Abstract

The marked interplay between the crystalline, electronic, and magnetic structure of atomically thin magnets has been regarded as the key feature for designing next-generation magneto-optoelectronic devices. In this respect, a detailed understanding of the microscopic interactions underlying the magnetic response of these crystals is of primary importance. Here, we combine model Hamiltonians with multireference configuration interaction wavefunctions to accurately determine the strength of the spin couplings in the prototypical single-layer magnet CrI$_3$. Our calculations identify the (ferromagnetic) Heisenberg exchange interaction $J = -1.44$ meV as the dominant term, being the inter-site magnetic anisotropies substantially weaker. We also find that single-layer CrI$_3$ features an out-of-plane easy axis ensuing from a single-ion anisotropy $A = -0.10$ meV, and predict $g$-tensor in-plane components $g_{xx} = g_{yy} = 1.90$ and out-of-plane component $g_{zz} = 1.92$. In addition, we assess the performance of a dozen widely used density functionals against our accurate correlated wavefunctions calculations and available experimental data, thereby establishing reference results for future first-principles investigations. Overall, our findings offer a firm theoretical ground to recent experimental observations.

1. Introduction

The first isolation of graphene back in 2004 represented a paradigm shift in condensed matter physics [1]. This discovery sparked a wealth of unexplored research directions, most notably the search for novel two-dimensional crystals [2–4], together with their controlled stacking for the assembling of van der Waals heterostructures in a layer-by-layer fashion [5–7]. Since then, the library of atomically thin materials is rapidly expanding, first starting from those parent 3D crystals which can be peeled off to the 2D limit (e.g. transition metal dichalcogenides [8] or hexagonal boron nitride [9]) and subsequently evolving into the synthesis of artificial monolayers (e.g. silicene [10–12] or its heavier group IV analogs [13, 14]), eventually covering a broad range of properties, including metals [15, 16], semi- and superconductors [17–21], as well as trivial or topological insulators [22–24].

Of particular interest in this context is the emergence of correlated electronic phases in ultrathin nanostructures, being the observation of magnetically ordered phases in some of these systems arguably the most striking of such phenomena [20, 21, 25]. Indeed, while magnetism in lattices of reduced dimensionality has hitherto been ascribed to native or engineered impurities [26–29], the isolation and characterization of two-dimensional CrI$_3$ (along with other ultrathin magnets, e.g. Fe$_2$GeTe$_2$, Cr$_2$Ge$_2$Te$_6$, FePSe$_3$, to mention but a few) have unambiguously demonstrated the realization of a long-range, intrinsic magnetism in atomically thin crystals [30–35]. This achievement is made possible as a consequence of the pivotal role played by the magneto-crystalline anisotropy, which preserves the magnetic order down to the monolayer limit, as explained by the Mermin-Wagner theorem [36]. Experimentally, ultrathin films of CrI$_3$ have been obtained upon exfoliation of their bulk counterpart, an insulating layered
crystal exhibiting magnetic order up to 61 K [30]. Interestingly, a competition between coexisting intralayer ferromagnetic and inter-layer antiferromagnetic exchange interactions in few-layer samples has been unraveled, giving rise to a thickness-dependent magnetic response [30]. In addition, switching between these two exchange interactions can widely be engineered in atomically thin samples, e.g. through applied external pressure [37, 38], electrostatic-gate control [39, 40], or lattice deformations [41]. Altogether, this pronounced interplay between crystalline, magnetic, and electronic structures paves the way towards prospective magneto-optoelectronic devices based on thin films of CrI$_3$ [34, 42–45]. In this vein, establishing the microscopic spin physics governing this system is of paramount importance.

On the computational side, the accurate description of magnetic interactions in two-dimensional CrI$_3$ comes as a challenging task, mainly due to the inherent inadequacy of semilocal density functionals in properly capturing electron-electron interactions. Several approximations have been devised for describing localization effects (e.g. Hubbard-corrected or hybrid density functionals), but they invariably rely on adjustable parameters, which in turn are system- and property-dependent and cannot be determined following universal protocols. These limitations can effectively be overcome by relying on many-body wavefunctions, which, though computationally demanding, enable to recover a substantial amount of the correlation energy. In addition, we stress that the nature and strength of numerous magnetic interactions occurring in monolayers of CrI$_3$ yet remain largely unknown, and their determination is essential in order to provide a detailed comprehension of the intriguing spin physics hosted by this crystal. Here, we report on the first ab initio quantum chemistry investigation of magnetic interactions in two-dimensional CrI$_3$ by carrying out multi-reference configuration interaction calculations. We further exploit such benchmark results to assess the performances of several density-functional approximations. Overall, our work portrays an unprecedentedly accurate picture of the spin interactions in monolayer CrI$_3$ which is instrumental in understanding its magnetic properties.

2. Crystal and electronic structure

We start by briefly reviewing the intertwining between the crystalline and electronic structure of CrI$_3$. Down to the monolayer limit, CrI$_3$ consists of a honeycomb plane of Cr atoms sandwiched between two planes of I atoms, as shown in figure 1. Each Cr atom exhibits a six-fold coordination, which gives rise to edge-sharing octahedra. According to a purely ionic argument, the Cr atoms present a formal oxidation state of +3 and a resulting valence electron configuration $3d^54s^1$. As a consequence of the crystal field associated with the octahedral environment, a splitting of the $d$ orbitals into three triply occupied $t_{2g}$ states and two higher-energy empty $e_g$ states occurs, the extent of which has not been ascertained yet and will be given in the following. However, on the basis of the Hund’s rule, such an electron occupation yields $S = 3/2$ [46]. This has been experimentally confirmed in single- and multilayer CrI$_3$, where a magnetization saturation of 3 $\mu_B$ per Cr$^{3+}$ ion has been observed [30, 45].

The scenario mentioned above suggests that Cr$^{3+}$ ions act as magnetic centers, which interact via non-magnetic iodine ligands through the so-called superexchange coupling theoretically proposed by P.W. Anderson [47]. On the experimental side, the hysteretic features emerging in magneto-optical Kerr effect (MOKE) measurements of single-layer CrI$_3$ are the hallmarks of a ferromagnetic spin order [30], which, given the Cr-I-Cr bond angle of $\sim$90°, is consistent with the Goodenough-Kanamori rule [48–50, 51]. Furthermore, such experimental investigations revealed that single-layer CrI$_3$ displays an out-of-plane easy axis and a critical temperature of 45 K, only slightly lower than its three-dimensional counterpart [30]. In the following, we accurately quantify the magnetic interactions underlying these effects.

3. Spin Hamiltonian from many-body wavefunctions

We consider a generalized, bilinear model Hamiltonian, which captures intra- as well as inter-site
exchange interactions between the \(i\)th and \(j\)th nearest-neighbor centers with spins \(\mathbf{S}_i\) and \(\mathbf{S}_j\), respectively. Such a Hamiltonian reads as

\[
\mathcal{H} = J \sum_{i<j} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_i \mathbf{I} \cdot \mathbf{S}_i + \sum_i AS_{i^+}^2 + \sum_{i<j} \mu_B \mathbf{g} \cdot \mathbf{S}_i \times \mathbf{S}_j
\]

with \(J\) corresponding to the isotropic Heisenberg exchange, \(\mathbf{I}\) the symmetric anisotropic tensor, \(A\) the single-ion anisotropy parameters, \(\mathbf{g}\) the \(g\)-tensor in the Zeeman term that accounts for the interaction of the lattice with the external magnetic field \(\mathbf{B}\), and \(\mathbf{D}\) the antisymmetric Dzyaloshinsky-Moriya interaction parameter. This latter term vanishes due to the inversion symmetry. Assuming a local Kitaev frame according to which the axis is perpendicular to the \(z\) axis, we perform multireference configuration interaction (MRCI) calculations to obtain the average of low-lying septet, quintet, triplet, and singlet states. Next, MRCI calculations are performed including single and double excitations involving the \(d\) \(t_{2g}\) valence shells of \(\text{Cr}^{3+}\) ion and the \(p\) valence shells of the bridging I ligands (see Supplementary Note 1). We anticipate that, while inessential for the intra-site magnetic interactions, an MRCI treatment of the electron correlation is crucial to accurately determine the inter-site magnetic parameters due to the important role of the super-exchange coupling, being this effect neglected in the CASSCF wavefunctions. Finally, we quantify the nature and magnitude of the magnetic parameters in CrI by mapping the resulting ab initio Hamiltonian onto the model Hamiltonian of equation (1) through the well-established procedure detailed in reference [56].

Before moving to spin interactions, we elucidate the electronic structure of the magnetic centers in single-layer CrI. The relative energies of the multiplet structure of the \(3d^3\) orbitals of the \(\text{Cr}^{3+}\) ion are given in Table 1. As discussed above, according to the crystal-field theory, one should expect a singlet ground state for the \(\text{Cr}^{3+}\) ion residing in an octahedral environment. This is confirmed by our correlated wavefunction calculations, which found \(4A_2(\mathbf{t}_{2g}^6\epsilon^3)\) to be the lowest-energy configuration. The higher-energy terms \(4T_2(\mathbf{t}_{2g}^6\epsilon^3)\) and \(2E(\mathbf{t}_{2g}^6\epsilon^3)\) can interact with the \(4A_2(\mathbf{t}_{2g}^6\epsilon^3)\) ground state in the presence of spin–orbit coupling, inducing a zero-field splitting of the spin quartet into \(m_s = \pm 1/2\) and \(m_s = \pm 3/2\) Kramers doublets, respectively. Our CASSCF results obtained including all 3d orbitals at the Cr site in the active space indicate that the \(4T_2(\mathbf{t}_{2g}^6\epsilon^3)\) configuration lies 1.48–1.49 eV higher in energy than the \(4A_2\) one. This quantity slightly increases to 1.62–1.67 eV at the MRCI level. We notice that the spin–orbit interactions affect the splittings given in Table 1 by only \(\sim 0.1\) meV.

The relative energies of the \(\text{Cr}^{3+}\) \(3d^3\) multiplet structure obtained with the many-body wavefunction CASSCF and MRCI methods on finite-size model systems. Energies are given in eV.

| Multiplet Structure | CASSCF | MRCI |
|---------------------|--------|------|
| \(4A_2(\mathbf{t}_{2g}^6\epsilon^3)\) | 0.00 | 0.00 |
| \(4T_2(\mathbf{t}_{2g}^6\epsilon^3)\) | 1.48; 1.49; 1.49 | 1.62; 1.67; 1.67 |
| \(2E(\mathbf{t}_{2g}^6\epsilon^3)\) | 2.34; 2.34 | 2.22; 2.22 |
| \(4T_2(\mathbf{t}_{2g}^6\epsilon^3)\) | 2.35; 2.42; 2.42 | 2.50; 2.58; 2.58 |
| \(2T_2(\mathbf{t}_{2g}^6\epsilon^3)\) | 2.45; 2.46; 2.46 | 2.33; 2.34; 2.34 |

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results of reference [37], in which a Kitaev interaction of magnitude comparable to $J$ was reported. It is worth noticing that the CASSCF method largely underestimates the inter-site exchange couplings, as compared to the MRCl method. This is especially true for the isotropic Heisenberg exchange, which at the CASSCF level is found to be 0.82 meV lower than that obtained at the MRCl level. This difference points towards (and, to some extent, quantifies) the significant role of the super-exchange channels between the $Cr^3^+$ ions occurring via the bridging I ligands in governing the magnetism of single-layer CrI$_3$.

We next discuss intra-site magnetic interactions. Even in the absence of magnetic field, the interplay between the spin–orbit coupling and the crystal field lifts the degeneracy of the electronic ground state for $S > 1/2$. The extent of such a zero-field splitting is quantified by the single-ion anisotropy. We derive this quantity by following the effective-Hamiltonian methodology presented in reference [60]. In this approach, the mixing of the $^4A_2^\pi$ components with the higher-energy states is treated in a perturbative manner, and the spin–orbit wavefunctions related to the high-spin $t^4_2g$ configurations are projected onto the $^4A_2^\pi$ $|S,M_S\rangle$ states. We then construct the effective Hamiltonian $\hat{H}_{\text{eff}} = \Sigma_k E_k (\tilde{\psi}_k | \tilde{\psi}_k \rangle$, where $\tilde{\psi}_k$ are the ortho-normalized projections of the low-lying quartet wavefunctions with corresponding eigenvalues $E_k$. A one-to-one correspondence between $\hat{H}_{\text{eff}}$ and the model Hamiltonian $\hat{H}_{\text{mod}} = \hat{S} \cdot \hat{A} \cdot \hat{S}$ leads to the $\hat{A}$ tensor, which, upon diagonalization, yields the commonly used axial parameter $A$ [60]. We obtain $A = -0.10$ meV, with the magnetic axis lying in the direction normal to the lattice plane. The negative sign of $A$ indicates that the easy axis of magnetization points along the magnetic axis, in accord with experiments [30]. We remark that this value is less than half than that obtained in reference [57] by means of density functional theory.

Finally, we quantify the response of the Cr sites to the external magnetic field $\vec{B}$ through the determination of the g-tensor appearing in the Zeeman term of the spin Hamiltonian in equation (1). This quantity can readily be accessed in experiments, i.e. electron spin resonance measurements [61]. From the quantum chemistry point of view, the multi-configuration wavefunctions are known to provide an accurate description of the spin–orbit multiplets. This allows one to evaluate the matrix elements of the total magnetic moment operator $\mu = -\mu_0 (g_\Sigma \vec{S} + \vec{L})$ in the basis of the multiplet eigenstates, with $\hat{L}$ and $\hat{S}$ being the angular momentum and spin operators, whose expectation values are obtained for a given Cr site, and $g_\Sigma$ being the free-electron Landé factor. The Zeeman Hamiltonian can be written in terms of total moment $\mu$ as $H_Z = -\mu \cdot \vec{B}$. In order to obtain the g-tensor, such $H_Z$ is mapped onto the Zeeman model Hamiltonian presented in equation (1) through the well-established procedure devised in references [62, 63]. To this end, we rely on an active space that encompasses all the five $d$ orbitals of Cr (with 3 electrons). We construct the initial wavefunction by averaging over the seven quartets and five doublets listed in table 1. We find an anisotropic g-tensor, with $g_{xx} = g_{yy} = 1.90$ and $g_{zz} = 1.92$, where the $x = y (z)$ axis lies in (perpendicular to) the CrI$_3$ lattice plane, in line with recent experimental observations [61].

### 4. Magnetic interactions from density functional theory

With the accurate many-body wavefunction results at hand, we are in a position to assess the performance of widely used exchange and correlation functionals in describing selected magnetic interactions occurring in single-layer CrI$_3$. We address by means of first-principles calculations in a periodic setting the isotropic Heisenberg exchange $J$, the magnetic anisotropy $E_{\text{MAE}}$, and provide an estimate of the Curie temperature ($T_C$), for which the experimental value (45 K) is available. Specifically, we climb the ladder of Density Functional Theory (DFT) by considering the local density approximation using the Ceperley and Alder (CA) parametrization [64], several flavors of the generalized gradient approximation (PBE [65], PBEsol [66], PW91 [67], revPBE [68]) and its Hubbard-corrected extension DFT+U [69] (with $1.0$ eV $\leq U \leq 3.0$ eV), some representative examples of meta generalized gradient approximations (SCAN [70], TPSS, and RTPSS [71]), and hybrid Fock-exchange/density-functionals, both in their plain (PBE0 [72]) and range-separated (HSE03 [73] and HSE06 [74]) formalisms. Further details of our DFT calculations are provided in the Supplementary Note II.

The main finding of our MRCI investigation is that, among the inter-site interactions listed in table 2, the dominant one is the Heisenberg exchange coupling. This indicates that single-layer CrI$_3$ can effectively be described as an isotropic Heisenberg magnet. Hence, we map the first-principles results onto the isotropic Heisenberg spin Hamiltonian $\hat{H} = J \sum_{i,j} \hat{S}_i \cdot \hat{S}_j$. 

### Table 2. Magnetic exchange coupling parameters in single-layer CrI$_3$: isotropic Heisenberg magnetic exchange ($J$), symmetric anisotropic ($\Gamma_{xy}$, $\Gamma_{yx}$, and $\Gamma_{xz}$), and Kitaev ($K$) interactions along with single-ion anisotropy ($A$) and the components of the $g$-tensor ($g_{xx}, g_{yy}, g_{zz}$) calculated by means of CASSCF and MRCI methods.

| Magnetic exchange coupling | CASSCF | MRCl |
|---------------------------|--------|------|
| $J$ (meV)                 | $-0.62$| $-1.44$|
| $K$ (meV)                 | $-0.01$| $-0.08$|
| $\Gamma_{xy}$ (meV)      | $1.0 \times 10^{-3}$| $2.3 \times 10^{-3}$|
| $\Gamma_{yx}$ (meV)      | $-2.1 \times 10^{-4}$| $1.2 \times 10^{-3}$|
| $\Gamma_{xz}$ (meV)      | $0.00$ | $1.90$ |
| $\Gamma_{yz}$ (meV)      | $1.92$ | $1.92$ |
| $g_{xx} = g_{yy}$        | $1.90$ | $1.92$ |
| $g_{zz}$                 | $1.92$ | $1.92$ |

This table provides a comprehensive overview of the magnetic exchange coupling parameters in single-layer CrI$_3$, including isotropic Heisenberg magnetic exchange ($J$), symmetric anisotropic ($\Gamma_{xy}$, $\Gamma_{yx}$, and $\Gamma_{xz}$), and Kitaev ($K$) interactions along with single-ion anisotropy ($A$) and the components of the $g$-tensor ($g_{xx}, g_{yy}, g_{zz}$) calculated by means of CASSCF and MRCI methods.
In brief, this expression reads as

$$J = \frac{E_{\text{FM}} - E_{\text{AFM}}}{2N_{\text{nn}}S^2}$$

where $E_{\text{FM}}$ ($E_{\text{AFM}}$) is the total energy of the out-of-plane ferromagnetic (antiferromagnetic) phase and $N_{\text{nn}}$ is the number of the nearest neighbors surrounding the magnetic site. In order to conduct a meaningful comparison between the many-body wavefunction and the density-functional results, we re-map the *ab initio* Hamiltonian onto the isotropic Heisenberg Hamiltonian. We obtain a benchmark value of $J = -1.48$ meV at the MRCI level, only slightly larger than that obtained on the basis of equation (1).

The upper panel of figure 2 compares the values of $J$ calculated with several density-functional approximations with our MRCI benchmark result. Notwithstanding their sharp differences in treating electron-electron interactions, all considered functionals provide a qualitative agreement with experiments, yielding a ferromagnetic ground state and an accompanying magnetic moment $\mu = 3 \mu_B$ per Cr$^{3+}$ ion [36, 46]. However, the magnitude of $J$ largely depends on the adopted approximation. For instance, both CA and (R)TPSS functionals severely underestimate the value of $J$ when compared with the MRCI result, despite their marked dissimilarities in describing exchange and correlation effects. Though to a lesser extent, an underestimation is observed when adopting the generalized gradient approximations as well. Among the meta-GGA functionals considered here, only SCAN is seen to lead to a satisfactory agreement with the benchmark value. Surprisingly, all hybrid functionals overestimate $J$ by $\approx$20%. The best agreement between DFT and MRCI results is achieved with the PBEsol, SCAN or DFT+U functionals – the latter matching the MRCI value upon the introduction of moderate values of Coulomb on-site repulsion (1.0–1.5 eV) – as they deviate from the benchmark value by less than 0.2 meV.

Next, we determine the magnetocrystalline anisotropy energy ($E_{\text{MAE}}$) per formula unit as

$$E_{\text{MAE}} = \frac{E(\mu_{\perp}) - E(\mu_{\parallel})}{2}$$

with $E(\mu_{\perp})$ and $E(\mu_{\parallel})$ being the total energy of single-layer CrI$_3$, with the magnetic moment $\mu$ pointing towards the out-of-plane and in-plane direction, respectively. Our results are overviewed in the middle panel of figure 2. MOKE investigations revealed that single-layer CrI$_3$ features an out-of-plane axis, albeit the magnitude of $E_{\text{MAE}}$ remains undetermined to date. Even though the results of our calculations appear to be spread over a quite broad interval depending on adopted the density-functional, for the ferromagnetic phase we obtain negative magnetocrystalline anisotropy energies irrespectively of the approximation considered. This finding lends support to MOKE observations [30], and is further consistent with our many-body wavefunction results concerning the single-ion anisotropy $A$ and $g$-tensor (see table 2). We then examine the spin orientation of the higher-energy antiferromagnetic phase. As compared to the stable ferromagnetic ordering, this configuration is found to exhibit an in-plane axis and a substantially lower magnetocrystalline anisotropy energy, being $E_{\text{MAE}} = 0.39, 0.90,$ and 0.70 meV at the PBE, SCAN and HSE06 levels, respectively.

Finally, we address the Curie temperature of CrI$_3$ from first principles and compare the results of our calculations with the experimental value of 45 K. To this end, we rely on the formalism developed in reference [58], in which an analytic expression of $T_C$ in the two-dimensional limit is derived on the basis of a fit to Monte Carlo results achieved on model lattices. In brief, this expression reads as

$$T_C = T_1f\left(\frac{\Delta}{J(2S - 1)}\right)$$

where $T_1$ is the critical temperature for the corresponding Ising model $T_1 = S^2/4T_C/k_B$ ($T_C = 1.52$ in the case of honeycomb lattices), $\Delta$ accounts for anisotropy parameters $\Delta = A(2S - 1) + B N_{\text{nn}}$, with $A = (\Delta E_{\text{FM}} + \Delta E_{\text{AFM}})/2S^2$ and $B = (\Delta E_{\text{FM}} - \Delta E_{\text{AFM}})/N_{\text{nn}}S^2$, with $\Delta E_{\text{FM}}$ ($\Delta E_{\text{AFM}}$) being the

$S^\|$, by determining $J$ according to the usual expression [75]
differences in energy between the in-plane and out-of-plane spin configurations in the ferromagnetic (antiferromagnetic) state, and $f$ is a function of the form $f(x) = \tanh\left(\frac{x}{\gamma}\right) \log(1 + e^{\gamma x})$, where $\gamma = 0.033$. Our results are shown in the lower panel of figure 2. Similarly to the investigation of $J$, we observe that the value of the Curie temperature obtained at the CA and (R)TPSS levels is about halved as compared the experimental benchmark, while it is only slightly underestimated when adopting gradient-corrected functionals, with the exception of the PW91 case. Also, we notice a good performance of both SCAN and DFT+U functionals. Contrary to the case of $J$, however, we remark that hybrid functionals yield an excellent agreement with the experimental $T_C$, differing only by $\sim \pm 2$ K. We suggest that the reason for this traces back to the favorable compensation between the overestimated $J$ and the underestimated $E_{\text{MAE}}$, as both these quantities enter equation (5). As DFT+U and SCAN density-functionals lead to a superior description of both the Heisenberg exchange coupling and the Curie temperature, it is likely that the resulting magnetocrystalline anisotropy energies should be reliable as well. Hence, we anticipate a $E_{\text{MAE}} \approx -0.87$ meV for ferromagnetic single-layer CrI$_3$.

5. Conclusion

In summary, we have combined CASSCF and MRCI calculations with model Hamiltonians to quantify the spin interactions in two-dimensional CrI$_3$. We have found that the inter-site magnetic interactions are primarily dictated by the ferromagnetic Heisenberg exchange coupling $J = -1.44$ meV, as inter-site magnetic anisotropies $\tilde{\Gamma}$ play a practically negligible role. Furthermore, our calculations indicate that single-layer CrI$_3$ features an out-of-plane easy axis, as confirmed by the determination of single-ion anisotropy $A = -0.10$ meV, $g$-tensor $\Gamma_{xx} = \Gamma_{yy} = 1.90$ and $\Gamma_{zz} = 1.92$, as well as first-principles calculations of the magnetocrystalline anisotropy energy. In addition, we have assessed the performance of various flavors of popular density-functionals against our accurate MRCI calculations and available experimental data, and found that DFT+U (with $U = 1.0$–1.5 eV) and SCAN functionals show an excellent description of exchange interactions. Overall, our work provides firm theoretical ground to recent experimental observations, unveils the magnitude of several magnetic interactions, and establishes reference results for future DFT studies, thereby offering a comprehensive picture of the microscopic spin physics in monolayer CrI$_3$.

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