic divergence, with

$$\phi_2(\boldsymbol{\rho}) = -\frac{e}{4\pi\epsilon_0} \frac{1}{r_0} \left(\gamma_E + \ln \frac{\rho\kappa}{2r_0} \right), \quad (\text{C.14})$$

where $\gamma_E \approx 0.578$ is the Euler's gamma constant. In the opposite limit, that is, for $\rho \rightarrow \infty$, the potential behaves as

$$\phi_2(\boldsymbol{\rho}) = \frac{e}{4\pi\epsilon_0} \frac{1}{\kappa\rho}, \quad (\text{C.15})$$

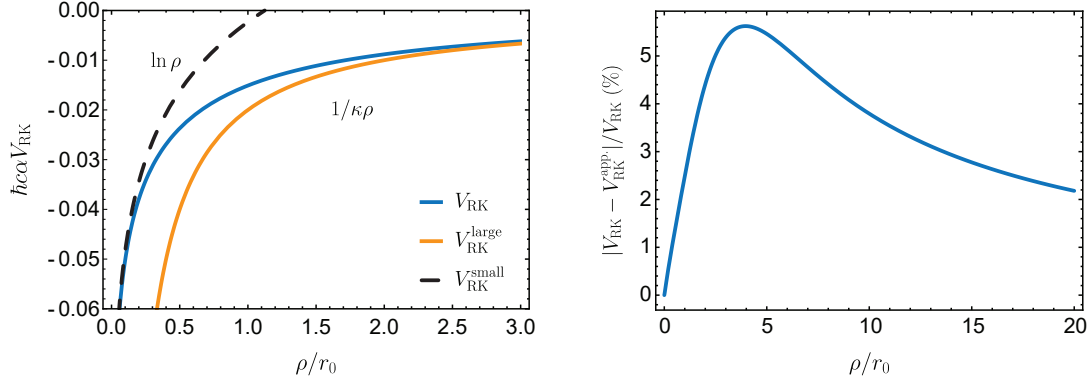


Figure 28: **Rytova-Keldysh potential.** (Left) Rytova-Keldysh potential as a function of the in-plane distance. Also depicted are the short and long range approximations. (Right) Comparison between the Rytova-Keldysh potential and its approximate expression. In both plots a value of $\kappa = 3$ and $r_0 = 50 \text{ \AA}$ was used.

which is nothing more than the Coulomb potential. Using these two limiting cases, and the results presented in Ref. [58], we introduce the following approximation for the Rytova-Keldysh potential

$$\phi_2(\boldsymbol{\rho}) \approx -\frac{e}{4\pi\epsilon_0} \frac{1}{r_0} \left[\ln \frac{\kappa\rho}{\kappa\rho + r_0} + (\gamma_E - \ln 2) e^{-\kappa\rho/r_0} \right], \quad (\text{C.16})$$

which is capable of describing the short and long range behavior with high accuracy, while also giving a good description of the intermediate region. In Fig. 28 we depict the Rytova-Keldysh potential as a function of the in-plane distance ρ ; the long-range Coulomb tail, and the logarithmic divergence near the origin are easily identifiable. Also depicted in Fig. 28 is the relative difference between Eq. (C.13) and (C.16). As expected, the two expressions agree well with each other, even in the region of intermediate distances.

Dynamical polarizability tensor from perturbation theory

For completeness, in this appendix we will introduce the different pictures of quantum mechanics, and how time evolution is described in each of them. Afterwards, we will derive the definition of the dynamical polarizability tensor from time dependent perturbation theory. The discussion of this appendix follows that of Ref. [79].

D.1 Time evolution operators

The study of the time evolution in quantum mechanics is associated with different pictures that place the time dependence in either the states, the operators, or both.

In the Schrodinger picture the time dependence is associated solely with the states. The differential equation governing their evolution in time reads

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi(t)\rangle, \quad (\text{D.1})$$

which is equivalent to the integral equation

$$|\psi(t)\rangle = |\psi(t_0)\rangle - \frac{i}{\hbar} \int_{t_0}^t H(\tau) |\psi(\tau)\rangle d\tau. \quad (\text{D.2})$$

One way of solving this equation is through successive iterations, yielding

$$\begin{aligned} |\psi(t)\rangle &= |\psi(t_0)\rangle - \frac{i}{\hbar} \int_{t_0}^t H(\tau) d\tau |\psi(t_0)\rangle - \frac{1}{\hbar^2} \int_{t_0}^t d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 H(\tau_1) H(\tau_2) |\psi(t_0)\rangle + \dots \\ &= \mathcal{T} \exp \left(-\frac{i}{\hbar} \int_{t_0}^t H(\tau) d\tau \right) |\psi(t_0)\rangle, \end{aligned}$$

where $\mathcal{T}$ is the time ordering operator, which ensures the correct ordering of the Hamiltonians. This relation between $|\psi(t)\rangle$ and $|\psi(t_0)\rangle$ suggests the introduction of an operator which describes the evolution of the state in time:

$$U(t, t_0) \equiv \mathcal{T} \exp \left(-\frac{i}{\hbar} \int_{t_0}^t H(\tau) d\tau \right). \quad (\text{D.3})$$

This time evolution operator can also be defined as the solution of the differential equation

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = H(t)U(t, t_0), \quad (\text{D.4})$$

or the integral equation

$$U(t, t_0) = \mathbb{I} - \frac{i}{\hbar} \int_{t_0}^t H(\tau)U(\tau, t_0)d\tau, \quad (\text{D.5})$$

where we used the initial condition $U(t_0, t_0) = \mathbb{I}$. One of the most important properties of this operator is the composition law, that is

$$U(t, t_1)U(t_1, t_0) = U(t, t_0). \quad (\text{D.6})$$

The composition law also leads to the following relation

$$U(t, t_0)U(t_0, t) = U(t, t) \equiv \mathbb{I} \Rightarrow U^{-1}(t, t_0) = U(t_0, t), \quad (\text{D.7})$$

that when combined with Eq. (D.3), yields

$$U^\dagger(t, t_0) = U^{-1}(t, t_0) = U(t_0, t). \quad (\text{D.8})$$

An alternative to the Schrodinger representation of quantum mechanics is the Heisenberg picture. In this formulation, the time dependence is shifted in its entirety from the states to the operators. The state vectors in the Schrodinger and Heisenberg representations are related according to

$$|\psi_H\rangle = |\psi_S(t_0)\rangle = U(t_0, t)|\psi_S(t)\rangle, \quad (\text{D.9})$$

where the indexes H and S refer to the Heisenberg and Schrodinger representations, respectively. To obtain the time dependence of an operator, $\hat{O}$, we consider its matrix element, that is

$$\langle\psi_S(t)|\hat{O}_S|\psi_S(t)\rangle = \langle\psi_H|U(t_0, t)\hat{O}_S U(t, t_0)|\psi_H\rangle,$$

where we now identify the operator in the Heisenberg picture as

$$\hat{O}_H(t) = U(t_0, t)\hat{O}_S U(t, t_0). \quad (\text{D.10})$$

The time evolution of the operator is given by the Heisenberg equation

$$\frac{d}{dt}\hat{O}_H(t) = U(t_0, t) \left(\frac{i}{\hbar} [H(t), \hat{O}_S(t)] + \frac{d}{dt}\hat{O}_S(t) \right) U(t, t_0). \quad (\text{D.11})$$

The final representation we will discuss is the interaction picture. This formulation of quantum mechanics is a middle term between the Heisenberg and the Schrodinger formulations, and is the most useful one in perturbation theory. This representation consists on separating the Hamiltonian into two

contributions: i) the free Hamiltonian, $H_0(t)$, which is solvable, and ii) the interaction term, $V(t)$, which is treated as a perturbation. The term H_0 is associated with the free time evolution operator, defined in an analogous way to Eq. (D.3),

$$U_0(t, t_0) = \mathcal{T} \exp \left(-\frac{i}{\hbar} \int_{t_0}^t H_0(\tau) d\tau \right). \quad (\text{D.12})$$

The states in the interaction picture are related to the ones of the Schrodinger picture according to

$$\begin{aligned} |\psi_I(t)\rangle &= U_0^\dagger(t, t_1) |\psi_S(t)\rangle \\ &= U_0^\dagger(t, t_1) U(t, t_0) |\psi_S(t_0)\rangle \\ &= U_0^\dagger(t, t_1) U(t, t_0) U_0(t_0, t_1) |\psi_I(t_0)\rangle, \end{aligned} \quad (\text{D.13})$$

which leads to the definition of the time evolution operator in the interaction picture:

$$U_I(t, t_0) = U_0^\dagger(t, t_1) U(t, t_0) U_0(t_0, t_1). \quad (\text{D.14})$$

The relation between the operators in the interaction and Schrodinger pictures can be once again obtained from the matrix element of the operator and reads:

$$\hat{O}_I(t) = U_0^\dagger(t, t_0) \hat{O}_S U_0(t, t_0), \quad (\text{D.15})$$

The differential equation governing their time evolution is:

$$i\hbar \frac{d}{dt} \hat{O}_I(t) = - [H_0(t), \hat{O}_I(t)]. \quad (\text{D.16})$$

Differentiating Eq. (D.13) with respect to t , and using the definition of Eq. (D.15) one finds the differential equation that determines the time evolution of the state in the interaction picture:

$$\begin{aligned} i\hbar \frac{d}{dt} |\psi_I(t)\rangle &= U_0^\dagger(t, t_1) [H(t) - H_0(t)] |\psi_S(t)\rangle \\ &= U_0^\dagger(t, t_1) V(t) U_0(t, t_1) |\psi_I(t)\rangle \\ &= V_I(t) |\psi_I(t)\rangle. \end{aligned}$$

This differential equation leads to the introduction of yet another time evolution operator

$$U_I(t, t_0) = \mathcal{T} \exp \left(-\frac{i}{\hbar} \int_{t_0}^t V_I(\tau) d\tau \right). \quad (\text{D.17})$$

Thus, the states in the interaction picture evolve with the perturbative term, while the operators evolve with the free part of the Hamiltonian.

D.2 Polarizability tensor

To compute the polarizability tensor we start by considering that at an initial time, $t = 0$, the system is described by the state vector $|\psi_v^{(0)}(0)\rangle$, with v an arbitrary index. At that same instant an external time dependent electric field, $\mathbf{E}(t)$, is applied to the system. The state vector describing the system in the presence of the electric field is $|\psi_v(t)\rangle$. Using time-evolution operators, we write

$$|\psi_v(t)\rangle - |\psi_v^{(0)}(t)\rangle = \Theta(t) [U(t) - U_0(t)] |\psi_v^{(0)}(0)\rangle, \quad (\text{D.18})$$

where $U(t)$ and $U_0(t)$ are the time evolution operators of the perturbed and unperturbed systems, respectively, such that $U(t)|\psi_v^{(0)}(0)\rangle = |\psi_v(t)\rangle$ and $U_0(t)|\psi_v^{(0)}(0)\rangle = |\psi_v^{(0)}(t)\rangle$. The Heaviside function, $\Theta(t)$, appears since the electric field is only applied at $t = 0$. This equation can be rewritten as

$$|\psi_v(t)\rangle - |\psi_v^{(0)}(t)\rangle = \Theta(t)U_0(t) \left[U_0^\dagger(t)U(t)U_0(0) - \mathbb{I} \right] |\psi_v^{(0)}(0)\rangle,$$

where $U_0(t)U_0^\dagger(t) = \mathbb{I}$ and $U_0(0) = \mathbb{I}$. We now note that $U_0^\dagger(t)U(t)U_0(0) = U_I(t)$, with $U_I(t)$ the time evolution operator in the interaction picture. Hence:

$$|\psi_v(t)\rangle - |\psi_v^{(0)}(t)\rangle = \Theta(t)U_0(t) [U_I(t) - \mathbb{I}] |\psi_v^{(0)}(0)\rangle. \quad (\text{D.19})$$

Expanding $U_I(t)$ up to first order, we find

$$\begin{aligned} |\psi_v(t)\rangle - |\psi_v^{(0)}(t)\rangle &\equiv |\psi_v^{(1)}(t)\rangle = -\frac{i}{\hbar}\Theta(t)U_0(t) \int_0^t d\tau H_I(\tau) |\psi_v^{(0)}(0)\rangle \\ &= -\frac{i}{\hbar}\Theta(t)U_0(t) \int_0^t d\tau U_0^\dagger(\tau)V(\tau)U_0(\tau) |\psi_v^{(0)}(0)\rangle \\ &= -\frac{i}{\hbar}\Theta(t) \int_0^t d\tau U_0(t-\tau)V(\tau)U_0(\tau) |\psi_v^{(0)}(0)\rangle, \end{aligned} \quad (\text{D.20})$$

where in the dipole approximation, $V(t) = -q\mathbf{x} \cdot \mathbf{E}(t)$. In the lowest order of perturbation, the induced dipole is given by

$$\begin{aligned} \mathbf{p}(t) &= \langle \psi_v^{(0)}(t) | q\mathbf{x} | \psi_v^{(1)}(t) \rangle + \langle \psi_v^{(1)}(t) | q\mathbf{x} | \psi_v^{(0)}(t) \rangle \\ &= q^2 \frac{i}{\hbar} \Theta(t) \int_0^t d\tau \langle \psi_v^{(0)}(0) | U_0^\dagger(t) \mathbf{x} U_0(t-\tau) \mathbf{x} \cdot \mathbf{E}(\tau) U_0(\tau) | \psi_v^{(0)}(0) \rangle \\ &\quad - q^2 \frac{i}{\hbar} \Theta(t) \int_0^t d\tau \langle \psi_v^{(0)}(0) | U_0^\dagger(\tau) \mathbf{x} \cdot \mathbf{E}(\tau) U_0^\dagger(t-\tau) \mathbf{x} U_0(t) | \psi_v^{(0)}(0) \rangle, \end{aligned}$$

using the composition law we write $U_0(t-\tau) = U_0(t)U_0^\dagger(\tau)$, and find

$$\begin{aligned} \mathbf{p}(t) &= \langle \psi_v^{(0)}(t) | q\mathbf{x} | \psi_v^{(1)}(t) \rangle + \langle \psi_v^{(1)}(t) | q\mathbf{x} | \psi_v^{(0)}(t) \rangle \\ &= q^2 \frac{i}{\hbar} \Theta(t) \int_0^t d\tau \langle \psi_v^{(0)}(0) | U_0^\dagger(t) \mathbf{x} U_0(t) U_0^\dagger(\tau) \mathbf{x} \cdot \mathbf{E}(\tau) U_0(\tau) | \psi_v^{(0)}(0) \rangle \\ &\quad - q^2 \frac{i}{\hbar} \Theta(t) \int_0^t d\tau \langle \psi_v^{(0)}(0) | U_0^\dagger(\tau) \mathbf{x} \cdot \mathbf{E}(\tau) U_0(\tau) U_0^\dagger(t) \mathbf{x} U_0(t) | \psi_v^{(0)}(0) \rangle. \end{aligned} \quad (\text{D.21})$$

At this point we introduce completeness relation of the unperturbed system, $\sum_{\lambda} |\psi_{\lambda}^{(0)}(0)\rangle \langle \psi_{\lambda}^{(0)}(0)| = \mathbb{I}$, and obtain

$$\begin{aligned} \mathbf{p}(t) = & q^2 \frac{i}{\hbar} \Theta(t) \sum_{\lambda} \int_0^t d\tau \langle \psi_{\nu}^{(0)}(0) | U_0^{\dagger}(t) \mathbf{x} U_0(t) | \psi_{\lambda}^{(0)}(0) \rangle \langle \psi_{\lambda}^{(0)}(0) | U_0^{\dagger}(\tau) \mathbf{x} \cdot \mathbf{E}(\tau) U_0(\tau) | \psi_{\nu}^{(0)}(0) \rangle \\ & - q^2 \frac{i}{\hbar} \Theta(t) \sum_{\lambda} \int_0^t d\tau \langle \psi_{\nu}^{(0)}(0) | U_0^{\dagger}(\tau) \mathbf{x} \cdot \mathbf{E}(\tau) U_0(\tau) | \psi_{\lambda}^{(0)}(0) \rangle \langle \psi_{\lambda}^{(0)}(0) | U_0^{\dagger}(t) \mathbf{x} U_0(t) | \psi_{\nu}^{(0)}(0) \rangle, \end{aligned}$$

which can be simplified as

$$\begin{aligned} \mathbf{p}(t) = & q^2 \frac{i}{\hbar} \Theta(t) \sum_{\lambda} \int_0^t d\tau \langle \psi_{\nu}^{(0)}(0) | \mathbf{x} | \psi_{\lambda}^{(0)}(0) \rangle \langle \psi_{\lambda}^{(0)}(0) | \mathbf{x} \cdot \mathbf{E}(\tau) | \psi_{\nu}^{(0)}(0) \rangle e^{-i\omega_{\nu\lambda}(t-\tau)} \\ & - q^2 \frac{i}{\hbar} \Theta(t) \sum_{\lambda} \int_0^t d\tau \langle \psi_{\nu}^{(0)}(0) | \mathbf{x} \cdot \mathbf{E}(\tau) | \psi_{\lambda}^{(0)}(0) \rangle \langle \psi_{\lambda}^{(0)}(0) | \mathbf{x} | \psi_{\nu}^{(0)}(0) \rangle e^{i\omega_{\nu\lambda}(t-\tau)}, \end{aligned} \quad (\text{D.22})$$

with $\omega_{\nu\lambda} = \omega_{\nu} - \omega_{\lambda}$. The induced dipole can thus be written as

$$\mathbf{p} = \int_0^{\infty} \bar{\bar{\alpha}}(t - \tau) \cdot \mathbf{E}(\tau) d\tau, \quad (\text{D.23})$$

where the temporal representation of the dynamical polarizability tensor is defined as

$$\begin{aligned} \bar{\bar{\alpha}}(t - \tau) = & q^2 \frac{i}{\hbar} \Theta(t - \tau) \sum_{\lambda} \left[\langle \psi_{\nu}^{(0)} | \mathbf{x} | \psi_{\lambda}^{(0)} \rangle \otimes \langle \psi_{\lambda}^{(0)} | \mathbf{x} | \psi_{\nu}^{(0)} \rangle e^{-i\omega_{\nu\lambda}(t-\tau)} \right. \\ & \left. - \langle \psi_{\lambda}^{(0)} | \mathbf{x} | \psi_{\nu}^{(0)} \rangle \otimes \langle \psi_{\nu}^{(0)} | \mathbf{x} | \psi_{\lambda}^{(0)} \rangle e^{i\omega_{\nu\lambda}(t-\tau)} \right]. \end{aligned}$$

We now assume that the applied electric field has an harmonic time dependence, that is

$$\mathbf{E}(t) = E_{\omega} (e^{i\omega t} + e^{-i\omega t}).$$

Using this, the the integral over τ in Eq. (D.23) can be explicitly evaluated, which yields

$$\begin{aligned} \mathbf{p} = & \frac{q^2}{2\hbar} \sum_{\lambda} \langle \psi_{\nu}^{(0)} | \mathbf{x} | \psi_{\lambda}^{(0)} \rangle \otimes \langle \psi_{\lambda}^{(0)} | \mathbf{x} | \psi_{\nu}^{(0)} \rangle \left(\frac{1}{\omega_{\nu\lambda} - \omega} + \frac{1}{\omega_{\nu\lambda} + \omega} \right) \mathbf{E}(t) \\ & + \frac{q^2}{2\hbar} \sum_{\lambda} \langle \psi_{\lambda}^{(0)} | \mathbf{x} | \psi_{\nu}^{(0)} \rangle \otimes \langle \psi_{\nu}^{(0)} | \mathbf{x} | \psi_{\lambda}^{(0)} \rangle \left(\frac{1}{\omega_{\nu\lambda} - \omega} + \frac{1}{\omega_{\nu\lambda} + \omega} \right) \mathbf{E}(t). \end{aligned} \quad (\text{D.24})$$

To obtain this result we assumed the field to oscillate slowly, that is, $\omega \ll |\omega_{\nu\lambda}|$, such that the dominant terms are the ones which are in phase with the electric field. Also, terms proportional to ω were dropped. Despite these assumptions the end result is valid for any value of ω as long as a small imaginary part is added in the denominator. The frequency dependent polarizability, $\bar{\bar{\alpha}}(\omega)$, is defined as

$$\mathbf{p} = \bar{\bar{\alpha}}(\omega) \mathbf{E}(t)$$

with

$$\begin{aligned} \bar{\bar{\alpha}}(\omega) = & \frac{q^2}{2\hbar} \sum_{\lambda} \left(\frac{1}{\omega_{v\lambda} - \omega} + \frac{1}{\omega_{v\lambda} + \omega} \right) \times \\ & \times \left[\langle \psi_v^{(0)} | \mathbf{x} | \psi_{\lambda}^{(0)} \rangle \otimes \langle \psi_{\lambda}^{(0)} | \mathbf{x} | \psi_v^{(0)} \rangle + \langle \psi_{\lambda}^{(0)} | \mathbf{x} | \psi_v^{(0)} \rangle \otimes \langle \psi_v^{(0)} | \mathbf{x} | \psi_{\lambda}^{(0)} \rangle \right] \end{aligned}$$

or equivalently

$$\begin{aligned} \alpha_{ij}(\omega) = & \frac{q^2}{2\hbar} \sum_{\lambda} \left(\frac{1}{\omega_{v\lambda} - \omega} + \frac{1}{\omega_{v\lambda} + \omega} \right) \times \\ & \times \left[\langle \psi_v^{(0)} | x_i | \psi_{\lambda}^{(0)} \rangle \langle \psi_{\lambda}^{(0)} | x_j | \psi_v^{(0)} \rangle + \langle \psi_{\lambda}^{(0)} | x_i | \psi_v^{(0)} \rangle \langle \psi_v^{(0)} | x_j | \psi_{\lambda}^{(0)} \rangle \right]. \end{aligned} \quad (\text{D.25})$$

Although at first it may not seem, this equation is identical to the one given in the main text. This is clearly seen when we set $i = j$, for example for $\alpha_{xx}(\omega)$, and

$$\alpha_{xx}(\omega) = \frac{q^2}{\hbar} \sum_{\lambda} \langle \psi_v^{(0)} | x | \psi_{\lambda}^{(0)} \rangle \langle \psi_{\lambda}^{(0)} | x | \psi_v^{(0)} \rangle \left(\frac{1}{\omega_{v\lambda} - \omega} + \frac{1}{\omega_{v\lambda} + \omega} \right). \quad (\text{D.26})$$

just like the result of the main text.

Exciton-phonon coupling

In this appendix we describe in a detailed manner how to obtain the exciton-phonon interaction Hamiltonian from the Hamiltonian describing the interaction of the individual carriers with phonons. The starting point is the following Hamiltonian:

$$H_{\chi-ph} = H_{e-ph} + H_{h-ph} = \sum_{\mathbf{q}, \mathbf{k}, \alpha} g_{\mathbf{k}, \mathbf{q}}^{(e), \alpha} c_{\mathbf{k}+\mathbf{q}, c}^{\dagger} c_{\mathbf{k}, c} \left(a_{-\mathbf{q}, \alpha}^{\dagger} + a_{\mathbf{q}, \alpha} \right) + \sum_{\mathbf{q}, \mathbf{k}, \alpha} g_{\mathbf{k}, \mathbf{q}}^{(h), \alpha} c_{\mathbf{k}+\mathbf{q}, v}^{\dagger} c_{\mathbf{k}, v} \left(a_{-\mathbf{q}, \alpha}^{\dagger} + a_{\mathbf{q}, \alpha} \right), \quad (\text{E.1})$$

where the first and second terms describe scattering with phonons in the conduction and valence band, respectively; $g_{\mathbf{k}, \mathbf{q}}^{(e/h), \alpha}$ are the carrier-phonon couplings, α refers to the phonon mode, $\mathbf{q}$ to the phonon momentum and $\mathbf{k}$ to the electron momentum; $c^{(\dagger)}$ and $a^{(\dagger)}$ refer to annihilation (creation) operators of electrons and phonons, respectively. Note that in this definition the momenta are measured relatively to the Γ point of the Brillouin zone. To describe intervalley scattering it is useful to measure the momenta relatively to different valleys of the BZ. To do so we transform the sums over the momenta which cover all the BZ, to a sum over the high symmetry points combined with a sum over the momenta in the vicinity of each points. This way we still cover the entire BZ, but it is easier to identify the valleys we are interested in. With this modification, and working in the deformation potential framework (which allows us to write $g_{\mathbf{k}, \mathbf{q}}^{(e), \alpha} \rightarrow g_{\mathbf{q}}^{(e), \alpha}$) we find

$$H_{\chi-ph} = \sum_{\mathbf{q}, \mathbf{k}, \alpha} \sum_{i, j} g_{j, \mathbf{q}}^{(e), \alpha} c_{\mathbf{k}+\mathbf{q}, c}^{\dagger, i+j} c_{\mathbf{k}, c}^i \left(a_{-\mathbf{q}, \alpha}^{\dagger, -j} + a_{\mathbf{q}, \alpha}^j \right) + \sum_{\mathbf{q}, \mathbf{k}, \alpha} \sum_{i, j} g_{j, \mathbf{q}}^{(h), \alpha} c_{\mathbf{k}+\mathbf{q}, v}^{\dagger, i+j} c_{\mathbf{k}, v}^i \left(a_{-\mathbf{q}, \alpha}^{\dagger, -j} + a_{\mathbf{q}, \alpha}^j \right), \quad (\text{E.2})$$

where the momenta in subscript are measured relatively to the symmetry points in superscript.

To quantize this Hamiltonian in terms of exciton operators, we write:

$$\hat{H}_{\chi-ph} = \sum_{\mathbf{K}, \mathbf{Q}} \sum_{\mu, \nu} \sum_{\zeta_e, \zeta_h} \sum_{\xi_e, \xi_h} \langle \mu, \zeta_h, \zeta_e, \mathbf{K} | H_{int} | \nu, \xi_h, \xi_e, \mathbf{Q} \rangle b_{\mu, \mathbf{K}}^{\dagger \zeta_h \zeta_e} b_{\nu, \mathbf{Q}}^{\xi_h \xi_e}.$$

Now, we introduce the definition of $|\nu, \xi_h, \xi_e, \mathbf{Q}\rangle$ given in the main text using Eqs. (4.1) and (4.2)

$$\begin{aligned} \hat{H}_{X-ph} = & \sum_{\mathbf{K}, \mathbf{Q}} \sum_{\mu\nu} \sum_{\zeta_e, \zeta_h} \sum_{\xi_e, \xi_h} \sum_{\mathbf{q}, \mathbf{k}, \alpha, \lambda} \sum_{i,j} \sum_{\mathbf{q}_1, \mathbf{q}_2} g_{j,\mathbf{q}}^{(\lambda), \alpha} \phi_{\mu, \mathbf{q}_2}^{\zeta_h, \zeta_e} \phi_{\nu, \mathbf{q}_1}^{\xi_h, \xi_e} \left(a_{-j, -\mathbf{q}, \alpha}^\dagger + a_{j, \mathbf{q}, \alpha} \right) \times \\ & \times \langle c_{\mathbf{q}_2 - \beta_{\zeta_h \zeta_e}}^{\dagger, \zeta_h} c_{\mathbf{q}_2 + \alpha_{\zeta_h \zeta_e}}^{\zeta_e} c_{\mathbf{k} + \mathbf{q}, \lambda}^{\dagger, i+j} c_{\mathbf{k}, \lambda}^i c_{\mathbf{q}_1 + \alpha_{\xi_h \xi_e}}^{\dagger, \xi_e} c_{\mathbf{q}_1 - \beta_{\xi_h \xi_e}}^{\xi_h} c_{\mathbf{Q}, v} \rangle b_{\mu, \mathbf{K}}^{\dagger \zeta_h \zeta_e} b_{\nu, \mathbf{Q}}^{\xi_h \xi_e}, \end{aligned} \quad (\text{E.3})$$

where $\langle \dots \rangle \equiv \langle GS | \dots | GS \rangle$. To compute the expectation value we use Wick's theorem, which unfolds this expectation value in the sum of different contributions. Most of the terms vanish since we are considering the $|GS\rangle$ to refer to an empty conduction band and a full valence band, and in the end we find.

$$\begin{aligned} & \langle c_{\mathbf{q}_2 - \beta_{\zeta_h \zeta_e}}^{\dagger, \zeta_h} c_{\mathbf{q}_2 + \alpha_{\zeta_h \zeta_e}}^{\zeta_e} c_{\mathbf{k} + \mathbf{q}, \lambda}^{\dagger, i+j} c_{\mathbf{k}, \lambda}^i c_{\mathbf{q}_1 + \alpha_{\xi_h \xi_e}}^{\dagger, \xi_e} c_{\mathbf{q}_1 - \beta_{\xi_h \xi_e}}^{\xi_h} c_{\mathbf{Q}, v} \rangle = \\ & = - \langle c_{\mathbf{q}_2 - \beta_{\zeta_h \zeta_e}}^{\dagger, \zeta_h} c_{\mathbf{k}, \lambda}^i \rangle \langle c_{\mathbf{q}_2 + \alpha_{\zeta_h \zeta_e}}^{\zeta_e} c_{\mathbf{q}_1 + \alpha_{\xi_h \xi_e}}^{\dagger, \xi_e} c_{\mathbf{Q}, v} \rangle \langle c_{\mathbf{k} + \mathbf{q}, \lambda}^{\dagger, i+j} c_{\mathbf{q}_1 - \beta_{\xi_h \xi_e}}^{\xi_h} c_{\mathbf{Q}, v} \rangle \\ & + \langle c_{\mathbf{q}_2 - \beta_{\zeta_h \zeta_e}}^{\dagger, \zeta_h} c_{\mathbf{q}_1 - \beta_{\xi_h \xi_e}}^{\xi_h} c_{\mathbf{Q}, v} \rangle \langle c_{\mathbf{q}_2 + \alpha_{\zeta_h \zeta_e}}^{\zeta_e} c_{\mathbf{k} + \mathbf{q}, \lambda}^{\dagger, i+j} \rangle \langle c_{\mathbf{k}, \lambda}^i c_{\mathbf{q}_1 + \alpha_{\xi_h \xi_e}}^{\dagger, \xi_e} c_{\mathbf{Q}, v} \rangle \\ & + \langle c_{\mathbf{q}_2 - \beta_{\zeta_h \zeta_e}}^{\dagger, \zeta_h} c_{\mathbf{q}_1 - \beta_{\xi_h \xi_e}}^{\xi_h} c_{\mathbf{Q}, v} \rangle \langle c_{\mathbf{k} + \mathbf{q}, \lambda}^{\dagger, i+j} c_{\mathbf{k}, \lambda}^i \rangle \langle c_{\mathbf{q}_2 + \alpha_{\zeta_h \zeta_e}}^{\zeta_e} c_{\mathbf{q}_1 + \alpha_{\xi_h \xi_e}}^{\dagger, \xi_e} c_{\mathbf{Q}, v} \rangle \end{aligned}$$

From each of the expectation values different Kronecker- δ appear

$$\begin{aligned} & \langle c_{\mathbf{q}_2 - \beta_{\zeta_h \zeta_e}}^{\dagger, \zeta_h} c_{\mathbf{q}_2 + \alpha_{\zeta_h \zeta_e}}^{\zeta_e} c_{\mathbf{k} + \mathbf{q}, \lambda}^{\dagger, i+j} c_{\mathbf{k}, \lambda}^i c_{\mathbf{q}_1 + \alpha_{\xi_h \xi_e}}^{\dagger, \xi_e} c_{\mathbf{q}_1 - \beta_{\xi_h \xi_e}}^{\xi_h} c_{\mathbf{Q}, v} \rangle = \\ & = - \delta_{\lambda, v} \delta_{i, \zeta_h} \delta_{\mathbf{q}_2 - \beta_{\zeta_h \zeta_e}} c_{\mathbf{k}, \lambda}^i \delta_{\zeta_e, \zeta_e} \delta_{\mathbf{q}_2 + \alpha_{\zeta_h \zeta_e}} c_{\mathbf{q}_1 + \alpha_{\xi_h \xi_e}} c_{\mathbf{Q}, v} \delta_{i+j, \zeta_h} \delta_{\mathbf{k} + \mathbf{q}, \mathbf{q}_1 - \beta_{\xi_h \xi_e}} c_{\mathbf{Q}, v} \\ & + \delta_{\zeta_h, \zeta_h} \delta_{\mathbf{q}_2 - \beta_{\zeta_h \zeta_e}} c_{\mathbf{q}_1 - \beta_{\xi_h \xi_e}} c_{\mathbf{Q}, v} \delta_{\lambda, c} \delta_{\zeta_e, i+j} \delta_{\mathbf{q}_2 + \alpha_{\zeta_h \zeta_e}} c_{\mathbf{k} + \mathbf{q}, \lambda}^{\dagger, i+j} \delta_{i, \zeta_e} \delta_{\mathbf{k}, \mathbf{q}_1 + \alpha_{\xi_h \xi_e}} c_{\mathbf{Q}, v} \\ & + \delta_{\zeta_h, \zeta_h} \delta_{\mathbf{q}_2 - \beta_{\zeta_h \zeta_e}} c_{\mathbf{q}_1 - \beta_{\xi_h \xi_e}} c_{\mathbf{Q}, v} \delta_{j, 0} \delta_{\lambda, v} \delta_{\mathbf{q}, 0} \delta_{\zeta_e, \zeta_e} \delta_{\mathbf{q}_2 + \alpha_{\zeta_h \zeta_e}} c_{\mathbf{q}_1 + \alpha_{\xi_h \xi_e}} c_{\mathbf{Q}, v}. \end{aligned}$$

The term with $\delta_{\mathbf{q}, 0}$ can be dropped since this contribution is implicitly excluded from the sums in the definition of the Hamiltonian. Hence:

$$\begin{aligned} \hat{H}_{X-ph} = & \sum_{\mathbf{K}, \mathbf{Q}, \mathbf{k}} \sum_{\mu\nu, \alpha} \sum_{\zeta_e} \sum_{\xi_e, \xi_h} g_{\zeta_e - \xi_e, \mathbf{K} - \mathbf{Q}}^{(e), \alpha} \phi_{\mu, \mathbf{k} - \mathbf{Q} + \beta_{\zeta_h \zeta_e}}^{\zeta_h, \zeta_e} \phi_{\nu, \mathbf{k} - \alpha_{\xi_h \xi_e}}^{\xi_h, \xi_e} b_{\mu, \mathbf{K}}^{\dagger \zeta_h \zeta_e} b_{\nu, \mathbf{Q}}^{\xi_h \xi_e} \times \\ & \times \left(a_{-(\zeta_e - \xi_e), -(\mathbf{K} - \mathbf{Q}), \alpha}^\dagger + a_{(\zeta_e - \xi_e), (\mathbf{K} - \mathbf{Q}), \alpha} \right) \\ & - \sum_{\mathbf{K}, \mathbf{Q}, \mathbf{k}} \sum_{\mu\nu, \alpha} \sum_{\zeta_h} \sum_{\xi_e, \xi_h} g_{\xi_h - \zeta_h, \mathbf{K} - \mathbf{Q}}^{(h), \alpha} \phi_{\mu, \mathbf{k} + \beta_{\zeta_h \xi_e}}^{\zeta_h, \xi_e} \phi_{\nu, \mathbf{k} + \mathbf{K} - \mathbf{Q} + \beta_{\xi_h \xi_e}}^{\xi_h, \xi_e} b_{\mu, \mathbf{K}}^{\dagger \zeta_h \xi_e} b_{\nu, \mathbf{Q}}^{\xi_h \xi_e} \times \\ & \times \left(a_{-(\xi_h - \zeta_h), -(\mathbf{K} - \mathbf{Q}), \alpha}^\dagger + a_{(\xi_h - \zeta_h), (\mathbf{K} - \mathbf{Q}), \alpha} \right). \end{aligned}$$

Performing the label changes $\zeta_e = \xi_e + j$, $\mathbf{K} = \mathbf{q} + \mathbf{Q}$ and $\mathbf{k} \rightarrow \mathbf{k} + \alpha_{\xi_h \xi_e} \mathbf{Q}$ on the first term, and

$\xi_h = \xi_h - j$, $\mathbf{K} = \mathbf{q} + \mathbf{Q}$ on the second one, leads to

$$\begin{aligned} \hat{H}_{X-ph} = & \sum_{\mathbf{Q}, \mathbf{q}, \mathbf{k}} \sum_{\mu, \nu, \alpha} \sum_j \sum_{\xi_e, \xi_h} g_{j, \mathbf{q}}^{(e), \alpha} \phi_{\mu, \mathbf{k} + \beta_{\xi_h}(\xi_e + j)}^{\xi_h, (\xi_e + j)} \mathbf{q} - \alpha_{\xi_h(\xi_e + j)} \mathbf{Q} \phi_{\nu, \mathbf{k} - \alpha_{\xi_h \xi_e} \mathbf{Q}}^{\xi_h, \xi_e} b_{\mu, \mathbf{q} + \mathbf{Q}}^{\dagger \xi_h, (\xi_e + j)} b_{\nu, \mathbf{Q}}^{\xi_h, \xi_e} \times \\ & \times \left(a_{-j, -\mathbf{q}, \alpha}^{\dagger} + a_{j, \mathbf{q}, \alpha} \right) \\ & - \sum_{\mathbf{K}, \mathbf{Q}, \mathbf{k}} \sum_{\mu, \nu, \alpha} \sum_{\xi_h} \sum_{\xi_e, \xi_h} g_{j, \mathbf{q}}^{(h), \alpha} \phi_{\mu, \mathbf{k} + \beta_{(\xi_h - j), \xi_e} \mathbf{q} + \beta_{(\xi_h - j), \xi_e} \mathbf{Q}}^{(\xi_h - j), \xi_e} \phi_{\nu, \mathbf{k} + \mathbf{q} + \beta_{\xi_h \xi_e} \mathbf{Q}}^{\xi_h, \xi_e} b_{\mu, \mathbf{q} + \mathbf{Q}}^{\dagger (\xi_h - j), \xi_e} b_{\nu, \mathbf{Q}}^{\xi_h, \xi_e} \times \\ & \times \left(a_{-j, -\mathbf{q}, \alpha}^{\dagger} + a_{j, \mathbf{q}, \alpha} \right). \end{aligned}$$

Thus, for a state with a given initial center of mass momentum $\mathbf{Q}$, quantum numbers ν and valley indexes ξ_e and ξ_h we obtain

$$\begin{aligned} \hat{H}_{X-ph} = & \sum_{\mathbf{q}} \sum_{\mu, \alpha, j} g_{\nu, \mu, \mathbf{q}, \mathbf{Q}}^{(e), \alpha, \xi_h, \xi_e, j} b_{\mu, \mathbf{q} + \mathbf{Q}}^{\dagger \xi_h, (\xi_e + j)} b_{\nu, \mathbf{Q}}^{\xi_h, \xi_e} \left(a_{-j, -\mathbf{q}, \alpha}^{\dagger} + a_{j, \mathbf{q}, \alpha} \right) \\ & - \sum_{\mathbf{q}} \sum_{\mu, \alpha, j} g_{\nu, \mu, \mathbf{q}, \mathbf{Q}}^{(h), \alpha, \xi_h, \xi_e, j} b_{\mu, \mathbf{q} + \mathbf{Q}}^{\dagger (\xi_h - j), \xi_e} b_{\nu, \mathbf{Q}}^{\xi_h, \xi_e} \left(a_{-j, -\mathbf{q}, \alpha}^{\dagger} + a_{j, \mathbf{q}, \alpha} \right). \end{aligned} \quad (\text{E.4})$$

where

$$\begin{aligned} g_{\nu, \mu, \mathbf{q}, \mathbf{Q}}^{(e), \alpha, \xi_h, \xi_e, j} &= g_{j, \mathbf{q}}^{(e), \alpha} \sum_{\mathbf{k}} \phi_{\mu, \mathbf{k} - \alpha_{\xi_h}(\xi_e + j)}^{\xi_h, (\xi_e + j)} \mathbf{q} - \alpha_{\xi_h(\xi_e + j)} \mathbf{Q} \phi_{\nu, \mathbf{k} - \alpha_{\xi_h \xi_e} \mathbf{Q}}^{\xi_h, \xi_e}, \\ g_{\nu, \mu, \mathbf{q}, \mathbf{Q}}^{(h), \alpha, \xi_h, \xi_e, j} &= g_{j, \mathbf{q}}^{(h), \alpha} \sum_{\mathbf{k}} \phi_{\mu, \mathbf{k} + \beta_{(\xi_h - j), \xi_e} \mathbf{q} + \beta_{(\xi_h - j), \xi_e} \mathbf{Q}}^{(\xi_h - j), \xi_e} \phi_{\nu, \mathbf{k} + \mathbf{q} + \beta_{\xi_h \xi_e} \mathbf{Q}}^{\xi_h, \xi_e}. \end{aligned}$$

Performing a label change on $\mathbf{k}$ we finally find

$$\begin{aligned} g_{\nu, \mu, \mathbf{q}}^{(e), \alpha, \xi_h, \xi_e, j} &= g_{j, \mathbf{q}}^{(e), \alpha} \sum_{\mathbf{k}} \phi_{\mu, \mathbf{k} - \alpha_{\xi_h}(\xi_e + j)}^{\xi_h, (\xi_e + j)} \mathbf{q} \phi_{\nu, \mathbf{k} - \mathbf{q}}^{\xi_h, \xi_e} = g_{j, \mathbf{q}}^{(e), \alpha} \sum_{\mathbf{k}} \phi_{\mu, \mathbf{k} + \beta_{\xi_h}(\xi_e + j)}^{\xi_h, (\xi_e + j)} \mathbf{q} \phi_{\nu, \mathbf{k}}^{\xi_h, \xi_e}, \\ g_{\nu, \mu, \mathbf{q}}^{(h), \alpha, \xi_h, \xi_e, j} &= g_{j, \mathbf{q}}^{(h), \alpha} \sum_{\mathbf{k}} \phi_{\mu, \mathbf{k} + \beta_{(\xi_h - j), \xi_e} \mathbf{q}}^{(\xi_h - j), \xi_e} \mathbf{q} \phi_{\nu, \mathbf{k} + \mathbf{q}}^{\xi_h, \xi_e} = g_{j, \mathbf{q}}^{(h), \alpha} \sum_{\mathbf{k}} \phi_{\mu, \mathbf{k} - \alpha_{(\xi_h - j), \xi_e} \mathbf{q}}^{(\xi_h - j), \xi_e} \mathbf{q} \phi_{\nu, \mathbf{k}}^{\xi_h, \xi_e}, \end{aligned}$$

resulting in the disappearance of the $\mathbf{Q}$ dependence.

A diagrammatic approach to the self energy

In this appendix we present an alternative technique to obtain the self energy associated with the exciton-phonon interaction. While in the main text the equation of motion approach was used, here the self energy will be obtained using imaginary time Green's functions (also known as Matsubara functions). The procedure here presented is an adaptation of the ideas of Ref. [118] where the electron-phonon interaction is studied.

F.1 Free phonon Matsubara function

As a first application of this formalism, let us determine the Matsubara function of non-interacting phonons. The starting point is the definition

$$d^0(\mathbf{q}\lambda, \tau) = - \left\langle T_\tau \phi_{\mathbf{q}\lambda}(\tau) \phi_{\mathbf{q}\lambda}^\dagger(0) \right\rangle_0, \quad (\text{F.1})$$

where $\phi_{\mathbf{q}\lambda} = a_{\mathbf{q}\lambda} + a_{-\mathbf{q}\lambda}^\dagger$, with $a_{\mathbf{q}\lambda}/a_{\mathbf{q}\lambda}^\dagger$ the annihilation/creation operator of a phonon with momentum $\mathbf{q}$ in the mode λ , T_τ is the time ordering operator acting on the imaginary time τ and the index 0 denotes a non-interacting system. The effect of the time ordering operator can be explicitly written as:

$$T_\tau \phi_{\mathbf{q}\lambda}(\tau) \phi_{\mathbf{q}\lambda}^\dagger(0) = \begin{cases} \phi_{\mathbf{q}\lambda}(\tau) \phi_{\mathbf{q}\lambda}^\dagger(0) & \tau > 0 \\ \phi_{\mathbf{q}\lambda}^\dagger(0) \phi_{\mathbf{q}\lambda}(\tau) & \tau < 0 \end{cases}$$

Just like any other Matsubara function, if one introduces the Lehmann representation of $d^0(\mathbf{q}\lambda, \tau)$, it is clear that the function is only defined in the interval $\tau \in [-\hbar\beta, \hbar\beta]$, with $\beta = 1/k_B T$. Besides this property, the Matsubara function for $-\hbar\beta < \tau < 0$ can be related with the one for $0 < \tau < \hbar\beta$. Considering $0 < \tau < \hbar\beta$ we have

$$d^0(\mathbf{q}\lambda, \tau) = d^0(\mathbf{q}\lambda, \tau - \hbar\beta), \quad 0 < \tau < \hbar\beta. \quad (\text{F.2})$$

Since $d^0(\mathbf{q}\lambda, \tau)$ is defined on a finite interval, we can expand it in a Fourier series as

$$d^0(\mathbf{q}\lambda, \tau) = \frac{1}{\hbar\beta} \sum_n e^{-i\omega_n\tau} d^0(\mathbf{q}\lambda, \omega_n). \quad (\text{F.3})$$

The periodicity of $d^0(\mathbf{q}\lambda, \tau)$ imposes a restriction on ω_n (the so called Matsubara frequencies). For $0 < \tau < \hbar\beta$ we write

$$\frac{1}{\hbar\beta} \sum_n e^{-i\omega_n\tau} d^0(\mathbf{q}\lambda, \omega_n) = \frac{1}{\hbar\beta} \sum_n e^{-i\omega_n(\tau-\beta\hbar)} d^0(\mathbf{q}\lambda, \omega_n), \quad (\text{F.4})$$

which is only satisfied if $e^{i\hbar\omega_n\beta} = 1$, or equivalently

$$\hbar\omega_n = \frac{2\pi n}{\beta}, \quad n = 0, 1, 2, \dots \quad (\text{F.5})$$

To obtain $d^0(\mathbf{q}\lambda, \omega_n)$ defined in terms of $d^0(\mathbf{q}\lambda, \tau)$ we multiply Eq. (F.3) by $e^{i\omega_m\tau}$ and integrate over τ from 0 to $\hbar\beta$. Doing so we find

$$d^0(\mathbf{q}\lambda, \omega_m) = \int_0^{\hbar\beta} d^0(\mathbf{q}\lambda, \tau) e^{i\omega_m\tau} d\tau \quad (\text{F.6})$$

Now that we introduced some of the properties of $d^0(\mathbf{q}\lambda, \tau)$ (which are quite general and apply to other Matsubara functions), we move on to its explicit computation. We start by noting that $d^0(\mathbf{q}\lambda, \tau)$, may be written as

$$\begin{aligned} d^0(\mathbf{q}\lambda, \tau) &= -\theta(\tau) \left\langle \phi_{\mathbf{q}\lambda}(\tau) \phi_{\mathbf{q}\lambda}^\dagger(0) \right\rangle - \theta(-\tau) \left\langle \phi_{\mathbf{q}\lambda}^\dagger(0) \phi_{\mathbf{q}\lambda}(\tau) \right\rangle \\ &= \theta(\tau) d^{0>}(\mathbf{q}\lambda, \tau) + \theta(-\tau) d^{0<}(\mathbf{q}\lambda, \tau). \end{aligned}$$

In terms of phonon operators we express $d^{0>}(\mathbf{q}\lambda, \tau)$ as

$$d^{0>}(\mathbf{q}\lambda, \tau) = - \left\langle \left(a_{\mathbf{q}\lambda}(\tau) + a_{-\mathbf{q}\lambda}^\dagger(\tau) \right) \left(a_{\mathbf{q}\lambda}^\dagger(0) + a_{-\mathbf{q}\lambda}(0) \right) \right\rangle_0, \quad (\text{F.7})$$

with $a_{\mathbf{q}\lambda}(\tau) = e^{H\tau/\hbar} a_{\mathbf{q}\lambda}(0) e^{-H\tau/\hbar}$, where $H = \sum_{\mathbf{q}\lambda} \hbar\omega_{\mathbf{q}\lambda} \left(a_{\mathbf{q}\lambda}^\dagger a_{\mathbf{q}\lambda} + 1/2 \right)$ is the phonon Hamiltonian.

Taking the derivative of $a_{\mathbf{q}\lambda}(\tau)$ with respect to τ we find:

$$\begin{aligned} \frac{\partial}{\partial \tau} a_{\mathbf{q}\lambda}(\tau) &= \frac{1}{\hbar} [H, a_{\mathbf{q}\lambda}(\tau)] \\ &= -\omega_{\mathbf{q}\lambda} a_{\mathbf{q}\lambda}(\tau). \end{aligned}$$

For $a_{-\mathbf{q}\lambda}^\dagger(\tau)$ we obtain

$$\frac{\partial}{\partial \tau} a_{-\mathbf{q}\lambda}^\dagger(\tau) = \omega_{\mathbf{q}\lambda} a_{-\mathbf{q}\lambda}^\dagger(\tau).$$

Thus, solving the differential equations

$$a_{\mathbf{q}\lambda}(\tau) = e^{-\omega_{\mathbf{q}\lambda}\tau} a_{\mathbf{q}\lambda}(0), \quad a_{-\mathbf{q}\lambda}^\dagger(\tau) = e^{\omega_{\mathbf{q}\lambda}\tau} a_{-\mathbf{q}\lambda}^\dagger(0). \quad (\text{F.8})$$

Inserting these in the definition of $d^{0>}(\mathbf{q}\lambda, \tau)$ the following result ensues

$$\begin{aligned} d^{0>}(\mathbf{q}\lambda, \tau) &= - \left\langle \left(e^{-\omega_{\mathbf{q}\lambda}\tau} a_{\mathbf{q}\lambda}(0) + e^{\omega_{\mathbf{q}\lambda}\tau} a_{-\mathbf{q}\lambda}^\dagger(0) \right) \left(a_{\mathbf{q}\lambda}^\dagger(0) + a_{-\mathbf{q}\lambda}(0) \right) \right\rangle_0 \\ &= - \left[e^{-\omega_{\mathbf{q}\lambda}\tau} \left\langle a_{\mathbf{q}\lambda}(0) a_{\mathbf{q}\lambda}^\dagger(0) \right\rangle_0 + e^{\omega_{\mathbf{q}\lambda}\tau} \left\langle a_{-\mathbf{q}\lambda}^\dagger(0) a_{-\mathbf{q}\lambda}(0) \right\rangle_0 \right] \\ &= -e^{-\omega_{\mathbf{q}\lambda}\tau} [1 + n_{\text{BE}}(\omega_{\mathbf{q}\lambda})] - e^{\omega_{\mathbf{q}\lambda}\tau} n_{\text{BE}}(\omega_{\mathbf{q}\lambda}), \end{aligned} \quad (\text{F.9})$$

with n_{BE} the Bose-Einstein distribution which describes the phonon population. For $d^{0<}(\mathbf{q}\lambda, \tau)$ a similar result is found

$$\begin{aligned} d^{0<}(\mathbf{q}\lambda, \tau) &= - \left\langle \left(a_{\mathbf{q}\lambda}^\dagger(0) + a_{-\mathbf{q}\lambda}(0) \right) \left(a_{\mathbf{q}\lambda}(\tau) + a_{-\mathbf{q}\lambda}^\dagger(\tau) \right) \right\rangle_0 \\ &= - \left[\left\langle a_{\mathbf{q}\lambda}^\dagger(0) a_{\mathbf{q}\lambda}(\tau) \right\rangle_0 + \left\langle a_{-\mathbf{q}\lambda}(0) a_{-\mathbf{q}\lambda}^\dagger(\tau) \right\rangle_0 \right] \\ &= -e^{-\omega_{\mathbf{q}\lambda}\tau} n_{\text{BE}}(\omega_{\mathbf{q}\lambda}) - e^{\omega_{\mathbf{q}\lambda}\tau} [1 + n_{\text{BE}}(\omega_{\mathbf{q}\lambda})]. \end{aligned} \quad (\text{F.10})$$

Finally, inserting Eq. (F.9) in Eq. (F.6) we obtain $d^0(\mathbf{q}\lambda, \tau)$ in terms of Matsubara frequencies

$$\begin{aligned} d^0(\mathbf{q}\lambda, \omega_m) &= - \int_0^{\hbar\beta} \left\{ e^{-\omega_{\mathbf{q}\lambda}\tau} [1 + n_{\text{BE}}(\omega_{\mathbf{q}\lambda})] + e^{\omega_{\mathbf{q}\lambda}\tau} n_{\text{BE}}(\omega_{\mathbf{q}\lambda}) \right\} e^{i\omega_m\tau} d\tau \\ &= \frac{2\omega_{\mathbf{q}\lambda}}{(i\omega_m)^2 - \omega_{\mathbf{q}\lambda}^2}, \end{aligned} \quad (\text{F.11})$$

where we used the fact that $e^{i\hbar\omega_m\beta} = 1$. The retarded Green's function can be obtain from $d^0(\mathbf{q}\lambda, \omega_m)$ by means of an analytical continuation

$$d^{0,R}(\mathbf{q}\lambda, \omega) = d^0(\mathbf{q}\lambda, i\omega_m \rightarrow \omega + i0^+). \quad (\text{F.12})$$

F.2 Exciton Matsubara function

Now that the Matsubara function of free phonons was derived, let us move on to the determination of the Matsubara function of the excitons. We are interested in two distinct functions: the Matsubara function of free excitons, that is, when no phonons are present in the system, and the full Matsubara function which contains the exciton-phonon interaction. Regarding the first one, we define as

$$G_0(\mathbf{Q}, \tau) = - \left\langle T_\tau b_{\mathbf{Q}}(\tau) b_{\mathbf{Q}}^\dagger(0) \right\rangle_0, \quad (\text{F.13})$$

with $b_{\mathbf{Q}}/b_{\mathbf{Q}}^{\dagger}$ the annihilation/creation operator of an exciton with center of mass momentum $\mathbf{Q}$. In analogy with what was done for the phonons we simply write

$$G_0(\mathbf{Q}, \omega_n) = \frac{1}{i\omega_n - E_{\mathbf{Q}}/\hbar}. \quad (\text{F.14})$$

To obtain the full exciton function, $G(\mathbf{Q}, \omega_n)$, we note that using the Matsubara formalism $G(\mathbf{Q}, \omega_n)$ can be expanded as a perturbation series in connected diagrams. Here we do not wish to prove this statement, and refer the reader to Refs. [118, 119]. A direct application of this result leads to

$$G(\mathbf{Q}, \tau) = - \sum_{n=0}^{\infty} \frac{(-1)^n}{\hbar^n n!} \int_0^{\hbar\beta} d\tau_1 \dots \int_0^{\hbar\beta} d\tau_n \left\langle T_{\tau} b_{\mathbf{Q}}(\tau) b_{\mathbf{Q}}^{\dagger}(0) V(\tau_1) \dots V(\tau_n) \right\rangle_{0,c}, \quad (\text{F.15})$$

where

$$V = \sum_{\mathbf{q}, \lambda} \sum_{\mathbf{Q}} g_{\mathbf{q}}^{\lambda} b_{\mathbf{Q}+\mathbf{q}1s}^{\dagger} b_{\mathbf{Q}1s} \phi_{\mathbf{q}, \lambda},$$

is the exciton-phonon interaction, and $\langle \dots \rangle_{0,c}$ indicates that only connected diagrams should be considered.

It is now clear that in order to find $G(\mathbf{Q}, \tau)$, we must study the different perturbation orders of Eq. (F.15). In the 0-th order of perturbation one trivially finds

$$G^{(0)}(\mathbf{Q}, \tau) = G_0(\mathbf{Q}, \tau). \quad (\text{F.16})$$

Taking the expansion in Eq. (F.15) to first order, we write

$$G^{(1)}(\mathbf{Q}, \tau) = \frac{1}{\hbar} \int_0^{\hbar\beta} d\tau_1 \left\langle T_{\tau} b_{\mathbf{Q}}(\tau) b_{\mathbf{Q}}^{\dagger}(0) V(\tau_1) \right\rangle_{0,c}, \quad (\text{F.17})$$

which can be evaluated using Wick's theorem. However, even without expanding the expectation value, we can already anticipate the result of the first order correction. Since we have a single operator $\phi_{\mathbf{q}, \lambda} = (a_{\mathbf{q}, \lambda} + a_{-\mathbf{q}, \lambda}^{\dagger})$, and the expectation value of a single phonon operators vanishes, the first order correction is automatically zero. In fact, this is the case for every odd correction order, and only even order corrections contribute to the full Matsubara function.

Moving up to the second order correction, we write

$$G^{(2)}(\mathbf{Q}, \tau) = -\frac{1}{2\hbar^2} \int_0^{\hbar\beta} d\tau_1 d\tau_2 \left\langle T_{\tau} b_{\mathbf{Q}}(\tau) b_{\mathbf{Q}}^{\dagger}(0) V(\tau_1) V(\tau_2) \right\rangle_{0,c}. \quad (\text{F.18})$$

In principle, this contribution is finite and it can be evaluated employing Wick's theorem. Introducing the definition of $V(\tau)$ we find for the expectation value:

$$\langle \dots \rangle_{0,c} = \sum_{\mathbf{q}, \mathbf{k}} \sum_{\lambda, \nu} \sum_{\mathbf{P}, \mathbf{K}} \left\langle T_{\tau} b_{\mathbf{Q}}(\tau) b_{\mathbf{Q}}^{\dagger}(0) g_{\mathbf{q}}^{\lambda} b_{\mathbf{P}+\mathbf{q}}^{\dagger}(\tau_1) b_{\mathbf{P}}(\tau_1) \phi_{\mathbf{q}, \lambda}(\tau_1) g_{\mathbf{k}}^{\nu} b_{\mathbf{K}+\mathbf{k}}^{\dagger}(\tau_2) b_{\mathbf{K}}(\tau_2) \phi_{\mathbf{k}, \nu}(\tau_2) \right\rangle_{0,c}.$$

To compute this expectation value we can proceed either analytically, by explicitly considering all the relevant contractions that appear in the application of Wick's theorem, or diagrammatically. The building

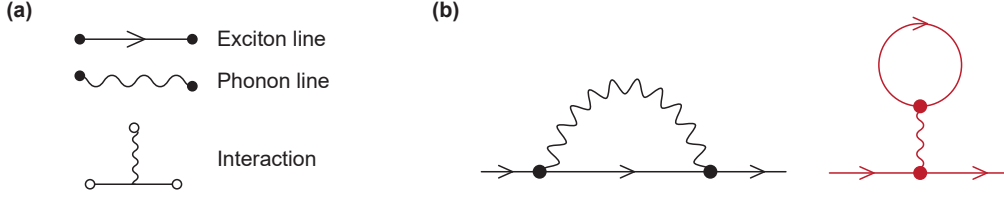


Figure 29: **Feynman diagrams.** (a) Building blocks to draw the Feynman diagrams. The black dots at the edges of the exciton and phonon lines should be connected to the whit dots of the interaction; (b) The two topologically distinct diagrams that appear in the second order correction to the Matsubara function. The one in red requires a vanishing transferred momentum (leading to no scattering) and is not included in the perturbative expansion.

blocks to follow a diagrammatic approach are depicted in Fig. 29a. In this order of perturbation we have to combine three exciton lines, with one phonon line and two interactions. Since we are restricted to connected diagrams, only two topologically distinct connected diagrams can be obtained, both with a degeneracy of two; these diagrams are depict in Fig. 29b. We now note that the diagram depicted in red requires the transferred moment to vanish, $\mathbf{q} = 0$, in order to guarantee momentum conservation in each vertex. As a result, we do not include this type of diagram in the perturbative expansion, since terms with $\mathbf{q} = 0$ do not contribute to scattering and are negligible in the exciton-phonon interaction. Analytically, the only relevant diagram is equivalent to the contribution

$$\langle \dots \rangle_{0,c} = 2 \sum_{\lambda, \mathbf{q}} \left| g_{-\mathbf{q}}^{\lambda} \right|^2 d^0(\mathbf{q}\lambda, \tau_1 - \tau_2) G_0(\mathbf{Q}, \tau - \tau_1) G_0(\mathbf{Q} - \mathbf{q}, \tau_1 - \tau_2) G_0(\mathbf{Q}, \tau_2),$$

where we identified the definition of the Matsubara functions after the application of Wick's theorem. The factor of 2 accounts for the degeneracy of the diagram. Inserting this into Eq. (F.18) leads to

$$G^{(2)}(\mathbf{Q}, \tau) = \frac{(-1)}{\hbar^2} \sum_{\lambda, \mathbf{q}} \left| g_{-\mathbf{q}}^{\lambda} \right|^2 \int_0^{\hbar\beta} d\tau_1 d\tau_2 \times d^0(\mathbf{q}\lambda, \tau_1 - \tau_2) G_0(\mathbf{Q}, \tau - \tau_1) G_0(\mathbf{Q} - \mathbf{q}, \tau_1 - \tau_2) G_0(\mathbf{Q}, \tau_2).$$

Introducing the Taylor expansions of the Matsubara functions we find:

$$G^{(2)}(\mathbf{Q}, \tau) = \frac{(-1)}{\hbar^2} \sum_{\lambda, \mathbf{q}} \left| g_{-\mathbf{q}}^{\lambda} \right|^2 \frac{1}{(\hbar\beta)^4} \sum_{l, m, n, o} \int_0^{\hbar\beta} d\tau_1 d\tau_2 e^{\tau_1(\omega_m - \omega_l - \omega_n)} e^{\tau_2(\omega_l + \omega_n - \omega_o)} \times e^{-\tau\omega_m} d^0(\mathbf{q}\lambda, \omega_l) G_0(\mathbf{Q}, \omega_m) G_0(\mathbf{Q} - \mathbf{q}, \omega_n) G_0(\mathbf{Q}, \omega_o).$$

We now perform the integrals over τ_1 and τ_2 and use the resulting Kronecker- δ 's to eliminate two of the sums. After some label changes we obtain

$$G^{(2)}(\mathbf{Q}, \tau) = \frac{(-1)}{\hbar\beta} \sum_n e^{-\tau\omega_n} \times \left[\frac{1}{\hbar^2} \sum_{\lambda, \mathbf{q}} \left| g_{-\mathbf{q}}^{\lambda} \right|^2 \frac{1}{\hbar\beta} \sum_l G_0(\mathbf{Q}, \omega_n) d^0(\mathbf{q}\lambda, \omega_l) G_0(\mathbf{Q} - \mathbf{q}, \omega_n - \omega_l) G_0(\mathbf{Q}, \omega_n) \right] \quad (\text{F.19})$$

where the term inside the brackets is nothing more than the representation of $G^{(2)}(\mathbf{Q}, \tau)$ in terms of Matsubara frequencies:

$$G^{(2)}(\mathbf{Q}, \omega_n) = \frac{1}{\hbar^2} \frac{(-1)}{\hbar\beta} \sum_{\lambda, \mathbf{q}} |g_{-\mathbf{q}}^\lambda|^2 \sum_l g_0(\mathbf{Q}, \omega_n) d^0(\mathbf{q}\lambda, \omega_l) g_0(\mathbf{Q} - \mathbf{q}, \omega_n - \omega_l) g_0(\mathbf{Q}, \omega_n). \quad (\text{F.20})$$

The diagrammatic representation of the second order correction is also depicted in Fig. 30.

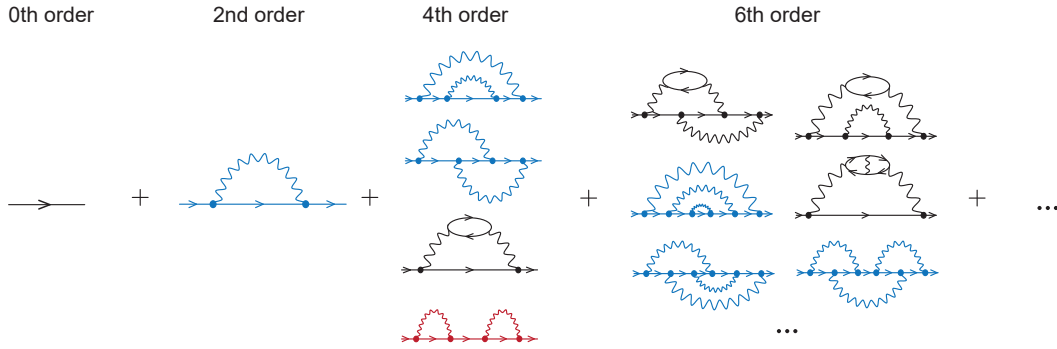


Figure 30: **Diagrammatic expansion.** Examples of connected Feynman diagrams that appear in the perturbative expansion of the Matsubara function. In red we give an example of a case where removing a single exciton line creates two distinct diagrams. In blue we present diagrams that share the same basic structure apart from vertex corrections.

Going to higher (even) orders in the interaction potential, new corrections to the full Matsubara function appear. The diagrammatic representation of some of the relevant diagrams in the fourth and sixth order of perturbation are depicted in Fig. 30. From these results we can already speculate that at order $2n$ in the interaction the diagrams present n phonon lines, two external exciton lines and $2n - 1$ internal exciton lines. It should also clear that all the diagrams have a similar structure, in the sense that all begin and end with an exciton line. Based on this observation, we may write the full exciton Matsubara function as

$$G(\mathbf{Q}, \omega_n) = G_0(\mathbf{Q}, \omega_n) + G_0(\mathbf{Q}, \omega_n) \Sigma(\mathbf{Q}, \omega_n) G_0(\mathbf{Q}, \omega_n), \quad (\text{F.21})$$

where $\Sigma(\mathbf{Q}, \omega_n)$ is known as the self energy, and is obtained by combining all the topological distinct diagrams of all orders in the perturbation. Furthermore, inspecting Fig. 30, we note that two types of diagrams exist: the ones that can be separated into two distinct diagrams by removing a single exciton line (e.g. the red one in Fig. 30); and the irreducible ones (the non red ones in Fig. 30). Diagrams belonging to this last group are the most relevant ones, since those of the first kind can be directly obtained from the irreducible ones by combining them with the introduction of an exciton line. Thus, we can express the self energy as

$$\Sigma(\mathbf{Q}, \omega_n) = \Sigma^*(\mathbf{Q}, \omega_n) + \Sigma^*(\mathbf{Q}, \omega_n) G_0(\mathbf{Q}, \omega_n) \Sigma^*(\mathbf{Q}, \omega_n) + \dots, \quad (\text{F.22})$$

where $\Sigma^*(\mathbf{Q}, \omega_n)$ is the proper or irreducible self energy, obtained from summing all the irreducible diagrams of all perturbation orders. Inserting Eq. (F.22) into Eq. (F.21) we find

$$\begin{aligned} G(\mathbf{Q}, \omega_n) &= G_0 + G_0 [\Sigma^* + \Sigma^* G_0 \Sigma^* + \dots] G_0 \\ &= G_0 + G_0 \Sigma^* [G_0 + G_0 \Sigma^* G_0 + \dots] \\ &= G_0(\mathbf{Q}, \omega_n) + G_0(\mathbf{Q}, \omega_n) \Sigma^*(\mathbf{Q}, \omega_n) G(\mathbf{Q}, \omega_n), \end{aligned} \quad (\text{F.23})$$

where for notation simplicity we omitted the arguments $(\mathbf{Q}, \omega_n)$, and in the last step we identified $G_0 + G_0 \Sigma^* G_0 + \dots$ as the full Matsubara function. This expression is known as the Dyson equation. Solving for $G(\mathbf{Q}, \omega_n)$ we obtain

$$\begin{aligned} G(\mathbf{Q}, \omega_n) &= \frac{1}{[G^{(0)}(\mathbf{Q}, \omega_n)]^{-1} - \Sigma^*(\mathbf{Q}, \omega_n)} \\ &= \frac{1}{i\omega_n - E_{\mathbf{Q}}/\hbar - \Sigma^*(\mathbf{Q}, \omega_n)}. \end{aligned} \quad (\text{F.24})$$

The retarded Green's function is recovered by applying an analytical continuation to this expression.

F.3 Self energy

We have just verified that the full Matsubara function of the exciton may be expressed in a rather simple form in terms of the irreducible self energy, $\Sigma^*(\mathbf{Q}, \omega_n)$. Now, our goal is to find the explicit form of the self energy. To that end, we return to Fig. 30 and note that from all the irreducible diagrams, some share a similar structure. Examples of this, are the diagrams marked in blue, which all present a similar form apart from some vertex corrections. This can be easily understood from Fig. 31a, where some of those diagrams, as well as the relevant vertex, are represented. According to the Migdal theorem [137], since the lattice ions are far heavier than the electrons and holes, the contribution of the vertex corrections may be neglected (see Fig. 31a). As a consequence, the self energy can be expressed as the sum of the diagrams depicted in Fig. 31b. Additionally, we approximate the self energy by the first term in that sum, such that it can be analytically written as

$$\begin{aligned} \Sigma^*(\mathbf{Q}, \omega_n) &= \frac{(-1)}{\hbar\beta} \sum_{\lambda, \mathbf{q}} |g_{-\mathbf{q}}^\lambda|^2 \sum_l d^0(\mathbf{q}\lambda, \omega_l) G_0(\mathbf{Q} - \mathbf{q}, \omega_n - \omega_l) \\ &= \frac{(-1)}{\hbar\beta} \sum_{\lambda, \mathbf{q}} |g_{-\mathbf{q}}^\lambda|^2 \sum_m \frac{2\omega_{\mathbf{q}\lambda}}{(i\omega_m)^2 - \omega_{\mathbf{q}\lambda}^2} \frac{1}{i(\omega_n - \omega_m) - E_{\mathbf{Q}-\mathbf{q}}/\hbar}, \end{aligned} \quad (\text{F.25})$$

in agreement with what we found in Eq. (F.20).

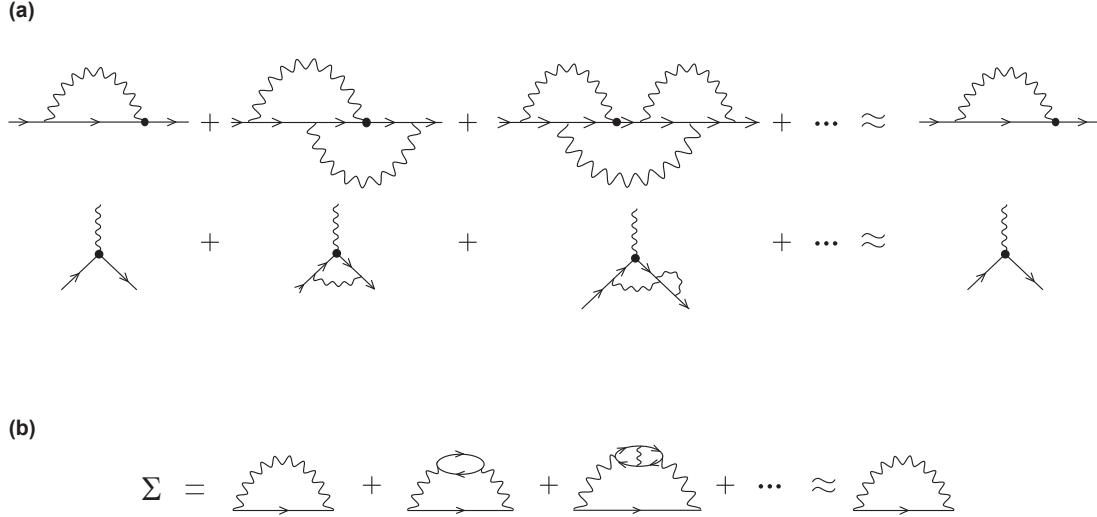


Figure 31: **Vertex corrections and self energy.** (a) Representation of the blue diagrams of Fig. 30 and the vertex corrections. (b) Diagrams that contribute to the self energy.

To obtain a compact expression for the self energy we have to evaluate the sum over the Matsubara frequencies:

$$S(\omega_n) = \frac{1}{\beta} \sum_m \frac{2\omega_{\mathbf{q}\lambda}}{(i\omega_m)^2 - \omega_{\mathbf{q}\lambda}^2} \frac{1}{i\omega_m - i\omega_n + E_{\mathbf{p}-\mathbf{q}}/\hbar}. \quad (\text{F.26})$$

Invoking once again a well known result from the literature [118, 119], this sum can be transformed into a sum over contour integrals:

$$S(\omega_n) = \sum_m \oint_{\gamma_m} n_{\text{BE}}(z) \frac{2\omega_{\mathbf{q}\lambda}}{z^2 - \omega_{\mathbf{q}\lambda}^2} \frac{1}{z - i\omega_n + E_{\mathbf{p}-\mathbf{q}}/\hbar} \frac{dz}{2\pi i}, \quad (\text{F.27})$$

where γ_m is a contour around $z = i\omega_m$ and $n_{\text{BE}}(z)$ is the Bose-Einstein function. We now note that the integrand has poles when $z = i\omega_n + E_{\mathbf{p}-\mathbf{q}}/\hbar \equiv z_0$ and when $z = \pm\omega_{\mathbf{q}\lambda} \equiv z_{\pm}$. To evaluate this expression we introduce a new contour integral, $\oint_{\gamma_{\infty}}$, where the integration path is a circle centered at the origin and with an infinite radius (see Fig. 32). From Cauchy's theorem, we schematically write

$$\oint_{\gamma_{\infty}} = \sum_m \oint_{\gamma_m} + \oint_{\gamma_0} + \oint_{\gamma_+} + \oint_{\gamma_-},$$

with γ_0 , γ_+ and γ_- the contours around z_0 , z_+ and z_- , respectively. Using Jordan's lemma, one shows that $\oint_{\gamma_{\infty}} \rightarrow 0$, and as a consequence

$$-\sum_m \oint_{\gamma_m} = \oint_{\gamma_0} + \oint_{\gamma_+} + \oint_{\gamma_-}.$$

Thus, to compute the sum over the Matsubara frequencies we only need to evaluate the integrals over γ_0 ,

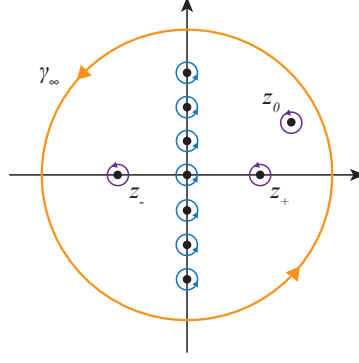


Figure 32: **Matsubara sum contour integral.** Integration path to evaluate the sum over Matsubara frequencies.

γ_+ and γ_- , which is easily achieved with an application of the residue theorem. Hence:

$$\begin{aligned} -S(\omega_n) &= \frac{2\omega_{q\lambda} n_{\text{BE}}(i\hbar\omega_n + E_{Q-q})}{(i\omega_n + E_{Q-q}/\hbar)^2 - \omega_{q\lambda}^2} + \frac{n_{\text{BE}}(\hbar\omega_{q\lambda})}{\omega_{q\lambda} - i\omega_n + E_{Q-q}/\hbar} - \frac{n_{\text{BE}}(-\hbar\omega_{q\lambda})}{-\omega_{q\lambda} - i\omega_n + E_{Q-q}/\hbar} \\ &= \frac{2\omega_{q\lambda} n_{\text{BE}}(i\hbar\omega_n + E_{Q-q})}{(i\omega_n + E_{Q-q}/\hbar)^2 - \omega_{q\lambda}^2} + \frac{n_{\text{BE}}(\hbar\omega_{q\lambda})}{\omega_{q\lambda} - i\omega_n + E_{Q-q}/\hbar} + \frac{1 + n_{\text{BE}}(\hbar\omega_{q\lambda})}{-\omega_{q\lambda} - i\omega_n + E_{Q-q}/\hbar}, \end{aligned}$$

where in the last step we used the relation $-n_{\text{BE}}(-x) = 1 + n_{\text{BE}}(x)$. This result can be further simplified as

$$\begin{aligned} S(\omega_n) &= \left[\frac{(-1)}{i\omega_n - \omega_{q\lambda} + E_{Q-q}/\hbar} + \frac{1}{\omega_{q\lambda} + i\omega_n + E_{Q-q}/\hbar} \right] n_{\text{BE}}(E_{Q-q}) \\ &\quad + \frac{n_{\text{BE}}(\hbar\omega_{q\lambda})}{i\omega_n - \omega_{q\lambda} - E_{Q-q}/\hbar} + \frac{1 + n_{\text{BE}}(\hbar\omega_{q\lambda})}{i\omega_n + \omega_{q\lambda} - E_{Q-q}/\hbar}. \end{aligned}$$

Setting $n_{\text{BE}}(E_{P-q}) \approx 0$, due to the large exciton energy, we finally find

$$\Sigma^*(Q, \omega_n) = \sum_{\lambda, q} |g_q^\lambda|^2 \left[\frac{n_{\text{BE}}(\hbar\omega_{q\lambda})}{i\hbar\omega_n - \hbar\omega_{q\lambda} - E_{Q+q}} + \frac{1 + n_{\text{BE}}(\hbar\omega_{q\lambda})}{i\hbar\omega_n + \hbar\omega_{q\lambda} - E_{Q+q}} \right], \quad (\text{F.28})$$

Performing an analytical continuation we obtain

$$\Sigma_Q^R(\omega) = \sum_{\lambda, q} |g_q^\lambda|^2 \left[\frac{n_{\text{BE}}(\hbar\omega_{q\lambda})}{\hbar\omega - \hbar\omega_{q\lambda} - E_{Q+q} + i0^+} + \frac{1 + n_{\text{BE}}(\hbar\omega_{q\lambda})}{\hbar\omega + \hbar\omega_{q\lambda} - E_{Q+q} + i0^+} \right], \quad (\text{F.29})$$

which is the same result we found in the main text using the equation of motion approach.