Quasiparticle Energies and Excitonic Effects of Chromium Trichloride: from Two Dimensions to Bulk

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Abstract

Layered van der Waals (vdW) magnetic materials have attracted significant research interest to date. In this work, we employ the first-principles many-body perturbation theory to calculate excited-state properties of a prototype vdW magnet, chromium trichloride (CrCl\textsubscript{3}), covering monolayer, bilayer, and bulk. Unlike usual non-magnetic vdW semiconductors, in which many-electron interactions and excited states are sensitive to dimensionality, many-electron interactions are always enhanced and dominate quasiparticle energies and optical responses of both two-dimensional and bulk CrCl\textsubscript{3}. The electron-hole (\textit{e}-\textit{h}) binding energy can reach 3 eV in monolayer and remains as high as 2 eV in bulk. Because of the cancellation effect between self-energy corrections and \textit{e}-\textit{h} binding energies, the lowest-energy exciton ("optical gap") is almost not affected by the change of dimensionality. Particularly, for the excitons with similar \textit{e}-\textit{h} binding energies, their dipole oscillator strength can differ by a few orders of magnitude. Our analysis shows that such a big difference is from a unique interference effect between \textit{e}-\textit{h} interactions and interband transitions. Finally, we find that the interlayer stacking sequence and magnetic coupling barely change quasiparticle band gaps and optical absorption spectra of CrCl\textsubscript{3}. Our findings give insight into the understanding of many-electron interactions and the interplay between magnetic orders and optical excitations in vdW magnetic materials.

I. Introduction

Many-electron interactions are known to be enhanced in low-dimensional structures, and they dominate corresponding excited-state properties. Because of the reduced screening, electronic self-energy and excitonic effects are dramatically enhanced. For instance, the electron-hole (\textit{e}-\textit{h}) binding energy of monolayer transition metal dichalcogenides (TMDs) [1–7] and black phosphorus [8–11] can be around a few hundred meV, which is about one to two orders of magnitude larger than those of typical bulk semiconductors [1,7,9–13]. This reduced screening effect stems from the surrounded vacuum and, thus, is sensitive to dimensionality. For example, \textit{e}-\textit{h} binding energy of bulk Tellurium is less than 10 meV while that of its monolayer structure is...
increased to be around 700 meV [14]. In addition to screening, the electronic band dispersion (effective mass) also impacts many-electron interactions. Particularly, flat bands contribute to a large joint density of states (JDOS), enhancing the chance of forming e-h pairs [15]. However, there have been very limited studies to clarify the roles of dimensionality and band-curvature effects on many-electron interactions and excited states to date.

Recently achieved two-dimensional (2D) magnetic materials [16–19] may provide a unique opportunity to answer this fundamental question because their electronic band edges are usually dominated by localized 3d orbitals and are flat for both 2D and bulk structures. With the help of magnetic anisotropy [20], these 2D structures hold a long-range magnetic order by gapping low-energy modes of magnons [21]. Because of enhanced light-matter interactions, layered vdW magnetic structures exhibit significant magneto-optical effects, such as the magneto-optical Faraday and Kerr effects and magnetic circular dichroism (MCD), which have been applied to identify magnetic orders [17,18,22] and give rise to optomagnetic applications based on vdW structures [23,24]. More recently, enhanced excitonic effects on magneto-optical responses have been calculated for monolayer magnetic structures [25,26]. These theoretical works showed that e-h binding energy can be 1.7 eV in monolayer CrI₃ [25], which is substantially larger than those of other non-magnetic semiconductors and satisfactorily explained available measurements.

Chromium trichloride (CrCl₃) is a good candidate to explore the relationship between many-electron interactions and dimensionality in correlated vdW magnetic structures. Unlike the widely studied CrI₃, whose bulk exhibits a ferromagnetic (FM) order [18,27], bulk CrCl₃ owns an interlayer antiferromagnetic (AFM) order with an intralayer FM order [19], the so-called A-type AFM order. Moreover, because of the significantly smaller spin-orbit coupling (SOC), the magnetic anisotropy energy (MAE) is small in CrCl₃ [19,21], and its 2D structure may exhibit an in-plane ground state magnetism [19,28,29] and rich topological spin textures, such as meron-like pairs at finite temperatures [30]. This weak SOC also substantially simplifies the optical spin selection rules, making CrCl₃ ideal to analyze many-electron interactions and corresponding optical activities.

In this work, we employed first-principles many-body perturbation theory (MBPT) to study many-electron interactions and excited-state properties of CrCl₃. Significant self-energy corrections and excitonic effects are discovered for monolayer, bilayer and bulk CrCl₃. The self-energy correction can be as large as 2.86 eV, and e-h binding energy of the lowest bright exciton amounts to around 2.94 eV for monolayer, making the effective “optical gap” close to the Kohn-Sham band gap. Importantly, for excitons with similar e-h binding energies within the same structure, their dipole oscillator strength can be different for a few orders of magnitude. Our analysis shows that this big difference is from a unique interference effect between exciton wavefunctions and interband transition matrices. Moreover, we show that many-electron interactions and excitonic effects are less sensitive to dimensionality in these vdW magnets. Thus, the flat bands and enhanced JDOS play an important role in deciding excited-state properties, giving hope to robust room-temperature excitons in bulk magnets. Finally, we find that these optical spectra and many-electron effects have little dependence on the interlayer crystallographic structure or magnetic
orders. Therefore, magneto-optical effects [18,22] or second-harmonic generation (SHG) [31,32] may be applied to identify those complex symmetries of ultra-thin magnets.

The remainder of this article is organized as follows: In Sec. II, we introduce the atomic and crystallographic structure of CrCl$_3$, as well as the simulation setups. The results on the electronic and optical properties for monolayer, bilayer and bulk CrCl$_3$ are presented in Sec. III, IV and V respectively. In Sec. VI, we made a comprehensive comparison of the evolution of band gaps and optical absorbance with dimensionality. Finally, the conclusions are summarized in Sec. VII.

II. Atomic Structures and Computational Details

The atomic structures of CrCl$_3$ are presented in Figure 1. Below 240 K [19], bulk CrCl$_3$ is a van der Waals layered material adopting the rhombohedral phase (space group $R\overline{3}$), which is formed by an interlayer shift along the $(\vec{a} - \vec{b})$ direction, as shown in Figures 1 (a1) and (a2). This is also known as the low-temperature (LT) phase. Above 240 K, it experiences a crystallographic phase transition into the monoclinic phase (space group $C2/m$), which is formed by an interlayer shift along the $-\vec{a}$ direction, as shown in Figures 1 (b1) and (b2). This is the high-temperature (HT) phase. Such a structural phase transition is similar to that observed in bulk CrI$_3$ [27]. Within each single layer of CrCl$_3$, the chromium atoms are arranged in a honeycomb structure, and each chromium atom is surrounded by six chloride atoms forming an octahedra. Below 17 K, an intralayer FM order is formed in bulk CrCl$_3$, followed by an interlayer AFM order below 14 K [19]. The magnetic moments are dominantly hosted on chromium atoms.

The ground-state properties are obtained by density functional theory (DFT) within the general gradient approximate (GGA) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [33] as implemented in the Quantum ESPRESSO package. The vdW interactions in bilayer and bulk CrCl$_3$ are included via the semiempirical Grimme-D3 scheme [34]. Semi-core 3$p$ and 3$d$ electrons of Chromium atoms are included in norm-conserving pseudopotentials, and the plane-wave energy cutoff is set to be 65 Ry. A vacuum distance of 18 Å between adjacent layers is used along the periodic direction in monolayer and bilayer calculations to avoid spurious interactions. SOC is relatively small in CrCl$_3$ due to the small atomic number of the ligand atom and, hence, is not considered in our calculations. [See supplementary information [35]]

The MBPT calculations are performed using the BerkeleyGW code [36] including the slab Coulomb truncation for monolayer and bilayer structures. Quasiparticle (QP) energy is calculated by using the single-shot $G_0W_0$ approximation within the general plasmon pole model [37]. The Bethe-Salpeter Equation (BSE) is employed to obtain excitonic effects and optical absorption spectra [38]. Because of the depolarization effect [39,40], only the incident light polarized parallel to the atomic plane is considered for the monolayer and bilayer cases. For monolayer CrCl$_3$, a coarse $k$-grid of 12x12x1 is adopted to calculate the dielectric function and QP energies, and it is interpolated to a fine $k$-grid of 24x24x1 for the $e$-$h$ interaction kernel and solving BSE. The coarse
In order to better describe the correlated 3d orbitals in chromium atoms in the DFT level ground state calculations, the on-site Hubbard interaction [41] is included with parameters U=1.5 eV and J=0.5 eV, which have been used in previous studies of CrI₃ and successfully explained available measurements [25,26]. To avoid the double-counting problem in this DFT+U/MBPT scheme, we have subtracted the DFT-level Hubbard potential $V_{Hub}$ together with the DFT exchange-correlation potential $V_{xc}$ from the conventional self-energy operator $\Sigma(E)$ within the GW approximation, following Ref. [25,42,43] by:

$$[T + V_{ext} + V_H + V_{xc} + V_{Hub}]\Psi(r) + \int dr'\Delta\Sigma(r, r'; E^{qp})\Psi(r') = E^{qp}\Psi(r),$$

(1)

and

$$\Delta\Sigma(E) = \Sigma(E) - V_{xc} - V_{Hub}.\quad (2)$$

The comparison of results adopting different Hubbard parameters is provided in the supplementary [35].

**III. Monolayer CrCl₃**

The DFT-calculated band structure of FM monolayer CrCl₃ is presented in Figure 2 (a). For FM monolayer CrCl₃, the valence band maximum (VBM) is located at the high-symmetry $M$ point and the conduction band minimum (CBM) is located around the middle point of the $K - \Gamma$ line, resulting in an indirect band gap of 1.98 eV and a direct band gap of 2.03 eV at $M$ point. According to the projected density of states (PDOS) in Figure 2 (a), the four lowest-energy conduction bands and the five highest-energy valence bands have a sizable amount of 3p orbital components of Cl atoms. Interestingly, those higher-energy conduction bands between 3 and 4 eV are nearly from pure 3d orbitals. Finally, both the valence and conduction band edges exhibit nearly flat dispersions and are composed of the same spin (up) states. This enhanced JDOS indicates stronger many-electron interactions and active interband transitions due to the spin-allowed selection rule [15].

We have calculated QP energies within the GW approximation. The DFT and GW band gaps are summarized in Table 1. The direct QP band gap is 4.89 eV, and the indirect QP band gap is 4.84 eV. The linear fit of GW-calculated QP energy to the DFT+U eigenvalues is presented in Figure 2 (b). Due to the reduced dielectric screening of the suspended 2D structure and enhanced JDOS, there are significant QP energy corrections in monolayer CrCl₃, rendering a 2.86 eV enlargement of the GW band gap from the DFT result. This enhancement is significantly larger than those in monolayer MoS₂ (~ 1.0 eV) [4,6] and black phosphorus (~ 1.2 eV) [10], indicating that correlated flat bands further enhance many-electron interactions in addition to the dimensionality factor. We also notice that the spin-up and spin-down states have slightly different self-energy corrections, as shown in Figure 2 (b).
We have further calculated the optical absorption spectrum of FM monolayer CrCl$_3$. To avoid the artificial effect from the choice of vacuum space in simulations, we plot the optical absorbance by $A(\omega) = \frac{n d c}{\varepsilon_2(\omega)}$, where $\varepsilon_2(\omega)$ is the calculated imaginary part of the dielectric function and $d$ represents the distance between adjacent CrCl$_3$ layers along the periodic direction of our calculation. Figure 3 (a) shows the optical absorbance of monolayer CrCl$_3$ with and without excitonic effects included. In the absence of $e$-$h$ interactions, the absorbance (blue dashed line) edge starts at around 4.9 eV, corresponding to the QP direct band gap at the $M$ point. This significant absorption edge is consistent with the enhanced JDOS and allowed spin-selection rule as shown in Figure 2 (a).

After $e$-$h$ interactions are included, the optical absorption spectrum is dramatically changed. The main optical absorption happens between 3 to 5 eV, which is a 2-eV red shift from the interband-transition result. More importantly, we observe two characteristic excitonic peaks in the optical spectrum at the low energy regime, which are marked as $X_1$ and $X_2$ in Figure 3 (a), respectively. It is worth mentioning that more excitonic states are around $X_1$ and $X_2$ while most of them are optically dark. In the inset of Figure 3 (a), we also mark the lowest-energy dark exciton, $X_0$, whose energy is about 35 meV below $X_1$ but dipole oscillator strength is about five orders of magnitude smaller than that of $X_1$. These low-energy excitons result in significant exciton binding energies of 2.98 eV, 2.94 eV, and 2.34 eV for $X_0$, $X_1$, and $X_2$, respectively. Such exciton binding energies are enormous compared with those of other typical 2D semiconductors such as monolayer MoS$_2$ ($\sim 960$ meV) [4] and black phosphorous ($\sim 800$ meV) [10], and they are almost two times larger than that of the sibling magnetic material, monolayer CrI$_3$ ($\sim 1.7$ eV [25]). Moving to higher excitation energies (between 3 eV to 5 eV), there are exciton states with much stronger dipole oscillator strength than those lower-energy exciton states. For example, the peak marked by $X_3$ has an oscillator strength one order larger than $X_1$. These bright excitons dominate the main optical absorption spectrum. Our calculated $e$-$h$ binding energies of monolayer CrCl$_3$ are in agreement with recent theoretical calculations [26].

To better understand these strongly bound excitons, we have plotted the real-space exciton wavefunctions of $X_0$, $X_1$ and $X_3$ with the hole positioned on a chromium atom in Figures 3 (b)-(d). Because of the large $e$-$h$ binding energy, all three excitons exhibit highly localized wavefunctions. Particularly, for $X_0$ and $X_1$, their wavefunctions are nearly confined within one unit cell. These highly localized real-space wavefunctions indicate a smearing of the $e$-$h$ pair contributions from the whole Brillouin zone (BZ) in reciprocal space. This also agrees with the argument that those flat bands around band edges actively contribute to the formation of strongly bound excitons. For $X_3$, because of its smaller $e$-$h$ binding energy, the wavefunction is slightly broader and roughly covers the size of three unit cells.

It is hard to tell any significant difference between the real-space wavefunctions of excitons $X_0$ and $X_1$, whose dipole oscillator strength differ, however, by five orders of magnitude. Following Ref. [44], we try to find the original contributions of dipole oscillator strength of these excitons. We rewrite the optical transition matrix element $\langle 0 | \hat{v} | i \rangle$ from the ground (vacuum) state $| 0 \rangle$ to an exciton state $| i \rangle = \sum_{vck} A_{vck}^i | v_c \rangle$, ($A_{vck}^i$ is the exciton amplitude solved from BSE [38]) to
analyze the contribution of interband transition matrix elements \( \langle vk | \hat{\varphi} | ck \rangle \) at a certain energy \( \omega \) to the optical transition matrix element

\[
\langle 0 | \hat{\varphi} | i \rangle = \sum_{vck} A_{vck}^i \langle vk | \hat{\varphi} | ck \rangle = \int S_i(\omega) \, d\omega,
\]

where

\[
S_i(\omega) = \sum_{vck} A_{vck}^i \langle vk | \hat{\varphi} | ck \rangle \delta(\omega - (E_{ck} - E_{vk})),
\]

and

\[
I_i(\omega) = \int_0^\omega S_i(\omega')d\omega'.
\]

Since monolayer CrCl\(_3\) is FM and lacks time reversal symmetry, \( S_i(\omega) \) and its integral \( I_i(\omega) \) are complex functions. The corresponding interference effect between interband transition matrices \( \langle vk | \hat{\varphi} | ck \rangle \) and exciton amplitude \( A_{vck}^i \) is essential for determining the overall dipole oscillator strength of excitons (note that the exciton dipole oscillator strength is proportional to the square of \( I_i(\omega) \)). To address main characters, we only plot the real part of \( S_i(\omega) \) and \( I_i(\omega) \) in Figures 3 (e)-(g) for the exciton states \( X_0 \), \( X_1 \) and \( X_3 \), respectively. The imaginary part is similar. These plots essentially show how e-h interactions obtain dipole oscillator strength from interband transitions at different energies and reform them into corresponding excitons. Like previous studies on graphene [44], the energy distribution of \( S_i(\omega) \) of all studied excitonic states is spread over a wide energy range, which is consistent with their large binding energies.

For the dark exciton \( X_0 \), there is a coherent cancellation of \( S_i(\omega) \). As shown in Figure 3 (e), \( S_i(\omega) \) fluctuates positively and negatively with similar amplitude at all energies. As a result, the integral of \( S_i(\omega) \) is not able to build up over the energy range and produce a small overall \( I_i(\omega) \). This is the reason for the tiny dipole oscillator strength of \( X_0 \). This interference effect between interband transition matrix elements and exciton wavefunctions is less prominent for the bright exciton state \( X_1 \), especially at the low energy side. As shown in Figure 3 (f), \( I_i(\omega) \) grows dominantly at around 5 eV and nearly saturates after 5.5 eV. This indicates that the dipole oscillator strength of the bright exciton \( X_1 \) is mainly contributed by those flat (3d) bands around band edges. Finally, for the bright exciton \( X_3 \) in Figure 3 (g), there is only minor interference effects. Particularly, the interband contributions above 5.5 eV have nearly the same positive sign. As a result, the integral \( I_i(\omega) \) builds consistently along the way to higher transition energies, resulting in a large oscillator strength. In a word, the dramatically different optical dipole oscillator strength of excitons with similar e-h binding energy is mainly from the interference effect between the interband transitions and exciton amplitude involved in forming excitons.

### IV. Bilayer CrCl\(_3\)

Compared with monolayer CrCl\(_3\), the interlayer magnetic order and stacking sequence in bilayer CrCl\(_3\) bring more degrees of freedom. First, as shown in Figure 1, there are two crystallographic structures of bulk CrCl\(_3\). Interestingly, unlike bulk CrCl\(_3\), recent experiments have shown that no
crystallographic transition was observed in few layer CrCl\textsubscript{3}, keeping a monoclinic HT phase structure at low temperatures [45]. Nevertheless, in order to identify the possible influence of crystallographic structures on the electronic and optical properties of bilayer CrCl\textsubscript{3}, we consider both stacking sequences in our calculations. Second, the energy difference of interlayer FM and AFM orders is small, less than 5 meV/Cr shown in previous calculations [19,46] and depends critically on the approach used [46]. Although the interlayer AFM order is widely observed in available measurements [19,28,29,45], the FM order can be achieved by applying a small magnetic field as shown by recent experiments [19,28,29]. Therefore, we will consider both interlayer AFM and FM orders in the following calculations of bilayer CrCl\textsubscript{3}.

The DFT-calculated band structures are summarized in Figure 4 for AFM/FM and LT/HT configurations of bilayer CrCl\textsubscript{3}. For the interlayer AFM order shown in Figures 4 (a) and (c), the bands of the two layers are almost degenerate, with opposite spin components from each layer. For the interlayer FM order shown in Figures 4 (b) and (d), the two layers have same spin components, resulting in an overall double-degenerated spin up band edge states. Meanwhile, the band structures and band gaps of LT and HT phases are similar, except that the monoclinic HT structure exhibits a little larger splitting of the bands than the rhombohedral LT structure.

The GW-calculated QP energy vs the DFT+U results are summarized in Table 1. Because of the similar reasons of enhanced self-energy corrections as in monolayer CrCl\textsubscript{3}, significant QP energy corrections are obtained in bilayer CrCl\textsubscript{3}. For example, the QP band gap of the bilayer rhombohedral LT phase AFM CrCl\textsubscript{3} is increased from a DFT value of 1.96 eV to 4.58 eV. As shown in Table 1, these self-energy corrections are not sensitive to the interlayer structure or magnetic order; the self-energy corrections are around 2.6 eV for all these configurations. On the other hand, this GW correction is about 240 meV smaller than that of monolayer. This is mainly from the increased screening in bilayer structures.

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The optical absorption spectra of these four configurations are presented in Figure 5. Like the results of QP energies, the optical absorption spectra are similar for all four configurations. Take the bilayer HT phase AFM CrCl\textsubscript{3} as an example (Figure 5 (c)). Without e-h interactions, the absorption edge starts at around 4.6 eV, which is due to the QP band gap. After including e-h interactions, a significant red shift of the optical spectrum is observed. Like the result of monolayer, the main optical spectrum is still located between 3 to 5 eV although the QP band gap is reduced by around 280 meV compared with monolayer. Moreover, the two characteristic excitonic peaks, \(X_1\) and \(X_2\), are observed in all spectra. Their energies are similar for all four configurations as well. Interestingly, the energies of \(X_1\) are averagely slightly higher than those of monolayer. As seen from Table 1, the GW correction for AFM rhombohedral (LT) bilayer is about 2.62 eV, which is about 240 meV smaller than that of monolayer. However, the e-h binding energy of bilayer is reduced by about 300 meV than that of monolayer. As a result, the e-h interaction is more sensitive than the band gap to the change of dimensionality, which increases the absolute value of exciton energy finally. This is an opposite trend according to usual quantum confinement effect, in which thinner samples show a blue shift of the optical spectrum [10,11,14].
V. Bulk CrCl₃

We have performed the GW-BSE calculations on bulk CrCl₃. Given the results from bilayer CrCl₃ that the GW QP energy corrections and absorption spectra are not sensitive to the interlayer stacking and magnetic order, we only consider the experimentally observed rhombohedral bulk structure with the AFM interlayer coupling [19] (see supplementary [35] for the results on the monoclinic structure). The DFT+U-calculated band structure of bulk CrCl₃ is presented in Figure 6 (a). Interestingly, quantum confinement effects are nearly negligible within DFT results: the band structure and band gap of bulk CrCl₃ is nearly the same as those of monolayer and bilayer structures.

The GW-calculated QP energy vs the DFT+U results are summarized in Table 1. Significant self-energy corrections are observed in bulk CrCl₃, and quantum confinement effects show up. Because of stronger screening in three dimensions, the GW enlargement of the band gap is around 2.1 eV, and it is smaller than those in monolayer (around 2.9 eV) and bilayer (around 2.6 eV). Nonetheless, this reduction of band gap from monolayer (~4.84 eV) to bulk (~4.03 eV) is significantly smaller than other typical semiconductors such as black phosphorous (~2 eV in monolayer and ~0.3 eV in bulk) [10] and tellurium (~2.35 eV in monolayer and ~0.41 in bulk) [14].

Further we have calculated the absorption spectrum $\varepsilon_2(\omega)$ of bulk CrCl₃. Because the depolarization effect is negligible in bulk structures, we include both in-plane and out-of-plane polarizations of incident light, as shown in Figures 6 (b) and (c), respectively. As expected, before including e-h interactions, both the optical absorption spectra start from the QP band gap around 4.1 eV. Excitonic effects substantially shift the main optical absorption spectrum to between 3 eV and 5 eV. For in-plane polarized incident light (Figure 6 (b)), those two characteristic excitonic peaks ($X_1$ and $X_2$) are similar to the monolayer and bilayer cases and are located at around 2.24 eV and 2.78 eV with e-h binding energies of 1.84 and 1.30 eV, respectively. Importantly, these exciton energies are significantly higher than those of bilayer (2.0 and 2.5 eV) and monolayer (1.9 and 2.5 eV), exhibiting an opposite trend of the usual quantum confinement effects. Moreover, the dipole oscillator strength of these two characteristic peaks is also enhanced. This can be from the stronger interlayer hybridization that enhances the overlap of electron and hole wavefunctions and corresponding transition matrices.

The dipole oscillator strength distribution is largely different for different incident-light polarizations, resulting in a highly anisotropic optical spectrum. For incident light polarized along the out-of-plane direction (Figure 6 (c)), the characteristic peak $X_2$ becomes optically dark, and the dipole oscillator strength of $X_1$ is further enhanced. Besides, the main absorption between 3 eV and 5 eV becomes more isolated absorption peaks around 3.4 eV and 4.6 eV. The redistribution of exciton dipole oscillator strength under different incident light polarization may be employed in experiments to detect the crystal orientation.

VI. Evolution of band gaps and excitons with dimensionality
Finally, we have summarized the evolution of band gaps and characteristic excitons of CrCl$_3$ from monolayer, bilayer, to bulk. Given available measurements and the insensitivity of electronic and optical properties to the interlayer stacking and magnetic configurations, we use the results of interlayer LT structures and AFM coupling, and the fitting results are universal for all configurations. In Figure 7 (a), the evolution of the DFT and QP band gaps as well as the “optical gap” (the first bright exciton peak $X_1$) is presented. To quantitatively provide the band gap dependence on the layer number, we employ the widely used empirical power law formula [10,11,47]:

$$E^N = E_{bulk}^{\infty} + \frac{A}{N^\alpha},$$

where $N$ is the layer number and $E_{bulk}^{\infty}$ represents the bulk value. The fitted results are included in Table 2. Although the DFT band gap barely changes from monolayer to bulk, the significant QP energy corrections reflect the trend of the increased dielectric screening effect. The failure of DFT in predicting the band gap as well as the dielectric screening effect indicates it is important to go beyond DFT in calculating the electronic properties of vdW layered magnetic materials even for obtaining qualitative trends of quantum confinement. Interestingly, the GW-calculated band gap follows the $1/N^{0.6}$ power law. This decay is slower than the usual quantum confinement case with $1/N^2$ [47] based on free-electron gas, and indicates that many-electron correlations are less sensitive to the quantum confinement in correlated CrCl$_3$. We have to point out that the unusual increase of “optical gap” from monolayer to bulk is evident in Figure 7 (a), which is evidenced by the negative sign of the fitting parameter A. This is opposite to the usual trend of quantum confinement [10,11,14] because of the magnetic exciton states, whose e-h binding energy is more sensitive to the screening than QP energies.

In Figure 7 (b), we focus on those two characteristic peaks ($X_1$ and $X_2$). As noticed in above presentations, the brightness of these two excitons are sensitive to the layer number of structures. As shown in Figure 7 (b), the absorbance of the lower-energy exciton ($X_1$) is more sensitive to the thickness, and it is increased from 0.26% in monolayer to 0.61% in bulk. Thus, we expect these two characteristic excitons can be useful to estimate the thickness of samples.

**VII. Summary**

In summary, we have systematically studied the electronic and optical properties from monolayer, bilayer to bulk CrCl$_3$ using first-principles MBPT approach. Unlike typical semiconductors, the increased dielectric screening in bulk CrCl$_3$ only renders a less than 20% decrease in the QP band gap relative to the monolayer case, and the energy of the lowest bright exciton is even slightly increased from monolayer to bulk. Besides, the absorption spectrum of bulk CrCl$_3$ resembles that of the monolayer, with significant e-h binding energy of around 2 eV compared with 3 eV in monolayer CrCl$_3$. The physics origin of different dipole oscillator strengths between excitons is discussed based on the interference effect between exciton wavefunctions and interband transition matrices. Finally, we find that the absorption spectra of the vdW magnet
CrCl$_3$ is not sensitive to the interlayer magnetic order or stacking structure. Magneto-optical probes such as Kerr effect and MCD may be needed in future experiments to probe the magnetic order in these magnetic materials.

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Tables:

**Table 1** Summary of DFT and GW band gaps, $X_1$ exciton energy and its e-h binding energy of monolayer, bilayer and bulk CrCl$_3$. The unit is eV.

|                  | DFT indirect band gap | DFT direct band gap | GW indirect band gap | GW direct band gap | $X_1$ exciton energy | $X_1$ binding energy |
|------------------|-----------------------|---------------------|----------------------|--------------------|---------------------|---------------------|
| Monolayer        | 1.98                  | 2.03                | 4.84                 | 4.89               | 1.95                | 2.94                |
| 2L               |                       |                     |                      |                    |                     |                     |
| Rhombohedral AFM | 1.96                  | 2.01                | 4.58                 | 4.63               | 1.97                | 2.66                |
| Rhombohedral FM  | 1.95                  | 1.98                | 4.56                 | 4.59               | 1.91                | 2.68                |
| Monoclinic AFM   | 1.95                  | 1.99                | 4.57                 | 4.61               | 1.98                | 2.63                |
| Monoclinic FM    | 1.94                  | 1.97                | 4.56                 | 4.59               | 1.93                | 2.66                |
| bulk             |                       |                     |                      |                    |                     |                     |
| (in-plane polarization) | 1.99             | 2.04                | 4.03                 | 4.08               | 2.24                | 1.84                |

**Table 2** Fitting parameters of DFT, QP band gaps, and “optical gap” (the energy of the first bright exciton $X_1$) to the layer number according to the power law formula $E_{bulk}^{∞} + A/N^\alpha$.

|      | DFT+U | QP   | “Optical gap” |
|------|-------|------|---------------|
| $\alpha$ | 0.07  | 0.59 | 0.16          |
| A    | -0.03 | 0.81 | -0.29         |
Figure 1 (a1) and (a2) Top and side views of the rhombohedral (LT) structure. (b1) and (b2) top and side views of the monoclinic (HT) structure. Cr atoms in different layers are shown with different colors. The Cl atoms are not shown in top views ((a1) and (b1)) for clarity. The arrows in (a1) and (b1) show the relative interlayer shift direction. The unit cells are marked by red dashed lines.
Figure 2 (a) DFT-calculated band structure (left panel) and projected density of states (right panel) of monolayer CrCl$_3$ with an intralayer FM order. The energy of the valence band maximum is set to be zero. (b) Linear fit of QP energy to DFT eigenvalues for monolayer CrCl$_3$. 
Figure 3 (a) Optical absorption spectra of monolayer CrCl$_3$ without e-h interaction (blue dashed line) and with e-h interaction (red solid line). The two characteristic absorption peaks are marked $X_1$ and $X_2$, respectively. A dark exciton state below $X_1$ is marked $X_0$ in the inset. An exciton state at higher energy is marked as $X_3$. (b-d) Real-space wavefunctions of exciton states $X_0$, $X_1$ and $X_3$, respectively. The hole positions are marked with red triangles. (e-g) $S_i(\omega)$ and its integral $I_i(\omega)$ for exciton states $X_0$, $X_1$ and $X_3$, respectively.
Figure 4 DFT-calculated band structure of bilayer CrCl$_3$: (a) LT rhombohedral stacking with an AFM interlayer coupling; (b) LT rhombohedral stacking with a FM interlayer coupling; (c) HT monoclinic stacking with an AFM interlayer coupling; (d) HT monoclinic stacking with a FM interlayer coupling. The energy of the valence band maximum is set to be zero.
Figure 5 Optical absorption spectra of bilayer CrCl$_3$ with and without e-h interactions: (a) those of the LT rhombohedral stacking with an AFM interlayer coupling; (b) those of the LT rhombohedral stacking with a FM interlayer coupling; (c) those of the HT monoclinic stacking with an AFM interlayer coupling; (d) those of the HT monoclinic stacking with a FM interlayer coupling. The two characteristic excitonic peaks are marked with $X_1$ and $X_2$, respectively.
Figure 6: Electronic and optical absorption spectra of bulk CrCl$_3$ in the LT rhombohedral stacking with an AFM interlayer coupling: (a) the DFT-calculated band structure. The energy of the valence band maximum is set to be zero. The optical absorption spectra with and without e-h interactions for incident light polarized in the (b) in-plane and (c) out-of-plane direction.
Figure 7 (a) Evolution of DFT, QP band gaps, and optical gap (the energy of the first bright exciton $X_1$) of CrCl$_3$ with the layer number. The dashed lines are power law fitting to the *ab initio* results. (b) Evolution of the optical absorbance of two characteristic peaks $X_1$ and $X_2$ with the layer number.
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