Supplementary Information

Electronic excitations and spin interactions in chromium trihalides from embedded many-body wavefunctions

Ravi Yadav, Lei Xu, Michele Pizzochero, Jeroen van den Brink, Mikhail I. Katsnelson, and Oleg V. Yazyev

†Institute of Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
‡National Centre for Computational Design and Discovery of Novel Materials (MARVEL), Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
¶Institute for Theoretical Solid State Physics, IFW Dresden, Helmholtzstr. 20, 01069 Dresden, Germany
§School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, United States
∥Institute for Theoretical Physics and Würzburg-Dresden Cluster of Excellence ct.qmat, Technische Universität Dresden, 01069 Dresden, Germany
⊥Institute for Molecules and Materials, Radboud University, 6525AJ Nijmegen, The Netherlands

E-mail: oleg.yazyev@epfl.ch
Supplementary Note 1: One-site quantum chemistry calculations

Multiplet structures (Table 1 in the main text) and intra-site magnetic interactions (Table 2 in the main text) are obtained using the finite-size model shown in Figure 1(b) in the main text. This model consists of a central unit that comprises a single CrX₆ (X=Cl, Br, I) octahedron treated with many-body wavefunctions, surrounded by the three nearest-neighbor octahedra. These latter octahedra account for the finite charge distribution in the vicinity of the central unit and are treated at the Hartree-Fock level. The remaining crystalline environment is modeled by arrays of point charges reproducing the ionic Madelung potential in the cluster region. All-electron basis functions of quadruple-zeta quality supplemented with f-polarization functions are used for the Cr³⁺ ion in the reference unit. The Cr³⁺ ions centered in the three nearest-neighbor octahedra are described as closed-shell Sc³⁺ ions with an all-electron basis set of triple-zeta quality. For Cl and Br ligands in CrCl₃ and CrBr₃, respectively, an all-electron basis set of triple-zeta quality is employed. The Cl and Br atoms in the octahedra surrounding the reference unit are represented with an all-electron basis sets of double-zeta quality. In the case of CrI₃, energy-consistent relativistic pseudopotentials along with quadruple-zeta quality basis sets for the valence shells of I atoms in the reference octahedron, while energy-consistent relativistic pseudopotentials along with triple-zeta quality basis sets are used for the I atoms in the nearest-neighbor octahedra.

CASSCF wavefunctions are variationally optimized for an average of low-lying seven quartet and five doublet states. In the subsequent MRCI calculations, we account for dynamic correlation effects by including single- and double-excitations involving the t₂g orbitals of the Cr³⁺ ions and the p valence shells of halogen ligands within the central unit. Calculations are performed using the MOLPRO package.
Supplementary Note 2: Quantum chemistry simulation of XAS and RIXS spectra

The simulation of XAS and RIXS spectra (Figure 2 in the main text) is carried out at the CASSCF level using the finite-size model shown in Supplementary Figure 1(a). This model consists of a single Cr$X_6$ ($X = \text{Cl, I}$) octahedron surrounded by an array of point charges to reproduce the ionic Madelung potential of the crystalline environment. For the Cr$^{3+}$ ion, we use an all-electron triple-zeta Douglas-Kroll basis sets with diffuse functions, along with weighted core-valence sets aug-cc-pwCVTZ-DK to describe core-valence correlation effects. For the halogen ligands, we employ an all-electron triple-zeta Douglas-Kroll basis sets with diffuse functions aug-cc-pVTZ-DK. To compute the Cr$^{3+}$ 3$d^3$ valence-excited states at the CASSCF level, we consider an active space comprising five 3$d$ orbitals ($t_{2g}$ and $e_g$) and three electrons. Ten spin-quartet and forty spin-doublet valence states associated with this manifold are obtained in the state-averaged complete active space self-consist field optimization. The Pipek-Mezey localization scheme, as implemented in Ref. 6, is adopted for localizing the orbitals of the halogen atoms. All these valence-excited states enter the spin-orbit coupling calculations at the CASSCF level. Spin-orbit coupling (SOC) effects are accounted for by diagonalizing the Breit-Pauli spin-orbit matrix in the basis of the scalar relativistic (SR) states. Calculations are performed with the MOLPRO package. The source code is modified and compiled in order to compute up to 800 SR states in the CASSCF module, thus allowing these states to be coupled in the subsequent SOC calculations. The resulting $d$ excitation energies up to 4 eV are listed in Supplementary Tables 2 and 3.

For the determination of the $2p^53d^4$ core-hole states, which are the final states in the L-edge X-ray absorption process and the intermediate states in the L-edge RIXS process, the active space is defined in terms of nine electrons and five Cr 3$d$ orbitals, in addition to three Cr 2$p$ orbitals. The self-consistent field optimization is performed for an average of 15 spin sextet, 160 spin quartet, and 325 spin doublet states associated with the $2p^63d^3$ and $2p^53d^4$ configurations (the first 10 quartet and 40 doublet states in lower energies correspond to the
2p⁶3d³ configurations). On top of this CASSCF reference, in the subsequent configuration interaction treatment, the occupation restriction of Cr 2p orbitals is defined as five electrons in order to exclude the 2p⁶3d³ valence-excited states, such that the corresponding CASSCF wavefunction including only 15 spin sextet, 150 spin quartet and 285 spin doublet states associated with the 2p⁵3d⁴ configurations. All these core-hole states further enter the SOC calculations, leading to a total of 1260 spin-orbit-coupled states.

The dipole transition matrix elements between wavefunctions expressed in terms of the nonorthogonal orbitals for the 3d³ and 2p⁵3d⁴ groups of states are derived according to the procedure described in Ref. 10. The XAS and RIXS scattering geometry and the directions of polarization are adjusted according to the setup of experimental measurements described in Ref. 11 also shown in Supplementary Figure 1(b). Linearly polarized x-rays are incident at an angle θ with the plane of the sample, this latter being oriented in such a way that the c-axis points to the surface normal. The scattering angle α between the incoming and outgoing light beams is set to 40° and the incident angle θ to 50°. The incoming light is linearly polarized, either perpendicularly to the scattering plane (σ polarization) or within the scattering plane (π polarization). For the outgoing radiation, we carry out a summation over the two independent polarization directions.

For the analysis of the ab initio wavefunctions, we rely on a local coordinate frame with the z component pointing along c axes of the CrX₃ unit cell. The rotation of the σ, π and π’ (introduced as outgoing π polarization) vectors as function of the angle θ is described by the following geometrical relations

\[ \vec{D}_\sigma = \vec{D}_y, \]
\[ \vec{D}_\pi = \vec{D}_x \sin \theta + \vec{D}_z \cos \theta, \]
\[ \vec{D}_{\pi'} = \vec{D}_x \sin(\theta + \alpha) + \vec{D}_z \cos(\theta + \alpha), \]

(1)

where \( \vec{D}_{x,y,z} = e \cdot \vec{R}_{x,y,z} \) are the dipole transition matrix elements. The expression of the
X-ray absorption cross section\textsuperscript{12,13} involves the summation over the ground state and core-excited states

\[ I^{XAS}(\hbar \omega, \epsilon, \theta) = 4\pi^2 \alpha \hbar \omega \sum_j \sum_l \frac{1}{g_{gs}} \left| \langle \Psi^l_{c*} \left| \vec{D}_{\epsilon} \right| \Psi^j_{gs} \rangle \right|^2 \times \frac{\Gamma_{c*}/2\pi}{(E_{gs} + \hbar \omega - E^l_{c*})^2 + (\Gamma_{c*})^2/4}. \]  

(2)

The RIXS double differential cross-section is obtained by summing over the outgoing polarization directions\textsuperscript{12,13}

\[ I^{RIXS}(\hbar \omega, \hbar \omega', \epsilon, \theta) = \frac{d^2 \sigma^{RIXS}_{k,e}}{d\Omega' d\hbar \omega'} = \frac{\alpha^2 \hbar^2}{e^4 c^2} \omega \omega' \sum_{\epsilon'} \sum_j \sum_{g_{gs}} \sum_{k} \left| \sum_{l} \langle \Psi^k_{fs} \left| \vec{D}_{\epsilon'} \right| \Psi^l_{c*} \rangle \langle \Psi^l_{c*} \left| \vec{D}_{\epsilon} \right| \Psi^j_{gs} \rangle \right|^2 \times \frac{\Gamma_{fs}/2\pi}{(E_{gs} + \hbar \omega - E^k_{fs} - \hbar \omega')^2 + (\Gamma_{fs})^2/4}. \]  

(3)

In Equations 2 and 3, \( \alpha \) is the fine structure constant, \( \hbar \omega \) is the energy of the incoming photons, \( \hbar \omega' \) is the energy of outgoing photons, while \( \epsilon \) and \( \epsilon' \) are polarizations of the incoming and outgoing photons, respectively. For \( I^{XAS} \), the summations take into account all core-hole (intermediate) states and the possible degeneracy of the ground state \( g_{gs} \). For \( I^{RIXS} \), the summations take into account all core-hole \( 2p^53d^4 \) (intermediate) states and \( 2p^63d^3 \) (final) states and the possible degeneracy of the ground state, \( g_{gs} \). The lifetimes of the core-excited and valence-excited states are \( \Gamma_{c*} \) and \( \Gamma_{fs} \), respectively. The natural widths \( \Gamma_{c*} \) are set to 0.4 eV for both CrCl\textsubscript{3} and CrI\textsubscript{3}. The natural widths \( \Gamma_{fs} \) are set to 0.3 eV for CrCl\textsubscript{3} and 0.35 eV for CrI\textsubscript{3}, that is, the same values adopted in the reference experimental work of Ref.\textsuperscript{11}. The RIXS spectra of \( \pi \)-polarization direction are directly compared to the corresponding experimental spectra.\textsuperscript{11}
Supplementary Note 3: Two-site quantum chemistry calculations

Inter-site magnetic interactions (Table 3 in the main text) are obtained using the finite-size model shown in Figure 1(c) in the main text. This model consists of a central unit that comprises two edge-sharing Cr$_2$X$_{10}$ ($X =$ Cl, Br, I) octahedra treated with many-body wavefunctions, surrounded by the four nearest-neighbor octahedra. These latter octahedra account for the finite charge distribution in the vicinity of the central unit and are treated at the Hartree-Fock level. The remaining crystalline environment is modeled by arrays of point charges reproducing the ionic Madelung potential in the cluster region. All-electron basis functions of quadruple-zeta quality were used for the Cr$^{3+}$ ions in the two-octahedra central unit. The bridging Cl and Br ligands are modeled with an all-electron quintuple-zeta quality basis set, while, for the bridging I ligand, energy-consistent relativistic pseudopotentials along with quintuple-zeta quality basis sets for the valence shells are employed. The remaining ligand atoms in the central region are described using a triple-zeta quality basis set in the case of Cl and Br atoms, and energy-consistent relativistic pseudopotentials along with triple-zeta quality basis sets in the case of I atoms. Cr$^{3+}$ ions centered at the octahedra adjacent to the reference unit are described as closed-shell Sc$^{3+}$ ions and an all-electron triple-zeta basis functions. The ligands belonging to these octahedra are modeled with double-zeta quality basis set for the Cl and Br atoms and energy-consistent relativistic pseudopotentials along with double-zeta quality basis sets for the I atoms.

CASSCF wavefunctions are variationally optimized for an average of one septet, quintet, triplet and singlet states, which are mainly of $t_{2g}^3 - t_{2g}^3$ character. In addition to $t_{2g}^3 - t_{2g}^3$ direct exchange between the nearest-neighbor sites, these wavefunctions consist of a finite-weight contribution that stems from inter-site excitations of the $t_{2g}^4 - t_{2g}^4$ type. MRCI calculations account for single- and double-excitations involving the $t_{2g}$ orbitals of the Cr$^{3+}$ ions and the $p$ valence shells of the bridging halogen ligands. In the treatment of spin-orbit effects, one septet, quintet, triplet and singlet states are considered, both in CASSCF and MRCI approaches. Calculations are performed using the MOLPRO package.
**Supplementary Table 1:** Effect of in-plane compressive and tensile lattice strain ($\epsilon$) on the multiplet structure of CrCl$_3$, as obtained at the MRCI level of theory, using the finite-size model shown in Figure 1(b) in the main text. Energies are given in eV and referenced to the ground state.

|        | $\epsilon = -2\%$ | $\epsilon = 0\%$ | $\epsilon = +2\%$ |
|--------|--------------------|--------------------|--------------------|
| $^4A_2$ ($t^3_{2g}e^0_g$) | 0.00               | 0.00               | 0.00               |
| $^4T_2$ ($t^2_{2g}e^3_g$) | 1.79, 1.79, 1.85   | 1.67, 1.68, 1.70   | 1.38, 1.45, 1.50   |
| $^2E$ ($t^3_{2g}e^0_g$)    | 2.39, 2.40         | 2.21, 2.21         | 2.36, 2.37         |
| $^4T_1$ ($t^2_{2g}e^1_g$) | 2.78, 2.80, 2.84   | 2.50, 2.52, 2.59   | 2.25, 2.35, 2.41   |
| $^2T_1$ ($t^3_{2g}e^0_g$) | 2.49, 2.51, 2.52   | 2.31, 2.33, 2.34   | 2.48, 2.49, 2.51   |
| $^2T_1$ ($t^2_{2g}e^1_g$) | 3.35, 3.36, 3.38   | 3.03, 3.05, 3.07   | 3.23, 3.26, 3.28   |
| $^2A_1$ ($t^2_{2g}e^1_g$) | 3.72               | 3.47               | 3.42               |
| $^2T_1$ ($t^2_{2g}e^1_g$) | 3.99, 4.01, 4.04   | 3.76, 3.77, 3.78   | 3.67, 3.70, 3.75   |
| $^4T_1$ ($t^1_{2g}e^2_g$) | 4.43, 4.44, 4.48   | 4.05, 4.07, 4.08   | 3.88, 3.93, 3.97   |
Supplementary Figure 1: (a) Embedding model used in the simulation of the XAS and RIXS spectra. Blue and orange spheres represent chromium and halogen atoms, respectively. The model is embedded in an array of points charges (not shown) to ensure charge neutrality and reproduce the crystalline environment. (b) RIXS scattering geometry used in our \textit{ab initio} calculations, analogous to the experimental setup adopted in Ref. 11.

Supplementary Figure 2: Convergence of the diagonal elements of the dipolar anisotropy tensor $D_{\text{dip}}^{\alpha\alpha}$ per transition metal ion for (a) CrCl$_3$, (b) CrBr$_3$ and (c) CrI$_3$ as a function of cutoff distance $r_{\text{cut}}$. 
**Supplementary Table 2:** Relative energies (in eV) at the CASSCF and CASSCF+SOC level of theory for the Cr$^{3+}$ $3d^3$ multiplet structure in CrCl$_3$, as obtained using the finite-size model shown in Supplementary Figure 1(a). Each CASSCF+SOC value denotes a spin-orbit doublet. For the $^4T$ and $^2T$ states, only the lowest and highest components are given.

|       | CASSCF | CASSCF+SOC |
|-------|--------|------------|
| $^4A_2(t_{2g}^3)$ | 0.00   | 0.00       |
| $^4T_2(t_{2g}^2e_{g}^1)$ | 1.62; 1.66; 1.66 | 1.61 ... 1.67 |
| $^2E(t_{2g}^3)$ | 2.27; 2.27 | 2.27; 2.28 |
| $^2T_1(t_{3g}^3)$ | 2.36; 2.41; 2.41 | 2.36 ... 2.42 |
| $^4T_1(t_{2g}^2e_{g}^1)$ | 2.56; 2.56; 2.67 | 2.55 ... 2.67 |
| $^2T_2(t_{3g}^3)$ | 3.19; 3.19; 3.29 | 3.18 ... 3.30 |
| $^2A_1(t_{2g}^3e_{g}^1)$ | 3.53 | 3.54 |
| $^2T_1(t_{2g}^2e_{g}^1)$ | 3.75; 3.83; 3.83 | 3.75 ... 3.84 |
| $^2T_2(t_{2g}^2e_{g}^1)$ | 3.95; 3.95; 4.01 | 3.93 ... 4.00 |

**Supplementary Table 3:** Relative energies (in eV) at the CASSCF and CASSCF+SOC level of theory for the Cr$^{3+}$ $3d^3$ multiplet structure in CrI$_3$, as obtained using the finite-size model shown in Supplementary Figure 1(a). Each CASSCF+SOC value denotes a spin-orbit doublet. For the $^4T$ and $^2T$ states, only the lowest and highest components are given.

|       | CASSCF | CASSCF+SOC |
|-------|--------|------------|
| $^4A_2(t_{2g}^3)$ | 0.00   | 0.00       |
| $^4T_2(t_{2g}^2e_{g}^1)$ | 1.37; 1.41; 1.41 | 1.36 ... 1.41 |
| $^2E(t_{2g}^3)$ | 2.19; 2.19 | 2.19; 2.19 |
| $^4T_1(t_{2g}^2e_{g}^1)$ | 2.22; 2.22; 2.29 | 2.22 ... 2.30 |
| $^2T_1(t_{3g}^3)$ | 2.29; 2.33; 2.33 | 2.30 ... 2.33 |
| $^2T_2(t_{3g}^3)$ | 2.99; 2.99; 3.09 | 2.99 ... 3.09 |
| $^2A_1(t_{2g}^3e_{g}^1)$ | 3.22 | 3.22 |
| $^2T_1(t_{2g}^2e_{g}^1)$ | 3.37; 3.45; 3.45 | 3.37 ... 3.45 |
| $^2T_2(t_{2g}^2e_{g}^1)$ | 3.59; 3.59; 3.63 | 3.58 ... |
| $^4T_1(t_{2g}^1e_{g}^2)$ | 3.59; 3.79; 3.79 | ... 3.79 |
| $^2E(t_{2g}^3e_{g}^1)$ | 3.91; 3.91 | 3.90; 3.92 |
**Supplementary Table 4:** \( \bar{D}_{\text{dia}} \) tensor as obtained from MRCI calculations in the units of \( cm^{-1} \) for \( \text{Cr}X_3 \) (\( X = \text{Cr, Br, I} \)).

|          | CrCl\(_3\)          | CrBr\(_3\)          | CrI\(_3\)          |
|----------|---------------------|---------------------|---------------------|
|          | \( \begin{bmatrix} 0.176 & -0.006 & -0.012 \\ -0.006 & 0.194 & 0.009 \\ -0.012 & 0.009 & -0.123 \end{bmatrix} \) | \( \begin{bmatrix} 0.360 & -0.003 & 0.002 \\ -0.003 & 0.442 & 0.012 \\ 0.002 & 0.012 & -0.304 \end{bmatrix} \) | \( \begin{bmatrix} 0.642 & -0.018 & -0.009 \\ -0.018 & 0.575 & 0.011 \\ -0.009 & 0.011 & -0.3596 \end{bmatrix} \) |

**Supplementary Table 5:** Heisenberg exchange parameter (in meV) in \( \text{Cr}X_3 \) (\( X = \text{Cr, Br, I} \)) obtained by considering the isotropic bilinear Heisenberg Hamiltonian (i.e., neglecting the biquadratic and inter-site anisotropic terms in Equation 3 of the main text).

|          | CrCl\(_3\) | CrBr\(_3\) | CrI\(_3\) |
|----------|------------|------------|------------|
|          | CASSCF     | MRCI       | CASSCF     | MRCI       | CASSCF     | MRCI       |
| \( J_1 \) (meV) | \(-0.69\)  | \(-1.08\)  | \(-0.67\)  | \(-1.28\)  | \(-0.66\)  | \(-1.42\)  |
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