Electronic Structure of Chromium Trihalides beyond Density Functional Theory

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We explore the electronic band structure of free standing monolayers of chromium trihalides, CrX3, X= Cl, Br, I, within an advanced ab-initio theoretical approach based on the use of Green’s function.

With the discovery of ferromagnetic order in CrI3, the family of chromium trihalides CrX3, X= Cl, Br, I, has emerged as a new class of magnetic 2D crystals. Ferromagnetism (FM) in a monolayer CrI3 was first reported in 2017 [12], which was followed by observation of FM in CrBr3 [13]. CrCl3 [14] and many other compounds [15–22] FM is intrinsic to these systems, which distinguishes them from traditional 2D sp-electron magnets where magnetism is induced by proximity to a FM substrate. Long range-order is typically suppressed in two-dimensional magnets [13] but it can be stabilized by magneto-crystalline anisotropy, which opens an energy gap in the magnon spectra and therefore protects the FM in two dimensions [12]. Due to their layered structure and their weak inter-layer van-der-Waals interactions these systems are loosely coupled to their substrates, which provides greater flexibility in functionalizing them and controlling their properties, e.g. by varying the layer-number or by applying a gate voltage. This offers new possibilities to make spintronic devices with high accuracy and efficiency [23].

CrX3 is a two-dimensional FM insulator with FM originating from the Cr-X-Cr superexchange interaction [13,23]. Six Cr3+ ions form a honeycomb structure with D3d point group symmetry and each Cr is surrounded by six X in an octahedral geometry (see Fig. 1). The edge-sharing geometry leads to first neighbor Cr atoms sharing a pair of ligands. This enables pathways for Cr-X-Cr super-exchange. In this crystal field geometry, the Cr d splits into a t2g triplet and an eg doublet. Cr3+ has a valence of three electrons, which fill the t2g majority-spin band according to Hund’s first rule, leaving all other d bands empty. The ionic model leads to the magnetic moment on each Cr3+ ion of ∼3μB which is confirmed by ab-initio calculations. All three CrX3 compounds have FM order down to the monolayer with Curie temperatures T1 = 45 K [20], TBr = 34 K [20] and TCl = 17 K [20] and the magnetization easy axis is normal to the plane for CrI3 and CrBr3 while it is in plane for CrCl3.

Recent Density Functional Theory (DFT) calculations [23, 25] confirm the qualitative understandings derived from the ionic model. However, at quantitative level details start to differ from the fully ionic picture; one important such factor is the degree of hybridization of the t2g levels with the p bands of the ligands. This degree of hybridization depends on the ligand, its atomic weight and the number of core levels, which turns out to be a crucially important factor in determining the detailed electronic band structure. This is the main
focus of the present paper which we carefully analyze on different levels of theory beyond conventional density functional theory. Our self-consistent GW (QSGW) and BSE (QSGW) implementations are independent of the starting point and, hence, allow us to study the roles of self-consistent charge densities and self-energies in determining the key features of the electronic structures at different levels of the theory.

Molecular Picture

Within the local-density approximation (LDA), we find the spin-polarized bandgaps of the three systems to be, 1.51 eV, 1.30 eV and 1.20 eV for X=Cl, Br, I respectively, in line with prior work. The qualitative trend is easily understood in terms of the splitting between Cr d and X p atomic levels. In the simplest two-level tight-binding description, the conduction and valence levels are given by $\epsilon_{d} \pm \epsilon_{p}$, where $\epsilon_{d}$ and $\epsilon_{p}$ are respectively the Cr $t_{2g}$, d and X p atomic levels and $v$ the hybridization matrix element. This results in a gap $E_{g} = \frac{\epsilon_{d} - \epsilon_{p}}{2\sqrt{2}}$ to the lowest order in $v/\epsilon_{d} - \epsilon_{p}$. Among all three halides iodine has the most core levels resulting in its p levels having the most nodes which thus sense the attractive nucleus most weakly. It has the shallowest $\epsilon_{p}$ of the three halogen, while Cl has the deepest. Thus, the qualitative trend in the bandgap is simply understood as following from the halide $\epsilon_{p}$ energies relative to the Cr $\epsilon_{d}$. As a slight elaboration on this picture that includes magnetochemistry, we can distinguish between the majority ($t_{2g}^{\uparrow}$) and minority ($t_{2g}^{\downarrow}$) Cr d levels. For the bandgap, the picture just sketched corresponds to the ($\epsilon_{d}^{\uparrow} - \epsilon_{p}^{\downarrow}$) bond. A similar picture applies to the $\epsilon_{d}^{\downarrow} - \epsilon_{p}^{\uparrow}$ bond, but in this channel both bond and antibond are occupied, and moreover $\epsilon_{d}^{\uparrow} - \epsilon_{p}^{\downarrow}$ need not be large in comparison to $v$. Indeed the Cr $t_{2g}$ and X p levels may overlap.

Energy band picture

The molecular picture qualitatively explains the trends in the bandgap and the admixture of X p in the highest valence states in the sequence Cl$\rightarrow$Br$\rightarrow$I. However, in the 2D crystal, the molecular levels broaden into bands which can alter the trends in both the bandgap and the merging of X p with Cr $t_{2g}^{\uparrow}$ in the valence bands. The corresponding orbital resolved density of states are shown in Fig. 2. The X p level becomes more shallow, and the highest lying valence band acquires increasing anion character as can be seen both in Table 1 and in Fig. 2. Spin-orbit coupling only slightly modifies the electronic structure for CrCl$_3$ and CrBr$_3$, while for CrI$_3$ the bandgap reduces by 150 meV to 1.06 eV in the LDA.

| theory  | bandgap (eV) | spectral weight |
|---------|--------------|----------------|
| DFT     | 1.51         | 24% 31% 50%    |
| QSGW    | 6.87         | 45% 69% 84%    |
| QSGW    | 5.55         | 27% 37% 71%    |

Table I. One particle electronic band gap at different levels of theory (with spin-orbit coupling). The gap increases from LDA to QSGW level. When when ladder diagrams are added two-particle interactions via a BSE, $W \rightarrow \hat{W}$ and screening is increased. This reduces the QSGW bandgap. Right columns show fraction of spectral weight that the Halogen contributes to the total DOS within an energy window of occupied states ($-0.6,0$) eV, relative to the valence band maximum.

Remarkably, the structure of the valence band is very...
sensitive to the level of theory used, which applies to both, the band energies and wave functions. Just for CrCl$_3$, the valence band maximum is independent of the theory and is consistently pinned to the M point (Fig. 3). In the sequence Cl→Br→I, there is an overall tendency for the valence band maximum to shift from the M point to the Γ point. In the LDA this transition occurs after Br and I, while in QSGW the valence band at Γ is above M already for Br. QSGW shows the same tendency as QS$_W$, but the change is less pronounced and the transition takes place between Br and I. This is a reflection of the softening effects of the ladder diagrams on W. Recent works implementing single-shot GW, with approximations different from QS$_W$, also finds the valence band maximum in CrI$_3$ at Γ [26,38], which also seems to be confirmed by a recent ARPES study [39].

While the band maximum is roughly similar across different levels of theory, there are sharp differences in the overall electronic dispersions and wave functions. Even though the QS$_W$ band structure more closely resembles DFT than QSGW, the eigenfunctions do not. This can be seen by inspecting the square of the wave function, $|\psi|^2$, corresponding to the highest-lying state at the M point (Fig. 4). The density is plotted in real space, and the abscissa and ordinate are defined by the inverse transpose of the $2 \times 2$ matrix composed of $b_1$ and $b_2$ of

Table II. Effective masses $m^*/m_0$ at the M point (as shown in Fig. 1) for CrCl$_3$ and CrBr$_3$, and at the Γ point for CrI$_3$, for three levels of approximation. These k points correspond to the valence band maximum except for CrBr$_3$ in the QS$_W$ approximation (see Fig. 5). $m_x$ and $m_y$ correspond to orientations perpendicular and parallel to the Γ-M line, respectively. $\infty$ is a shorthand for an effective mass larger than 10$m_0$.
Figure 6. CrBr$_3$ : Square of wave function $|\psi|^2$, in real space, of the highest valence band state at the M point. All the left panels pass through a Cr plane and right panels pass through a Br plane. Top panels display constant-amplitude contours for DFT eigenfunctions. Contours are taken in half-decade increments in $|\psi|^2$, with a factor of 300 between highest contour (red) and lowest (blue). In the Cr plane, the atomic $d_{xy}$ character centered at Cr nuclei stand in sharp relief; in the Br plane the Br atomic $p$ character is evident. Middle panels show the change in $|\psi|^2$ passing from DFT to QSGW eigenfunctions; bottom panels show the corresponding change passing from DFT to QSGW$^*$ eigenfunctions. In the bottom four panels, blue→red has a similar meaning as in the top panels (increasing positive $\delta|\psi|^2$), while contours of negative $\delta|\psi|^2$ are depicted by increasing strength in the change blue→green.

Fig. I. Throughout this paper x and y are defined by aligning b$_2$ parallel to y. In this notation the M point is on the b$_2$ line, or the y axis. Contour plots in two planes are shown, passing through Cr and Br, respectively. At the LDA level (top panels), the wave function resembles an atomic $d_{xy}$ state centered at each Cr nucleus. In the Br plane some Br $p$ character is evident, and the bond is partially directed along $x$. The middle panels depict the change in $|\psi|^2$ when passing from DFT to QSGW. Two effects are prominent: first there is a transfer of spectral weight from Cr to Br (mostly green contours on Cr, red on Br) as also noted in Table I. Second, the bonding becomes more directional, forming one-dimensional chains along $x$. This reflects an enhancement of the Cr-Cr coupling mediated through the Br. It is especially apparent in the Br plane, but it is also reflected in the asymmetry between the $x$ and $y$ directions in the Cr plane. The bottom two panels show the change in $|\psi|^2$ when passing from DFT to QSGW$^*$. The effect is similar to DFT→GW, but the magnitude of the change is softened.

The directionality in the wave function is also reflected in strong anisotropy in the valence band mass at the point M, particularly in CrBr$_3$ (see Table II). By symmetry, there is no anisotropy at the $\Gamma$ point, but at M it becomes quite pronounced at the highest level of theory.

Finally, we analyze the dynamic and momentum dependent self energies $\Sigma(k, \omega)$ from QSGW and QSGW$^*$. The results were interpreted in terms of a simplified tight-binding model to elucidate the trends in Cr→Br→I, in particular the bandgap and the orbital character of the valence band. Many-body effects both enhance the bandgap, and make the valence band eigenfunctions

Figure 7. CrX$_3$ : Real part of $\Sigma(k, \omega)$ is analyzed to extract the quasi-particle renormalization factor $Z_k$ from QSGW and QSGW$^*$. (a) and (b) show the weak momentum dependence of the $Z_k$ for the top most valence band at the quasi-particle peaks at the $k$ points chose along the high symmetry directions of the first Brillouin zone for the up and down spin sectors respectively. (c) and (d) show the relative suppression of the $Z_k$ factor in QSGW$^*$, compared to QSGW for the up and down spin sectors respectively.
more directional. We also showed that addition of ladder diagrams to improve $W$ increases the screening, thus softening the many body corrections to DFT. Further we quantify the momentum dependence of the self-energies at different levels of the theory and show explicitly how excitonic correlations lead to re-normalization of the electronic bands and localization of charges. Summarily, we show how a starting point independent implementation of $GW$ and BSE leads to changes in electronic band energies and wavefunctions via complicated interplay between charge and self-energy self-consistencies in CrX$_3$.

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Appendix A: Numerical Details

Single particle calculations (DFT, and energy band calculations with the static quasiparticlized QSGW self-energy $\Sigma^0(k)$) were performed on a $16 \times 16 \times 1$ k-mesh while the (relatively smooth) dynamical self-energy $\Sigma(k)$ was constructed using a $6 \times 6 \times 1$ k-mesh and $\Sigma^0(k)$ extracted from it. For each iteration in the QSGW self-consistency cycle, the charge density was made self-consistent. The QSGW cycle was iterated until the RMS change in $\Sigma^0$ reached $10^{-5}$ Ry. Thus the calculation was self-consistent in both $\Sigma^0(k)$ and the density. Numerous checks were made to verify that the self-consistent $\Sigma^0(k)$ was independent of starting point, for both QSGW and QSGW calculations; e.g. using LDA or Hartee-Fock self-energy as the initial self energy for QSGW and using LDA or QSGW as the initial self-energy for QSGW.

For the present work, the electron-hole two-particle correlations are incorporated within a self-consistent ladder-BSE implementation with Tamm-Dancoff approximation. The effective interaction $W$ is calculated with ladder-BSE corrections and the self energy, using a static vertex in the BSE. $G$ and $W$ are updated iteratively until all of them converge and this is what we call QSGW. Ladders increase the screening of $W$, reducing the gap besides softening the LDA→QSGW corrections noted for the valence bands.

For all materials, we checked the convergence in the QSGW band gap by increasing the size of the two-particle Hamiltonian. We increase the number of valence and conduction states that are included in the two-particle Hamiltonian. We observe that for all materials the QSGW band gap stops changing once 24 valence and 24 conduction states are included in the two-particle Hamiltonian. While the gap is most sensitive to the number of valence states, 14 conducting states produces results within 2% error of the converged results from 24 conduction states.

In Tab. III we list the Cr-d occupancies for different materials at different levels of the theory.

| CrX$_3$ | DFT | QSGW | BSE |
|---------|-----|------|-----|
| CrCl$_3$ | 4.23 | 4.08 | 4.11 |
| CrBr$_3$ | 4.44 | 4.3  | 4.35 |
| CrI$_3$  | 4.66 | 4.66 | 4.64 |

Table III. Shown are the Cr-d occupancies.

Figure 8. CrBr$_3$ and CrCl$_3$: Scaling of the one particle band gap from QSGW with vacuum size $L$.

Appendix B: Vacuum Distance Scaling

Periodic boundary conditions were used in all directions, introducing an unwanted coupling between CrBr$_3$ slabs. To minimize this coupling a vacuum of length $L$ was inserted between slabs, and $L$ was varied.

As is well known, the QSGW is known to fix the infamous ‘gap problem’ in insulators, we observe that the band gap increases significantly in all three compounds within QSGW: 6.87 eV in Cl, 5.73 eV in Br and 3.25 eV in I (see [1]). We change the vacuum length from 10 Å to 80 Å, and observe the scaling of the band gap with vacuum size ($L$). We observe an almost perfect 1/L scaling (see Fig. 3) of the gap as noted earlier in a separate work on V$_2$O$_5$ [13]. This also allows us to check the dielectric constant ($\epsilon_\infty$) and its vacuum correction. In the limit of a purely free standing monolayer all three direc-
tional components of the macroscopic dielectric response in the static limit approaches 1, suggesting the absence of screening. We use this vacuum length (60 Å) for the rest of the discussions in the present work.

Appendix C: Full Band Structures

In Fig. 1 we show the band structures for all materials over larger energy windows.

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Figure 9. CrX₃: Top panels is for X= Cl, middle one for Br and bottom one for I. The colors correspond to X-pₓ + pᵧ (red), X pₓ (green), Cr-d (blue) (From left to right: DFT, QS\textit{GW} and QS\hat{\textit{GW}} respectively).