Excitonic States in Atomically Thin WSe_2 Semiconductor Beata Kardynał

1 SEMICONDUCTORS - BACKGROUND

Introduction

Electronic properties of crystals derive from the symmetries of their periodic lattice as much as the properties of the constituent atoms. If the crystal size in any direction is comparable to the electron wavelength, its properties become strongly affected by quantum confinement. Advances in growth techniques of semiconductor crystals that exhibit quantum confinement (sometimes called nanostructures) have lead to many discoveries and facilitated technological developments over past decades. Quantum integer and fractional Hall effects, Bose-Einstein condensation of excitons are examples of phenomena observed in two dimensional systems (in which quantisation affects only one direction). Quantised conductance and Coulomb blockade are examples of the phenomena observed in one- and zero dimensional systems, respectively. Most modern (opto)electronic devices that you find in computers, mobile phones etc make use of semiconductor nanostructures.

There are however limits to scaling down the sizes of standard semiconductors (Si,GaAs, InP etc) since their surfaces have dangling bonds which start interfering with the properties derived from their band structure even when their nanostructures are encapsulated in heterostructures.¹. With the discovery of graphene it became clear that isolated monolayers can be used as an ultimate two dimensional (2D) system. This is possible because layered materials are composed of monolayers bonded with each other with van der Waals forces to form bulk crystals. Not only does it mean that it is easy to isolate the monolayer but even more importantly there are no dangling bonds in the monolayer. A number of different monolayer materials have been studied since the emergence of graphene a couple of decades ago and many exhibit unique properties that may lead to development of devices with new functionalities.

WSe₂ monolayer is an example of semiconducting 2D material with fascinating optoelectronic properties. It has been chosen for this exercise due to its rich physics and as well suited example to give you an insight into optical spectroscopy as a method to study materials of any dimensionality. This text gives you a background to the physics addressed in the exercise. The first section summarises the relevant basic properties of semiconductors and introduces the terminology and conventions used in later sections. WSe₂ monolayer crystal, electronic and optical band structure are introduced in the second section. Before discussing what one can expect from the photoluminescence and reflectance spectroscopy of WSe₂ monolayer in section 4, optical selection rules that govern the processes of photon absorption and emission are summarised in section 3. Feel free to skip sections that you are familiar with such as section 1 or 5 or the general part of section 3. If something catches your interest you will find a list of suggested further reading at the end of this text. Footnotes that you find in the text serve as a reminder of more basic concepts or contain information beyond what you need for the exercise.

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Figure 1 shows a Brillouin zone of a GaAs that crystallizes in a zinc blende structure. GaAs is chosen here due to its known optoelectronic properties. The band structure of GaAs along k-directions defined in figure 1 is shown in a figure 2. One can see that electrons in the semiconductor can occupy states with energies below some energy E_v (a valence band edge)

 $^{^{1}}$ A heterostructure is a crystal composed of layers of different materials or compositions which have very similar lattice constant. They are selected to have different band gaps and confine electrons in the space protecting them from surfaces

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Figure 1: A Brillouin zone of zinc-blende crystal structure. Figure adapted from [1]

or above some energy E_c (a conduction band edge). The valence and conduction bands are separated by a band of forbidden for an electron energies, a so called band gap of a width: $E_q = E_c - E_v$. The band gap must be at most a few eV for a material to be classified as a semiconductor rather than an insulator although this is more a guide than a strict definition. For example, a zero-temperature band gap of the best known semiconductors, Si and GaAs, are 1.17 eV and 1.52 eV, respectively. The band gaps of all semiconductors decrease by at most 10%with heating them to the room temperature. The band structure of GaAs, shown in figure 2a has the minimum energy of conduction band and maximum energy of the valence band at the same point Γ of the Brillouin zone. This makes GaAs a *direct band gap* semiconductor because electrons can be transferred across the band gap directly by photon absorption / emission without involvement of phonons. This will be elaborated on later in this text. Details of the band structure of the GaAs near Γ point are shown in figure 2b; the states in this range of k-vectors are responsible for most optical and many electronic properties of GaAs. Si is an example of *indirect band qap* semiconductor, in which minimum energy of conduction band and maximum energy of the valence band occur at different points of the Brillouin zone. Optical transitions across the band gap need to be assisted by phonon emission or absorption.

For any semiconductor, an occupation of the conduction and valence band with electrons and its electrochemical potential are determined by the density of electronic states in the relevant bands and Fermi-Dirac distribution 2 taking into consideration charge neutrality. At zero temperature, Fermi-Dirac distribution is a step function. In this case, a monocrystalline semiconductor, which contain no impurities or defects except the thermodynamically unavoidable ones, a so called *intrinsic* semiconductor, has the valence band fully occupied with electrons and the conduction band completely empty; its Fermi level is located in the middle of the band gap. At higher temperatures, some electrons are present in the conduction band. Charge neutrality requires that the number of electrons in the conduction matches the number of vacant states in the valence band. This is shown in figure 3a for GaAs at room temperature. One can see that electrons can be found above the band gap (1.42 eV) in the conduction band with probability

²According to Fermi-Dirac distribution, an average number of electrons, n_i , that occupy an energy state E_i is given by $n_i = (e^{\frac{-(E_i - \mu)}{k_B T}} + 1)^{-1}$, where μ is the electrochemical potential, k_B is the Boltzman constant and T is the temperature. The electrochemical potential is a generalization of the Fermi level that includes external electrical potentials that can be introduced for example by applying voltages to the semiconductor sample. In the absence of those, μ is simply the Fermi level.



Figure 2: a) Band structure of GaAs in the crystal structure of zinc-blende. b) Band structure near the Γ point at energies close to the band gap. Conventionally, the energy of the valence band edge is set to 0 eV.*Figures adapted from* [1]

decreasing with electron energy. Similarly one can find that probability of finding an empty state in the valence band (located at $E_v = 0$ eV) decreases for lower energies.

This symmetry in the behaviour of electrons in the conduction band and empty states in the valence band lead to the introduction of a concept of a *hole*. The hole is a quasi-particle formed in the valence band by a removal of an electron. In order to use the concept of the hole one has to be able to define its wave function, energy, charge and spin etc. - in short the quantities that determine their properties in semiconductors. Since the properties of crystals are derived from those of electrons on the atomic orbitals of the component atoms, electron wave functions and other parameters are know from the theoretical calculations (and experimental data). It is intuitive³ that the hole behaves as a particle of the charge +e, where -e if the charge of the electron. The spin up or down of a hole, denoted as \uparrow or \downarrow is opposite to the spin of the removed electron, \downarrow or \uparrow . In other words, a hole with spin up, $\uparrow(\Downarrow)$ is obtained by removing an electron with spin $\downarrow(\uparrow)$. The wave function of a hole in the valence band, $|u_v\rangle$: $|u_h\rangle = |u_v\rangle^*$. Setting the valence band edge energy to zero let us express the energy of the hole as $E_h(k) = -E_v(k)$. A decreasing energy of an electron is an increasing energy of holes.

Figure 3 captures the feature of semiconductors that differentiates it from metals and insulators: a strong dependence of the electron and hole concentration on a very small change of the crystal's electrochemical potential (see footnote 2). In figure 3b and 3c, the electrochemical potential has been shifted by 50 meV from the level found in unperturbed intrinsic GaAs at 300K (figure 3a. These changes of less than $\pm 4\%$ of the band gap cause an order of magnitude increase in the concentration of electrons or holes, which can conduct electrical current. There are many ways in which one can shift the electrochemical potentials, among them the ones already mentioned: applying voltage, building heterostructures. The simplest but very powerful

 $^{^{3}}$ If one applied an electric field to a semiconductors, electrons will drift towards the more positive potential, which will result in the hole drifting in the opposite direction.



Figure 3: Electron and hole concentration per unit energy for a) intrinsic b) n-type c) p-type GaAs at 300K. Red, vertical line shows the position of the Fermi level.

method relies on the introduction of certain impurities in their crystal lattice. Even very small levels of impurities, as low as one impurity atom per 10^9 host atoms can lead to measurable changes of semiconductor properties. At these levels, the crystal structure is not damaged or even distorted; the impurities simply introduce additional energy levels in the band structure from figure 2. Impurities which affect the properties of the host semiconductor are called dopant atoms, or *dopants*. The impurities of interest are the ones that introduce energy levels in the band gap of the semiconductor, near (within a few k_BT) from the conduction or valence band as they are able to shift the Fermi level and thus the concentration of *charge carriers* (collective name for electrons and holes). This feature of semiconductors (combined with the technologies to introduce the impurities locally) is one of the key reasons that we have transistors, lasers and other electronic and optoelectronic devices.

Let's consider the case of an atom containing one extra valence electron that replaces an atom of the host semiconductor. This could be P atom in Si or Si atom replacing Ga atom in GaAs. If the energy of this extra electron on the dopant atom is close to, but below the conduction band edge E_c (on the scale of the thermal energy)⁴, it can be thermally excited into the conduction band (the dopant can be ionised). An electron in the conduction band is delocalized which means that it can move in the crystal upon some stimulus. The motion of an electron in the conduction band defined as $m_e(k) = \frac{1}{\hbar^2} \frac{1}{\delta^2 E_c/\delta k^2}$, where k is an electron wave vector at which the mass is calculated. This substitution of m_e for m_0 takes into account for the effect of the periodic potential of the lattice atoms on an electron's motion and only external forces need to be considered. m_e is a function of the crystal momentum k, but near E_c , energy is a quadratic function of k, which means that m_e is constant.

Even when only a small fraction of atoms of a semiconductor is replaced by dopants and a fraction of them is ionised, the Fermi level shifts towards the impurity energy level and the likelihood of the electron being excited to the conduction band is even higher. Dopants which supply delocalized electrons to the conduction band are called shallow *donors*, donor-doped semiconductors are referred to as *n-doped*. It is thus clear that the case depicted in the figure 3b refers to the n-doped semiconductor. One finds that most electronic properties of n-doped semiconductors can be explained simply by considering the electrons in the conduction band

 $^{^{4}}$ Note that since an impurity level is completely localized in real space, it is fully delocalized in the k-space. It is a flat line in the dispersion relation as the one in figure2

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from the donor doping and the occupancy states of the donors.

Similarly, dopant atoms which have one less valence electron that atoms of the host semiconductor can trap electrons from the valence band. Again the condition is that the energy level of the electron on the impurity level is just above the valence band edge to allow for thermal excitation of the electron from the valence band (or the hole from the impurity). Such dopants are called *acceptors*, and semiconductors doped with acceptors are referred to as *p*-doped. Trapping of electrons on the acceptor level leaves delocalized holes in the valence band and most electronic properties of p-doped semiconductors can be explained simply by considering these holes and occupancy of acceptors. In the analogy to electrons, the hole mass can be defines as $m_h(k) = \frac{1}{\hbar^2} \frac{1}{\delta^2 E_h/\delta k^2}$, where k is a hole wave vector. Irrespective of the doping, optical properties of semiconductors depend on both conduction and valence bands and the dopants.

Free (delocalized) charge carriers in materials interact with each other. For example electronelectron (or hole-hole) interactions can impact the electrical and heat transport in the semiconductors ⁵. Similarly, an electron in the conduction band and a hole in the valence band are attracted to each other and if brought close enough, they will be bound by Coulomb interactions into a so called *exciton*: a quasi-particle with zero electric charge, spin of zero or one and a reduces mass, $\mu^* = m_e m_h/(m_e + m_h)$. As a consequence of having no charge, excitons in the first approximation are not accelerated by electric field. With their integer spin, they are bosons. An exciton can be thought of as a hydrogen atom in the semiconductor represented by its relative dielectric constant, ϵ . It can occupy only discrete states, indexed by the shell number, n, with the binding energies of:

$$E_{b,n} = -\frac{\mu^* e^4}{32\pi^2 \epsilon_0 \epsilon \hbar^2} \times \frac{1}{n^2} = -\frac{R^*}{n^2}$$
(1.1)

where R^* a Rydberg constant. The energy of the exciton in its *n*-excited state is therefore lower than the total energy of the pair of free electron and hole by $E_{b,n}$. The lowest energy of the electron-hole pair is E_g , so the energy of the exciton is $E_X = E_g - E_{b,n}$.

Binding energy of excitons depends on the dielectric constant of the host material. Semiconductor such as Si, GaAs and related ones have high dielectric constants and binding energies of excitons are low. As the results, excitonic effects are observed only at the cryogenic temperatures. At higher temperatures they dissociate into free electron-hole pairs.⁶

In a further analogy to hydrogen atom, one can calculate the separation between the probability densities of the electron and the hole. For the excitonic ground state, n = 1 it is give as:

$$\Psi^X(r) = \frac{1}{\sqrt{\pi}a_0^{3/2}} e^{-\frac{r}{a_0}}$$
(1.2)

where $a_0 = \frac{4\pi\epsilon\epsilon_0\hbar^2}{\mu^*e^2}$ is a Bohr radius and a measure of the extend of the exciton wave function. If the exciton is generated in a (nano)crystal of the size(s) comparable with a_0 , the confinement will affect its energy.

Let's consider an exciton in GaAs with the energy: $E_{X,n} = E_g - E_{b,n}$. It is composed of an electron from a Γ point in the conduction band and a hole from the Γ point of the valence

⁵Coulomb blockade is the simplest and striking example of such interactions.

⁶This is why Si and GaAs based solar cells have such high efficiencies: at high temperatures light creates free electron-hole pairs that can be separated by applying voltages.



Figure 4: An exciton dispersion relation for excitons in GaAs. Since $m_h = 0.47m_0$ and $m_e = 0.063m_0$, the reduced mass of excitons, μ^* , is very close to the mass of an electron and the energy of excitons and electrons have very similar dependence on the momentum. Figure adapted from [1]

band (see figure 2). The resulting exciton has zero momentum. It can acquire kinetic energy and its total energy is related to the momentum according to the following dispersion relation:

$$E_{X,n}(\mathbf{k} - \mathbf{k}_X) = E_X + \frac{\hbar^2 (k - k_X)^2}{2M}$$
(1.3)

In GaAs, exciton reduced and total mass, μ^* and $M = m_e + m_h$, near minimum energy are constant but in general they are functions of the momentum. Here $\mathbf{k}_X = 0$, as the exciton is in Γ valley but it does not have to be the case. Excitons formed from electrons in L valley and holes in Γ valley may not be longed lived but can be generated. In this case the dispersion relation would have its minimum at k of the L valley (since k in the Γ valley is zero). A dispersion relation for Γ valley excitons in GaAs is shown in Figure 4.

Since excitons are often generated by optical excitation, there are two ways of viewing interactions of light with semiconductors. If the Coulomb interactions are weak and can be treated as a perturbation, one can consider interactions of light with electrons and holes and include Coulomb interactions as an energy correction. Alternatively, interaction of light with excitons can be considered and then exciton dispersion relations used. Very often even when the Coulomb interactions are strong, qualitative understanding of the main optical transitions can be gained from considering free electron-hole pairs.

2 Crystal and band structure of monolayer WSe₂

Graphene, a monolayer of graphite, is the simplest and best known 2D material. It is a single sheet of covalently bonded carbon atoms arranged in a hexagonal lattice. The interest in graphene has its origin in its unique properties. Unlike graphite, graphene is a semimetal with unusual linear dispersion near the Fermi level (so called Dirac cone). This qualitative difference between the properties of graphite and graphene has triggered an interest in other monolayer materials.



Figure 5: Arrangement of atoms in 1H phase of the WSe₂ monolayer in a) across-section, b) a plan view, with blue balls representing tungsten atoms and yellow, selenium. Note that in the plan view there are two atoms of Se on top of each other. Atom positions and the centre of a hexagon, marked as h are centres of rotational symmetry of the structure around z-axis. c) First Brillouin zone of WSe₂ monolayer with directions for the calculations of the dispersion relations to follow marked in green. Blue arrows mark unit vectors in the k- space.

Monolayer materials can be obtained from any, also compound materials, in which monolayers of atoms are bonded by van der Waals forces. In the case of compound materials, the monolayer can be composed of several sheets of atoms, with saturated covalent of ionic bonds between the atoms. WSe₂ and more generally transition metal dichalcogenides (TMDCs) with the composition MX₂ where M= Mo or W and X=S, Se or Te, are examples of layered compound materials. Their monolayers contains three sheets of atoms. The central sheet is composed of metal atoms in a hexagonal lattice. A metal layer is embedded between two sheets of chalcogen atoms, also in hexagonal lattices. Metal-chalcogen bonds are polar and form electric dipoles. Depending on the relative shift of the chalcogen and metal layers, TMDCs monolayers are either metals (1T crystal phase) or semiconductors (in 1H crystal phase).

Since the properties of crystals are determined in a large degree by their symmetry, let's look at the symmetry of the 1H WSe₂ monolayer, depicted in figures 5a and 5b. The cross sectional view shows a mirror symmetry with the sheet of metal atoms being the plane of symmetry. The asymmetric arrangement of Se atoms around W atom means that it lacks inversion symmetry. Figure 5b shows threefold rotational symmetry with the rotation centre on M or X atoms or at the centre of the hexagon (point h in the figure). This combination of symmetries is responsible for some of the remarkable properties of the monolayer TMDCs that will be observed in this exercise.

The first Brillouin corresponding to 1H crystal is shown in figure 5c. The six K-points of the hexagonal Brillouin zone are split into two groups of alternating K and -K points as a result of metal atoms occupying two non-equivalent locations in the metal sheet lattice.⁷

A band structure of WSe₂ calculated without spin-orbit interactions is shown in Figure 6a. The conduction and the valence band edges are both located at the corners of the first Brillouin zone, at K and -K points of the reciprocal space. This means that WSe₂ monolayer is a direct band gap semiconductor unlike multilayer WSe₂ (or even bilayers) which is an indirect semiconductor.

The conduction band edge electronic states are derived predominantly from d_{z^2} orbitals of the tungsten atoms. The valence band edge electronic states are derived predominantly from

⁷As in the case of graphene, metal lattice has to be split into two sublattices in order to be able to construct 1H structure by periodic translation of the atom positions. These sub-lattices correspond to K or -K points.



Figure 6: Band structure of WSe₂ a) without b) with spin orbit interactions, both calculated using *ab-initio* methods. *Courtesy of Stefan Rost.*



Figure 7: a) Band structure of WSe₂ at energies close to the band gap. (Courtesy of Stefan Rost.) b) Schematic diagram of the spin-resolved band structure near K/-K points.

the $d_{x^2+y^2,xy}$ orbitals of the metal atoms. In the first approximation, the small admixture of p-states of chalcogen atoms can be neglected. The basis wave functions are then $|\phi_c\rangle = |d_{z^2}\rangle$ and $|\phi_v\rangle = 1/\sqrt{2}(|d_{x^2+y^2}\rangle + i\tau |d_{xy}\rangle)$ where $\tau = \pm 1$ is the valley index corresponding to the K/-K valleys, respectively. The valley index is one of the quantum numbers that describe the state of an electron (or a hole). Unlike other quantum numbers it is the same for both particles. This band structure can be summarised in the following Hamiltonian:

$$\hat{H}_0 = at \left(\tau \hat{\sigma}_x k_x + \hat{\sigma}_y k_y\right) + \frac{\Delta}{2} \hat{\sigma}_z \tag{2.1}$$

where a is the lattice constant of 1H WSe₂, t is the hopping integral (related to the coupling between atomic sites), $k_{x,y}$ are the electron wave vectors, $\hat{\sigma}_{x,y,z}$ - the Pauli matrices, Δ is the band gap.⁸ The calculated single particle band gap of WSe₂ monolayer is 2.2 eV and varies between 2.1 eV and 2.4 eV for other TMDCs monolayers, all of which are direct band gap

⁸In the previous section the value of the band gap was denoted by E_g as conventionally used in semiconductor physics. Here, a symbol Δ is used as typically used in Hamiltonians of two hybridizing states. The two different symbols refer to the same quantity.

semiconductors.

The presence of massive metal atoms in the structure translates into very strong spin-orbit interactions, $\lambda L \cdot S$, which must be included in the full Hamiltonian:

$$\hat{H} = \hat{H}_0 - \lambda \tau \frac{\hat{\sigma}_z - 1}{2} \hat{s}_z \tag{2.2}$$

where 2λ is the spin splitting of the valence band at K/-K point, \hat{s}_z is the spin Pauli vector. The band structure of the WSe₂ with spin-orbit interactions included is shown in figure 6b. The most noticeable change introduced by spin-orbit interactions is the removed spin degeneracy of the valence band at K and -K points. The spin up and down valence band subbands are separated by 400 meV (and between 200 meV and 400meV for other TMDCs), energy large enough that even at room temperature only one spin-split subband with lower energy can be occupied by holes. Non-equivalence of the K and -K points of the Brillouin zone extends to the spin resolved states: the lowest hole energy subband at K point is occupied by a spin-down hole (\Downarrow) and at -K point by a hole with spin up (\Uparrow).⁹ This property of TMDCs is referred to as spin-valley locking.

Spin-orbit interactions also split the conduction band, as seen in figure 7. Even though d_{z^2} orbital has zero magnetic moment, second order spin-orbit interactions involving earlier neglected p orbitals of the chalcogen atoms split the conduction band at K / -K points by up to a few tens of meV. In WSe₂, the spin splitting of the conduction band is about 30 meV and thus of the order of kT at room temperature.¹⁰

In $MoSe_2$, the ordering of the spin states in the conduction band is opposite to the one in WSe_2 and this seemingly small difference has very strong implications for their interactions with light.

2.1 Excitons in 2D, the case of WSe_2 monolayer

The binding energy of excitons confined in two dimensions is given as:

$$E_{b,n} = -\frac{\mu^* e^4}{32\pi^2 \epsilon_0 \epsilon \hbar^2} \times \frac{1}{(n-0.5)^2} = -\frac{R^*}{(n-0.5)^2}$$
(2.3)

The energy of the 2D exciton in its lowest energy state (n = 1) is four times larger than the one of the 3D exciton in the medium of the same dielectric constant. Considering that the exciton's electrostatic field extends in all three dimensions, the effective dielectric constant depends strongly on the material in which the monolayer is embedded. If the monolayer is suspended in vacuum (air), the dielectric constant is small giving even larger enhancement of the binding energy compared with the bulk semiconductors. The measured binding energies of excitons in TMDCs monolayers are of the order of 500 meV, much higher than kT so the excitonic effects are important even at room temperature.

The orbital wave function of the excitonic n = 1 state is:

$$\Psi^X(r) = \sqrt{\frac{2}{\pi}} \frac{2}{a_0} e^{-\frac{2r}{a_0}}$$
(2.4)

⁹Again, one has to remember that spin of a hole is opposite to the spin of an electron.

¹⁰To put it in a perspective, this is the same as spin-splitting of the valence band of GaAs (2b. The valence band spin splitting is always larger than the conduction band spin splitting.

ground state



Figure 8: Dispersion relation of excitonic states. Labels show the electron and hole spin- and valley-indices that contribute to these states. Only n=1 excitonic states are shown.

where $a_0 = \frac{4\pi\epsilon\epsilon_0\hbar^2}{\mu^*e^2}$ is a Bohr radius of the exciton and a measure of the extend of the exciton wave function in the 2D plane. It is of the order of 2 nm for TMDC monolayers. This is much smaller than the Bohr radius in e.g. GaAs (20 nm) but it still extends over many unit cells of the lattice meaning that excitons in the TMDC are considered to be delocalized.

Considering the band structure of WSe₂ monolayer in figure 7, one can see that a number of different excitons can be formed with a hole in the lowest energy state. A hole in K valley with spin down (\Downarrow) can bind an electron with a spin up, (\uparrow) or down, (\downarrow) from either K or -K valley. This means that excitons have so called fine structure. It is thus often useful to label the excitonic states as X^{β}_{α} , where α (β) gives the valley and spin indices of the hole (electron). Accordingly, the four excitons can be labelled, $X^{K/-K\uparrow/\downarrow}_{K\Downarrow}$. Each of the excitons can have kinetic energy which results in the exciton dispersion relation depicted in figure 8. Both $X^{K\uparrow/\downarrow}_{K\Downarrow}$ occupy Γ valley but are split in energy and have different masses inherited from the properties of electrons in the different subbands. $X^{-K\uparrow/\downarrow}_{K\Downarrow}$ on the other hand occupy K valley.

The weak screening of Coulomb interactions which results in these high exciton binding energies in the 2D materials means that even larger charge complexes can be observed in the TMDC monolayers. For example, in the n- or p-doped 2D system, an exciton binds an extra electron or hole to form a three-particle complex called a trion. Pauli exclusion principle limits the number of trion configurations requiring that two electrons in the negatively charged trion, X^- , or holes in the positively charged trion, X^+ , have to be in a different quantum state. For the electrons and holes in their lowest energy states, it means different valley or/and spin -indices. The binding energies of trions are of the order of 25 - 30 meV in the TMDC monolayers. Two excitons can also bind each other to form a biexciton, X + X = XX, an exciton-negatively charged trion bound complex is called a charged biexciton, $X + X^- = XX^-$. Note, that just like excitons and trions, these complexes (some of which have only a few meV binding energies) can have different spin and momentum configurations.

3 Spontaneous recombination and optical selection rules

Light can exchange energy with electrons through the processes of absorption and radiative recombination. Both processes are widely used to get insight into electronic properties of materials. Light absorption in semiconductors has found its applications in variety of light sensors (most familiar perhaps being CCDs) or solar cells. Radiative recombination of electrically injected electrons and holes in direct band gap semiconductors lead to development of light emitting diodes and lasers. The former make use of spontaneous recombination while stimulated radiative recombination produces lasing in diode lasers. Radiative recombination is also a process behind single photon or entangled photon (or other non-classical light) sources and as such is an active field of research.

Absorption of a photon causes a transfer of an electron from an initial state in the valence band (or any lower energy state) to the final state in the conduction band (or any higher energy state) with the energy difference between the two states. Radiative recombination of an electron and a hole is a process opposite to absorption with the energy difference between the two states emitted as a photon. Quantum mechanical analysis of spontaneous radiative recombination (and absorption) starts from considering probability $W_{1->2}$ of electron transition between two levels, |1 > and |2 > as given by the Fermi golden rule:

$$W_{1->2} = \frac{2\pi}{\hbar} |M_{12}|^2 g(\hbar\omega)$$
(3.1)

where M_{12} is the matrix element for the transition and $g(\hbar\omega)$ is the density of final states. [4] Depending on the system in which the transition takes place, the density of states can refer to photon or/and electronic density of states. Qualitative understanding of the radiative recombination processes can be gained by looking at the transition matrix element, which depends on the wave functions of electrons in the initial $|1\rangle$ and final $|2\rangle$ states:

$$M_{12} = \langle \psi_2 | H_i | \psi_1 \rangle = \int \psi_2^*(\boldsymbol{r}) H_i(\boldsymbol{r}) \psi_1(\boldsymbol{r}) d^3 \boldsymbol{r}$$
(3.2)

Light interacts with matter via its electromagnetic field. In the presence of electromagnetic field with the vector field \mathbf{A} , the momentum operator of an electron, $\hat{\mathbf{p}}$, becomes $\hat{\mathbf{p}} = -i\hbar\nabla - e\mathbf{A}$. Expanding the terms of the momentum operator in the Schrödinger equation gives the interaction Hamiltonian as:

$$\hat{H}_i = \frac{e}{m} \boldsymbol{A} \cdot \boldsymbol{\hat{P}}$$
(3.3)

 $\hat{P} = -i\hbar\nabla$ is a canonical momentum operator. Normally, the strongest interaction of electrons with light is a dipole interaction with the electric field of the light.¹¹ Other interactions, both with magnetic field and higher order interactions with electric field can therefore be neglected. Now, M_{12} can be calculated by substituting H_i into equation 3.2:

$$M_{12} \propto \langle \psi_2 | \boldsymbol{A} \cdot \hat{\boldsymbol{P}} | \psi_1 \rangle = \boldsymbol{A} \langle \psi_2 | \hat{\boldsymbol{P}} | \psi_1 \rangle$$
(3.4)

For the transition to be possible, this matrix element has to be non-zero. This requires that wave functions of the initial and final states, $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$, must be of different parity (operating with $\hat{\mathbf{P}} = -i\hbar\nabla$ means differentiating ψ_1). This leads to the first selection rule: *optical transition requires a change of parity of the electron wave function*. For example, it is possible for a photon to be absorbed by an electron on an atomic *s*-orbital and be transferred to *p*-orbital but not to another *s*-orbital.

¹¹Another, often found form of the dipole interactions Hamiltonian is $\hat{H}_i = -\mathbf{d} \cdot \mathbf{E}_o$, where \mathbf{d} is the electric dipole of the transition and \mathbf{E}_0 is the electric field of the photon.

Apart from energy, photons carry spin angular momentum along the propagation direction. Left /right handed circularly polarized photons $(1/\sqrt{2}(\sigma^+/\sigma^-))$ carry spin angular momenta of $\hbar/-\hbar$.¹² Light beams whose state can be expresses as $|\sigma_+\rangle \pm i |\sigma_-\rangle$ in some coordinate system are linearly polarized and carry no angular momentum. Conservation of total angular momentum leads to the next selection rule: the total angular momentum of an electron has to change by one or 0 (in units of \hbar) for a transition to occur. In the absence of spin-orbit mixing of electronic bands, in electric dipole interactions approximation, the spin of electrons has to be conserved - there are no magnetic or pseudo-magnetic fields that could interact with the spin.

The above derived selection rules are valid for electric dipole interactions between light and matter (not limited to semiconductors but also for atoms, molecules of single electrons). They can be different for other types of interactions which we are not addressing here.

Implicitly assumed, and common for all types of interactions, are the energy and momentum conservation rules. Since momentum carried by a photon $(= E_{ph}/\hbar c)$ is very small compared with the possible momenta of electrons in crystals, $\hbar k$, optical transitions practically do not change momentum of an electron; optical transitions are referred to as "vertical' in the k - E space. It is however possible that emission of a photon is accompanied by emission of phonons. In this case, since the momenta of phonons and electrons are comparable, radiative recombination between different k-states is also possible. In direct band gap semiconductors, such multi-particle transitions are typically weaker than direct, vertical transitions.

The time between the photon absorption and spontaneous radiative recombination of the electron and the hole is random and therefore described by Poisson statistics. The probability that an electron - hole pair will not recombine radiatively before time, t, is then equal:

$$P(t) = P(0)e^{-\frac{t}{\tau_0}}$$
(3.5)

where τ_0 is the average time before recombination, so called radiative lifetime of the electron. This temporal distribution means that the energy of a photon that is going to be emitted is expressed by a Lorentzian function:

$$S(\omega) = \frac{1}{\pi} \frac{\frac{1}{2}\gamma}{(\omega - \omega_0)^2 + (\frac{1}{2}\gamma)^2}$$
(3.6)

where $\hbar\omega_0$ is the energy of emitted photon and $\gamma = 1/(2\pi\tau_0)$ is a so called lifetime broadening of the line.

This section analysed a transition of an electron between two discrete levels such as found in atoms or on isolated defects in crystals or in very small crystals. In typical crystals several different transitions are possible for a given energy/polarization of the photon and broadening of the states has to also be considered. This difference is captured mostly in the density of final states entering Fermi golden rule. The selection rules are however generic and are therefore a useful tool to determine electronic properties of mateirals. Detailed analysis of spontaneous recombination and properties of light relevant for absorption/spontaneous recombination processes can be found in references [1,2].

¹²Momentum operators entering equations for matrix element for σ^+/σ^- photons are $\hat{\boldsymbol{P}}^+ = \hat{\boldsymbol{P}}_x + \hat{\boldsymbol{P}}_y / \hat{\boldsymbol{P}}^- = \hat{\boldsymbol{P}}_x - \hat{\boldsymbol{P}}_y$.

3.1 Optical selection rules for WSe₂ monolayer

In this section we will apply the considerations from the last section to the optical transitions in WSe₂ monolayers ignoring Coulomb interactions between electrons and holes. Figure 9 shows the dispersion relation near the bottom of the conduction band and the top of the valence band around K and -K points for electrons and holes with both spin directions. Also shown are all possible optical transitions involving photons propagating normal to the monolayer which are discussed in this and the next sections.

Energy conservation requires that only photons with energy above semiconductor band gap can be emitted following radiative recombination from intrinsic WSe₂ monolayer. For photon energies close to the band gap, momentum conservation limits the number of possible optical transitions to so called intravelley transitions in either K or in -K valley. In other words electrons in K(-K) valley recombine with holes in K(-K) valley. There are four possible transitions to consider for each valley. Here we will limit the discussion to the transitions in the K valley; the conclusions can be adapted for the -K valley taking into account that the two are linked by time-reversal symmetry.

While we do not know the exact wave functions of the states involves in the optical transitions, we do know their symmetries at the K-point (a great description of the relationship between symmetry and conservation laws leading to selection rules can be found in reference [3]). The conduction band wave function, $|\psi_c\rangle$ has the symmetry of d_{z^2} orbitals while the valence band electron wave function, $|\psi_v\rangle$ of $d_{x^2+y^2} \pm i d_{xy}$ orbitals of W atoms. The wave functions can be separated into parts with a threefold rotational symmetry upon rotation around the axis normal to the 2D plane (z-direction) and a translational symmetry of the Bloch wave function $(\psi((\mathbf{r} + \mathbf{R}) = \psi(\mathbf{r}), \text{ with } \mathbf{R}$ - lattice vector). Both parts can contribute to the orbital angular momentum. Operation of rotation around the centre of the orbital, C_3 , results in the phase factor of $e^{-i\frac{2m\pi}{3}}$ added to the state wave function.¹³ The index m takes value of 0 for the d_{z^2} orbital, ± 2 for $d_{x^2+y^2} \pm i d_{xy}$ hybridized orbitals. If the centre of rotation is placed on the metal atom, Bloch wave function is invariant upon C_3 operation and does not contribute to the total orbital angular momentum.¹⁴

Operating with C_3 on the momentum operator of the circularly polarized photons, $\hat{\boldsymbol{P}}^{\pm}$ introduces a phase of $e^{i\frac{2m\pi}{3}}$ with $m = \pm 1$ for $\sigma^{+/-}$ photons respectively and m = 0 for linearly polarized light.

We can now use the symmetry of $|\psi_c\rangle$, $|\psi_v\rangle$ and $\hat{\boldsymbol{P}}^{\pm}$ to see how the matrix element M_{12} (equation 3.4) for radiative recombination between conduction band and valence band states with an emission of left/right handed polarized photon will transform upon two rotations that cancel each other $C_3^{-1}C_3$:

$$\begin{aligned} \langle \psi_v | \hat{\boldsymbol{P}}^{\pm} | \psi_c \rangle &= \langle \psi_v | C_3^{-1} C_3 \hat{\boldsymbol{P}}^{\pm} C_3^{-1} C_3 | \psi_c \rangle \\ &= \langle \psi_v C_3^{-1} | C_3 \hat{\boldsymbol{P}}^{\pm} C_3^{-1} | C_3 \psi_c \rangle \\ &= e^{-i\frac{2\pi}{3}(m_v - m_c)} \langle \psi_v | C_3 \hat{\boldsymbol{P}}^{\pm} C_3^{-1} | \psi_c \rangle \\ &= e^{-i\frac{2\pi}{3}(m_v - m_c \mp 1)} \langle \psi_v | \hat{\boldsymbol{P}}^{\pm} | \psi_c \rangle \end{aligned}$$

¹³Infinitesimal rotation around z-axis is given by $(1 - \frac{i}{\hbar}\Delta\Theta z \cdot L)$ where $z \cdot L$ is a projection of the angular momentum on z axis, m.

¹⁴Centre of rotation can be also placed on a chalcogen atom or the central point of a hexagon of the lattice (see figure 7b. In these cases, the rotation operation will lead to different phase factors but the same selection rules.



Figure 9: a) Direct optical transitions in the monolayer WSe_2 for light propagating normal to the monolayer. b) Phonon-assisted transitions from momentum dark states (only the lowest energy transitions shown for clarity) c)-d) Equivalent transitions for MoSe₂.

For the transition to be possible, the phase factor has to be equal to one because the operation should not introduce any changes, we only multiplied \hat{P}^{\pm} by one. This means that $(m_v - m_c + 1) \mod 3 = 0$. This condition is true for σ^+ but not for σ^- photons for the transition between conduction and valence bands in the K valley, so only left handed polarized photons can be emitted, absorbed in K-valley. Since $m_v = -2$ in -K valley, optical transitions can be mediated with right handed polarized photons but not with left handed polarized photons.

Spin conservation limits the number of possible transitions in each valley to the ones with electron spin up \uparrow (\downarrow) and hole spin down \Downarrow (\uparrow). The energy of the two photons for these transitions differ by over 300 meV in WSe₂, so the transitions can be isolated from each other.

For the lowest energy transition, the above derived and depicted in figure 9 selection rules mean that polarization of light can be used to optically select a specific valley in WSe₂. Since valley and spin indices are coupled for the states addressed in the transitions, one finds that photon polarization is locked to the valley and spin of the electron it can interact with. This remarkable property renders WSe₂ (TMDCs) monolayers unique for spin- and valley-optoelectronics.

From this point on we will limit the discussion to the transitions involving only the lowest energy subband of holes. Following very similar analysis as above, one can show that optical transitions between the lowest electron energy subband of the -K(K) conduction band and the lowest hole energy subband in the valence band satisfy all the selection rules except the conservation of momentum. The momentum can be conserved if the optical transition is accompanied by an emission of a phonon.¹⁵ This is shown in figure 9b. Since conduction band states have zero angular momentum, the polarization of photons depends on the valley-state of the hole and this means that recombination of an electron from -K(K) valley with hole in K(-K)valley generates a photon with left (right) handed circular polarization. The phonons which can facilitate the transition carry not only momentum but also an energy of about 30 meV so photons emitted from this phonon assisted process have lower energy (longer wavelength) than those that would be emitted in the direct transitions.

3.2 Many body effects in optical selection rules for WSe₂

The discussion above considered independent electrons and holes rather than excitons. We know, however, that excitonic effects are very strong and cannot be ignored. Luckily, it turns out that the selection rules derived in the previous section are not changed for the excitons: excitons in the K valley can recombine emitting left handed polarized photons and excitons in the -K valley, right handed polarized photons. The energy of the emitted photons is $E_X = E_g - E_{b,1}$, as discussed in section 2.3. Optical transitions involving excitons are shown graphically in figure 10a. The lowest energy exciton in dark, the bright exciton of the lower energy is known as an A-exciton, the one of the higher energy as a B-exciton.

Superimposed on the dispersion relation in the figure 10a is the dispersion relation of light, a so called light cone. Only excitons within this cone can emit photons directly (with no phonons involved in the process). Excitons in the K valley, e.g. $X_{K\downarrow\downarrow}^{-K\uparrow}$ are momentum dark, they are located outsize the light cone. Having the lowest energy, the K valley may have a large population of excitons generated by phonon scattering of optically excited bright excitons (process labelled $\gamma_{\Gamma-K}$ in the figure) or by electrical injection of charge carriers. As discussed in the previous section, such a momentum dark exciton can emit a photon with the simultaneous

¹⁵In phonon assisted transitions, selection rules have to be applied to both photons and phonons. This is beyond this exercise, but for completeness, we should add that the phonon mediating this optical transition needs to be fully symmetric (carry zero angular momentum) for the process to be possible.



Figure 10: a) Selection rules for the optical transitions for the excitons. The ground state corresponds to no excitation. Excitons can occupy different valleys and they will interact with photons with corresponding polarization. Emission/absorption of a phonon, $\gamma_{K,-K}$, accompanies recombination of photons from the K-valley excitons. Light grey area marks a light cone: photons with a given momentum will have energy in the shaded area. b) Higher energy levels of excitons, here shown for the A-excitons, obey the same selection rules as the lowest energy state one provided that they are have the same shell symmetry (in analogy to atoms referred to as s-, p- etc). The energy of the photons changes with the shell number.

emission of a phonon, ($\gamma_{K,-K}$ in the figure). The energy of emitted photons is lowered by the phonon energy.

The final configuration of an exciton, $X_{K\downarrow}^{K\downarrow}$ is spin forbidden, which means that spin would not be conserved in the optical transitions with photons with momentum normal to the mono-layer plane.

Typically, only the A-excitons are observed in the photoluminescence spectra and also in the case of low energy reflectance spectra. Therefore only A-excitons will be considered from now on.

Figure 11 shows a dispersion relation for trions. The ground state of the trion is a hole or an electron; the mass of the trion is the weighed average of the three component particles. In a p-doped WSe₂ monolayer an absorption of a σ^+ photon generates a $X_{K_{\psi},-K_{\uparrow}}^{K\uparrow}$ trion. This is the only possibility as the A-exciton $X_{K_{\psi}}^{K\uparrow}$ can only bind a hole from -K valley (see lower panel in figure 11a. Although there are two possible recombination paths for $X_{K_{\psi},-K_{\uparrow}}^{K\uparrow}$ (see figure 10), the direct (intravalley) recombination is much more likely:

$$\left|X_{K_{\downarrow},-K_{\uparrow}}^{K\uparrow}\right\rangle = \left|\sigma^{+},h_{-K\uparrow}\right\rangle$$

We can see that due to the spin conservation, the photon emitted from a positive trion has a polarization entangled with the spin of the remaining hole.¹⁶

 $^{^{16}}$ We can also see that the energy of the trion can now be distributed between the emitted photon and the remaining hole. While momentum conservation limits how much energy the hole will retain, it is clear that this sharing will cause broadening of the photon energy distribution with the lower energy tail in the otherwise Lorentzian distribution.



Figure 11: a) Positively charged bright trion and two negatively charged bright trion configurations with an extra electron in b) the opposite and c) the same valley. Top row shows the excitonic states. Only trions formed with a bright exciton interacting with σ^+ photons are shown. Bottom row shows the valley occupancy of electrons and holes. Notice that the bright exciton in a) and c) can easily convert into a dark exciton with the electron in the top subband of K valley being scattered into the bottom subband of -K valley.

Small spin splitting of the conduction band results in a rich fine structure of the negatively charged trions in n-doped WSe₂. Two examples of bright X^- s are shown in the figure 11b and 11c. Radiative recombination of these trions generates photons with polarizations defined by the valley index of the hole. There is a small but measurable difference (a few meV) in the energy of these two trions that is a result of different Coulomb and exchange energies. In addition, there is a difference in the probability of radiative recombination. The trion in the configuration from figure 11b is in its lowest energy state and it can only decay by radiative recombination. The trion in figure 11c can lower its energy by emitting a phonon that would scatter the electron from the state $|K\uparrow\rangle$ into the state $|-K\uparrow\rangle$. The resulting trion $X_{K\downarrow}^{K\downarrow,-K\uparrow}$ is momentum dark.

As discussed above, Coulomb interactions responsible for binding of excitons and trions do not affect the selection rules.¹⁷ However interactions between them can lead to emission/absorption of photons with properties that cannot be understood by solely applying optical selection rules to basis states.

In the simplest example let us consider what happens if WSe_2 monolayer is excited with

¹⁷Coulomb interactions do not affect the selection rules but they do affect the overlap of electron and hole wave functions entering the equation for matrix element, M_{12} . The separation between free electrons and holes will vary randomly (and with no bounds) from one free pair of carriers to another since they move independently. On the other hand, an exciton has a specific Bohr radius and the deviations of the electron-hole separation between excitons are small. This difference demonstrates the limitation of considering only the symmetries of the system rather than the wave functions.



Figure 12: Superposition of intravalley spin-dark excitons (here schematically indicated by the grey ellipses) interacts with z-polarized light.

horizontally polarized light, $|H\rangle = \frac{1}{\sqrt{2}}(|\sigma^+\rangle + |\sigma^-\rangle)^{18}$, a coherent superposition of two beams with opposite circular polarizations. It turns out that as a consequence of photon polarization valley - spin locking for A-excitons, $|H\rangle$ polarized light interacts with a coherent superposition of the A-excitons in K and -K valleys:

$$\left|X_{K,-K}\right\rangle = \frac{1}{\sqrt{2}} \left(\left|X_{K\downarrow}^{K\uparrow}\right\rangle + \left|X_{-K\uparrow}^{-K\downarrow}\right\rangle\right)$$

It means that excitation of a WSe₂ monolayer with linearly polarized light at time zero will generate a coherent superposition of the valley-spin excitons. In the absence of magnetic fields or impurities, of spin or valley selective scattering, or other sources of decoherence, the energy of the two excitons is the same and this state as the whole acquires a phase, $|X_{K,-K}(t)\rangle = e^{-iE_x t} |X_{K,-K}(0)\rangle$ but does not dephase. Radiative recombination from $|X_{K,-K}(t)\rangle$ will generate an $|H\rangle$ polarized photon. This phenomenon is referred to as valley-coherence.¹⁹ Let me remark, that in contrast to excitons, no valley coherence can be observed from the recombination of trions because of the spin-photon polarization entanglement on recombination. Linear polarization cannot not observed in the photon emission spectra of bright trions.

It turns out that z-polarized light (linearly polarized with out of the plane electric field vector) can be absorbed at the energy of spin forbidden excitons, $X_{K\downarrow}^{K\downarrow}$ ($X_{-K\uparrow}^{-K\uparrow}$). A detailed discussion of interactions leading to this phenomenon is beyond the scope of the exercise and can be found in reference [6]. Here it suffices to say that using a mirror symmetry argument one can see that if light propagating in the plane of the monolayer was to interact with excitons, its polarization would have to have a mirror symmetry making a z-polarization the only option. As there is no reason why only one of the two excitons was to allow the interaction but not the other, z-polarized light must interact with a superposition of the two spin forbidden excitons. It

¹⁸By choosing a specific linear polarization we have not lost generality because the polarization is defined in an arbitrary coordinate system.

¹⁹The observed photon generated valley coherence led to a proposal that $X_{K\downarrow}^{K\uparrow}$ and $X_{-K\uparrow}^{K\downarrow}$ can be used as valleyqubit for quantum computation. However, short lifetimes of excitons limit the time for operations performed on the qubit rendering the proposal impractical.

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does interact with $1/\sqrt{(2)}(X_{K\downarrow}^{K\downarrow} + X_{-K\uparrow}^{-K\uparrow})$ schematically shown in figure 12 enables by spin-orbit interactions with higher hole energy bands.

Biexcitons, XX = X + X can be found in the WSe₂ monolayer at high density of excitons. They can form in different valley and spin configurations. In two of those configurations, XX formed from two bright A-excitons in the two valleys, can recombine producing a cascade of photons:

$$\left|X_{K\Downarrow,-K\Uparrow}^{K\uparrow,-K\downarrow}\right\rangle => \left|X_{K\Downarrow}^{K\uparrow},\sigma_{r}^{-}\right\rangle => \left|\sigma_{b}^{+},\sigma_{r}^{-}\right\rangle$$

or

$$|XX\rangle => \left| X_{K\downarrow}^{K\uparrow}, X_{-K\uparrow}^{-K\downarrow} \right\rangle => \left| \sigma_r^+, X_{-K\uparrow}^{-K\downarrow} \right\rangle => \left| \sigma_r^+, \sigma_b^- \right\rangle$$

The subscript r indicates that the first photon of the cascade will recombine with the energy lower than the second exciton (whose energy is marked with the subscript b) by the biexciton binding energy. The two excitons of the pair have different polarizations. This means that the two photons are entangled in energy and polarization. In other configurations, at least one of the excitons is momentum dark.

Similar analysis can be performed for a charged biexciton, $XX^- = X + X^-$. In all possible configurations of the charged biexciton, at least one exciton is bright. When two excitons are bright, one way in which a charged biexciton with an extra electron in the K valley can recombine is:

$$\left| X X_{K\downarrow}^{-} \right\rangle => X_{K\downarrow}^{K\uparrow,K\downarrow} + \sigma_r^+ => \sigma_t^- + \sigma_r^+ + e_{K\downarrow}$$

The two photons have different energies, the second of the trion, the first energy lower than that of the trion by the binding energy of the complex.

4 Optical spectroscopy

The band gap of WSe_2 and other TMDCs monolayer lies in the range of optical photons energy (visible or near infrared light) so optical spectroscopy is a natural way to study them. In this exercise, photoluminescence and reflectance spectroscopies are performed to gain insight into the properties of excitons and other complexes made of electrons and holes in WSe_2 . The next two sections will introduce the general idea behind the techniques, detailed description of the experiments is enclosed in the separate instructions.

4.1 Photoluminescence

Luminescence is a name for emission of photons from the radiative recombination of electron hole pairs or excitons that follows external excitation. Different methods can be used to generate the excited states. For example, in electroluminescence charge carriers are injected electrically into a region of recombination, while energetic electrons are used in cathodoluminescence.

Photoluminescence relies on generation of excited electrons by absorption of light with lasers being the most common source of light. The energy of the photons in the excitation beam typically exceeds the energy of the recombining excitons (see figure 13). This means that photon

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Figure 13: Absorption of a photon with energy, $\hbar\omega_b$, generates an exciton of the same energy and momentum $k \neq 0$. Rapid emission of phonons (t < 10s fs) removes excess energy from the exciton and it is transferred to the lowest energy state at k = 0. After this process, the exciton has the temperature of the crystal lattice hence the process is called thermalization. In the absence of fast non-radiative recombination the exciton will recombine radiatively. The average radiative recombination time depends on the system (material, dimensionality) and is of the order of a few ps in WSe₂ monolayer.

absorption generates so called hot excitons (having non-zero kinetic energy). The excess energy is distributed between electrons and holes in the conduction and valence bands, respectively to maintain zero momentum change. These hot carriers undergo rapid thermalisation with the lattice, meaning that they dissipate the kinetic energy by phonon emission to reach the bottom of the conduction and valence bands. Typically, thermalisation occurs within a few to tens of fs although it can be longer if energy states are quantised. This rapid thermalisation is the reason why it is often sufficient to consider radiative recombination between the bottom of the conduction band and the top of the valence band.

Measurements of the properties (energy, polarization, wave vector) of the light emitted during radiative recombination that follows thermalisation gives an insight into the optical transitions in the measured system. The measurements are performed mostly at cryogenic temperatures, preferably liquid helium temperature (~ 4.2 K) to reduce the phonon population and thermal broadening of energy levels. Measurements at low temperatures also help reducing other, non-radiative, recombination channels that would reduce the intensity of the measured signal.

Figure 14 shows an example of a spectrum of MoSe₂. It consist of two broadened lines of emission. In a perfect case the lines of emission from excitons would have Lorentzian shape (see equation 3.6) and Lorentzian with a tail at low energy from trions recombination. However, the recombining species are often influenced by their environment and lines acquire in lower or higher degree a character of a Gaussian curve. The lines can also be superimposed on a non-zero background caused by defects or spurious signals. Identification of the lines requires that additional variable is introduced in the measurement. This can be a modulation of the excitation beam or perturbation of the system under study. For example, by measuring the intensity of PL as a function of the excitation intensity, one can distinguish excitons from biexcitons. In the first case one expects a linear dependence of PL on excitation intensity; in the latter, quadratic. This type of measurement provides even more information. While we only discussed a radiative recombination, excitons or excited electron - hole pairs can dissipate their energy as phonons. They can also be removed from the sample as an electrical current. This happens in solar cells: as soon as high enough voltage is applied to the solar cell, photogenerated electrons / holes



Figure 14: a) PL and b) reflectance spectra of $MoSe_2$ monolayer with identified emission/absorption lines from X and X⁻. Note that reflectance signal is weak so it is plotted as its derivative. The simple spectra of $MoSe_2$ reflect the fact that the lowest exciton energy state is bright.

are removed from the semiconductor into the contacts, there is no photoluminescence signal.²⁰ Such non-radiative recombination channels will cause deviation of the measured PL excitation power dependence from the expected value.

Temperature dependent photoluminescence can be used to measure the change of semiconductor band gap with the temperature. It can also measure activation energies of electrons and holes localized on dopants, impurities, defects or excitons trapped in dark states. It can provide further insight into non-radiative recombination processes, many of which are thermally activated.

One can change the electrochemical potential in the measured semiconductor by incorporating it in a metal-oxide-semiconductor device. Application of a voltage to the metal (called a gate) changes the electrochemical potential of the grounded semiconductor and the concentration of electrons and holes in the sample via capacitive coupling. PL spectra acquires from a semiconductor with varied background charge levels will have different ratios of exciton and trion line intensities helping to distinguish them.

An application of a magnetic field to the samples causes Zeeman splitting of electronic states and gives information about their magnetic moments. It can also rotate spins or mix states, leading to changes in optical selection rules.

In the final example, excitation by using very short laser pulses, much shorter than the recombination rate of excited states, can be used to measure this recombination rate. In such measurements, histograms of photon detection times are acquired and fitted with appropriate models. If electrons lose their energy only by radiative recombination, the measured histogram follows an exponential curve given by equation 3.5. In the presence of other decay mechanisms (electron trapping on defects, non-radiative recombination, electrical current), the measured curve may still be exponential but the measured decay rate, k_{tot} is a sum of decay rates of all relevant decay processes. Most generally, the decay curves can be non-exponential.

In this exercise, we will use spectrally resolved photoluminescence in order to determine the

 $^{^{20}}$ Since we earlier learnt that excitons do not respond to electric field, the remark here is needed. Materials in which electron - hole pairs are bound into excitons can also be used for solar cells. In this case to extract the excitons as an electric current, sharp potential changes are introduced (e.g. junctions between two materials) which break apart the excitons.

5 REFERENCES

energies of various electron-hole complexes in WSe_2 that decay by emission of photons. We will then analyse their properties and compare with the optical selection rules to identify them.

4.2 Reflectance

While the photoluminescence gives insight into the lowest energy optical transitions, reflectance can be used to get insight into the higher energy transitions as it monitors the process of carrier generation in figure 13, a process occurring before carrier thermalization.

The reflectance spectra of a material are related to its complex dielectric function, $\epsilon(\omega)$, which is derived by considering all possible optical transitions involving photons of the energy $h\omega$. The imaginary part of the dielectric function, $\epsilon''(\omega)$, is linked to the absorption of photons by the material. The real part, $\epsilon'(\omega)$, is related to $\epsilon''(\omega)$ by Kramers–Kronig relations.

The relationship between reflectance and the dielectric function becomes clear when rewriting $\epsilon(\omega)$ as $(n(\omega) + i\kappa(\omega))^2$ where $n(\omega)$ is the refractive index of material and $\kappa(\omega)$ its extinction coefficient (and measure of absorbance). Reflection of light on an interface between two media is related to their refractive indices by Fresnel equations. Reflection of light at the interface between a non-absorbing (e.g. air) and absorbing medium (e.g. semiconductor above the band gap) carries information about the absorption on the latter.

Reflectance spectra of solids tend to be smoothly varying functions of the photon energies with superimposed lines at the energies where absorption is particularly strong. Bright excitons, having large oscillator strengths, are very efficient photon absorbers and their reflectance spectra follow the equation 3.6. Often, a comparison of the reflectance and the photoluminescence spectra is used to get insight into electron energy relaxation processes and into oscillator strengths of optical transitions. Optical transitions from states with low oscillator strength can be observed in PL spectra as long as there is a large population of excitons occupying these states. This can certainly be the case if the lowest excited state of electrons is "dark" (it is the case in WSe₂ as you will see in the exercise). These states do not however contribute to the absorption spectra. Comparing the PL and reflectance spectra in figure 14, we see that two lines are present in both of them and do therefore originate from states with large oscillator strengths, from bright states.

As expressed by equations 1.1 and 2.3 for 3D and 2D materials, bright exctions can be thought of as hydrogen atoms with a multiple shells of different energies. Reflectance spectroscopy can be used to reveal these states and gain further insight into the electronic structure of materials. Plotting the exciton energy as a function of the shell number n can reveal dimensionality of the system $(n^{-2} \text{ vs. } (n - 1/2)^{-2}$ relationship). It can also be extrapolated to measure the single particle band gap, E_g .

Typically, reflectance spectra are measured at 4.2K to avoid thermal broadening of the energy states even for materials such as WSe₂. Limiting the angle of incidence of light to close to normal is also required to avoid spectral broadening. Under such conditions, one commonly observes both excitons and trions in TMDCs. As in PL, variations in the excitation light and external perturbations can be used to get deeper insight into the observed optical transitions.

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