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Finite-momentum exciton landscape in mono- and bilayer transition metal dichalcogenides

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Monolayers and bilayers of transition metal dichalcogenides (TMDCs) are currently being intensively scrutinized not least due to their rich opto-electronic properties which are governed by strongly bound excitons. Until now the main focus has been on excitons with zero momentum. In this study we employ *ab initio* many-body perturbation theory within the *GW*/*BSE* approximation to describe the entire Q -resolved exciton band structure for mono- and bilayers of the MX_2 ($M = \text{Mo}, \text{W}$ and $X = \text{Se}, \text{S}$) TMDCs. We find that the strong excitonic effects, i.e. strong electron-hole interactions, are present throughout the entire Q -space. While the exciton binding energies of the lowest excitons do not vary significantly with Q , we find a strong variation in their coupling strength. In particular, the latter are strongly peaked for excitons at $Q = 0$ and $Q = \Lambda$. For MoX_2 monolayers the $\text{K} \rightarrow \text{K}'$ excitons constitutes the exciton ground state, while in WX_2 monolayers direct transitions at K are lowest in energy. Our calculations further show that the exciton landscape is highly sensitive to strain and interlayer hybridization. For all four bilayers the exciton ground state is shifted to $\Gamma \rightarrow \Lambda$ or $\text{K} \rightarrow \Lambda$ transitions closely following the trends of the single-particle band structures.

I. INTRODUCTION

Over the past few years atomically thin two-dimensional (2D) materials, in particular transition metal dichalcogenides (TMDCs) have attracted tremendous interest within several research areas including batteries, (electro-)catalysis, electronics, and photonics [1, 2]. Special attention has been given to the opto-electronic properties which can change drastically from the monolayer to the multilayer/bulk material (e.g. the transition from a direct to indirect gap semiconductor in TMDCs) [3, 4]. However, until now the main focus has been on the selective valley- and spin-excitations [5–9] close to the direct gap at K , i.e. on excitons coupling to photons with vanishingly small momentum Q .

While already this small subspace of possible excitations around $Q = 0$ has led to many interesting phenomena, a complete picture including excitations with nonzero momenta is only beginning to emerge. Especially for time-dependent phenomena (e.g. photoluminescence) the relative energetic alignment of zero and nonzero momentum excitons is important. Moreover, the exciton energy and coupling strength to electric field at finite Q is important for modeling and understanding how excitons in TMDCs couple to localized electric fields, which is relevant for e.g. electron energy loss spectroscopy and localized plasmon-exciton coupling phenomena [10]. Only recently first principles studies on excitons with nonzero momenta have been presented [11, 12][13]. A key finding of these studies was the non-analytic dispersions of the excitons in MoS_2 and hBN close to the K point, i.e. for small momentum transfer Q .

Furthermore, based on model calculations Feierabend

et al. have proposed the usage of excitons with a non vanishing momentum for sensing and have underlined the role of such excitons for the line width and shape of the bright excitons [14–16]. However, the employed models rely on many parameters. In the present study we use *ab-initio* methods to describe the momentum resolved optical properties of the four most popular TMDCs, namely MoS_2 , WS_2 , MoSe_2 , and WSe_2 . After a short introduction to the methodology in Sec. II we focus on the investigation of monolayer TMDCs in Sec. III as well as its bilayer form in Sec. IV.

II. METHODS

Our first principles investigations are carried out within the framework of density-functional theory (DFT) and many-body perturbation theory. In the DFT we employ norm-conserving pseudopotentials in the Kleinman-Bylander form [17, 18] and a basis of localized atom-centered Gaussian orbitals of s , p , d and s^* symmetry [19]. For a detailed discussion of the many-body approach we refer to Ref. [20] and restrict ourselves here to the less conventional description of excitons with nonzero momenta. Thus we assume that we have already solved the quasi-particle Hamiltonian

$$\hat{H}^{\text{QP}} \psi_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} \psi_{n\mathbf{k}} \quad (1)$$

in the *GW* or *GdW* approximation [21, 22] and obtained the quasi-particle energies $\epsilon_{n\mathbf{k}}$ and the wave functions $\psi_{n\mathbf{k}}$ for all bands n and points $\mathbf{k}$ of interest. In the next step we set up the Bethe-Salpeter equation [23–25] in the

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FIG. 1. (a) 2D hexagonal Brillouin zone including special points. The red arrows denote the momentum transfer Q . Three different transitions ($\Gamma \rightarrow \Lambda'$, $K' \rightarrow M$, and $K' \rightarrow \Lambda'$) are shown. We note that Q and $-Q$ transitions are equivalent due to time inversion symmetry. (b) Representation of the momentum transfer Q in the band structure (here: MoS₂ in the *GdW* approximation).

Tamm-Dancoff approximation

$$(\epsilon_{c\mathbf{k}+\mathbf{Q}} - \epsilon_{v\mathbf{k}})A_{v\mathbf{c}\mathbf{k}}^{(S,\mathbf{Q})} + \sum_{v',c',\mathbf{k}'} K_{v\mathbf{c}\mathbf{k},v'\mathbf{c}'\mathbf{k}'}(\mathbf{Q})A_{v'\mathbf{c}'\mathbf{k}'}^{(S,\mathbf{Q})} = \Omega^{(S,\mathbf{Q})}A_{v\mathbf{c}\mathbf{k}}^{(S,\mathbf{Q})}. \quad (2)$$

Here, $\Omega^{(S,\mathbf{Q})}$ are the exciton energies and $A_{v\mathbf{c}\mathbf{k}}^{(S,\mathbf{Q})}$ the amplitudes. The dependence on Q enters via the single-particle energies and the electron-hole interaction kernel $K_{v\mathbf{c}\mathbf{k},v'\mathbf{c}'\mathbf{k}'}(\mathbf{Q})$. This kernel includes the screened direct as well as the exchange interaction. The real-space exciton wave functions can be calculated by

$$\Phi^{(S,\mathbf{Q})}(x_h, x_e) = \sum_{v,c,\mathbf{k}} A_{v,c,\mathbf{k}}^{(S,\mathbf{Q})} \phi_{v,\mathbf{k}}^*(x_h) \phi_{c,\mathbf{k}+\mathbf{Q}}(x_e) \quad (3)$$

and their amplitude in the excitation spectra is given by the generalized dipole operator

$$\langle 0 | e^{-i\mathbf{Q}\mathbf{r}} \hat{\mathbf{p}} | S, \mathbf{Q} \rangle = \sum_{v\mathbf{c}\mathbf{k}} A_{v\mathbf{c}\mathbf{k}}^{(S,\mathbf{Q})} \times \sum_{\sigma} \int \phi_{v,\mathbf{k}}^*(\mathbf{r}, \sigma) e^{-i\mathbf{Q}\mathbf{r}} \hat{\mathbf{p}} \phi_{c,\mathbf{k}+\mathbf{Q}}(\mathbf{r}, \sigma) d\mathbf{r}. \quad (4)$$

Note that the amplitude for nonzero momentum is not directly related to the optical absorbance.

The *GW*+*BSE* method has previously been shown to yield excellent agreement with experiments [26–29]. While the absolute accuracy has been found to be about 0.1 eV the relative accuracy of different excitons is typically 10 meV or less [20, 22].

To investigate the entire exciton landscape all possible momenta $\mathbf{Q}$ in the irreducible part of first Brillouin zone need to be taken into account. However, as we are interested in the low energy excitations only, the investigation of momentum transfer between regions close to the band extrema is sufficient. In this study we consider $\mathbf{Q} \equiv (0, 0, Q)$ with $Q = 0 \dots \overline{\Gamma K'}$ as shown in Fig. 1(a).

This choice is sufficient to cover all momenta relevant for the low-energy excitations. As $\mathbf{Q}$ is a vector connecting the valence and conduction band, the highlighted momentum of $\sim \frac{1}{2}\overline{\Gamma K'}$ can lead to transitions for instance from $\Gamma \rightarrow \Lambda'$, $K' \rightarrow M$, or $K \rightarrow \Lambda$. The latter one is shown inverted to $-Q$ in Fig. 1(b) which depicts the band structure of a monolayer of MoS₂ along $\Gamma \rightarrow K' \rightarrow K$.

III. TMDC MONOLAYERS

After having recapitulated the employed methodology we discuss the results for the four most common TMDC monolayers. In Fig. 2 the calculated exciton spectra for the MoS₂ monolayer are shown for several different momenta Q . At the bottom the well known case of $Q \approx 0$ is depicted corresponding to the optical absorption spectrum. It contains the prominent spin-orbit split so called A and B excitons. All the energetically low lying excitations correspond to transitions at K and K', i.e. $K \rightarrow K$ and $K' \rightarrow K'$. With increasing momentum Q the excitons raise in energy and their oscillator strength rapidly decreases. We note that this strong decrease is caused by the varying orbital character of the valence and conduction bands which enter quadratically. Close to the middle of the plot the oscillator strength start to rise again and an excitation just above the A exciton becomes vis-

FIG. 2. Momentum dependent exciton spectra for the monolayer MoS₂. The bottom spectrum shows the results for $Q \approx 0$ (i.e. $K \rightarrow K$ and $K' \rightarrow K'$). With increasing momentum Q the offset is increased. The red line marks the energy of the optical bright A exciton.

ible. In this exciton we find the hole in the valence band maximum at K and the electron at the minimum in the conduction band at the Λ point. Close to the top of the plot an excitation with small oscillator strength shows up with a similar energy as the A exciton. This is an exciton with a hole in the valence band maximum at K' and the electron in the conduction band minimum at K.

Due to the different spin polarization of the split valence and conduction bands, the transitions at $\pm K$ ($Q = 0$) can be selectively excited with circular polarized light [9]. In the direction $K \rightarrow \Gamma$ the spin polarization of the bands remains equally strong, e.g. at Λ . However, the excitation/decay of the $Q \neq 0$ excitons relies on an additional momentum transfer (e.g. by phonons). The details of this transfer process can strongly influence the valley selectivity of the calculated excitations.

To be able to track all excitations with vanishing and nonzero expectation value of the dipole operator, we turn to the representation of an “exciton band structure” in Fig. 3(a).

For each momentum, the exciton peaks are represented by a dot with the color of the dots denoting the strength of the dipole operator, i.e. red correspond to excitons with high oscillator strengths while black corresponds to excitons with vanishing oscillator strength. For MoS_2 we can clearly identify minima at $Q = 0$ and $Q = 2/3$ (we use reciprocal units, i.e. $2\pi/a_{\text{lat}}$, if not explicitly stated differently). We find that the transition $K \rightarrow K'$ is about 30 meV lower than the optically bright A exciton, and thus also 10 meV below the lowest dark exciton at $Q = 0$. We note that the ordering agrees well with the previous results of Qiu et al. which reported a difference of 5 meV for the lowest state with momentum $Q = 2/3$ [11].

In Fig. 3(b-d) similar plots are shown for the other TMDC monolayers WS_2 , MoSe_2 , and WSe_2 . The general trend is the same for all materials, namely we find a parabolic dispersion with minima at $Q = 0, 1/3$, and $2/3$. These characteristic shapes of the exciton band structure are largely inherited from the underlying single-particle band structures with minima at K, Λ , and Γ . However, a more detailed view highlights some important differences. While MoSe_2 shows a similar ordering compared to MoS_2 the $Q = 2/3$ excitation is 40 meV below that at $Q = 0$ while $Q = 1/3$ is 40 meV above. On the other hand, for WX_2 all three minima are energetically much closer. This is a consequence of the smaller difference of the single-particle energies at K and Λ , i.e. the exciton binding energies var only little with Q . A detailed comparison of the energy differences is shown in Tab. I [30]. We emphasize that the lowest energy transitions refer to zero momentum excitations with electrons and holes located at K/ K' . For $Q = 1/3$ we find a further transition from $\Gamma \rightarrow \Lambda'$ in addition to the lowest transition from $K \rightarrow \Lambda$. For the monolayer this transition is higher in energy, however, this will change for the case of the bilayers discussed in Sec. IV. We note that the band gaps and exciton binding energies obtained here with the *GdW* approximation quantitatively are larger compared to those

TABLE I. Direct gap at K, energy difference between K and Λ (conduction band) $\Delta_{K-\Lambda}^{\text{CB}}$ and K and Γ (valence band) $\Delta_{K-\Gamma}^{\text{VB}}$ for the four TMDC monolayers. The effective masses for holes m_h and electron m_e are given at K, Λ , and Γ . Furthermore, the energy of optical bright A exciton, the dark-bright splitting Δ_{DA} , and the exciton energies for $K \rightarrow \Lambda$ and $K' \rightarrow K$ are listed.

TMDC	MoS_2	WS_2	MoSe_2	WSe_2
Gap at K (eV)	2.90	2.81	2.60	2.40
$\Delta_{K-\Lambda}^{\text{CB}}$ (meV)	40	10	20	-10
$\Delta_{K-\Gamma}^{\text{VB}}$ (meV)	410	610	610	810
m_h at K (m_0)	0.53	0.34	0.55	0.34
m_h at Γ (m_0)	4.28	3.09	9.54	4.16
m_e at K (m_0)	0.48	0.36	0.52	0.38
m_e at Λ (m_0)	0.58	0.54	0.60	0.42
“A” $K \rightarrow K$ (eV)	2.16	2.17	1.80	1.78
Δ_{DA} (meV)	20	60	10	70
$K \rightarrow \Lambda$ (eV)	2.18	2.11	1.83	1.72
$K' \rightarrow K$ (eV)	2.13	2.12	1.75	1.72

in our recent *GW* study [29]. However, the qualitative features such as the relative variation in energies with Q are in good agreement. For a detailed comparison and further discussions of the accuracy of the *GdW* method we refer to Ref. [20].

We stress that for $Q \rightarrow 0$ we find an increased slope of the exciton dispersion, but we do not observe a linear dispersion for the bright exciton as found in Refs. [11, 12]. However, this deviation can be expected due to the fact that we do not truncate the Coulomb interaction (in 3D $\propto 1/Q^2$), which is required to simulate a truly isolated 2D layer ($\propto 1/Q$). On the other hand, in practice 2D materials will be placed on a substrate, i.e. the Coulomb interaction is not strictly 2D anyway.

In the next step we analyse the influence of the electron-hole interaction on the exciton band structure. We pick the example of WS_2 (from Fig. 3(b)) and compare to the bare transition energies between valence and conduction bands (green dashed lines, corresponds to zero electron-hole interaction) in Fig. 4. For better comparison the latter is shifted by 0.7 eV (i.e. by the exciton binding energy) to match the energetically lowest dark exciton at $Q = 0$. The bare transition energies show similar trends as the previously discussed exciton dispersions. The lowest transitions have a quadratic shape close to all three extrema. For all minima the influence of the electron-hole interaction is almost the same, i.e. the excitons experience a similar exciton binding energy independent of Q .

In previous *GW*+BSE calculations of TMDCs, the band gap and excitonic energies have been found to depend quite sensitively on the lattice constant [31, 32]. Here we compare the influence of different lattice constants on the momentum dependent spectra, see Fig. 5. While the previous results for WS_2 (Fig. 3(b)) have been calculated for the experimental lattice constant, we show the results for our theoretical optimized lattice constant

FIG. 3. Exciton band structure of monolayer MoS₂, WS₂, MoSe₂, and WSe₂. The grey dashed lines are a guide to the eye for the dots which denote the calculated peaks. The color corresponds to the expectation value of the dipole operator ranging from red (high amplitude) to black (zero amplitude). The horizontal red line shows the energy of the lowest bright A exciton ($Q = 0$).

(in LDA) in blue. The results are shifted down by 30 meV for an easier comparison. While most transitions at $Q = 0$ are only rigidly shifted those at $Q = 1/3$ have moved down relatively by 30 meV. This is a result of the modified band structure at Λ which is very sensitive to the lattice constant.

To get a more general picture of the dependency of the excitons on the applied strain in WS₂, we evaluate strain dependent QP band structures and exciton spectra. The resulting trends for biaxial strain between -2 and 2% are shown in Fig. 6. For this small compression/expansion we find a nearly perfect linear response of the band gap at K and between K- Λ . The corresponding deformation potentials are in good agreement with previous results [29, 33]. Interestingly, the trends are reversed in sign and the changes at K are larger by about a factor of 3. For the three excitons shown ($Q = 0, 1/3$, and $2/3$) we find that they closely follow the behaviour of the band gap at the point with the largest contributions to the exciton. That means that the exciton binding energy is nearly constant. This results in an exciton ground state at K for the experimental lattice constant as well as for expanded WS₂. On the other hand, the indirect $Q = 1/3$ exciton is lower in energy if the material is compressed.

This behaviour could be interesting for pressure/strain sensors and similar applications [34].

In Ref. [15] Malic et al. have applied a Wannier model to describe the excitations close to the minima at $Q = 0$, $1/3$ (Λ), and $2/3$ (K). For MoX₂ we find $Q = 2/3$ excitons to be lowest in energy. In contrast to this, the excitons at $Q = 0$ and $2/3$ are at similar energies in [15] due to the neglected exchange in the Wannier model. For WX₂ Malic et al. observe distinctly lower excitons at $Q = 1/3$ (compared to $Q = 0$). Within our ab-initio approach we cannot reproduce this finding, however, the exact relative alignment also depend on the chosen lattice constant (see Fig. 6).

In addition to a possible strain field, a substrate leads to an enhanced dielectric screening and a hybridization of monolayer and substrate states. While the dielectric screening strongly effects band gaps and the exciton binding energies in opposite directions, the excitons typically only undergo a small redshift [35]. This shift is similar for all momenta Q for excitons located around K and Λ [36]. On the other hand, the hybridization can differ greatly for different Q . For instance the modification of the band structure due to hybridization with substrates or other 2D materials, is much larger at Γ than at K. In

FIG. 4. Momentum dependent exciton spectrum of monolayer WS_2 . In addition to the previous result with electron-hole interaction (grey dashed line and points) the resulting transitions without electron-hole interaction are shown as green dashed line. The latter have been shifted by the exciton binding energy of the lowest (dark) $Q = 0$ exciton. In addition to the green bands which indicate possible transitions at the employed k -points, the green area indicates the continuous region of possible transitions for infinite k -points.

FIG. 5. Momentum dependent exciton spectrum of monolayer WS_2 with different lattice constants. For an easier comparison the results using the theoretical lattice constant ($a_{\text{Lat}} = 3.146 \text{ \AA}$, blue) are shifted downward by 30 meV to match the $Q = 0$ result.

the next Sec. IV we observe these effects for the bilayer materials. Due to the typically less perfect lattice match of the monolayer and a general substrate at the atomic level, the observed shifts in a bilayer should be seen as an upper limit to the hybridization in a supported or encapsulated monolayer.

FIG. 6. Strain dependent changes of the QP gaps (relative to the minimal direct gap) and exciton energies (relative to the A exciton) in monolayer WS_2 . The QP gaps at K (red dashed line) and between K- Λ (blue dashed line) show a reversed trend. The resulting excitons at $Q = 0, 1/3$, and $2/3$ reciprocal units (red, blue, and black dots, respectively) closely follow the corresponding QP gaps. The shown lines are linear fits. Note that $Q = 0$ is overlaid by $Q = 2/3$.

IV. TMDC BILAYERS

Now we turn to the discussion of the bilayers of MoS_2 , WS_2 , MoSe_2 , and WSe_2 . All four bilayer materials show clear indirect gaps (see Tab. II). Therefore, the bilayer materials are also prototypes for thicker multilayer systems up to the bulk.

Fig. 7 shows the momentum resolved exciton spectra for all four bilayers analogous to the monolayer spectra in Fig. 3. A comparison of the excitations at $Q = 0$ for bilayers and monolayers shows very similar results for the lowest energy excitations, which experience a small redshift of up to 60 meV (for WSe_2). The most obvious difference is observed around $Q \approx 1/3$ where the energies of the excitons are distinctly shifted downwards by up to 330 meV (for MoS_2). This shift is a consequence of the modified band structure which becomes indirect

TABLE II. Direct gap at K, energy difference $\Delta_{\text{K}-\Lambda}^{\text{CB}}$ and $\Delta_{\text{K}-\Gamma}^{\text{VB}}$ for the four TMDC bilayers. In addition to the energy of optical bright A exciton and the dark-bright splitting Δ_{DA} the energies for various possible transitions are listed.

TMDC	MoS_2	WS_2	MoSe_2	WSe_2
Gap at K (eV)	2.63	2.51	2.30	2.18
$\Delta_{\text{K}-\Lambda}^{\text{CB}}$ (meV)	-190	-140	-150	-170
$\Delta_{\text{K}-\Gamma}^{\text{VB}}$ (meV)	-130	90	10	280
“A” $\text{K} \rightarrow \text{K}$ (eV)	2.12	2.10	1.76	1.76
Δ_{DA} (meV)	20	50	10	60
$\text{K} \rightarrow \Lambda$ (eV)	2.00	1.94	1.70	1.58
$\Gamma \rightarrow \Lambda$ (eV)	1.84	1.99	1.70	1.82
$\text{K}' \rightarrow \text{K}$ (eV)	2.09	2.06	1.72	1.71
$\Gamma \rightarrow \text{K}$ (eV)	2.00	2.15	1.82	1.98

FIG. 7. Exciton band structure of bilayer MoS₂, WS₂, MoSe₂, and WSe₂. The horizontal red line shows the energy of the lowest bright A exciton, see caption of Fig. 3.

(150-300 meV, see Tab. II). E.g. for MoS₂ we find an A exciton energy of 2.12 eV while the energetically lowest exciton is found at 1.84 eV for $\Gamma \rightarrow \Lambda$. The energy difference of the excitons is nearly identical to the difference between the direct and indirect band gaps. Beyond this general tendency for $Q \approx 1/3$ the details are different for all materials. In MoS₂ and MoSe₂ the $\Gamma \rightarrow \Lambda$ excitation is lowest in energy. This is most pronounced for MoS₂ for which the valence band at Γ is 130 meV higher in energy compared to K. On the other hand, for WS₂ and WSe₂ the $K \rightarrow \Lambda$ transitions are energetically lowest. We note that we find a vanishing oscillator strength for $\Gamma \rightarrow \Lambda$ excitons while it is nonzero for $K \rightarrow \Lambda$. The latter oscillator strengths are similar to those found in monolayers.

A further special feature is observed at $Q = 2/3$ for MoS₂. While for all other materials the energetically lowest excitation occurs from $K' \rightarrow K$ the strong hybridization of the valence band at Γ leads to a lower $\Gamma \rightarrow K$ transition by about 90 meV.

Analogous to the investigation of strain induced effects for monolayers (Fig. 6) we investigate the bilayer WS₂ in Fig. 8. In agreement with previous studies based on DFT (see e.g. [37, 38] and the references therein), we find that bilayer WS₂ has an indirect gap. Close to 0.7% biaxial strain the $\Gamma-K$ gap drops below the $K-\Lambda$ gap. As observed for the monolayer, the exciton energies closely

FIG. 8. Strain dependent changes of the QP gaps (relative to the minimal direct gap) and exciton energies (relative to the A exciton) in bilayer WS₂. The colors are chosen similar to Fig. 8. Note that the additional excitations (blue and black dots which do not follow the lines) represent excitations from $\Gamma \rightarrow \Lambda$ and $\Gamma \rightarrow K$, respectively.

follow the trends of the related gaps, i.e. the exciton binding energies are almost independent of the applied strain.

V. CONCLUSIONS

We have studied the exciton band structure of the four prototypical transition metal dichalcogenides employing many-body perturbation theory within the *GdW*/BSE approximation. Throughout the entire *Q*-space strong electron-hole interactions are present which do not vary significantly. This results in an exciton ground state with $K \rightarrow K'$ transitions for MoX_2 monolayers and zero momentum transitions for WX_2 monolayers. For bilayers the lowest energy transitions are shifted to $Q = \Lambda$ closely following the trends of the single-particle band struc-

tures. At the same time, the coupling strength varies significantly depending on the character of the corresponding wave functions and *Q*.

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