Optical fingerprint of dark 2p-states in transition metal dichalcogenides

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Abstract

Atomically thin transition metal dichalcogenides exhibit a remarkably strong Coulomb interaction. This results in a fascinating many-particle physics including a variety of bright and dark excitonic states that determine optical and electronic properties of these materials. So far, the impact of dark states has remained literally in the dark to a large extent, since a measurement of these optically forbidden states is very challenging. Here we demonstrate a strategy to measure a direct fingerprint of dark states even in standard linear absorption spectroscopy. We present a microscopic study on bright and dark higher excitonic states in the presence of disorder for the exemplary material of tungsten disulfide (WS₂). We show that the geometric phase cancels the degeneration of 2s and 2p states and that a significant disorder-induced coupling of these bright and dark states offers a strategy to circumvent optical selection rules. As a proof, we show a clear fingerprint of dark 2p states in the absorption spectrum of WS₂. The predicted softening of optical selection rules through exciton-disorder coupling is of general nature and therefore applicable to related two-dimensional semiconductors.

Atomically thin transition metal dichalcogenides (TMDs) are in the focus of a rapidly growing scientific community due to their exceptional optical and electronic properties [1, 2]. In contrast to two dimensional graphene, the inversion symmetry is broken, resulting in a band gap at the K and K' points [3–5]. In optical absorption spectra, the extraordinarily strong Coulomb interaction gives rise to the formation of excitonic states with binding energies in the range of 500 meV [6–11]. Due to their complex electronic bandstructure including strong spin–orbit splitting of valence and conduction bands, TMDs exhibit a great variety of bright and dark excitonic states. The existence of dark states is experimentally supported by the measured low quantum yield in photoluminescence suggesting a strong coupling between bright and dark states [12]. Unfortunately, in optical experiments the dark states are not directly accessible. As a result, the investigation of their impact on optical and electronic properties of TMDs is rather challenging. Here, we demonstrate a strategy to reveal dark states even in standard linear optical spectroscopy on disordered TMD samples. Disorder is known to play an important role in TMDs [13], and is the first responsible for the broad inhomogeneous line widths in optical spectra that can exceed the homogeneous line width by one order of magnitude [14, 15]. We show that disorder-induced coupling between dark and bright states leaves a measurable fingerprint of dark states in the linear absorption spectrum providing a relatively easy experimental access to dark excitons.

We apply a microscopic many-particle approach [16, 17] to investigate the impact of disorder on dark 2p-like excitonic states. We address the question whether exciton-disorder coupling can circumvent optical selection rules and make these dark excitonic states optically active. The discussed principle is not only applicable to 2p excitonic states but may also be used to fully characterize the full spectrum of dark and bright states in the TMD material class. Dark states are not directly optically accessible. This can have several
reasons: a photon can not change the spin of a fermion and has only a negligibly small momentum, therefore it can only transfer a particle between states with the same momentum or spin. In the present work, we focus on optically forbidden transitions between 1s and 2p states that exhibit a non-zero angular momentum. The gained insights can also be applied to dark intervalley excitons, where the hole and the electron are located at different points in the Brillouin zone [18]. TMDs are excellent candidates to investigate this generally interesting question, since they (i) show a significant inhomogeneous broadening of the absorption spectrum indicating a disorder landscape in the semiconductor [14, 15], (ii) exhibit a strong Coulomb interaction resulting in experimentally accessible Rydberg-like series of higher excitonic states [10], and (iii) are characterized by a non-vanishing geometric phase, which cancels the degeneration of 2s and 2p excitonic states making both states detectable in optical spectra [19–23]. As a result, provided that the exciton-disorder coupling is efficient enough to mix bright and dark states, we expect an optical fingerprint of dark states in optical spectra, i.e. optical selection rules suppressing the excitation of these states would be circumvented. Signatures of such mixing of s- and p-like states might have been already observed in recent experiments comparing two-photon and direct absorption of TMDs [24–26]. The experimental results show that resonances from single and two-photon absorption coincide implying that the 2s and 2p states are energetically degenerate. However, this contradicts theoretical calculations predicting a lifting of this degeneracy [19–23]. Another explanation of the experimental results is the mixing of dark and bright states which would lead to a simultaneous optical response of both states.

To investigate the impact of exciton-disorder coupling on the absorption spectra [27, 28], we calculate the frequency-dependent absorbance \( \alpha(\omega) \) that is proportional to the imaginary part of the linear response function \( \chi(\omega) \) [17]. The latter is determined by the microscopic polarization \( \mathbf{p} = \langle a^\dagger \mathbf{a} \rangle \), which describes the optical transition between the states \( j \) and \( i \). Here, we have used the formalism of second quantization introducing the creation and annihilation operators \( a^\dagger \) and \( a \). The interacting states are described by the compound indices \( i, j \) containing the electronic momentum \( \mathbf{k}_i, \mathbf{k}_j \), the electronic band \( \lambda = v, c \) (denoting the conduction and the valence band) as well as the spin valley index \( \xi_c \). Note that we restrict our study to the energetically lowest A exciton and we do not consider interlayer interactions or doping effects but focus on a finite center-of-mass motion \( \mathbf{k} = \mathbf{k}_1 - \mathbf{k}_2 \).

As a first step, we derive semiconductor Bloch equations for the entire class of TMDs within the Heisenberg picture based on the many-particle Hamilton operator consisting of the interaction-free carrier contribution \( H_0 = \sum_{\alpha} \epsilon_{\alpha} a^\dagger_{\alpha} a_{\alpha} \), the light–matter interaction \( H_{\text{LM}} = \sum_{\alpha \beta} M_{\alpha \beta} a^\dagger_{\alpha} a_{\beta} \), the Coulomb interaction \( H_C = \sum_{\alpha \beta} V_{\alpha \beta} a^\dagger_{\alpha} a^\dagger_{\beta} a_{\beta} a_{\alpha} \), and the disorder interaction \( H_d = \sum_{\alpha} U_{\alpha} a^\dagger_{\alpha} a_{\alpha} \). Here, we have introduced compound indices \( \alpha, \beta, \gamma, \delta \) which represent all quantum numbers characterizing the system including the momentum \( \mathbf{k} \), the band index \( \lambda = c, v \) for conduction or valence band, the valley index \( \xi \) for \( K \) or \( K' \)-valley, and the spin index \( s \) for spin-up and spin-down states. The electronic dispersion \( \epsilon_{\alpha} \), the optical matrix element \( M_{\alpha \beta} \), the Coulomb potential \( V_{\alpha \beta} \) and the disorder potential \( U_{\alpha} \) are calculated within a tight binding approach [11]. Then, we project the solution for the microscopic polarization \( \mathbf{P}_{\xi, \mathbf{k}} \) into an excitonic basis using the transformation \( \mathbf{p} = \sum_{n, m} n^m n^m n^m n^m \mathbf{P}_{\xi, \mathbf{k}} \) with the excitonic polarization \( n^m n^m n^m n^m \) characterized by the excitonic quantum number \( n \) and the angular momentum or azimuthal quantum number \( m \). The appearing excitonic wave function \( \phi_{\xi, \mathbf{k}} \) can be determined with the Wannier equation [11, 16]. Note that for the study of the Wannier equation we only need to consider microscopic polarizations containing the relative motion \( \mathbf{k} = \alpha \mathbf{k}_j + \beta \mathbf{k}_d \) denoting direct optical transitions.

Before we further discuss the results of the Wannier equation, we first address the lifting of the degeneracy of 2s and 2p states, which is of crucial importance to be able to detect these states in optical spectra. The lifting has two origins, which are both accounted for in the present study: the momentum-dependent screening of the Keldysh Coulomb potential, and the geometrical phase that is present in two-dimensional systems, where the optically active region is located at the \( K \) points and not, as in conventional semiconductors, at the \( \Gamma \) point. While at the latter, the crystal symmetry effects cancel and one can find a perfect analogy between the excitonic and the two-dimensional hydrogen problem, at the \( K \) points the excitonic states and the eigenfunctions are influenced by the lattice symmetry appearing as a geometric phase. It enters via the overlap integrals of the matrix elements [19–21]. In our approach, the phase is inherently included in the tight-binding wave functions [11] \( \phi_{\xi, \mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{R}} C_{\xi, \mathbf{k}}^{\mathbf{R}} e^{i \mathbf{k} \cdot \mathbf{R}} \phi_{\xi, \mathbf{k}}^{\mathbf{R}}(\mathbf{r} - \mathbf{R}) \). Here, \( \phi_{\xi, \mathbf{k}}^{\mathbf{R}}(\mathbf{r} - \mathbf{R}) \) is the orbital integral of the irreducible basis of the atom type \( j \), which can be \( M \) denoting the transition metal or \( X \) denoting the chalcogen atom in TMD structures \( MX_2 \). The wave function of TMDs explicitly includes the lattice symmetry via the tight-binding coefficients [11]

\[
C_{\xi, \mathbf{k}}^{\mathbf{R}} = C_{\xi, \mathbf{k}}^M g_{\mathbf{k}}^X C_{\xi, \mathbf{k}}^X = \pm (1 + |s_{\mathbf{k}}^X|^2)^{-\frac{1}{2}}
\]

with \( g_{\mathbf{k}}^X = t^\chi e^{i \mathbf{k} \cdot \mathbf{\zeta}_c} (\Delta s_{\xi_c}^X/2 - s_{\mathbf{k}}^X) -1 \). The appearing nearest-neighbor tight-binding function \( e^{i \mathbf{k} \cdot \mathbf{\zeta}_c} \) can be Taylor-approximated for small momenta close to the \( K \) points resulting in \( e^{i \mathbf{k} \cdot \mathbf{\zeta}_c} \approx \frac{e^{i \mathbf{k} \cdot \mathbf{\zeta}_c}}{1 + s_{\mathbf{k}}^X} \) with the geometric phase \( e^{i \mathbf{k} \cdot \mathbf{\zeta}_c} \). This phase enters all coupling elements including the optical matrix
element with optical selection rules and the Coulomb matrix element that describes the formation of excitonic states. In combination, they give rise to the lifting of the degeneracy between 2s and 2p states and they determine which excitonic states are optically bright (s-states) and dark (p-states).

The optical matrix element \( M^0_{\lambda}(k) = \langle \Psi^\lambda_{\xi,q}(k, r) | P^\pm | \Psi^{\lambda',\xi}(k, r) \rangle \) is the expectation value of the impulse \( P^\pm \) projected to the direction of circularly polarized light. Inserting the tight-binding wave functions, we can obtain an analytic expression [11]

\[
M^0_{\xi,q}(k) = M_0 e^{i\phi_{\xi,q}} (1 \pm \tau_\xi) \tag{2}
\]

with the geometric phase \( e^{i\phi_{\xi,q}} \), where \( \tau_\xi = +/-1 \) denotes the \( K'/K \) point. The strength of the coupling is determined by \( M_0 = c_0 C_{\xi,k}^0 p_{\xi,k} + C_{\xi,k}^0 \) with \( c_0 = 1.04 \) meV that has been adjusted to obtain a light absorption of 10% in agreement with recent measurements [14]. The optical matrix element determines the linear response function \( \chi(\omega) \) that is given by the macroscopic polarization for circularly left (\( \sigma_- \)) or right (\( \sigma_+ \)) polarized light

\[
P_{\xi,q}(t) = \sum_{n,m,k} \theta_{n,m,\xi,k} \rho_{n,m}(t) M^0_{\xi,q}(k) + cc
\]

\[
= \sum_{n,m,k} \rho_{n,m}(t) M_0 \sum_{q_\xi} \theta_{n,m,\xi,k} e^{-i\phi_{\xi,q}} (1 \pm \tau_\xi) + cc.
\]

Besides the optical matrix element, the excitonic wave function \( \rho_{n,m} \) and its angle dependence play a crucial role for the optical response. For isotropic systems, the appearing sum over the angle \( \phi_\xi \) is only non-zero if its argument is symmetric. Since the azimuthal quantum number \( m_l \) is representing the phase of the eigenfunction \( e^{im_l\phi_{\xi,q}} \), we can rephrase equation (3) by shifting \( m_l \) by \( \tau_\xi \) resulting in \( m_l \rightarrow m_l - m_l = m_l - \tau_\xi \) and \( \theta_{n,m,\xi,k} e^{-i\phi_{\xi,q}} = \theta_{n,m,\xi,k} \). One might argue that since we find bright states for \( m_l = 0 \) resulting in \( m_l = \tau_\xi \), the geometric phase leads to a non-zero optical response only for p-like excitonic states with \( m_l = 0 \). However, to obtain a complete picture, one has to take into account also the geometric phase in the Coulomb interaction.

In agreement with kp-theory and many-body Bethe–Salpeter approach [19, 20, 23], the geometric phase enters the Coulomb matrix element \( \Gamma_{\xi,q}^{\lambda',\lambda}(k) = \Gamma_{\xi,q}^{\lambda',\lambda}(k') \) via the overlap integrals appearing in the tight-binding coefficients \( \Gamma_{\xi,q}^{\lambda',\lambda}(k) = \sum_{k} C_{\xi,k}^{\lambda'} C_{\xi,k}^{\lambda} C_{\xi,k+q}^{\lambda'} C_{\xi,k+q}^{\lambda} \). This term leads to an angular dependence of the Coulomb interaction and hence to the cancellation of the energy degeneration of excitonic states with the same excitonic index \( n \), but different azimuthal quantum number \( m_l \), see the supplementary material for more details.

To evaluate equation (3), we solve the Wannier equation to obtain the excitonic wave function \( \theta_{\xi,m} \) and the Bloch equation to obtain the excitonic polarization \( P_{\xi,q} \). The Wannier equation reads [11]

\[
\tilde{\theta}_{k,q;\xi} = \sum_{k} \Gamma_{k,k'}^{\xi,q} \theta_{\xi,m_{k'}} + E_{\xi,m_{k'}} \theta_{\xi,m_{k'}} \tag{3}
\]

with the excitonic eigenstates \( \theta_{\xi,m} \) and eigenvalues \( E_{\xi,m} \). Here, the electronic dispersion relation \( \epsilon_{k,q;\xi} = \epsilon_{k,\xi} - \epsilon_{k,\xi} \) appears, as well as the tight-binding coefficient \( \Gamma_{k,k'}^{\xi,q} \) that contains the geometric phase. To be more exact, the summation over atomic sublattice \( j \) in \( \Gamma_{k,k'}^{\xi,q} \) leads to three terms: one without any phase and two with phase expressed by \( e^{i\theta_{\xi,m_{k'}}} \) and weighted by differently strong Coulomb interactions within the the Keldysh potential [29], see the supplementary material.

Evaluating the Wannier equation for different azimuthal quantum numbers \( m_l \) we find the corresponding excitonic eigenenergies and eigenfunctions, which are illustrated in figure 1. To determine which states are optically active, we use the shifted \( m_l \).
introduced above (containing the geometric phase from the optical matrix element) and consider the three different phase terms appearing in $\Gamma_{qQ}^{\xi}$. We find that one of these terms cancels the geometric phase from the optical matrix element, since $\theta_{\xi k}^{nm} + \xi k = \theta_{\xi k}^m + \xi k = \theta_{\xi k}^{nm}$ with $m_l = m_l + \xi q$, i.e. we have shifted the azimuthal quantum number back to normal order. This results in strongly bound and bright excitonic states with $m_l = 0$, see first row of figure 1(a). To sum up, although the geometric phase lifts the degeneracy between excitonic states of different angular momentum, it does not change the optical selection rules.

In agreement with recent experimental data [10], our calculations reveal that higher excitonic states are stronger bound than expected in the 2D Rydberg series. This can be traced back to the relatively weak Keldysh screening of the Coulomb interaction in atomically thin TMDs [10, 11]. Furthermore, we find that due to the phase-dependent Keldysh interaction, the degeneracy between 2s and 2p states is lifted with 2p states now lying about 35 meV below the 2s states, which is also in line with recent studies [19, 20]. The 2p states themselves are split by approximately 15 meV depending on the sign of the phase, see figure 1(a). The latter is given by the azimuthal quantum number $m_l$ and prohibits their coupling to an external light field. This is manifested by their vanishing contribution to the macroscopic polarization in equation (3) due to the appearing integral over the angle $\phi_k$.

The energy difference of the 2p states is also reflected by a different radial component of the corresponding excitonic wave functions, see figures 1(b) and (c). Our calculations show that in analogy to the ideal hydrogen model the stronger the excitonic state is bound, the broader is its eigenfunction in the momentum space and the more localized it is in the real space. As a result, the 1s state is much broader in momentum space compared to the 2s state, while the stronger bound 2p exciton is slightly broader than the 2p exciton, see figures 1(b) and (c).

Having determined the excitonic eigenvalues and eigenfunctions, we have all ingredients to formulate TMD Bloch equations for the time- and momentum-dependent microscopic polarization within the excitonic basis. Since the disorder-exciton coupling induces polarization $p_{\xi k}^{xc}(t)$ with $k_j = k_i$, we introduce the relative momentum $q = \alpha k_i + \beta k_j$ and the center-of-mass momentum $Q = k_i - k_j$ with $\alpha = \frac{m_l}{m_l} = \frac{m_l + m_q}{m_l + m_q}$ and $\beta = \frac{m_q}{m_l + m_q}$ where $m_{\lambda_i \lambda_j}$ is the effective mass of the band $\lambda_i$, taken from [6]. Then, the transformation of the microscopic polarization into the excitonic basis is more general, yielding $p_{\xi k}^{xc}(t) = \sum_{n,m} P_{\xi k}^{nm} \theta_{\xi k}^{nm}$. The corresponding TMD Bloch equation reads:

$$ih\frac{\partial}{\partial t} P_{\xi Q}^{nm}(t) = (E_{\xi Q} + E_{\xi Q}^{nm}) P_{\xi Q}^{nm}(t) + \delta_{Q,0} \delta_{m_l,0} a_{\xi Q}^{mp} + \sum_{Q'\mu,\nu} D_{\xi \xi Q'Q}^{mq} P_{\xi Q'}^{\mu \nu}(t).$$

Here, the excitonic dispersion is given by $E_{\xi Q} = hQ^2/(2M)$ with $M = m_l + m_q$. Since the focus of our work lies on a qualitative investigating of fundamental aspect of exciton-disorder coupling, we do not include the effects of the Coulomb exchange coupling on excitonic dispersion [21, 22, 30]. The TMD Bloch equation allows us to calculate the excitonic absorption as well as to study the impact of exciton-disorder coupling on optical selection rules. It includes all excitonic states with eigenenergies $E_{\xi Q}^{nm}$, the coupling of the system with incoming light determined by the Rabi frequency $\Omega_{\xi Q}^{nl}(t) = \sum_{A}(t)M_{nl}(Q)\theta_{\xi Q}^{nm}a_\xi Q$, and exciton-disorder coupling determined by the matrix element $D_{\xi \xi Q'Q}^{mq}$.

The latter is given by the azimuthal quantum number $m_l$ and prohibits their coupling to an external light field. However, the exciton-disorder term in equation (4) couples p- and s-like excitonic states, which crucially changes the optical selection rules. Since in TMDs the 2s and 2p states are not degenerate due to the non-vanishing geometric phase, the disorder-induced coupling is expected to lead to pronounced effects even in linear absorption spectra.

The disorder contribution is averaged on the macroscopic level by calculating the microscopic polarization for a large number of random disorder realizations. The method has been implemented following the approach of Glutsch and Bechstedt [27].

The exciton-disorder matrix element entering equation (4) reads:

$$D_{\xi \xi Q'Q}^{mq} = \sum_{\lambda} U(Q')\Gamma_{\xi \lambda}^{ll}(Q)\theta_{\xi \lambda}^{nm} \theta_{\xi \lambda Q}^{mq} + \theta_{\xi \lambda Q}^{mq}$$

with $q$ describing the relative and $Q$, $Q'$ the center-of-mass motion. The disorder potential $U(Q') = R(Q')Ae^{-iQ'Q''/\beta}$ is determined by the amplitude $A$ giving the maximal strength of the disorder, the correlation length $\lambda = 1$ nm according to the excitonic Bohr radius [31], and $R(Q')$ being a random number on the complex unitary circle fulfilling the condition $R(Q'') = R(-Q'')^{\alpha}$ [27]. Furthermore, the tight-binding coefficients directly enter in $\Gamma_{\xi \lambda}^{ll}(Q) = \sum_{\alpha,M} C_{\xi \lambda}^{\alpha M}(Q + \alpha \xi Q)$ with $\alpha_{\xi} = \beta_{\xi} = \alpha$. For perfect crystals or for isolated atoms, one finds $\Gamma_{\xi \lambda}^{ll}(Q) = \delta_{\xi \lambda} \theta_{\xi \xi}^{nm}$ due to the orthogonality of the wave functions. The term vanishes.
for wave functions with \( m_l = \mu_l \), since the phase difference results in \( \sum_{l} e^{i\mu_q - i\mu_q l} = 0 \). However, under the influence of disorder the microscopic quantities gain a center-of-mass momentum, which enters the wave function and breaks the symmetry of the angular integral. In systems with center-of-mass motion the azimuthal quantum number is not conserved. For wave functions with a conserved quantity the angular integral. In systems with center-of-mass motion the azimuthal quantum number is not symmetric resulting in a non-conservation of angular momentum. To illustrate this, figures 2(b)–(d) show the absolute value of the microscopic polarizations. The frequency of the relatively fast oscillation of 2p \( \pm \) polarizations in figure 2(c) corresponds to \( \omega = 2\pi (E_{1s} - E_{2p})/\hbar \) reflecting the role of the optically driven 1s polarization. The slower frequency scaling with \( \omega = 2\pi (E_{2p_+} - E_{2s})/\hbar \) reflects the coupling of 2p with the 2s states. Calculating \( R_{Q=0}^{1s/2s} \) without exciton-disorder coupling (black lines in figure 2(b)) shows a slower dephasing of the 2s polarization. Note that the disorder-induced coupling of the bright 1s and 2s states with the dark 2p states give both a non-negligible contribution to the spectrum. While the 1s state couples more efficiently to the light pulse exhibiting a larger oscillator strength, the spectral overlap of 2s and 2p states is higher. In total the coupling of 1s and 2s to the dark 2p states both lead to measurable signatures of the 2p state in the absorption spectrum.

The crucial quantity for the occurrence of these effects is the disorder strength. Depending on the quality of the material, the degree of disorder (reflected by the inhomogeneous broadening) can strongly vary. Most samples investigated so far show inhomogeneous line widths at low temperatures of some tens of meV [14]. In line with these investigations, we assume a disorder strength of 6.5 meV. Here, the disorder couples states with center-of-mass momentum to the optically excited state resulting in multiple resonances and an inhomogeneous broadening of the

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**Figure 2.** Microscopic polarizations of higher excitonic states. (a) Schematic illustration of the optically excited 1s and 2s polarization \( R_{Q=0}^{1s} \) and \( R_{Q=0}^{2s} \) and the generation of disorder-induced 2p polarization \( R_{Q=0}^{2p} \). (b) Temporal evolution of the absolute value of \( R_{Q=0}^{1s} \) and \( R_{Q=0}^{2p} \), where the black lines show the case without the coupling to 2p states. (c) Direct comparison between the polarization of 2s, 2p+, and 2p− states. Note that the 2p\( \pm \) states have been multiplied by a factor of 10. (d) Temporal evolution of \( R_{Q=0}^{2p} \) as a function of the disorder strength.
1s excitonic resonance of 30 meV. To investigate the impact of disorder, figure 2(d) shows the temporal evolution of $p^\pm$ as a function of disorder. The stronger the disorder, the more pronounced is the induced microscopic polarization of the initially dark 2p state and the weaker is the decay of the appearing oscillations.

Next, we study the influence of the disorder-induced polarizations of dark 2p states on the experimentally accessible optical absorption of the exemplary WS$_2$ material. Figure 3 illustrates the spectrum in the vicinity of the 1s and 2s excitonic resonance in the presence of disorder. Although p-like polarizations with $m = 0$ do not directly contribute to the absorption spectrum (see equation (3)) they do leave visible fingerprints via exciton-disorder coupling. We observe a clearly enhanced absorption at the position of $2p^\pm$ excitonic states, see the inset of figure 3. How pronounced this effect is, depends on the disorder strength, as illustrated in the contour plot in figure 3(b). The stronger the disorder, the larger is $p^\pm$ (see figure 2(d)), and the more pronounced is the enhancement of the absorption appearing at the position of $2p^\pm$ excitons and the larger is the red-shift of the 1s excitonic peak.

The appearance of additional oscillator strength can be understood in a straightforward way by reducing the complexity of the equations to the most important aspects: considering a situation of two states $E_1$, $E_2$ coupled via the coupling element $C_{12}$, where only one state is driven by an external source (representing the 1s or the 2s state), we find an analytic solution for resonances appearing in the absorption spectrum

$$\hbar \omega_{\pm} = (E_1 + E_2)/2 \pm \sqrt{(E_1 - E_2)^2/4 + |G_{12}|^2}.$$ 

Although only one state is directly driven, we find a resonance at both states with $\hbar \omega_{\pm} = E_2$ and $\hbar \omega_{\pm} = E_1$ for $(E_1 - E_2)^2 \gg |G_{12}|^2$. This is exactly what happens, when exciton-disorder interaction couples the optically active 1s or 2s state to the initially dark 2p states. Here, we have assumed the same homogeneous broadening for the higher excitonic states. However, it can be expected that the higher states exhibit a larger broadening due to availability of additional relaxation channels. As a consequence, a larger spectral overlap of the 2s and 2p states is expected and would lead to a stronger mixing of the states. Note also that the additional resonances found in the spectrum can be better separated at low temperatures, where the homogeneous broadening of the main 2s peak via phonons is smaller allowing a better resolution of the weak disorder-induced peaks.

In conclusion, we have presented a microscopic study on the impact of exciton-disorder coupling on the temporal dynamics and the absorption spectra of TMDs. We find that the non-vanishing geometric phase lifts the degeneracy between 2s and 2p states and that the significant exciton-disorder interaction softens optical selection rules in these materials. It induces a microscopic polarization of optically dark $2p^\pm$ states leaving an optical fingerprint in linear absorption spectra. The gained insights on the impact of exciton-disorder coupling on optical selection rules are of general nature and therefore applicable to related materials with a strong Coulomb interaction and significant degree of disorder.

Figure 3. Absorption spectrum of WS$_2$. (a) The blue-shaded spectrum shows the absorption including disorder-induced bright-dark-state coupling. For comparison, the black line describes the spectrum without the coupling demonstrating a clearly enhanced absorption in the vicinity of the 2p states (see the inset) and a red-shift of 1s and 2s resonances. Contour plot (b) with and (c) without exciton-disorder coupling shows the absorption as a function of energy and disorder strength illustrating the increasing absorption in the vicinity of the 2p states (vertical lines) for higher disorder. The horizontal blue line marks the case plotted in part (a).
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