Optical absorption by indirect excitons in a transition metal dichalcogenide/hexagonal boron nitride heterostructure

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Received 14 February 2018, revised 9 April 2018
Accepted for publication 16 April 2018
Published 9 May 2018

Abstract

We study optical transitions in spatially indirect excitons in transition metal dichalcogenide (TMDC) heterostructures separated by an integer number of hexagonal boron nitride (h-BN) monolayers. By solving the Schrödinger equation with the Keldysh potential for a spatially indirect exciton, we obtain eigenfunctions and eigenenergies for the ground and excited states and study their dependence on the interlayer separation, controlled by varying the number of h-BN monolayers. The oscillator strength, optical absorption coefficient, and optical absorption factor, the fraction of incoming photons absorbed in the TMDC/h-BN/TMDC heterostructure, are evaluated and studied as a function of the interlayer separation. Using input parameters from the existing literature which give the largest and the smallest spatially indirect exciton binding energy, we provide upper and lower bounds on all quantities presented.

Keywords: optical absorption, excitons, 2D materials

(Some figures may appear in colour only in the online journal)
To this end, there has been a significant amount of experimental work dedicated to understanding the electronic structure of TMDCs [11, 12], in particular the properties of direct excitons, such as their quasiparticle band structure [13, 14], binding energies [15, 16], and optical properties [17–19]. As a compliment to the experimental efforts to determine the properties of the energy band structure of charge carriers and the optical properties of excitons in TMDC monolayers, there have been a wide variety of analytical and numerical approaches [10, 15, 20–28] which seek to reproduce experimental results as well as to provide a theoretical framework capable of predicting behavior which has not yet been witnessed.

TMDC/h-BN/TMDC heterostructure structures have attracted attention for many of the same reasons as monolayer TMDCs, and the scope of experimental and theoretical studies has expanded to fill a variety of niche scenarios which are inaccessible in the case of single TMDC monolayers. Many studies of TMDC/h-BN/TMDC heterostructures have focused on spatially indirect excitons, and in particular on their optical properties [16, 29–45] or on the formation and properties of Bose–Einstein condensates and superfluids of spatially indirect excitons [46–49]. Complexes of spatially indirect excitons, such as trions and biexcitons, can be excited by high intensity light in TMDC/h-BN/TMDC heterostructures [50].

In this paper, we study optical absorption by excitons in TMDCs due to intraexcitonic transitions, that is, transitions from the excitonic ground state to the excited states. This is accomplished by solving the Schrödinger equation for the electron and hole to obtain the eigenfunctions and eigenenergies of the spatially indirect exciton. The obtained solutions allow us to calculate optical quantities such as the oscillator strength, absorption coefficient, and absorption factor, which gives the fraction of incoming photons absorbed by spatially indirect excitons in a TMDC/h-BN/TMDC heterostructure.

This paper is organized as follows: in section 2, we present a theoretical description of a spatially indirect exciton formed via the Keldysh potential in a TMDC/h-BN/TMDC heterostructure separated by a dielectric. In section 3 we derive expressions for the optical properties under consideration. A summary of our methodology for obtaining numerical solutions for the electron–hole system with the Keldysh potential is presented in section 4. We present and discuss all relevant results in section 5. In section 6, we compare the optical properties of spatially indirect excitons in a TMDC/h-BN/TMDC heterostructure to the optical properties of direct excitons in monolayer TMDCs, as well as to spatially indirect excitons in coupled quantum wells (CQWs). We discuss our numerical results in the context of experimental research of intraexcitonic optical transitions in semiconductors in section 7. Our conclusions follow in section 8.

2. The spatially indirect exciton in a TMDC/h-BN/TMDC heterostructure

We begin by considering two TMDC monolayers separated by a distance $D$, with many-layer h-BN encapsulating the TMDC/h-BN/TMDC heterostructure on the top and bottom, and few-layer h-BN acting as a dielectric between the two TMDC monolayers. The schematic of the TMDC/h-BN/TMDC heterostructure is presented in figure 1. The electrons and holes which constitute the spatially indirect excitons are contained in different TMDC monolayers. The two-body Schrödinger equation for an electron and hole is

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{1}{m_e} \nabla^2 + \frac{1}{m_h} \nabla^2 + V(r_e, r_h) \right] \Psi(r_e, r_h) = E\Psi(r_e, r_h),$$  \hspace{1cm} (1)

where $m_e$ and $m_h$ are the effective electron and hole masses, respectively, $r_e$ and $r_h$ are the position vectors for the electron and hole, and $V(r_e, r_h)$ is the interaction potential between the electron and hole. While the electron and hole interact via the Coulomb potential, in TMDCs the electron–hole interaction is affected by screening which causes the electron–hole attraction to be described by the Keldysh potential [51]. Following the standard procedure for the separation of the relative motion of the electron–hole pair from their center-of-mass motion, one can introduce variables for the center-of-mass of the electron–hole pair, $R = \frac{m_e r_e + m_h r_h}{m_e + m_h}$, and the relative motion of the electron and hole, $r = r_e - r_h$. After separation of the electron–hole center-of-mass motion, the Schrödinger equation for the relative motion of the electron and hole becomes

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \Psi(r) = E\Psi(r),$$  \hspace{1cm} (2)

where $\mu = \frac{m_e m_h}{m_e + m_h}$ is the exciton reduced mass.

The quantum mechanical properties of the exciton are the subject of this investigation and from this point forward we will examine the eigenfunctions and eigenenergies of the spatially indirect exciton using equation (2). We further note that the Keldysh potential has spherical symmetry and only depends on the relative coordinate between the electron and hole. Using cylindrical coordinates with the longitudinal axis perpendicular to the planes of the two TMDC monolayers forming a TMDC/h-BN/TMDC heterostructure, the relative position vector between the electron and the hole is $r = r_e - r_h = \rho z$, where $\rho$ and $z$ are unit vectors, $D$ is the fixed interlayer separation, and $\rho$ is the radial separation between the hole and the projection of the electron position onto the TMDC layer with holes. In these coordinates
the potential \( V(r) \equiv V\left(\sqrt{\rho^2 + D^2}\right) \), and the Schrödinger equation reads,

\[
\left[ \frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right) + V\left(\sqrt{\rho^2 + D^2}\right) \right] \Psi(\rho, \phi) = E\Psi(\rho, \phi).
\]

(3)

Multiplying equation (3) by \( \rho^2 \) and performing separation of variables \( \Psi(\rho, \phi) = R(\rho)\Phi(\phi) \), we obtain,

\[
\Phi(\phi) = \frac{e^{-i\phi}}{\sqrt{2\pi}}, \quad l = 0, \pm 1, \pm 2, \ldots.
\]

(4)

and \( R(\rho) \) is a solution of the following equation:

\[
\frac{d^2 R}{d\rho^2} + \frac{1}{\rho} \frac{dR}{d\rho} + \left\{ \frac{2\mu}{\hbar^2} (E - V(\rho)) - \frac{l^2}{\rho^2} \right\} R(\rho) = 0.
\]

(5)

The potential \( V(\rho) \) is the Keldysh potential \[51\], which in the case of the electron and hole occupying different monolayers is written as

\[
V(\rho) = \frac{\pi ke^2}{2\kappa \rho_0} \left[ H_0 \left( \sqrt{\rho^2 + D^2} \right) \rho_0 - Y_0 \left( \sqrt{\rho^2 + D^2} \right) \rho_0 \right],
\]

(6)

where \( e \) is the charge of an electron, \( k = 9 \times 10^9 \text{ N m}^2/\text{C}^2 \), \( \kappa = \varepsilon_1/\varepsilon_2 \) describes the surrounding dielectric environment (here \( \varepsilon_1 \) and \( \varepsilon_2 \) refer to the dielectric constant of the medium between and surrounding the TMDC/h-BN/TMD heterostructure, respectively), \( \rho_0 = \frac{2\pi \lambda_{\text{TMDC}}}{\kappa} \) is the screening length, where \( \chi_{2D} \) is the 2D polarizability of the medium, and \( H_0 \) and \( Y_0 \) are the Struve and Bessel functions of the second kind, respectively. Note that \( \chi_{2D} \) is a material property while \( \rho_0 \) also depends on the environment via the inclusion of \( \kappa \) in the denominator.

We refer to the eigenstates of the spatially indirect exciton for the Keldysh potential by their analogues in the hydrogen atom, that is, 1s refers to \((n, l) = (1, 0)\), 2s is \((n, l) = (2, 0)\), 2p refers to \((n, l) = (2, \pm 1)\), and so on. This convention of describing the eigenstates of the 2D exciton in TMDC monolayers (or heterostructures) is used, for example, in \[10, 13, 16, 19, 25, 52–57\] despite the qualitative differences between the 2D hydrogen atom and the 2D exciton. The biggest difference between the two systems is that the local screening effects described by the Keldysh potential break the degeneracy of states with the same principal quantum number but different angular momentum quantum numbers, e.g. the 2s and 2p states, or the 3s/3p/3d eigenstates. Conceptually, the reason for this degeneracy breaking is due to the different excitonic radii amongst, for example, the 2s/2p states. The 2s state, which has a smaller radius than the 2p state, is more strongly screened by the TMDC in which the exciton is located. On the other hand, the 2p state, with its larger radius, is screened more by the surrounding h-BN relative to the 2s state. The end result is that the 2p state, with its larger radius, is actually more strongly bound than the 2s state due to the inhomogeneous dielectric environment.

The result described above is a characteristic feature of the Keldysh potential, and indeed our own calculations bear this pattern out, even for large principal quantum numbers. Experimentally, however, there has been some difficulty in simply observing whether or not this degeneracy breaking exists. Indeed, our calculations show that the difference between the 2s and 2p states can be anywhere from 10–15 meV at \( N_{h-BN} = 1 \), decreasing to as small as 6 meV as \( N_{h-BN} \to 9 \), which is at best approximately equal to, and at worst more than three times smaller than, the optical excitonic broadening (see section 4). It is understandable, then, that some experiments do report degeneracy breaking \[58\] while others do not \[19\]. From a theoretical perspective, however, there seems to be very little uncertainty over whether or not this degeneracy breaking should exist, with both \textit{ab initio} studies \[13\] and studies employing a screened 2D potential \[59\] concluding that the 2s eigenstate has a smaller binding energy than the 2p eigenstate.

Equation (5) with the Keldysh potential (6) is not solvable in closed form. It is therefore necessary to turn to numerical methods to solve the Schrödinger equation (2) with the Keldysh potential (6), allowing us to obtain the eigenfunctions and eigenenergies of the spatially indirect exciton in a TMDC/h-BN/TMD heterostructure. Results of the numerical solutions of the Schrödinger equation (2) for a spatially indirect exciton, and the subsequent calculations of the relevant optical properties, are presented in section 5.

3. Optical absorption by spatially indirect excitons

To calculate the optical absorption coefficient and related quantities for optical transitions of spatially indirect excitons in TMDC/h-BN/TMD heterostructures, we need only make slight modifications to the well-established form for the optical absorption due to individual atoms. Therefore, the expressions that describe the optical properties of spatially indirect excitons have the same functional form as those for the hydrogen atom, even though the dynamics of the underlying eigensystem are quite different. Additionally, some aspects of this theoretical framework were applied to obtain optical absorption due to magnetoexcitons in semiconductor CQWs in \[60\].

The theoretical treatment of optical absorption by atoms is well-known \[61\]. Following \[61\], the oscillator strength, \( f_{i\to f} \), for the transition of the exciton from the initial state \(|i\rangle\) to the final state \(|f\rangle\) can be written as:

\[
f_{i\to f} = \frac{\left(2\mu\omega_{i\to f}/\hbar\right)|\langle f|x|i\rangle|^2}{\hbar},
\]

(7)

where \( \mu \) is the exciton reduced mass, \( \omega_{i\to f} = (E_f - E_i)/\hbar \) is the Bohr angular frequency of the transition, and \( E_i \) and \( E_f \) are the eigenenergies of the initial and final states, respectively. The oscillator strength, \( f_{i\to f} \), is a dimensionless quantity and obeys the sum rule, \( \sum_{\neq f} f_{i\to f} = 1 \). The oscillator strength is interesting from a theoretical viewpoint because it can be used to analyze solely the relative likelihood of a particular system undergoing a particular optical transition. Furthermore, calculation of the matrix element \( \langle f|x|i\rangle \) yields the allowed and forbidden transitions. In this work, we assume that all
incident light is normal to the plane of the TMDC monolayer, and that it is linearly polarized. Due to the in-plane isotropy of TMDCs, we arbitrarily choose the polarization of the electric field along the x-axis, without loss of generality.

For optical transitions in spatially indirect excitons induced by linearly polarized light, the only allowed transitions are to states in which \( l_f = l_i \pm 1 \), and \( n_f \neq n_i \). When specifically considering optical transitions from the excitonic ground state \( 1s \) to the excited states, the only allowed transitions are therefore the excited states \( 2p, 3p \), and so on.

We use \( f_0 \) to refer to the oscillator strength, and \( \omega_0 \) to refer to the corresponding Bohr angular frequency, in the cases where the specific states \( |i \rangle \) and \( |f \rangle \) under consideration are clear from context, or when speaking generally about the nature of the functions themselves.

Both the dielectric function \( \epsilon(\omega) \) and the electric susceptibility \( \chi(\omega) \) are commonly obtained using \textit{ab initio} techniques \[20, 21, 38, 46, 62–64\]. The imaginary part of the electric susceptibility \( \text{Im} \chi(\omega) \) is related to the oscillator strength \( f_0 \) as

\[
\text{Im} \chi(\omega) = -\frac{\pi e^2}{2\omega_0 \mu_0 \omega} \frac{n_0}{2\hbar} \left( \frac{\Gamma/2}{(\omega_0^2 - \omega^2)^2 + (\Gamma/2)^2} \right),
\]

(8)

where \( n_0 \) is the 2D concentration of excitons in the TMDC/h-BN/TMDC heterostructure, \( h \) is the thickness of one TMDC monolayer, and \( \Gamma \) is the damping or homogeneous line-broadening, whose primary physical origin is due to exciton-phonon interactions. The fraction \( n_0/(2\hbar) \) represents the 3D concentration of spatially indirect excitons in the TMDC/h-BN/TMDC heterostructure, and the factor of two is included because the single exciton is spread across two TMDC monolayers, each containing either an electron or a hole. Unlike the oscillator strength, the imaginary part of the electric susceptibility contains information about the material within which the spatially indirect excitons exists—indeed, it may be more accurate to say that the imaginary part of the electric susceptibility is fundamentally a property of the TMDC itself, and a sufficiently thorough calculation of \( \text{Im} \chi(\omega) \) will consider how the TMDC interacts with an incoming photon of any wavelength, and will therefore incorporate the contribution of quasiparticles on the full spectrum \( \text{Im} \chi(\omega) \). The presence of quantities such as \( n_0, h, \) and \( \Gamma \) demonstrate that \( \chi \) is a quantity which depends not only on the specific behavior of the spatially indirect exciton—which is encapsulated within \( f_0 \)—but also on material properties such as the thickness of the TMDC monolayer, \( h \), the concentration of spatially indirect excitons in the TMDC/h-BN/TMDC heterostructure, \( n_0 \), and the rate at which these excitons interact dissipatively with their surroundings, \( \Gamma \). It is especially noteworthy that these latter two quantities may be controlled experimentally: \( n_0 \) by changing the intensity of the pump laser which is creating the spatially indirect excitons, and the damping \( \Gamma \) is sensitive to the temperature of the sample, among other things.

Experimental values for the 2D concentration of spatially indirect excitons in TMDC/h-BN/TMDC heterostructures is scarce. Recently, \( n_0 = 5 \times 10^{13} \text{ m}^{-2} \) was reported for a WSe\(_2\) monolayer [65]. Below, we are using this experimental value in our calculations, assuming that it is representative of typical concentrations of spatially indirect excitons in a TMDC/h-BN/TMDC heterostructure.

The second free parameter, \( \Gamma \), may in principle be calculated by analyzing an experimentally obtained absorption spectrum—in this way, \( \Gamma \) is understood as the ‘line broadening’ of each absorption peak, and is thus defined as the full-width half-maximum of each absorption peak. Therefore, we must again turn to prior literature to obtain a reasonable value to use for our purposes. Optical absorption experiments on spatially indirect excitons in GaAs/GaAlAs quantum wells [66] provide a value on the order of \( \Gamma \approx 10^{13} \text{ Hz} \), which corresponds to 41 meV. Values of the line broadening from recent TMDC optical absorption experiments include for MoS\(_2\) phenomenological fits of 30 meV [67], 50 meV [64], and 20 meV [21], which corresponds to \( 7.2 \times 10^{12} \text{ Hz}, 1.2 \times 10^{13} \text{ Hz}, \) and \( 4.8 \times 10^{12} \text{ Hz} \), respectively. Because \( \Gamma \) appears in the denominator of equation (8), a larger \( \Gamma \) corresponds to a smaller maximal value of the absorption, a physically logical result—as the damping in an oscillating system grows stronger, its response to the driving force decreases in amplitude. Therefore, we use \( \Gamma = 10^{13} \text{ Hz} \) throughout our calculations as a conservative approximation of the line broadening in order to avoid overstating the absorption properties of any or all of the TMDC materials studied here.

The imaginary part of the electric susceptibility is primarily interesting for us because of its close relation to the optical absorption coefficient, \( \alpha(\omega) \) [68, 69]:

\[
\alpha(\omega) = -\frac{\omega}{n(\omega)\varepsilon} \text{Im} \chi(\omega).
\]

(9)

In equation (9), \( n(\omega) \) refers to the refractive index of the environment surrounding the TMDC. In the case where the environment (here, we consider exclusively h-BN) interacts weakly with photons in the frequency range of the corresponding optical transition, we approximate \( n(\omega) \approx \sqrt{\varepsilon} \), where \( \varepsilon \) is the static dielectric constant of the environment [69], and rewrite equation (9) as

\[
\alpha(\omega) = \frac{\omega}{n_0 c \sqrt{\varepsilon}} \frac{\pi e^2}{2\omega_0 \mu_0 \omega} \frac{n_0}{2\hbar} \left( \frac{\Gamma/2}{(\omega_0^2 - \omega^2)^2 + (\Gamma/2)^2} \right).
\]

(10)

In much the same way that \( f_0 \) describes solely how the spatially indirect exciton itself interacts with an incoming photon of a particular frequency, and the imaginary part of the dielectric susceptibility describes how the TMDC material itself interacts with incoming photons of any frequency, the absorption coefficient \( \alpha \) further contextualizes the interaction of the photon with the exciton by adding the factor \( n(\omega) \) which takes into account the effect of the environment on the exciton-photon interaction.

It is also important to recognize that equation (10) describes the absorption coefficient for a single allowed transition, for example to the \( n = 1 \rightarrow 2 \), \( l = 0 \rightarrow 1 \) eigenstate. However, as was mentioned previously, ground state excitons may transition to two degenerate states, that is, states with \( l_f = \pm 1 \). Therefore, when considering the effect that a photon with angular frequency \( \omega_{1 \rightarrow n_f} \) will have as it interacts with
the spatially indirect exciton, we must multiply our absorption coefficient \( \alpha \) by a factor of two to properly reflect the fact that the photon may induce a transition to either the \( \ell_f = 1 \) or \( \ell_f = -1 \) eigenstate.

Using equations (8) and (10) to obtain the full spectrum of, correspondingly, the imaginary part of the dielectric susceptibility and the absorption coefficient, it is now possible. To do so, however, one needs a complete theoretical description of how the TMDC in its entirety interacts with an incoming electromagnetic wave of arbitrary frequency, necessarily including knowledge of the band structure of the material as well as any optically accessible phonon modes.

Instead, let us calculate the maximal value of the absorption coefficient for any given optical transition. This maximal value is obtained from equation (10) when \( \omega = \omega_0 \), that is, when the incoming photon’s frequency matches exactly with the Bohr angular frequency of the transition in question. In this case, the expression for the maximum value of the absorption coefficient, \( \alpha(\omega = \omega_0) \), is:

\[
\alpha(\omega = \omega_0) = \left( \frac{\pi e^2}{2\hbar c \varepsilon_0 \varepsilon \mu} \frac{n_0}{\varepsilon_0} \right) \left( \frac{2z}{\ell} \right).
\]

Equation (11) is defined by the oscillator strength of the transition, and depends on the following input parameters: the exciton reduced mass, the dielectric constant of the environment, the 2D concentration of spatially indirect excitons, the thickness of the TMDC monolayer, and the value of the line broadening.

Consider that the absorption coefficient \( \alpha \) features prominently in the expression for the intensity of an electromagnetic wave as it propagates a distance \( z \) through a homogeneous material, e.g.:

\[
I(z, \omega) = I_0 e^{-\alpha(\omega)z},
\]

where \( I_0 \) is the initial intensity of the wave. In equation (12), the physical meaning of the absorption coefficient is clear: it is the inverse of the propagation distance that would correspond to the intensity of the electromagnetic wave decreasing by a factor of 1/e. This form is useful when the electromagnetic wave may propagate any arbitrary distance \( z \) through the material described by the absorption coefficient \( \alpha \), as is the case in bulk 3D materials, but becomes less useful when the distance \( z \) is known and fixed, for example in the case of TMDC/h-BN/TMDC heterostructures. Hence, it may be more useful to consider what fraction of the incoming electromagnetic wave is absorbed by a single TMDC/h-BN/TMDC heterostructure system containing a 2D concentration \( n_0 \) of ground state spatially indirect excitons.

Let us call this quantity the absorption factor and denote it by \( A \):

\[
A(\omega = \omega_0) = 1 - \frac{I(z = 2\hbar, \omega = \omega_0)}{I_0} = 1 - e^{-2\alpha(\omega=\omega_0)z}.
\]

The absorption factor \( A \) simplifies the process of comparing how strongly each TMDC/h-BN/TMDC heterostructure system absorbs incoming light, while taking into account the variety of thicknesses of each TMDC material.

### 4. Methodology of numerical calculations

Let us outline the methodology of numerical calculations for finding the eigenfunctions and eigenenergies of spatially indirect excitons using the Keldysh potential \([51]\). First, we consider equation (2) for large interlayer separation \( D \) and numerically solve the Schrödinger equation with the approximate harmonic oscillator potential \((A.1)\) for different interlayer separations and compare our results to the analytical solutions shown in equations \( (A.4) \) and \( (A.3) \). Next, we solve the Schrödinger equation with the Keldysh potential for a direct exciton using the same input parameters as in \([71]\) and compare the solution with results from \([71]\). Finally, the Schrödinger equation for the spatially indirect exciton is then solved with the Keldysh potential to obtain the eigenfunctions and eigenenergies of spatially indirect excitons in a TMDC/h-BN/TMDC heterostructure for different values of the interlayer separation \( D \).

Let us check that our numerical calculations in the case of the harmonic oscillator approximation accurately reproduce the analytical solutions given in appendix. Verifying the accuracy of the numerical eigenenergies is achieved by straightforwardly comparing the numerically obtained binding energy as a function of \( D \) to the binding energy given analytically in equation \((A.4)\). Performing such a comparison shows that the numerical values agree with the analytical values to at least four decimal places.

Verifying the accuracy of the numerical eigenfunctions is best done by comparing the results of a calculated value based on the eigenfunctions themselves. To accomplish this, we calculate the in-plane gyration radius of the spatially indirect exciton in the ground state, \( r_X = \sqrt{\langle \rho^2 \rangle} = \left[ \int \Psi_{1s}^*(r) \rho^2 \Psi_{1s}(r) \, dr \right]^{1/2} \), where \( \Psi_{1s}(r) \) and \( \Psi_{1s}^*(r) \) represent the ground state excitonic wave function and its complex conjugate, respectively. By calculating \( r_X \) using both the numerical and theoretical \((A.3)\) solutions in the harmonic oscillator approximation presented in appendix, we can verify that the numerical calculation produces accurate results. Upon comparing these two values, we again find excellent agreement to better than four decimal places.

To further emphasize that our computational method is sound, we sought to use our computational framework to emulate the results of previously published literature. In \([71]\) the authors used density functional theory to obtain \( \mu \) and \( \chi_D \) for MoS\(_2\), MoSe\(_2\), WS\(_2\), and WSe\(_2\), and calculated the corresponding binding energy of direct excitons. Using the same material parameters from \([71]\) to calculate the binding energy of direct excitons yields results that agree to better than 1%.

Based on the robust agreement between the numerical and analytical results, as well as the robust agreement between our calculations and results from \([71]\), there is strong evidence that the code produces accurate eigenfunctions and eigenenergies. Given the functional forms of the optical quantities \( f_0 \), \( \alpha \), and \( A \) presented in section 3, we can be assured of accurate calculations of optical absorption provided we are using the correct eigenvalues and eigenfunctions.
Throughout the previous sections, we have carried out the theoretical analysis of a system consisting of spatially separated electrons and holes under the assumption that the exciton system is dilute enough that it is reasonable to ignore the electrostatic dipole–dipole interaction between the spatially indirect excitons themselves. We justify this assumption by comparing the in-plane gyration radius, \( r_X \), to the average distance between the excitons themselves, \( r_S \). Rearranging \( r_S \), we may write the 2D concentration of spatially indirect excitons in the plane of the TMDC monolayers as \( n_0 = 1 / (\pi r_S^2) \). If \( r_S \gg r_X \), then the electrostatic interaction between the electron and hole forming a spatially indirect exciton would be much stronger than any dipole–dipole interactions between neighboring excitons. It would therefore be reasonable to consider each exciton as effectively isolated from its neighbors, which in turn justifies treating the exciton in section 2 as a purely two-body system, and furthermore justifies in section 3 the decision to not modify the eigensystem obtained in section 2.

Using the numerical results for the spatially indirect exciton formed via the Keldysh potential in a TMDC/h-BN/TMDC heterostructure, we find that for \( n_0 = 5 \times 10^{15} \text{ m}^{-2} \) the ratio \( r_X/r_S \) falls between 0.25 for \( N_{h-BN} = 1 \) and 0.5 for \( N_{h-BN} = 9 \). These results do not necessarily satisfy the condition that \( r_S \gg r_X \), nor do they immediately invalidate the assumption that the spatially indirect excitons can be treated as non-interacting. It could be argued that the ratio \( r_X/r_S \) approaches 0.5 at larger interlayer separations that the assumption that the excitons are non-interacting breaks down. However, it is worth mentioning again that no experiment yet has used a TMDC/h-BN/TMDC heterostructure with more than five layers of h-BN, and \( r_X/r_S \approx 0.35 - 0.45 \) for \( N_{h-BN} = 5 \). It is therefore reasonable to assume that our calculated optical quantities, presented in section 5, are accurate enough to produce experimentally verifiable results.

5. Results and discussion

Let us now turn our attention to the calculation of the binding energies, transition energies, oscillator strengths, absorption coefficients, and absorption factors for the \( 1s \rightarrow 2p \) and \( 1s \rightarrow 3p \) transitions using the solution of equation (5) with the Keldysh potential (6). As the input parameters for calculations of the aforementioned values we use the data listed in table 1 and the dielectric constant of h-BN, \( \epsilon_{h-BN} = 4.89 \) [46]. With reference to table 1, we see that there is still non-trivial disagreement as to the precise value of the material parameters which define each of our TMDC systems. For that reason, to avoid arbitrarily choosing one value for each parameter and presenting those results as a definitive prediction of the behavior of the systems, we choose the largest and smallest values found in the literature for the material parameters \( \mu \) and \( \chi_{2D} \), and use these extreme values to provide upper and lower bounds on each of the quantities we calculate. Specifically, we find that the largest value of \( \mu \) and the smallest value of \( \chi_{2D} \) corresponds to the largest binding energy. The binding energy is an increasing function of \( \mu \) as in the case of the bare Coulomb potential, while the binding energy is a decreasing function of \( \chi_{2D} \). A small value of \( \chi_{2D} \) corresponds to highly localized screening effects—indeed, the Keldysh potential tends exactly to the Coulomb potential in the limit \( \chi_{2D} \rightarrow 0 \). Therefore, in the scenario where the TMDC has a higher dielectric constant than the environment, small values of the 2D polarizability \( \chi_{2D} \) correspond to a more Coulomb-like environment, which yields larger binding energies.

Figure 2 presents the range of binding energies for the four TMDC materials. Results of the calculations show that the binding energy of spatially indirect excitons in each TMDC/h-BN/TMDC heterostructure decreases monotonically as a function of the interlayer separation. We see that MoSe\(_2\) has the most tightly constrained upper and lower bounds for the binding energy, which is simply due to MoSe\(_2\) having the smallest range of material parameters found in the literature. The binding energies for the other three materials are strikingly similar despite the differences in the particular values of \( \mu \) and \( \chi_{2D} \) found in table 1. We also note that the upper and lower bounds of \( E_b \) for MoS\(_2\), WS\(_2\), and WSe\(_2\) can differ by nearly 20% for \( N_{h-BN} = 1 \), but as the number of h-BN monolayers increases to 9, we see that the difference in binding energy between the upper and lower bounds decreases to roughly 10%.

The energies at which transitions into the excitonic excited states occur are given in figure 3. It is clear that for both excited states, the transition energy decreases monotonically as the interlayer separation \( D \) increases. It is notable that there is no overlap between the upper and lower bounds for the \( 1s \rightarrow 2p \) and \( 1s \rightarrow 3p \) transitions for a given value of \( N_{h-BN} \), which suggests that any experimental observation of optical transitions occurring at photon energies given in figure 3 should unambiguously identify the particular transition which occurred. The difference between the upper and lower bounds on the energies of the two transitions shown in figure 3 is, in general, smaller than the corresponding difference between the upper and lower bounds on the binding energy as shown in figure 2. This suggests that the values of the eigenergies themselves are more sensitive to changes in the material parameters than the relative change in energy between successive eigenstates. Figures 2 and 3 also demonstrate that TMDC/h-BN/TMDC heterostructures may be engineered such that the binding energies and transition energies fall within a particular energy range.

Figure 4 presents the dependence of the oscillator strengths for the \( 1s \rightarrow 2p \) and \( 1s \rightarrow 3p \) transitions on the interlayer separation. The behavior of the oscillator strengths for the two transitions are drastically different: the oscillator strengths for the \( 1s \rightarrow 2p \) transition increase monotonically with increasing \( D \), while the oscillator strengths for the \( 1s \rightarrow 3p \) transition decrease monotonically. Moreover, the oscillator strengths for the \( 1s \rightarrow 2p \) transition are roughly an order of magnitude larger than for the \( 1s \rightarrow 3p \) transition. The upper and lower bounds of the oscillator strengths for a given transition and interlayer separation show much less variability overall than either the binding energies or transition energies, however the
difference between the upper and lower bounds remains relatively constant as the interlayer distance increases. This may be due in part to the fact that the sum of the oscillator strengths for all allowed transitions must be unity, fundamentally constraining the range of possible values.

Now that the results for the oscillator strength $f_0$ have been presented, we turn our attention again to equation (11), and recognize that we may rewrite the expression for $\alpha$ as:

$$\alpha = C_\alpha f_0, \quad (14)$$

where

$$C_\alpha = \frac{\pi e^2}{2 \epsilon_0 \sqrt{\epsilon_c \mu_i}} n_0 \frac{2}{2h \Gamma}, \quad (15)$$

is the absorption coefficient scale factor and $i = \text{MoS}_2, \text{MoSe}_2, \text{WS}_2, \text{WSe}_2$. Hence, one may simply use the value of $f_0$ found in figure 4 paired with the appropriate scale factor given in table 2 to obtain $\alpha$. The absorption factor $\mathcal{A}$ may then be straightforwardly calculated using equation (13).

Though our calculations show that MoSe$_2$ has the largest oscillator strength, it actually has the smallest absorption coefficient of the four TMDC materials. We also find that WS$_2$ has the largest absorption coefficient, with MoS$_2$ and WSe$_2$ being roughly equal. Since $\mathcal{A}$ is very closely related to the absorption coefficient $\alpha$, we draw many of the same conclusions as for $\alpha$. For the $1s \rightarrow 2p$ transition, WS$_2$ and WSe$_2$ absorb the most strongly, showing between 2.0% and 3.5% absorption in the case of one h-BN monolayer, increasing to between 2.5% and 4.1% absorption when $D$ increases to 9 layers of h-BN. MoSe$_2$ again exhibits the weakest and least variable absorption, barely surpassing an upper bound of 2.5% absorption for 9 layers of h-BN. In general, the absorption coefficients and absorption factors for the $1s \rightarrow 3p$ transition are about an order of magnitude less than the corresponding values for the $1s \rightarrow 2p$ transition.

We have also been made aware of a very recent experimental work in which 'inter-layer' (i.e. spatially indirect) excitons were observed in MoSe$_2$ single crystals [74]. The authors report that spatially indirect excitons in bilayer MoSe$_2$ encapsulated by h-BN have a binding energy of 153 meV. Using the range of material parameters given in table 1, the upper and lower bounds of the spatially indirect exciton binding energy are 132–140 meV. Our calculations are within $\approx 10\%$ of the reported value.

6. Comparison of results to optical absorption in TMDC monolayers and coupled quantum wells

Despite the fundamental differences between interband optical absorption in TMDC monolayers and the intraexcitonic optical absorption studied here, it may still prove instructive to examine the underlying physical differences between the two processes. In light of the fundamental differences between interband and intraexcitonic optical absorption, it may be helpful to place our results in the broader context of optical absorption in TMDCs. It was previously reported [6, 45, 67, 75] that interband absorption leading to the creation of direct excitons in monolayer MoS$_2$ is nearly 10%, e.g., $\mathcal{A} = 0.10$. The creation of spatially indirect excitons in TMDC/h-BN/TMDC heterostructures, on the other hand, is a multi-step process—first, direct excitons are created in a TMDC monolayer via optical excitation in the presence of an electric field perpendicular to the plane of the monolayers. The electric field separates the electron and hole into the spatially separated TMDC monolayers of the TMDC/h-BN/TMDC heterostructure system, at which point the excited state transitions studied here may be accessed optically. Therefore, despite the fact that the aforementioned studies on interband transitions leading to the creation of direct excitons focused specifically on TMDC monolayers, the full absorption spectrum for TMDC/h-BN/TMDC heterostructure systems will include both the full absorption spectrum for direct-exciton-creating interband transitions plus the absorption spectrum corresponding to the transitions to spatially indirect excitonic excited states considered in this paper. Semiconductor CQWs such as GaAs/GaAlAs have enjoyed intensive experimental [76–79] and theoretical [66, 80–83] study. Experimental results for the optical absorption coefficient for interband optical transitions in CQWs, when not presented in arbitrary units, show that the first interband optical transition [76] has an absorption coefficient of around $4 \times 10^4$ m$^{-1}$. This value of $\alpha$ for interband transitions is therefore roughly an order of magnitude smaller than our current results for intraexcitonic transitions. TMDCs are a topic of intense study precisely because they exhibit exceptionally strong absorption. In comparison to quantum wells, we see that

| Parameter | MoS$_2$ | MoSe$_2$ | WS$_2$ | WSe$_2$ |
|-----------|---------|---------|--------|---------|
| $\mu, (m_0)$ | 0.16 [72] | 0.28 [27] | 0.27 [27] | 0.31 [27] |
| $\chi_{2D}, (\text{Å})$ | 7.112 [71] | 6.60 [25] | 8.461 [71] | 8.23 [25] |
| $h, (\text{Å})$ | 6.18 | 6.527 | 6.219 | 6.575 |

Table 1. Table of relevant material parameters for the calculation of eigenvalues, eigenenergies, and optical properties of various TMDC/h-BN/TMDC heterostructure systems. For each material, two values of $\mu$ and $\chi_{2D}$ are given and $h$ is the thickness of the corresponding TMDC monolayer. The value of the left sub-column corresponds to the value found in the literature which minimizes the spatially indirect exciton binding energy, while the value in the right sub-column maximizes the binding energy. Because these minimal/maximal values represent the range of values found in the literature, it is highly likely that the true value of each parameter for a given material falls somewhere within the range given, and therefore that the true magnitude of the calculated quantities studied in this paper lies somewhere between the calculated values.
the absorption coefficients $\alpha$ for interband optical transitions in TMDCs are roughly an order of magnitude greater than the absorption coefficients $\alpha$ for the corresponding transitions in semiconductor CQWs.

7. Relation to experiment

Intraexcitonic optical transitions have been studied experimentally since at least 2004, when such a study was performed.
in Cu$_2$O [84–87]. Additional experiments were performed in GaAs/GaAlAs quantum wells [88, 89]. More recently, similar experiments were performed in monolayer TMDCs [52, 54, 57] in which the excited states of the direct exciton were probed. However, it appears that these types of studies have not yet been performed for spatially indirect excitons in TMDC/h-BN/TMDC heterostructure systems. Therefore, while we are unable to directly compare our results with previously published literature, we state with confidence that our theoretical approach is sound, and that it is certainly possible to design an experiment which could probe exactly the types of optical transitions that are studied here.

Though our computational results are limited by the accuracy of the input parameters shown in table 1, this general disagreement as to the precise values of the material properties of TMDCs does not invalidate the predictive power of our calculated values of the binding energy, transition energies, oscillator strengths, absorption coefficients, and absorption factors for spatially indirect excitons in TMDC/h-BN/TMDC heterostructures. On the contrary, by surveying the range of possible values for experimentally verifiable quantities ranging from the binding energies to the absorption coefficients, we provide here convenient upper and lower bounds for all optically relevant quantities for the benefit of future experimentalists who seek to observe the phenomena predicted here. In principle, the transition energies shown in figure 3 may be verified experimentally by first creating the spatially indirect excitons in the 1s (ground) state, and using a second laser to probe the excited states. Direct observation of absorption or photoluminescence at photon frequencies corresponding to the transition energies presented in figure 3 should be an unambiguous confirmation of predicted transitions, as well as a demonstration of the feasibility of taking advantage of these types of optical transitions for future optoelectronic applications.

**8. Conclusions**

To conclude, we provide experimentally verifiable predictions for the binding energies, and the transition energies, oscillator strengths, absorption coefficients, and absorption factors for the 1s → 2p and 1s → 3p transitions. Using solutions of the Schrödinger equation with the Keldysh potential for a spatially indirect exciton in a TMDC/h-BN/TMDC heterostructure, we calculated binding energies, transition energies,
oscillator strengths, absorption coefficients, and absorption factors and their dependence on interlayer separation for four different TMDC materials.

We emphasize the following conclusions, which are generally applicable to each of the TMDC materials studied here: (i) The binding and transition energies for a spatially indirect exciton in TMDC/h-BN/TMDC heterostructures monotonically decrease as the interlayer separation is increased: binding energies decrease by nearly a factor of two, while energies for the $1s \rightarrow 2p$ and $1s \rightarrow 3p$ transitions decrease by nearly a factor of three as the number of h-BN monolayers is increased from 1 to 9. (ii) The oscillator strengths for the $1s \rightarrow 2p$ transition increase monotonically with increasing $D$, while the oscillator strengths for the $1s \rightarrow 3p$ transition decrease monotonically. Moreover, the oscillator strengths for the $1s \rightarrow 2p$ transition are roughly an order of magnitude larger than the $1s \rightarrow 3p$ transition for a single h-BN monolayer, becoming about 20 times larger when the interlayer separation is increased to 9 layers of h-BN. (iii) The absorption coefficients and absorption factors show that spatially indirect excitons in TMDC/h-BN/TMDC heterostructures should exhibit exceptionally strong absorption.

While our calculations are limited by the range of values of the input parameters presented in table 1, our predicted values for the binding and transition energies, oscillator strengths, absorption coefficients, and absorption factors are, in principle, accurate enough to be verified experimentally. In fact, the deliberate decision to present these calculations in principle, accurate enough to be verified experimentally.

In equation (A.2b), $H_{-1}$ and $Y_{-1}$ are the Struve and Bessel functions of the second kind, of order $\nu = -1$. Having recast the potential in the form of the quantum harmonic oscillator, we now have a Schrödinger equation which has an analytical solution [90] in terms of the associated Laguerre polynomials $L_n^\mu$:

$$
\Psi(\rho) = (-1)^{n+\mu} \left( \frac{2}{\gamma} \right)^{1/2} \left( \frac{\gamma}{\rho} \right)^{n+\mu} e^{-\rho/2} L_n^\mu(\gamma \rho) \frac{e^{i\phi}}{\sqrt{2\pi}}.
$$

(A.3)

where $L_n^\mu$ is the associated Laguerre polynomial of degree $n$. The corresponding eigenenergies are:

$$
E_n = \left[ \frac{2\hbar^2 \gamma^2}{\mu} \right] (n + 1) - V_0,
$$

(A.4)

where $V_0$ and $\gamma^2$ are defined by equations (A.2a) and (A.2b), respectively and the quantum numbers $n = 0, 1, 2, \ldots$ and $\lambda = -n, -n + 2, \ldots, n$ are the principal and angular momentum quantum numbers, respectively.

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