



# Nonanalyticity, Valley Quantum Phases, and Lightlike Exciton Dispersion in Monolayer Transition Metal Dichalcogenides: Theory and First-Principles Calculations

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Exciton dispersion as a function of center-of-mass momentum  $\mathbf{Q}$  is essential to the understanding of exciton dynamics. We use the *ab initio* *GW*-Bethe-Salpeter equation method to calculate the dispersion of excitons in monolayer  $\text{MoS}_2$  and find a nonanalytic lightlike dispersion. This behavior arises from an unusual  $|Q|$ -term in both the intra- and intervalley exchange of the electron-hole interaction, which concurrently gives rise to a valley quantum phase of winding number two. A simple effective Hamiltonian to  $Q^2$  order with analytic solutions is derived to describe quantitatively these behaviors.

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An exciton is a neutral excitation of an interacting electron system, consisting of a bound excited electron and hole pair with energy depending on its center-of-mass momentum,  $\mathbf{Q}$ . In crystals, the exciton dispersion relation (energy vs  $\mathbf{Q}$ ) forms an exciton band structure. In optical absorption, the momentum of a photon is converted to that of an exciton, resulting in a small  $\mathbf{Q}$  exciton for visible light. Recent model Hamiltonian calculations predict that the dispersion of the lowest energy optically active exciton bands in monolayer  $\text{MoS}_2$  form a Dirac cone (as in graphene) due to the exchange interaction coupling electron-hole states in different valleys (the intervalley exchange) [1]. Another study based on a tight-binding formulation of the Bethe-Salpeter equation (BSE) approach hinted at also linear dispersion for the lowest energy excitons near  $\mathbf{Q} = 0$ , although the dispersion relation (on a  $45 \times 45$  finite- $\mathbf{Q}$  grid) was not resolved at the length scale of the momentum of light [2]. The effects of the interplay of inter- and intravalley exchange and local fields are not explicitly investigated in these model calculations, which also miss terms in both  $Q$  and  $Q^2$  orders.

In this work, we calculate the exciton dispersion of  $\text{MoS}_2$ , a prototypical transition metal dichalcogenide (TMD), from first principles, using the *ab initio* *GW*-BSE method [3,4], and find a highly unusual low-energy dispersion consisting of a nonanalytic *v*-shaped upper band that is degenerate with a parabolic lower band at  $\mathbf{Q} = 0$ , consistent qualitatively with extrapolation of previous tight-binding results [2]. We show that the physical origin of this highly nonanalytic behavior (the  $|Q|$  dependence) comes from  $|Q|$ -dependent terms in both the intravalley and intervalley exchange interaction, which arise from the unique electronic structure and the quasi-2D nature of the Coulomb interaction in atomically thin TMDs. Local-field effects introduce additional interaction terms and are responsible for the splitting of optically bright and dark

excitons. Moreover, the theory gives a valley quantum phase of winding number two (or chirality two), which we show should manifest in optical experiments as a phase difference between the longitudinal and transverse response. A similar winding number is found in Ref. [1], although in this model Hamiltonian study, intravalley exchange is neglected resulting in a Dirac cone dispersion.

Transition metal dichalcogenides are layered, weakly coupled materials. In the 2H monolayer form, TMDs are direct band gap semiconductors with the gap at the  $K$  and  $K'$  points of the 2D hexagonal Brillouin zone [5,6]. Because of a lack of inversion symmetry and the presence of threefold rotational symmetry, a valley selective response emerges: the  $K$  and  $K'$  valley couples, respectively, only to left or right circularly polarized light [7–10]. Moreover, as a result of confinement and reduced screening, excitons have very large binding energies [11–26].

The quasiparticle (QP) band structure of monolayer  $\text{MoS}_2$  calculated within the *GW* approximation [3,15] (see Supplemental Material [27]) is shown in Fig. 1. The direct gap of 2.67 eV is at the  $K$  and  $K'$  points. Spin-orbit coupling splits the valence band edge by 147 meV and the conduction band edge by 3 meV. Over an extended range in the  $K$  and  $K'$  valleys,  $s_z$ , the spin of the electron along the direction perpendicular to the layer is a good quantum number [8]. Thus, the concept of singlet and triplet exciton states is no longer well defined. Instead, the electron-hole Hamiltonian or BSE matrix can be decoupled into transitions between bands of like spin [Figs. 1(b)–(1d)] that are optically allowed and transitions between bands of unlike spin that are optically forbidden. We calculate the exciton dispersion of both the like-spin transition states and the unlike-spin transition states within the BSE formalism following Ref. [4]. The resulting exciton dispersion near  $\mathbf{Q} = 0$  and  $\mathbf{Q} = K$  is shown in Fig. 2. Figure 2 only presents exciton states involving

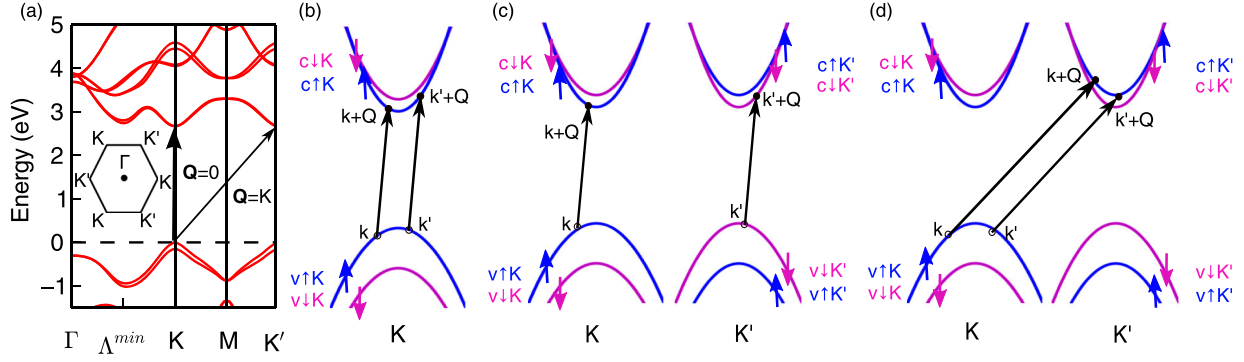


FIG. 1 (color online). (a) QP band structure of monolayer MoS<sub>2</sub>. Lowest energy transitions corresponding to electron-hole excitations with momentum transfers of  $\mathbf{Q} = 0$  and  $\mathbf{Q} = \mathbf{K}$  are shown with the labeled arrows. (b)–(c) Schematics of interactions between two electron-hole pairs with momentum near  $\mathbf{Q} = 0$ , corresponding to BSE matrix elements  $\langle v\mathbf{c}\mathbf{k}\mathbf{Q}|H^{\text{BSE}}|v'\mathbf{c}'\mathbf{k}'\mathbf{Q}\rangle$  for (b) two like-spin transitions within one valley and (c) two like-spin transitions from different valleys. (d) Schematic of two electron-hole pairs with momentum near  $\mathbf{Q} = \mathbf{K}$  giving rise to BSE matrix elements for like-spin transitions.

predominantly transitions from the topmost valence band (the  $v\uparrow K$  and  $v\downarrow K'$  bands in Fig. 1), which is the so-called *A* series in the literature. Similar results are obtained for the spin-orbit split *B* series (see Supplemental Material [27]).

In Fig. 2, near  $\mathbf{Q} = 0$ , the lowest energy exciton complex shown is the “1s”-like states of the *A* series excitons, which has a binding energy of 0.63 eV for the like-spin transition states and 0.65 eV for the unlike-spin transition states. At  $\mathbf{Q} = 0$ , the twofold degeneracy of the exciton states due to *K* and *K'* valley degeneracy is protected by the time-reversal symmetry. Away from  $\mathbf{Q} = 0$ , for optically active like-spin transition states, the degenerate bands split as  $|\mathbf{Q}|$  increases. Consistent with previous model calculations [1,2,32,33], this splitting of the like-spin transition states is due to intervalley exchange. The exciton bands for unlike-spin states, which have zero exchange interaction, remain doubly degenerate (the blue lines in Fig. 2). However, contrary to previous model predictions [1], our *ab initio* results do not find a Dirac cone near  $\mathbf{Q} = 0$  in the dispersion of the like-spin transition 1s bands. In fact, we find a “*v*-shaped” nonanalytic upper band with a velocity of  $3 \times 10^5$  m/s or 0.001 *c* and a parabolic lower band, with both bands increasing monotonically with  $|\mathbf{Q}|$  down to the smallest sampled  $|\mathbf{Q}|$  of  $4 \times 10^{-3} \text{ \AA}^{-1}$ , which corresponds to 0.3% of the distance from  $\Gamma$  to *K* in the Brillouin zone.

We also calculate the dispersion of the intervalley excitons [Fig. 2(b)]—i.e., an exciton with the electron and hole in different valleys (with  $\mathbf{Q} = \mathbf{K}$ )—and find that the unlike-spin transition state is slightly lower in energy than the similar exciton at  $\mathbf{Q} = 0$  as a consequence of the spin-orbit splitting of the conduction bands and the screened Coulomb interaction (see Supplemental Material [27]).

We now provide the physical origin of the nonanalytic behavior of the dispersion seen in Fig. 2(a) [closeup in Fig. 3(a)]. The exciton dispersion is obtained from first principles by solving the BSE [4,34] for electron-hole pair excitations with finite center-of-mass momentum  $\mathbf{Q}$

$$(E_{c\mathbf{k}+\mathbf{Q}} - E_{v\mathbf{k}})A_{v\mathbf{c}\mathbf{k}\mathbf{Q}}^S + \sum_{v'\mathbf{c}'\mathbf{k}'} \langle v\mathbf{c}\mathbf{k}\mathbf{Q}|K^{\text{eh}}|v'\mathbf{c}'\mathbf{k}'\mathbf{Q}\rangle A_{v'\mathbf{c}'\mathbf{k}'\mathbf{Q}}^S = \Omega_{\mathbf{Q}}^S A_{v\mathbf{c}\mathbf{k}\mathbf{Q}}^S. \quad (1)$$

Here, *S* indexes the exciton states,  $A_{v\mathbf{c}\mathbf{k}\mathbf{Q}}^S$  is the amplitude of the free electron-hole pair consisting of an electron in  $|c\mathbf{k} + \mathbf{Q}\rangle$  and one missing from  $|v\mathbf{k}\rangle$ ,  $\Omega_{\mathbf{Q}}^S$  is the exciton excitation energy,  $E_{c\mathbf{k}+\mathbf{Q}}$  and  $E_{v\mathbf{k}}$  are the quasiparticle energies, and  $K^{\text{eh}}$  is the electron-hole interaction kernel. The kernel consists of a direct term and an exchange term [4]:  $\langle v\mathbf{c}\mathbf{k}\mathbf{Q}|K^{\text{eh}}|v'\mathbf{c}'\mathbf{k}'\mathbf{Q}\rangle = \langle v\mathbf{c}\mathbf{k}\mathbf{Q}|K^d + K^x|v'\mathbf{c}'\mathbf{k}'\mathbf{Q}\rangle$ . The exchange term is

$$\langle v\mathbf{c}\mathbf{k}\mathbf{Q}|K^x|v'\mathbf{c}'\mathbf{k}'\mathbf{Q}\rangle = \sum_{\mathbf{G}} M_{cv}(\mathbf{k}, \mathbf{Q}, \mathbf{G}) v(\mathbf{Q} + \mathbf{G}) M_{c'v'}^*(\mathbf{k}', \mathbf{Q}, \mathbf{G}), \quad (2)$$

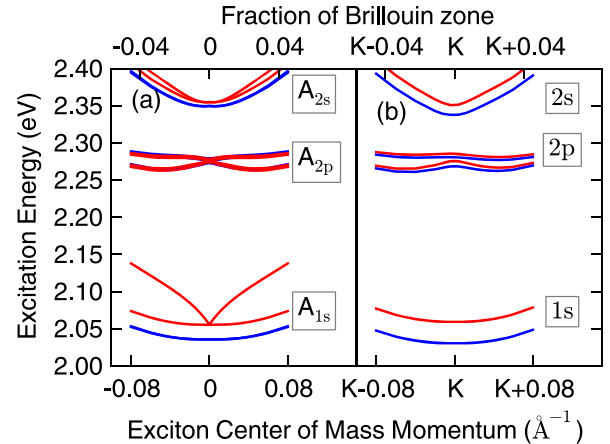


FIG. 2 (color online). Exciton dispersion of monolayer MoS<sub>2</sub> near (a)  $\mathbf{Q} = 0$  and (b)  $\mathbf{Q} = \mathbf{K}$  along the  $K$ – $\Gamma$ – $K'$  direction. Red (blue) lines indicate states arising from like-spin (unlike-spin) transitions. The label *A* refers to states involving transitions from the highest valence band at *K*/*K'*. “*B*” states involving transitions from the second highest valence band are similar and shown in the Supplemental Material [27].

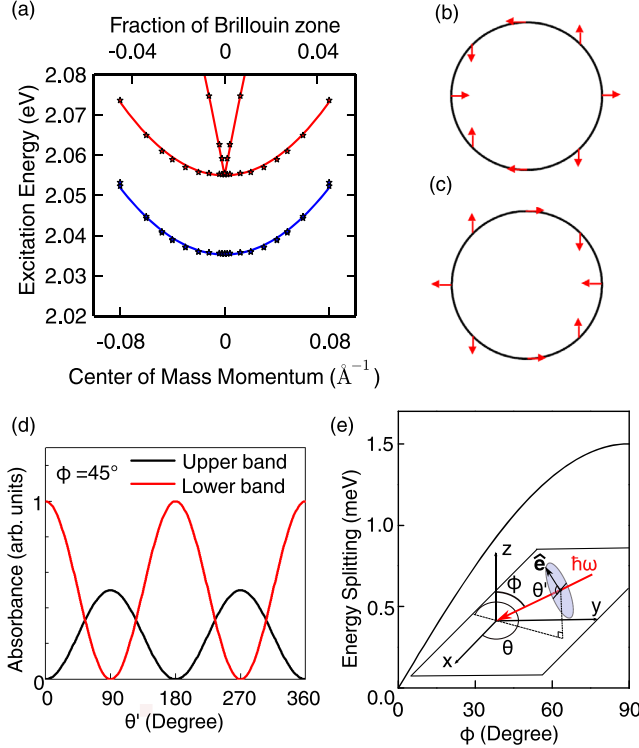


FIG. 3 (color online). (a) Closeup of dispersion of  $A_{1s}$  near  $\mathbf{Q} = 0$ . *Ab initio* values are stars. Fit to effective Hamiltonian [Eq. (11)] are solid lines. Red (blue) lines indicate states arising from like-spin (unlike-spin) transitions. (b) Valley pseudospin texture of the (upper) nonanalytic like-spin transition band around  $\mathbf{Q} = 0$  for states of fixed energy in  $\mathbf{Q}$  space. (c) Valley pseudospin texture of the (lower) parabolic like-spin transition band. (d) Optical absorbance of linearly polarized light at fixed incidence as the polarization vector  $\hat{\mathbf{e}}$  is rotated over  $360^\circ$ . The angle of the polarization vector,  $\theta'$ , is defined with respect to the vector formed by the intersection of the polarization plane (blue) and the  $xy$  plane. Red (black) indicates the absorbance of states arising from the lower (upper) like-spin band. (e) Energy difference between the upper and lower like-spin bands that is probed as  $\phi$ , the angle between the wave vector of light and the  $z$  axis is changed, for light of  $\hbar\omega \approx 2$  eV. The inset shows how  $\theta$ ,  $\phi$ , and  $\theta'$  are defined.

where  $\mathbf{G}$  are reciprocal lattice vectors,  $v$  is the bare Coulomb interaction, and  $M$  is defined as  $M_{nm'}(\mathbf{k}, \mathbf{Q}, \mathbf{G}) = \langle n\mathbf{k} + \mathbf{Q} | e^{i(\mathbf{Q}+\mathbf{G})\cdot\mathbf{r}} | n'\mathbf{k} \rangle$ . The exchange term is only non-zero for like-spin transitions (i.e., excitons with total spin along  $z$  equal to zero). The direct term is

$$\langle v\mathbf{c}\mathbf{k}\mathbf{Q} | K^d | v'\mathbf{c}'\mathbf{k}'\mathbf{Q} \rangle = -\sum_{\mathbf{G}\mathbf{G}'} M_{cc'}^*(\mathbf{k} + \mathbf{Q}, \mathbf{q}, \mathbf{G}) W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) M_{vv'}(\mathbf{k}, \mathbf{q}, \mathbf{G}), \quad (3)$$

where  $\mathbf{q} = \mathbf{k} - \mathbf{k}'$  and  $W$  is the screened Coulomb interaction.

The solutions of the BSE matrix are exciton states  $|S_{\mathbf{Q}}\rangle = \sum_{v\mathbf{c}\mathbf{k}} A_{v\mathbf{c}\mathbf{k}\mathbf{Q}}^S |v\mathbf{c}\mathbf{k}\mathbf{Q}\rangle$ . In the subspace spanned by the two lowest energy states, at exactly  $\mathbf{Q} = 0$ , the exchange matrix elements are also diagonal. At  $\mathbf{Q} = 0$ , the exchange term is the diagonal constant

$$C \equiv \langle S_0 | K^x | S_0' \rangle = \delta_{SS'} 2\pi e^2 \sum_{\mathbf{G} \neq 0} \sum_{v\mathbf{c}\mathbf{k}v'\mathbf{c}'\mathbf{k}'} A_{v\mathbf{c}\mathbf{k}\mathbf{0}}^{S*} A_{v'\mathbf{c}'\mathbf{k}'\mathbf{0}}^S \times \frac{\langle u_{\mathbf{c}\mathbf{k}} | e^{i\mathbf{G}\cdot\mathbf{r}} | u_{v\mathbf{k}} \rangle \langle u_{v'\mathbf{k}'} | e^{i\mathbf{G}\cdot\mathbf{r}} | u_{\mathbf{c}'\mathbf{k}'} \rangle^*}{|\mathbf{G}|}, \quad (4)$$

where for small  $\mathbf{Q}$ 's in 2D,  $v(\mathbf{Q} + \mathbf{G}) = [2\pi e^2 / (|\mathbf{Q} + \mathbf{G}|)] \approx (2\pi e^2 / |\mathbf{G}|)$ . This constant term is 20 meV in our *ab initio* calculation. It is purely a local-field effect and is responsible for the splitting between the like-spin (bright) and unlike-spin (dark) states at  $\mathbf{Q} = 0$ .

We now derive an effective Hamiltonian ( $H^{\text{BSE}}$ ) to describe the main physics for the  $1s$  complex in a basis of "excitonic" functions from the individual valleys in the tight-binding limit, given in Eq. (5) below. At  $\mathbf{Q} = 0$ , both the like- and unlike-spin excitonic levels are doubly degenerate, with the amplitude  $A_{v\mathbf{c}\mathbf{k}\mathbf{0}}^S$  of one state ( $|S_0^K\rangle$ ) confined to the  $K$  valley and that of the other ( $|S_0^{K'}\rangle$ ) confined to the  $K'$  valley. Near  $\mathbf{Q} = 0$ , it is sufficient to use the following basis functions (which are of the Bloch form of excitons from a specific valley in the tight-binding limit) to expand the true exciton state  $|S_{\mathbf{Q}}\rangle$ :

$$|S_{\mathbf{Q}}^K\rangle \approx |e^{i\mathbf{Q}\cdot\mathbf{R}} S_0^K\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}_{\mathbf{Q}}, \quad |S_{\mathbf{Q}}^{K'}\rangle \approx |e^{i\mathbf{Q}\cdot\mathbf{R}} S_0^{K'}\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}_{\mathbf{Q}}, \quad (5)$$

where  $\mathbf{R} = [(\mathbf{r}_e + \mathbf{r}_h)/2]$ ,  $\begin{pmatrix} 1 \\ 0 \end{pmatrix}_{\mathbf{Q}}$  and  $\begin{pmatrix} 0 \\ 1 \end{pmatrix}_{\mathbf{Q}}$  are pseudospinors denoting, respectively, basis functions on  $K$  and  $K'$  valleys, and  $|e^{i\mathbf{Q}\cdot\mathbf{R}} S_0^K\rangle = \sum_{v\mathbf{c}\mathbf{k}} A_{v\mathbf{c}\mathbf{k}\mathbf{0}}^S |v\mathbf{c}\mathbf{k}\mathbf{Q}\rangle$ .

In this basis,  $H^{\text{BSE}}$  is a  $2 \times 2$  matrix and the intravalley exchange term (matrix element between basis functions in the same valley) is

$$\langle S_{\mathbf{Q}}^K | K^x | S_{\mathbf{Q}}^K \rangle = \sum_{v\mathbf{c}\mathbf{k}v'\mathbf{c}'\mathbf{k}'} A_{v\mathbf{c}\mathbf{k}\mathbf{0}}^{S*} A_{v'\mathbf{c}'\mathbf{k}'\mathbf{0}}^S \langle v\mathbf{c}\mathbf{k}\mathbf{Q} | K^x | v'\mathbf{c}'\mathbf{k}'\mathbf{Q} \rangle. \quad (6)$$

Using a  $\mathbf{Q} \cdot \mathbf{p}$  expansion of the QP states in the  $M$  matrix elements [Eq. (2)] to second order in  $\mathbf{Q} \cdot \mathbf{p}$ , the intravalley exchange term [Eq. (6)] becomes

$$\begin{aligned} \langle S_{\mathbf{Q}}^K | K^x | S_{\mathbf{Q}}^K \rangle &= \langle S_{\mathbf{Q}}^{K'} | K^x | S_{\mathbf{Q}}^{K'} \rangle \\ &= \sum_{v\mathbf{c}\mathbf{k}v'\mathbf{c}'\mathbf{k}'} A_{v\mathbf{c}\mathbf{k}\mathbf{0}}^{S*} A_{v'\mathbf{c}'\mathbf{k}'\mathbf{0}}^S (\mathbf{Q} \cdot a(\langle u_{v\mathbf{k}} | \mathbf{p} | u_{\mathbf{c}\mathbf{k}} \rangle)^* \mathbf{Q} \\ &\quad \cdot a' \langle u_{v'\mathbf{k}'} | \mathbf{p} | u_{\mathbf{c}'\mathbf{k}'} \rangle v(\mathbf{Q}) + \sum_{\mathbf{G} \neq 0} v(\mathbf{Q} + \mathbf{G}) \\ &\quad \times \{c + O(\mathbf{Q} \cdot \mathbf{p}) + O[(\mathbf{Q} \cdot \mathbf{p})^2]\}). \end{aligned} \quad (7)$$

Here, we have separated contributions from the  $\mathbf{G} = 0$  and  $\mathbf{G} \neq 0$  Fourier components. (Higher order terms are described explicitly in the Supplemental Material [27].) We note that  $a$ ,  $a'$ , and  $c$  are factors that depend on the QP states but are independent of  $\mathbf{Q}$  [35]. In Eq. (7), the  $\mathbf{G} = 0$ -term has a nonanalytic dependence on  $|\mathbf{Q}|$

$$|\mathbf{Q} \cdot \sum_{v\mathbf{k}} aA^{S^k} \langle u_{v\mathbf{k}} | \mathbf{p} | u_{c\mathbf{k}} \rangle|^2 v(\mathbf{Q}) \propto A|Q|. \quad (8)$$

Here,  $A$  is a proportionality constant, and we have made use of the fact that for small  $\mathbf{Q}$  in  $2D$ ,  $v(\mathbf{Q}) \approx (2\pi e^2/|Q|)$ , and the fact that  $\langle 0 | \mathbf{p} | S_0^K \rangle \propto \hat{x} + i\hat{y}$  due to the  $C_3$  symmetry [7], which eliminates the dependence on the orientation of  $\mathbf{Q}$ . Up to order  $Q^2$ , the intravalley exchange [Eq. (6)] has the form

$$\langle S_Q^K | K^x | S_Q^K \rangle = \langle S_Q^{K'} | K^x | S_Q^{K'} \rangle = C + A|Q| + \beta Q^2. \quad (9)$$

$C$  is the splitting of bright and dark states given in Eq. (4), and  $\beta$  is a proportionality constant that is a real number, which arises from the local fields. Likewise, the intervalley exchange may be shown to be

$$\langle S_Q^K | K^x | S_Q^{K'} \rangle = (\langle S_Q^{K'} | K^x | S_Q^K \rangle)^* = A|Q|e^{-i2\theta} + \beta' Q^2, \quad (10)$$

where  $\theta$  is the angle of  $\mathbf{Q}$  defined with respect to the  $x$  axis and  $\beta'$  is a complex number.

After performing a similar analysis of the direct term, we find an effective Hamiltonian

$$\begin{aligned} H^{\text{BSE}}(\mathbf{Q}) = & \Omega_0 \mathbb{1} + A[\mathbb{1} + \cos(2\theta)\sigma_x + \sin(2\theta)\sigma_y] |Q| \\ & + \left\{ \left( \frac{\hbar^2}{2M} + \alpha + \beta \right) \mathbb{1} + |\beta'| [\cos(2\theta)\sigma_x \right. \\ & \left. + \sin(2\theta)\sigma_y] \right\} Q^2, \end{aligned} \quad (11)$$

where  $\Omega_0$  is the excitation energy of the exciton with  $\mathbf{Q} = 0$ ,  $M = m_e + m_h$  is the QP band mass of the free electron-hole pair at  $K$  or  $K'$ ,  $\alpha$  is a constant from the order of the  $Q^2$  contribution from the direct term,  $\beta$  and  $\beta'$  are constants from the order of the  $Q^2$  contribution from the intravalley and intervalley exchange, respectively, and  $\sigma_x$  and  $\sigma_y$  are the Pauli matrices (see Supplemental Material for a detailed derivation [27]). An effective Hamiltonian may be obtained for the other exciton complexes through similar analyses.

Diagonalizing the effective Hamiltonian [Eq. (11)] gives us two solutions: one with a parabolic dispersion

$$\Omega_-(\mathbf{Q}) = \Omega_0 + \left( \frac{\hbar^2}{2M} + \alpha + \beta - |\beta'| \right) Q^2, \quad (12)$$

and the other with a nonanalytic dispersion

$$\Omega_+(\mathbf{Q}) = \Omega_0 + 2A|Q| + \left( \frac{\hbar^2}{2M} + \alpha + \beta + |\beta'| \right) Q^2. \quad (13)$$

Hence, it is the combination of intervalley and intravalley exchange that results in a lower band with a parabolic dispersion [Eq. (12)] and an upper band with a nonanalytic dependence on  $|Q|$  [Eq. (13)], as seen in our *ab initio* calculation [Fig. 3(a)]. We emphasize that this  $|Q|$  dependence at small  $\mathbf{Q}$  is a consequence of the  $2D$  Coulomb interaction and the opposite angular polarization of the electronic states in the  $K$  and  $K'$  valleys, which removes the dependence on the direction of  $\mathbf{Q}$ .

We fit Eqs. (12) and (13) to our *ab initio* calculation [Fig. 3(a)] to obtain the values of the proportionality constants,  $A$ ,  $\alpha$ ,  $\beta$ , and  $\beta'$ . From the slope of the linear branch, we find  $A = 0.9 \text{ eV \AA}$ . Normally, the dominant  $Q^2$ -term comes from the QP effective mass term  $\hbar^2 Q^2/2M$ .  $M$  for monolayer MoS<sub>2</sub> is roughly  $1.1m_0$ . From the dispersion of the unlike-spin states in which exchange interaction is zero, we find that  $\alpha = -0.9 \text{ eV \AA}^2$ , and the effective mass of the unlike-spin transition (dark) 1s exciton is roughly  $M^* = 1.5m_0$ . The effective mass of the parabolically dispersing like-spin transition (bright) 1s exciton is  $M^* = 1.4m_0$ , indicating that  $\beta - |\beta'|$ , the difference between quadratic terms in the intervalley and intravalley exchange, is small, only about  $0.2 \text{ eV \AA}^2$ , while the magnitude of  $\beta$  is about  $4 \text{ eV \AA}^2$ . Our results demonstrate an enhancement of about 30% in the center-of-mass effective mass  $M^*$  of the parabolic band excitons due to the electron-hole interaction [36].

Since the difference between the magnitude of the quadratic terms in the intervalley and intravalley exchange,  $\beta - |\beta'|$ , is small, we may to good approximation neglect this difference (i.e., we take  $\beta' = e^{-i2\theta}\beta$ ; see Supplemental Material [27]). Then, the solution for the parabolic like-spin transition exciton band simplifies to

$$\frac{1}{\sqrt{2}} (e^{-i\theta} |S_Q^K\rangle - e^{i\theta} |S_Q^{K'}\rangle), \quad (14)$$

and the solution for the nonanalytic like-spin transition exciton band simplifies to

$$\frac{1}{\sqrt{2}} (e^{-i\theta} |S_Q^K\rangle + e^{i\theta} |S_Q^{K'}\rangle). \quad (15)$$

For both states, the valley pseudospin winding number around  $\mathbf{Q} = 0$  is 2. The pseudospin texture of these states in a circle in  $\mathbf{Q}$  space is shown in Figs. 3(b)–3(c). To study the optical response, we project the momentum and polarization of incident linearly polarized light into the layer  $2D$  plane. The momentum  $\mathbf{Q}$  of the excited exciton is equivalent to the in-plane component of the wave vector of the light. The in-plane projection of the electric field polarization vector can be decomposed into components perpendicular (transverse) to and parallel (longitudinal) to the momentum transfer  $\mathbf{Q}$ . We define the angle of the polarization vector with respect to the transverse projection as  $\theta'$ . The absorbance of the upper and lower bands with respect to  $\theta'$  has a phase difference of  $90^\circ$ , and the intensity of each band peaks twice as the polarization angle is rotated over  $360^\circ$  [Fig. 3(d) and Supplemental Material [27]]. The different pseudospin texture results in the upper band coupling to the longitudinal component of the in-plane projection of the electric field and the lower band coupling to the transverse component of the in-plane electric field (see Supplemental Material [27]). Since the transverse projection is always in the  $2D$  plane, only the intensity of optical absorbance from the upper band changes with the angle of the incident light with respect to the  $z$  axis ( $\phi$ ). Intensity is maximum at normal incidence ( $\phi = 0$ ) and

minimum at grazing incidence ( $\phi \approx 90^\circ$ ). The energy difference between the upper and lower band for different  $\mathbf{Q}$  on the dispersion curve can also be probed by changing  $\phi$ . For photons with  $\hbar\omega \approx 2$  eV, the largest energy difference is about 1.5 meV when the wave vector of the light is nearly parallel to the plane.

In summary, we have computed the exciton dispersion of MoS<sub>2</sub> from first principles and find an unusual dispersion with a parabolic lower band and a  $v$ -shaped upper band for the lowest energy like-spin transition exciton complex near  $\mathbf{Q} = 0$ . This dispersion is due to the interplay of the intervalley and intravalley exchange, both of which have a  $|\mathbf{Q}|$ -dependent behavior. We have derived a simple effective Hamiltonian and analytic solutions describing this physics and predict that the splitting of the exciton bands can be measured with a linearly polarized optical beam tilted away from normal incidence. We expect any 2D semiconductor with excitons with an amplitude concentrated in a small portion of the Brillouin zone to exhibit similar nonanalytic exciton dispersion near  $\mathbf{Q} = 0$ . We also show that interaction effects increase the exciton mass  $M^*$  by  $> 30\%$ . First-principles results for the intervalley excitons with  $\mathbf{Q} = K$  and other finite- $\mathbf{Q}$  excitons are also obtained.

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