Signatures of trions in the optical spectra of a doped MoS$_2$ monolayer

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Abstract. Two-dimensional transition metal dichalcogenides is a novel class of semiconductor materials with remarkable properties due to the interplay of the valley and spin degrees of freedom controlled by the optical helicity. Optical spectra of those direct band-gap materials are influenced by a variety of complex multi-particle tightly bound excitonic states. In this work, we report first-principles calculations within the Tamm-Dancoff approach for the absorption spectra of the doped monolayer MoS$_2$, as determined by neutral direct and indirect two-particle excitons as well as charged three-particle trions. Our study reveals a large doping dependence of the lowest energy spectral peaks due to the direct exciton and trion, in excellent quantitative agreement with the available experimental data. At finite doping, the indirect dark exciton brightens with its optical oscillator strength becoming comparable to the conventional trion and direct exciton states at moderately low doping levels, offering the novel interpretation of the observed complex spectra of MoS$_2$ monolayer.

Monolayers of MoS$_2$, first created in 2010, are non-centrosymmetric 2D semiconductors with two degenerate direct gaps in the single-particle spectrum at the ±$K$ points of the Brillouin zone [1, 2, 3, 4]. Such structures have many properties that are of interest to both fundamental research and practical applications. In particular, they are strongly coupled to light, yielding strong photoluminescence [1, 5], and have a large spin-orbit interaction which allows one for efficient manipulation of their spin and valley degrees of freedom [6, 7, 8, 9]. A combination of optical and electric characteristics of those materials makes them very attractive for a variety of opto-electronic applications [10, 11] including logic circuits [12, 13], phototransistors [14], light sensors [15] as well as light-producing and harvesting devices [16, 17, 18, 19, 20].

The 2D geometry of such materials enhances the Coulomb interaction, giving rise, in particular, to a much larger exciton binding energy [1, 5, 21, 16, 22, 23] than in bulk semiconductors [24]. This enhancement also facilitates other many-body states including three-particle charged excitons $X^\pm$ or trions [25, 20, 26, 27, 28, 29, 30, 31, 32, 33]. Signatures of trions, consisting of two electrons and one hole, were previously
Signatures of trions in the optical spectra of a doped MoS$_2$ monolayer observed in the photoluminescence spectrum of a field-effect transistor based on MoS$_2$ monolayer [25]. It must be noted that the existence of two degenerate valleys in the band structure results in many different types of exciton and trion states, such that a reliable interpretation of experiments is possible only alongside comprehensive theoretical calculations [11].

A direct solution of the three-body problem requires enormous computation efforts even for a 2D system. This forced researchers to look for approximate methods, such as the variational [34, 35] and stochastic approaches [36, 37, 38], perturbation expansions [39, 40, 41, 42], path integral [43, 44] and diffusion Monte Carlo methods [45]. Recently a direct solution of the three-body problem within the Tamm-Dancoff approach become possible [46, 47, 48, 49, 50, 51, 52, 53]. However, a solution of the pure three-body problem is of limited use, if one wants to describe real experiments where trions are excited in doped materials with finite excess carrier densities [25, 54, 29, 55].

In this work, we overcome this shortcoming and present calculations of trions in an electrically doped MoS$_2$ monolayer using results of the ab-initio electronic structure calculations. Our results are in excellent agreement with the available experimental data. Moreover, we predict that at finite doping indirect exciton brightens and, at a moderately low doping level of $2.5 \times 10^{12}$ cm$^{-2}$, its optical strength becomes similar to that of the conventional trion and direct exciton.

The band structure of a single-layered MoS$_2$ is calculated using the DFT approach as implemented in the GPAW [56, 57] code with the PBE exchange-correlation functional [58]. The spin-orbit interaction is taken into account within the first-order perturbation contribution [59]. The calculations are done using the plane-wave basis with the $12 \times 12 \times 1$ grid in the $k$ space with the energy cutoff 600 eV. The calculated band structure is used to construct a tight-binding model Hamiltonian following Ref. [60] using a standard approach implemented in the Wannier90 code [61] with the $24 \times 24 \times 1$ mesh of the Brillouin zone. The resulting Hamiltonian has 22 bands, of which 10 bands correspond to Mo atoms and 6 valence bands correspond to each of the S atoms in the elementary cell. We also apply a scissor procedure $\Delta_{\text{scissor}} = 0.497$ eV to get the correct energy peak of the ground exciton state in the BSE calculation. The lattice constant of MoS$_2$ is assumed 3.14 Å, the vacuum distance between MoS$_2$ layers is 20 Å.

We employ the approach, which allows us to consider the influence of doping while avoiding solving the full many-body problem. The method is based on the fact that for delocalized Fermi particles, the Coulomb interaction is taken into account by considering the problem in the phase-space that is reduced by the Pauli blocking principle due to the presence of the Fermi sea of free carriers. This method is similar to the famous Cooper treatment of the superconducting pairing phenomenon, where a similar reduction of the available phase-space gives rise to the particle interaction enhancement and the Cooper pair formation [62]. Details of the trion calculations are given in the Supplementary Information.

The linear absorption spectra of a monolayer MoS$_2$ deposited on a SiO$_2$ substrate
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Figure 1. Absorption spectra of a monolayer MoS$_2$. (a) shows three lowest energy absorption peaks calculated as optical transitions between the three-particle states and single-electron states for different carrier densities $n$ given on the right of the figure. The corresponding Fermi levels are shown on the left. The spectra are offset vertically for clarity. The peaks correspond to the three-particle states: “Trion” (T), “Indirect exciton” (IE), and “Direct exciton” (DE) (see text). (b) shows zoomed-in absorption spectra (blue) for the lowest doping level in (a) in comparison with the BSE solution (red) for the two-particle exciton state (red). (c) shows the doping dependence of the oscillator strengths corresponding to the three peaks in (a). The IE peak becomes visible for $n > 5 \times 10^{11}$ cm$^{-2}$ and exceeds DE peak intensity at $n > 2 \times 10^{12}$ cm$^{-2}$. The dashed horizontal line corresponds to the oscillator strength from the two-particle BSE solution, which agrees fairly well with the sum of the oscillator strengths of the three peaks (magenta circles). (d) shows the doping (Fermi level) dependence of the three peak positions from (a). The theoretical calculations (filled circles) are in excellent agreement with the experiment [25] (empty circles) for the T and DE states. The IE peak appears in between the T and DE peaks. The two dashed horizontal lines are results of the two-particle BSE solution for the direct and indirect excitons.
Figure 2. Band structure and trion wave functions in a monolayer MoS$_2$. The zoomed-in band structures near the $K$ and $-K$ points, where the open circle sizes correspond to the wavefunction weights for the trion (a), indirect exciton (b), and direct exciton (c) states from the three-particle solution at $n = 0.36 \times 10^{12}$ cm$^{-2}$. (d) demonstrates the concept of using a variable k-point mesh to mimic doping level dependence of free carriers contribution to the three-particle wavefunction.
Signatures of trions in the optical spectra of a doped MoS$_2$ monolayer are presented in Fig. 1a and b. First, we note that at a small doping level, $n \lesssim 5 \times 10^{11}$ cm$^{-2}$, the lowest part of the spectrum has two peaks that correspond to the trion (T) and direct exciton (DE) states. However, as the doping increases, a third peak, due to the indirect exciton (IE), appears between the T and DE peaks. The IE peak intensity increases rapidly with the doping and, at $n > 2 \times 10^{12}$ cm$^{-2}$, it overwhelms the decreasing DE peak.

More detailed doping dependences of the intensities are shown in Fig. 1c. One can see that the oscillator strengths of both the T and IE peaks are negligible at small doping but they increase as carrier density grows. On the contrary, the oscillator strength of the DE state is maximal at zero doping, but it decreases when the doping level increases. Remarkably, the combined oscillator strength of all three peaks is practically constant and is equal to that of the direct two-particle exciton, as calculated using Bethe-Salpeter Equation (BSE) [63] as shown in Fig. 1d. The absence of the IE peak at small doping does not imply this state does not exist, but it is simply a manifestation of the fact that the corresponding optical transitions are suppressed. This observation matches the results of the BSE calculations for the spectrum of two-particle excitons in Fig. 1b, which demonstrates that the indirect exciton state is optically dark.

The doping dependencies of the spectral peak positions are plotted in Fig. 1d. Remarkably, the doping affects states T, IE, and DE in a qualitatively different way. When the doping increases, only the T peak shifts to lower energies, whereas the energies of both the IE and DE peaks increase. Comparing positions of the T and DE peaks with the available experimental results [25], reproduced in Fig. 1d, reveals a perfect quantitative agreement. The corresponding data for the IE peak is missing which is probably explained by its much lower visibility, especially at smaller doping densities.

For comparison, in Fig. 1d we also plot transition energies of the corresponding two-particle exciton states obtained by solving the BSE equation. One can see that the results for the IE and DE states in the zero doping limit converge to that of the two-particle BSE solution, illustrating that the two- and three-particle states are practically equivalent in this limit. This equivalence is also manifested in the match between the optical spectra of the two- and three-particle states in the undoped system, as illustrated in Fig. 1b. The peaks that correspond to the trion and indirect exciton three-particle states are both invisible at a vanishingly low doping level approaching the results of the BSE calculations for the two-particle states.

The properties of the low energy peaks follow from the details of the internal structure of those states. It has two degenerate direct gaps $E_g \approx 2.184$ eV at two valley points $K$ and $-K$ of the Brillouin zone, in full agreement with the other calculations [3] [22] [17]. For the lowest-energy T state, the electrons are distributed symmetrically over the valley states. This is shown in Fig. 2a, which plots relative contributions of the single-particle states to the trion wavefunction. In contrast, the single-particle distributions for the DE and IE states are highly non-symmetric approaching that of the two-particle direct and indirect exciton states, see Fig. 2b and c. Furthermore, one notes that distributions of single-particle states in the IE and DE wavefunctions comprise two qualitatively dif-
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Different contributions: a quasi-continuous part, which spreads over many single-particle states, and a singular part with essentially one contributing single-particle state. The quasi-continuous part yields a spatially localized component while the singular part a spatially extended one. Without the singular part, distributions of single-particle weights in Figs. 2b and c are very similar to that of the indirect and direct two-particle excitons, calculated using the BSE. One can thus conclude, that in the limit of vanishing doping the IE and DE trion states are in fact products of the corresponding two-particle exciton wavefunction and the free (delocalized) electron state. On the contrary, the T state does not have a singular part, which implies that it is always tightly bound.

Finally, we demonstrate how the spectra of trion states can be engineered by changing the dielectric properties of the underlying substrate, which modifies the strength of the Coulomb interaction. Fig. 3 shows trion binding energies, relative to the DE exciton peak position, calculated as a function of the substrate dielectric constant $\varepsilon$ at two doping levels. For $n = 0.58 \times 10^{12}$ cm$^{-2}$ the binding energies decreases monotonically with increasing $\varepsilon$. However, at larger doping $n = 1.3 \times 10^{12}$ cm$^{-2}$ it tends to saturate at $\varepsilon \gtrsim 8$. This behavior can be rationalized by the fact that, at large $\varepsilon$, free carriers dominate screening of the Coulomb interaction, such that the effect of the environmental screening diminishes. The variational approach does not show the binding energy saturation at large $\varepsilon$ since it does not take into account the screening due to the free carriers. This explains why the deviation between the exact and the variational approach is relatively small for an undoped system, but it grows at larger doping thereby limiting the applicability of the variational approach for trions at finite densities.

In contrast, the $\varepsilon$ dependence of the oscillator strength differs for the three-particle states qualitatively, as shown in Fig. 3b and c. While the oscillator strength of the DE state monotonically decreases with increasing $\varepsilon$, the strengths of the IE and T peaks increase with $\varepsilon$ for small values of the dielectric constant and saturates at larger values of $\varepsilon$. The decrease of the DE optical strength is attributed to the increasing exciton radius, which means a smaller spatial overlap between the localized electron and the localized hole. In the case of the IE state, an optical transition is due to the radiative decay of the delocalized electron and the localized hole. As the hole radius increases, the overlap between the delocalized electron and the less localized hole increases as well, which leads to a larger oscillator strength. Note, that the total oscillator strength follows the behavior of that of the DE state and it is almost the same as obtained from the BSE calculations for the two-particle exciton.

In conclusion, our calculations of the optical spectra of a monolayer MoS$_2$ offer a novel interpretation of its low energy peaks and their doping dependence. In particular, they reveal that transitions due to the indirect excitons brighten with finite doping, so that the corresponding spectral peak becomes visible at $n \gtrsim 10^{12}$ cm$^{-2}$. We demonstrate how contributions by different many-particle excitonic states to the spectrum can be engineered by varying the doping and by choosing the dielectric environment of a
Figure 3. Dependence of the peak positions and oscillator strengths on the dielectric constant of an underlying substrate. (a) shows the binding energies of the trion states relative to the direct exciton energy as a function of the substrate dielectric constant $\varepsilon$ for two carrier densities $n = 1.3 \times 10^{12} \text{ cm}^{-2}$ and $n = 0.58 \times 10^{12} \text{ cm}^{-2}$. The variational calculations (magenta open circles) agree well with the Tamm-Dancoff approach at a smaller doping. (b) and (c) show the corresponding oscillation strengths from the three-particle solution for the same densities as in (a) along with the sum of the oscillator strengths (magenta circles). Note, that the indirect exciton is not visible for the smaller density and is not shown in (c).

monolayer. Our approach, that combines \textit{ab initio} calculations for the band structure, a direct solution of the three-body problem, and the discretization to take into account the Pauli blocking, can easily be extended to other transition metal dichalcogenides. Our qualitative conclusions are general and should hold for other transition metal dichalcogenides layered structures with the valley degeneracy in the single-particle spectrum.
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Supplemental Materials: Signatures of trions in the optical spectra of a doped MoS$_2$ monolayer

Trion states

Quantum states for trions are obtained by solving a three-body problem for two electrons and one hole by direct diagonalization of the Hamiltonian [46]:

$$H = H_0 + H_{cc} + H_{vv} + H_{cv},$$

where $H_0$ is the tight-binding Hamiltonian for the single-particle states, while $H_{cc}$, $H_{vv}$ and $H_{cv}$ describe the electron-electron and electron-hole interactions, respectively. The explicit form of $H$ in term of the creation (annihilation) operators for electrons $a_c^\dagger$ ($a_c$) and holes $a_v^\dagger$ ($a_v$) is given by:

$$H_0 = \sum_c \varepsilon_c a_c^\dagger a_c + \sum_v \varepsilon_v a_v^\dagger a_v,$$

$$H_{cc} = \frac{1}{2} \sum_{c_1c_2c_3c_4} V_{c_1c_2}^c a_{c_1}^\dagger a_{c_2}^\dagger a_{c_3} a_{c_4},$$

$$H_{vv} = \frac{1}{2} \sum_{v_1v_2v_3v_4} V_{v_1v_2}^v a_{v_1}^\dagger a_{v_2}^\dagger a_{v_3} a_{v_4},$$

$$H_{cv} = - \sum_{c_1v_1c_2v_2} V_{c_1v_1}^v a_{c_1}^\dagger a_{v_1}^\dagger a_{v_2} a_{c_2}.$$  

where $\varepsilon_c$ and $\varepsilon_v$ are the conduction and valence band energies, respectively. The matrix elements in $V$ correspond to the Coulomb interactions. The trion quantum states $T$ are obtained as the eigenstates of the Hamiltonian, in which the basis is restricted to the three-particle states. In other words, the trion state is constructed as a linear combination:

$$|T\rangle = \sum_{c_1c_2v} A_{c_1c_2v}^T |c_1c_2v\rangle, \quad |c_1c_2v\rangle = a_{c_1}^\dagger a_{c_2}^\dagger a_v^\dagger |0\rangle.$$  

Then a solution for the trions is reduced to an eigenvalue problem:

$$\sum_{c_1c_2v} \mathcal{H}_{c_1c_2v}^{c_1'c_2'} A_{c_1c_2v}^T = E_T A_{c_1c_2v}^T,$$

where the Hamiltonian $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{cc} + \mathcal{H}_{cv} + \mathcal{H}_{cv}^-$ is given by:

$$\mathcal{H}_0 = (\varepsilon_{c_1} + \varepsilon_{c_2} - \varepsilon_v)\delta_{c_1c_1'}\delta_{c_2c_2'}\delta_{vv'},$$

$$\mathcal{H}_{cc} = (W_{c_1c_2}^{c_1'c_2'} - W_{c_1c_2}^{c_1c_2'})\delta_{vv'},$$

$$\mathcal{H}_{cv}^- = -(W_{v'c_1}^{v'c_1'} - V_{v'c_2}^{v'c_2'})\delta_{c_2c_2'} - (W_{v'c_2}^{v'c_2'} - V_{v'c_2}^{v'c_2'})\delta_{c_1c_1'},$$

$$\mathcal{H}_{cv}^+ = (W_{v'c_1}^{v'c_1'} - V_{v'c_1}^{v'c_1'})\delta_{c_2c_2'} + (W_{v'c_2}^{v'c_2'} - V_{v'c_2}^{v'c_2'})\delta_{c_1c_1'}..$$
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where $W$ and $V$ are the screened and bare Coulomb potentials, respectively. This is a direct extension of the Tamm-Dancoff Hamiltonian that is used to calculate two-particle excitons. The momentum of a trion state $\mathbf{K} = \mathbf{k}_{c_1} + \mathbf{k}_{c_2} - \mathbf{k}_v$ is a conserved quantity.

To reduce the otherwise very large computational efforts, we use the following approach. First, we utilize the fact that the Hamiltonian matrix is sparse by employing the corresponding algorithms to store and manipulate it \[46\]. Second, we use the Arnoldi iterative algorithm \[64\] to find the lowest energy states. Third, we restrict the single-particle basis to the vicinity of the $K^\pm$ points by the following constraint:

$$|\mathbf{k}_{c_1} \pm \mathbf{K}|, |\mathbf{k}_{c_2} \pm \mathbf{K}|, |\mathbf{k}_v \pm \mathbf{K}| < q_{cut}$$

where $q_{cut} = 0.4$ ˚A$^{-1}$ ensures the convergence of our results. For the screened Coulomb potential we assume the Keldysh expression

$$W(q) = \frac{2\pi e^2}{\varepsilon q(1 + r_0 q)},$$

where $r_0 = 33.875$ ˚A/ε is the screening length \[34\] and ε is the effective dielectric constant of the monolayer on a substrate. For the layered system SiO$_2$ - MoS$_2$ - vacuum, we take $\varepsilon = 2.45$ \[65\] - \[66\] - \[34\]. The bare Coulomb interaction $V$ is obtained by setting $r_0 = 0$.

Absorption spectrum

The linear optical absorption $L(E)$ is calculated as a sum of the Fermi’s Golden rule transition rates:

$$L(E) \propto \sum_{c,T} |\langle T|\hat{P}|c \rangle|^2 \delta(E - \varepsilon_T + \varepsilon_c),$$

where we omit the exact pre-factor. The summation here runs over single-particle electrons $c$ and trion $T$ states of equal momenta. The transition dipole matrix elements are calculated as:

$$\langle T|\hat{P}|c \rangle = \sum_{c_1c_2v} A_{c_1c_2v}^T (p_{c_1v}\delta_{c_2c} - p_{c_2v}\delta_{c_1c}) .$$

there are $p_{c,v}$ - transition dipole matrix element between the conduction $c$ and valence $v$ states. The delta functions in Eq. () are replaced by the Gaussian functions with the width of 1 meV to model the finite lifetime of trions.

Accounting for the doping

Analysis of trion states in doped systems with excess electrons is a very non-trivial problem which should ideally involve many-body calculations. However, there is a simple way to bypass this difficulty by using a numerical scheme which is no more complex than a standard three-body problem. The main idea is to solve the problem on a discrete grid in the momentum space. The discretization is done in all numerical calculations, however, additional effects introduced by it are commonly regarded as an
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Figure 4. Schematic discretization of the Brillouin zone with the basis vectors $\vec{b}_{1,2}$ and the $6 \times 6$ mesh. A blue filled polygon shows an elementary area of a k-point: $\Delta k^2 \sqrt{3}/2$. Points $\Gamma$, $K$, $K'$ and $M$ are shown for reference.

artifact that must be eliminated by choosing a sufficiently small discretization interval $\Delta k$.

At the same time, the discretization is related to the doping density and can be used to investigate how the latter affects the trions properties. This approach can be intuitively understood by recalling that the discretization in the $k$-space is equivalent to considering a system in a finite box of size $L$. The discretization can thus be loosely interpreted as if each $L$-sized box in the periodic system has a trion and, hence, a single excess electron. For the $N \times N$ k-point mesh of the Brillouin zone, shown in Fig. 4 this yields an estimate for the doping density $n = g_s g_v / (A N^2)$, where $g_s$ and $g_v$ are spin and valley degeneracies, respectively, $A = \sqrt{3}a^2/2$ is the unit cell area, and $a = 3.14 \ \text{Å}$ is the lattice constant.

One can also see the discretization from a different perspective, which clarifies its physical origin. The excess electrons are Fermi particles, which, following the Pauli’s exclusion principle, occupy all the single-particle states below the Fermi level $E_F$ (if we assume that the system temperature $k_B T << E_F$). The interaction-induced scattering to the occupied states is thus blocked and such states must be excluded from the consideration. Therefore, the $k$-discretization effectively models the Pauli-blocking by restricting the available phase-space to states with energy $E \geq E_F = \hbar^2 \Delta k^2 / 2 m^*_c$, where $\Delta k = 4\pi / (\sqrt{3}aN)$ gives the correct area of the Brillouin zone $(N\Delta k)^2 \sqrt{3}/2 = 4\pi^2 / A$. An effective mass of the conduction band in MoS$_2$ in our calculations $m_c = 0.524 \ m_e$ is consistent with the earlier works [3, 34]. For example, for the $36 \times 36$ $k$-mesh, we get the carrier density $n = 3.6 \times 10^{12} \ \text{cm}^{-2}$ and the Fermi energy $E_F = 31 \ \text{meV}$. Note, that the usual relationship $E_F = \hbar^2 \pi n / 2 m_e$ between the Fermi energy and the carrier density does not hold in our case, because an effective Fermi area on a discretized mesh is $\Delta k^2 \sqrt{3}/2$ and not $\pi \Delta k^2$. 

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