Magnetoelectric Response of Antiferromagnetic Van der Waals Bilayers

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We predict that antiferromagnetic bilayers formed from van der Waals (vdW) materials, like bilayer CrI3, have a strong magnetoelectric response that can be detected by measuring the gate voltage dependence of Faraday or Kerr rotation signals, total magnetization, or anomalous Hall conductivity. Strong effects are possible in single-gate geometries, and in dual-gate geometries that allow internal electric fields and total carrier densities to be varied independently. We comment on the reliability of density-functional-theory estimates of interlayer magnetic interactions in van der Waals bilayers, and on the sensitivity of magnetic interactions to pressure that alters the spatial separation between layers.

Introduction—Spintronics is the study of the interplay between electrical and magnetic properties, and underlies an important technology, based so far almost exclusively on the properties [1–4] of magnetic metals. There has long been interest in expanding spintronics to semiconductors, which tend to have properties that are more subject to electrical control [5]. In this Letter we address electrical control of magnetization in vdW semiconductor bilayers with antiferromagnetic interlayer coupling, which have been fabricated for the first time recently [6–9]. Indeed tunneling magnetoresistance [10–12] and electrical control [13–15] of magnetic configurations, have already been demonstrated in CrI3 bilayers. We predict that antiferromagnetic van der Waals (vdW) bilayers, like bilayer CrI3, will also have strong magnetoelectric responses that can be detected by measuring the gate voltage dependence of Faraday rotation, anomalous Hall conductivity, or bulk magnetization.

Mean-Field Theory—Antiferromagnetic vdW bilayers have interlayer magnetic interactions that are weak compared to their intralayer counterparts. To establish that this property implies strong magneto-electric response, we first apply mean-field theory to an intrinsic bilayer magnetic semiconductor. The low energy degrees are then spin S local moments. If we assume for simplicity one spin per layer per unit cell, the spin Hamiltonian can be expressed in the momentum-space form

\[ H = -\sum_{i',i} J_{i',i}(k) S_{i'}(-k) \cdot S_i(k), \]

where \( i', i = 0, 1 \) are layer labels, \( S_i(k) \) is the appropriately normalized Fourier transform of the spin operators in layer \( i \), and

\[ J_{i',i}(k) = \sum_L \exp(-i k \cdot L) J_{i',i}(L) \]

is a Fourier sum of exchange interactions between spins localized at the origin in layer \( i \) and at lattice site \( L \) in layer \( i' \). In mean-field theory the temperature dependent

\[ (S)_i = (-1)^{i} S_{i'} S_i = (-1)^{i} 2 S_B \beta \hbar k_i \]

In Eq. 3 \( \beta = 1/k_B T \) is inverse temperature, \( B_S(x) \) is the Brillouin function, and we have assumed that the magnetization points in the \( \hat{z} \) direction, that \( \hat{J}_{ii} \) corresponds to ferromagnetic alignment of spins within each layer, and that \( J_{01} = J_{AF} < 0 \) corresponding to
antiferromagnetic coupling between layers.

The magneto electric coupling on which we focus is due to mirror-symmetry breaking by a gate electric field $E$. Since $\tilde{J}_{00} + \tilde{J}_{11}$ and $\tilde{J}_{01}$ must be even functions of $E$, we can describe linear magneto-electric response by letting $\tilde{J}_{ij} = J_F + (-)^i \delta E_F$. It follows that the linear response to $E$ of the total spin per unit cell, $f = S(n_0 - n_1)$, is

$$\alpha \equiv \frac{df}{dE} = 2S \chi_F s_{AF}$$

where $s_{AF}$ is the average local moment on each site in the $E = 0$ antiferromagnetic bilayer state, and $\chi_F$ is the magnetic susceptibility

$$\chi_F \equiv \frac{df}{dH} = \frac{\beta B_S^0(\beta h_0)}{1 - \beta(SF - |J_{AF}|)B_S^0(\beta h_0)},$$

where $B_S^0(x)$ is the derivative of $B_S(x)$. Note that $\beta(SF + |J_{AF}|)B_S^0(\beta h_0) = 1$ at the antiferromagnetic critical temperature and, as we discuss at greater length below, $|J_{AF}|$ is always very small compared to $J_F$ in antiferromagnetic bilayers. The critical divergence in $\chi$ that would occur at the critical temperature if the ground state were ferromagnetic is therefore only weakly truncated in the antiferromagnetic state [16]. For $T_N/T - 1 > |J_{AF}|/J_F$ the mean-field magneto electric response grows like $(T_N - T)^{-1/2}$. Fig. 1 compares the bilayer magnetoelectric response calculated using this mean-field-theory with the results of numerically exact classical Monte Carlo calculation discussed in the supplementary material. As we discuss more fully below, the Monte Carlo results are strongly sensitive to magnetic anisotropy which must be present to endow the mean-field calculations with qualitative validity. In antiferromagnetic bilayers with uniaxial anisotropy of the size present in CrI$_3$, the mean-field predictions are largely validated by Monte Carlo. The magneto electric response is largest close to but below the antiferromagnetic transition temperature.

**Interlayer Magnetic Interactions in CrI$_3$ Bilayers**—Surprisingly, CrI$_3$ bilayers have [13–15] antiferromagnetic interlayer interactions [6] even though bulk CrI$_3$ is ferromagnetic. As discussed below, the the reliability of ab initio density functional theory estimates of $\tilde{J}_{AF}$ is uncertain because of the vdW character of the material. The strength of the interlayer interaction can however be reliably extracted from the magnetic field $B_c \approx 0.65T$ [6], needed to drive the bilayer’s metamagnetic transition to a ferromagnetic state. This consideration implies that $\tilde{J}_{AF} \approx 2g\mu_B S B_c \approx -0.23$ meV, nearly two orders of magnitude smaller than the bilayer’s ferromagnetic intralayer magnetic interaction parameter $J_F$.

Bulk CrI$_3$ is a layered semiconductor with the low-temperature R3 rhombohedral structure [9–11, 18] illustrated in the supplementary material [16] and a high temperature C2/m monoclinic structure. Because CrI$_3$ bilayers are prepared by room temperature mechanical exfoliation of bulk crystals on a silicon oxide substrate they are likely [21–24] to maintain the stacking arrangement of the high temperature structure even when cooled to low temperature. To shed light on the bilayer’s surprising antiferromagnetic state, we have applied plane wave density-functional-theory as implemented in the Vienna Ab initio simulation package (VASP) [25] and Quantum Espresso(QE) [8] to bilayer CrI$_3$, using semi-local PBE-GGA [27] with the vdW-D2 correction proposed by Grimme [28]. Technical details of these calculations can be found in the supplementary material [16].

In Fig. 2 (b), the DFT total magnetic interaction energy is plotted as a function of $d$, the spatial vdW gap $d$ illustrated in Fig. 2(a). For each curve we measure $d$ from the corresponding theoretical equilibrium vdW gap $d_0$ of the layer-ferromagnetic bilayer configuration. The bulk experimental vdW gap in the ferromagnetic configuration is $\sim 6.6$ Å [9]. Calculations were performed using both LDA and LDA+U DFT approximations, for both R3 and C2/m energy stacking arrangements, and with and without spin-orbit coupling. The predicted inter-
layer magnetic interactions are most often ferromagnetic and much stronger than the strength inferred from experiment. Within LDA we find that the monoclinic C2/m structure is ferromagnetic at \( d = d_0 \), becoming antiferromagnetic only at larger values of interlayer separation distance \( d - d_0 \). The change in sign as \( d \) varies is expected, since direct ferromagnetic exchange interactions are expected to decline more rapidly with \( d \) than antiferromagnetic superexchange interactions. For LDA+U, \( U = 3 \) eV substantially alters the the total energy differences. Additional DFT results are summarized in Fig. S4 [16].

Note that the antiferromagnetic and ferromagnetic states reach their minimum energies at different layer separations [16] and that the vdW gaps of the encapsulated bilayers studied experimentally [13–15] are likely smaller than those of the isolated bilayers we have studied theoretically. It follows that the field-driven meta-magnetic transition should be accompanied by an area change, and that the critical field of the transition should be pressure dependent and altered by encapsulation.

This confusing landscape of DFT predictions establishes that the interlayer magnetic interaction in CrI\(_3\) bilayers is weak and sensitive to layer separation and stacking arrangement [16, 21–24]. If confident in the DFT+U estimate, one could conclude that the stacking arrangement must be monoclinic and that the very weak interlayer exchange interaction in CrI\(_3\) case is an accident due to an approximate coincidence of the experimental vdW gap and the value of \( d \) at which the interaction changes sign. This coincidence does however require a finely-tuned value of the +U interaction correction parameter, and is not consistent with the theoretically estimated influence of spin-orbit interactions. The alternate view, and the one that we favor, is that interlayer magnetic interactions in vdW multilayers are intrinsically weak because of the same correlation effects responsible for the van der Waals energy correction, and have values that are not reliably estimated by DFT. It is noteworthy that the vdW-D2 correction changes the total energy at a given layer separation in a crucial way, but does not change the magnetic energy \( \Delta E \). It seems clear that the large vdW correction should in fact have a substantial spin-dependence. Correlations reduce hybridization between layers and should therefore also reduce magnetic interactions. If so, this new class of materials motivates work to develop van der Waals corrections that not only account for changes in how the energy depends on total density, but also for changes in how the energy depends on spin-density. Below we view the interlayer magnetic interaction as a parameter that is presently most reliably estimated from experiment. The DFT calculations do reliably predict important details of the intralayer magnetic interactions that are related to the covalent intralayer bonding network.

**Magnetic Properties of CrI\(_3\) multilayers —** Our \textit{ab initio} calculations show that each Cr atom has a magnetic moment close to \( 3\mu_B \), consistent with full \( d \)-electron spin-polarization in Cr\(^{3+}\) ions. We therefore map the DFT magnetic energy landscape in the intrinsic limit to that of a Cr-ion spin Hamiltonian:

\[
H = -\frac{1}{2} \sum_{i,R,R'} J_i (R - R') S_i R \cdot S_{iR'} - \frac{1}{2} \sum_{i \neq j} J_{ij} S_i R \cdot S_j R - D \sum_R (S^z_R)^2 - g \mu_B \sum_R BS^z_R
\]

(6)

where \( i \) labels layer, \( R \) is an in-plane Cr \_ position, \( S \) is a spin operator, \( D \) is the crucial uniaxial anisotropy constant, \( g \) is the Cr ion \( g \)-factor, \( \mu_B \) is the Bohr magneton, and \( B \) is the strength of a magnetic field applied along the \( \hat{z} \) (out-of-plane) direction.

In agreement with experiment, we find that the energy is lowest when the spins have an out-of-plane orientation. We find that the anisotropy constant for bilayer CrI\(_3\) is \( D = 660 \mu eV \) according to VASP, and \( D = 730 \mu eV/Cr \) atom according to QE. These values are smaller than the corresponding monolayer values \( (D = 960 \mu eV) \) reported in the literature. Magnetic anisotropy plays a critical role in limiting the thermal fluctuations that lower the monolayer and bilayer critical temperatures relative to their mean field values. The increase in \( T_c \) with \( \Delta \) is illustrated in Fig. S11 [16].

Intralayer exchange constants can be extracted from ground state total energies calculated for different metastable magnetic configurations as detailed in the supplementary material [16] and sum to give a value for \( J_F \approx 14.6 \mu eV \), corresponding to a mean field critical temperature \( T_{MF} \approx 94K \). This size of exchange interaction is in reasonable agreement with experiment since it would imply a ratio of the critical temperature to its mean field value, \( \sim 0.50 \), slightly smaller than the ideal two-dimensional Ising model value \( T_c/T_{MF} \approx 0.56 \). The Monte Carlo Curie temperature we obtain for monolayers is \( 30 \) K, and the Néel temperature for bilayers is \( 31 \) K when we use the experimental antiferromagnetic interlayer coupling \( J_{AF} \approx -0.23 \) meV. We observe that although \( T_c \) is mainly governed by intralayer exchange parameters, interlayer coupling can help suppress thermal fluctuations and help increase \( T_c \). (See Figs. S12-S14 [16]).

**Magneto-electric Coupling in CrI\(_3\)** The influence of gate electric fields on total magnetization, and on other magnetic properties, depends very much on whether or not electrostatic doping occurs. For dual gated bilayers the carrier density and the internal electric field can be varied independently. In the absence of carriers we find [16] that in CrI\(_3\) the coupling constant \( \lambda \) defined above Eq. 4 has the value

\[
|\lambda| = \frac{1}{2} \frac{d(\tilde{J}_{11} - \tilde{J}_{22})}{dE} \approx 0.12(\text{meV})\text{nmV}^{-1}.
\]

(7)
The sign of $\lambda$ is such that the layer with the lower electric potential and higher charge density has stronger exchange interactions. Strong gate electric fields $\sim 1$ Vnm$^{-1}$ yield intralayer magnetic interactions that are $\sim 2\%$ higher in the high density layer than in the low density layer. As expected on symmetry grounds and illustrated in Fig. 3, the dependence of the ground energy on $E$ is quadratic and the dependence of interlayer exchange on $E$ is negligible for practical electric field strengths. This relatively small variation in the exchange coupling parameters slightly increases the Curie temperatures ($T_c$) estimated by mean field and Monte Carlo calculations [16]. Combining the DFT result for $\lambda$ with either the Monte-Carlo or the mean-field theory results illustrated in Fig. 1 yields values for the ratio of the net magnetization per volume to the electric field, which is dimensionless in cgs units, $\sim 1 \times 10^{-3}$, comparable to the corresponding values in classic magnetoelectric materials like chromia [30, 31].

In dual gated bilayer CrI$_3$ samples the external electric fields above and below the bilayer, and hence via Poisson’s equation also the sign and magnitude of the electrostatic doping, can be controlled independently. The possibility of electrostatic doping expands the phenomenon of magnetoelectric response beyond the di-electric case, since the magnetization depends separately on two electric fields. Finite carrier density is in fact already experimentally relevant because of unintended doping which is reported to range from $4.4 \times 10^{12}$ cm$^{-2}$ [15] to $2.3 \times 10^{13}$ cm$^{-2}$ [14]. At finite but low carrier densities, the $T = 0$ energies of the FM and AF states at a given average electric field are given by:

$$E_{\text{FM}} = E_{0}^{\text{FM}} - \theta(n)E_n^F nA + \theta(n)E_n^F nA$$

$$E_{\text{AF}} = E_{0}^{\text{AF}} - \theta(n)E_n^F nA + \theta(n)E_n^F nA$$

(8)

where $E_{0}^{\text{FM/AF}}$ is the ground state energy per 2D unit cell from DFT, $n$ is the carrier density per unit cell defined as negative for electrons and positive for holes, $A$ is the unit cell area $\sqrt{3}a^2/2$ where $a = 6.863$ Å is the lattice constant, and $E_c/v$ are the conduction/valence band edge energies. Doping generally favors ferromagnetic states because the ferromagnetic state has a smaller band gap, allowing carriers to be introduced with a smaller band energy cost. The ground state energy is a quadratic function of field in the absence of electrostatic doping, but has a cusp at neutrality when gate fields are adjusted to vary the total carrier density. As show in Fig. 3(b), we estimate that carrier densities of around $1.5 \times 10^{12}$ cm$^{-2}$ for electrons and $3 \times 10^{12}$ cm$^{-2}$ for holes are sufficient to induce transitions between the two magnetic ground states.

Discussion—Because the magnetic interactions between van der Waals bilayers with adjacent ferromagnetic materials are expected to be weak, the Faraday and Kerr effects associated with the intrinsic semiconductors magnetoelectric response on which we have focused on in this article are expected to be easier to measure and more technologically relevant than proximity induced magnetism and anomalous Hall effects in adjacent non-magnetic conductors. When carriers are present however, because of either impurity or electrostatic gating, gate voltage modulated anomalous Hall effects will be present and should be easily measured. Applications await the development, still in progress [8, 9], of well controlled magnetic van der Waals bilayers that order at room temperature. Electric fields in van der Waals bilayers also alter the magnon dispersion [12], opening a gap between bands associated with the two spins per unit cell in the two-dimensional honeycomb lattices and opening up the possibility of topological magnon bands when electric field breaks the inversion symmetry and generate Dzyaloshinskii-Moriya interactions [33, 34]. Based on DFT calculations, the magnon energies in bilayer CrI$_3$ are in the range below $15$ meV, and the magnon gap is around $1$ meV [16], at a $1$ V nm$^{-1}$ electric field.

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Methods of calculations

The density functional theory (DFT) calculations were performed using the Vienna Ab initio simulation package (VASP) [S1–S4] using Generalized Gradient Approximation PBE [S5, S6] pseudopotentials. Since CrI$_3$ is a van der Waals (vdW) crystal, we use the DFT-D2 dispersion correction introduced by Grimme to account for vdW bonding [S7]. For the plane wave expansion of the DFT calculation we used a cutoff energy of 520 eV, a total electronic energy convergence threshold of $10^{-8}$ eV per unit cell, a $6 \times 6 \times 1$ k mesh is used for structure relaxation calculations, and a $12 \times 12 \times 1$ k mesh for self-consistent calculations with a fixed structure. A gaussian smearing parameter of 0.05 eV was used to assign partial occupancies. A conjugate-gradient algorithm was used to relax nuclear positions with forces less than 0.0005 eV/Å. The ground-state energy calculations are also carried out using plane-wave density functional theory as implemented in Quantum Espresso. [S8] We have used the Rappe-Rabe-Kaxiras-Joannopoulos ultrasoft (RRKJS) pseudopotentials for the semi-local Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [S5, S6] together with the VdW-D2 [S7]. The structures were optimized until the forces on each atom reached $10^{-5}$ Ry/a.u. using self-consistency criteria for total energies at $10^{-10}$ Ry.

The momentum space integrals for unit cells were performed using a regularly spaced k-point sampling density of $16 \times 16 \times 1$ for triangular and $8 \times 16 \times 1$ for rectangular cells, with a plane wave energy cutoff 60 Ry.

| Method          | ∆E (meV) | $d_o$ (Å) |
|-----------------|----------|-----------|
|                 | FM AF    | FM AF     |
| **Bulk (R3)**   |          |           |
| PBE             | 0.000    | 194.0 7.422 6.825 |
| DFT-D2          | 0.000    | 9.153 6.497 6.538 |
| **Bulk (C2/m)** |          |           |
| PBE             | 0.000    | 206.0 7.516 7.799 |
| DFT-D2          | 0.000    | 159.0 6.534 6.524 |
| **Bilayer (R3)**|          |           |
| PBE             | 0.000    | 249.0 7.334 7.384 |
| DFT-D2 (Non-Collinear) | 0.000 | 15.01 6.531 6.533 |
| DFT-D2 (U)      | 0.000    | 1.718 6.522 6.547 |
| DFT-D2 (Non-Collinear) | 0.000 | 4.337 6.512 6.516 |
| DFT-D2 (Non-Collinear + U) | 0.000 | 4.500 6.548 6.552 |
| **Bilayer (C2/m)** |          |           |
| PBE             | 0.000    | 13.65 7.400 6.817 |
| DFT-D2          | 0.000    | 0.626 6.571 6.548 |
| PBE (Non-Collinear) | 0.353 | 0.000 7.752 7.763 |
| DFT-D2 (Non-Collinear) | 0.000 | 0.646 6.544 6.561 |
| DFT-D2 (U)      | 0.000    | 0.059 6.616 6.674 |
| DFT-D2 (Non-Collinear + U) | 0.000 | 0.302 6.616 6.617 |

TABLE I: Ground state energies for bulk and bilayer CrI$_3$ (Rhomboedral (R3) and monoclinic (C2/m) structures) obtained with fully relaxed geometries using different approximate exchange-correlation energy functionals. The structural relaxations were performed separately for ferromagnetic (FM) and layer antiferromagnetic (AF) configurations. The energies are normalized per Cr atom in each case. The comparison of interlayer distance between PBE and DFT-D2 indicates a strong vdW dispersion force between layers in CrI$_3$. A reduction of nearly 1 Å in the vdW gaps of both bulk and bilayer CrI$_3$ using the vdW corrected methods (DFT-D2 and optB86b). The layer AFM is favored over the layer FM magnetic configuration case only for the C2/m structure and only when the equilibrium interlayer distance is larger due to the absence of vdW corrections and non-collinear spins are used.
Crystal Structure Optimization

Bulk Structure

The ferromagnetic semiconductor bulk CrI$_3$ is a vdW layered structure, with two different phases with rhombohedral (R3, BiI$_3$-type, we will label as R3 in the follow) at low-temperatures ($< 210 - 220$ K) and with monoclinic (C2/m, AlCl$_3$-type, and we will label as C2m in the follow) at high temperature ($> 210-220$ K) structure [S9–S11]. In Fig. S1(a), we describe the low temperature rhombohedral R3 phase of bulk CrI$_3$, with each layer having a structure as shown in Fig. S1(b). In the Fig. S1(c-e) we describe bilayer structure at low temperature (R3) and at high temperature (C2m). We performed volume and atomic position relaxations using the DFT framework, with and without vdW corrections, for both bulk rhombohedral (R3) and monoclinic (C2m) structures. We list the total energy per metal atom relative to that of the ground state structure and magnetic configurations, ferromagnetic (FM) and antiferromagnetic (AF), and the interlayer equilibrium distances ($d_0(A)$) in Table I for both bulk and bilayer. The bulk R3 and C2m phase are found to be ferromagnetic ground states, and are compared against exchange functional PBE and DFT-D2.

![FIG. S1: Rhombohedral (R3, BiI$_3$-type) crystal structure: (a) The hexagonal unit cell consists of three layers, each with two Cr atoms and six I atoms. (b) The Cr (blue color) atoms in each layer form a honeycomb network, and each Cr atom is surrounded by six I atoms, 3 above (yellow color) and 3 below (red color) with a distorted octahedral crystal fields. The top view of monolayer represent the 60° off-set rotation between top and below I atoms within a monolayer. (c) Bilayer: The top view of a CrI$_3$ bilayer in which the corresponding atoms in adjacent layers are separated by $(a + b + c)/3$, where a/b and c are respectively in plane and out-of-plane primitive lattice vectors: $a/b = \sqrt{3}/2 ax \pm 1/2 ay$, and $c = cz$. The black vector is the inter-layer displacement connecting two Cr atoms in different layers. (d) Bilayer CrI$_3$ with the low temperature phase stacking, AB’ in R3 phase (see Fig. S2). (e) and the high temperature phase stacking, AC in C2/m phase (see Fig. S3). Note: Here the translation is to the most adjacent Iodine (I) atom in the bottom layer, not to the Chromium (Cr) atom. Translation to the most adjacent Cr atom will not lead to the high temperature stacking as shown in Fig. S2.

Bilayer Structure

Two layers of CrI$_3$ are truncated from the low and high temperature phase structures by introducing a vacuum not less than 15 Å between the bilayers to avoid the periodic interactions. The low and high temperature are related by a translation in one of the layers as explained in Fig. S1. The total energies of each bilayer is calculated within
the DFT framework along with the introduction of the influence of dispersion forces on the vdW gap, as listed in Table. I. It is evident that vdW corrections substantially decrease the vdW gap $d_0$ between layers and it is found to be large in the absence of vdW corrections. The DFT predicted ground states are ferromagnetic (FM) for both R3 and C2m phase bilayer.

In the case of bilayers fabricated by exfoliation, it is likely that the structure observed experimentally replicate the bulk structure at the exfoliation temperature, instead of being determined thermodynamically. In order to find the interlayer distance influence on the interlayer exchange interaction for R3 and C2m stacking, we considered the AF relaxed R3 phase and C2m phase bilayers and obtained the FM order total energy within self-consistent field (SCF) calculations with the hard shift in the interlayer vdW gap, and no relaxation of Cr atoms imposed during the energy calculations, fully relaxing the FM coordinates of I atoms.

As mentioned in the Fig. S1, the translation of the top layer to the most adjacent I atom in the bottom layer leads to the C2m phase (see Fig. S3). However, translation to most adjacent Cr atom leads to different stacking as explained in Fig. S2. In Fig. S2 and S3 we compare the energies of a variety of different metastable stacking and magnetic configurations, including the ferromagnetic (FM), Néel-AF, Zigzag-AF, and Stripy-AF magnetic configurations for the stacking resulting from the translation to most adjacent Cr atom. The ground-state energy calculations are carried out using plane-wave density functional theory as implemented in Quantum Espresso. [S8] We have used the Rappe-Rabe-Kaxiras-Joannopoulos ultra-soft (RRKJUS) pseudopotentials for the semi-local Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [S5, S6] together with the VdW-D2 [S7]. For all metastable structures parallel spins in opposite layers were energetically favored over opposite spins, except for the case of the meta-stable layer AFM configuration which has lower energy than the corresponding FM structure for AA stacking. We found that the AB stacking in the FM phase have lowest energy for the R3 phase stacked bilayer. In Fig. S3 we compare the energies of a variety of different metastable stacking with the translation to most adjacent I atom i.e C2m phase stacking. The AC stacking which C2m phase stacking has lowest energy compared to other metastable stacking with FM order. The AB′ and AB′′ show layer AF as local minima.

Inter layer distance dependent total energy calculations

Our calculations show no evidence of AF lower energy or transition from AF to FM when performing collinear (no spin-orbit) calculations as shown in Fig. S4. However, using non-collinear calculations we obtain an FM to AF transition for both R3 and C2m stacking. The difference with the main text is that no relaxation in main text is performed when change vdW gap and the $d_0$ is got from the relaxation of R3 stacking.

Parameters of spin Heisenberg Hamiltonian

Although DFT theory is not able to reliably predict all physical properties related to the magnetic and magneto electric properties of CrI$_3$ bilayers, it is able to provide reliable estimates for intra-layer magnetic exchange interactions and magnetic anisotropies energies and their dependence on gate electric fields. In this section we explain how we estimate these quantities and provide more details on DFT predictions for structure and interlayer exchange interactions which illustrate the associated uncertainties.

Magnetic exchange coupling

The magnetic exchange interactions ($J$) in CrI$_3$ bilayers can be estimated by comparing the energies of different meta-stable spin configurations and mapping the resulting energy landscape to a Heisenberg model with $S = 3/2$ spins, near-neighbor interlayer interactions, and interlayer interactions truncated at third neighbors. For the case of zero electric field, the spin interaction parameters for the top and bottom layers are identical by symmetry.

The metastable DFT states for which we calculate energies have the spin configurations illustrated in Fig. S5. The interlayer exchange parameter is calculated from the energy difference between the interlayer ferromagnetic (FM) and antiferromagnetic (AF) spin configurations (a).

In the Heisenberg model the energies of the F and AFM states are

$$E_{AF/FM}^{cell} = E_0 - 4(3J_{11} + 6J_{12} + 3J_{13})|S|^2 - 4(3J_{b1} + 6J_{b2} + 3J_{b3})|S|^2 \pm 4z_v J_v |S|^2.$$  \hspace{1cm} (S1)
FIG. S2: Total energy difference $\Delta E$ between the ground state Layer Ferromagnetic (L-FM) and other possible metastable spin and stacking configuration states in bi-layer CrI$_3$ obtained within our DFT calculations. The metastable stacking is drawn from the translation of top layer with reference to the most adjacent Chromium (Cr) atom in the bottom layer. Our DFT calculations carried out for bilayer geometries show that the total energies for FM and AFM phases for the same atomic structure have minimal differences barely visible, where generally the FM phase is favored, except for the AA$'$ stacking where AFM is preferred but its structure is energetically not favorable. The top panel shows the amount of energy per Cr atom is different from the ground state. Layer Ferro (L-FM) and layer anti-Ferro (L-AFM) spin arrangement for possible in-plane magnetic order such as Néel-AF, Zigzag-AF, and Stripy-AF are considered to determine the ground state. The bottom panel shows the top (XY-plane) and side views (XZ-plane) for all possible symmetric stacking arrangements. The red panels show the stacking arrangement from in-plane sliding, and the green panels show the stacking arrangement that arises due to the three-fold rotation symmetry. Note: AB'(1) and AB'(2) are the same energetically as well as structure wise, hereafter we call it AB$'$.

The ground-state energy calculations are carried out using plane-wave density functional theory as implemented in Quantum Espresso. [S8] We have used the Rappe-Rabe-Kaxiras-Joannopoulos ultrasoft (RRKJUS) pseudopotentials for the semi-local Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [S5, S6] together with the VdW-D2 [S7].

Here $E_{\text{cell}}$ is the DFT total energy normalized to per unit cell, $J_{t/bi}$ is the exchange coupling between $i$-th nearest neighbors, top $t$ and bottom $b$ layers are distinguished in anticipation of the case in which the two layers are distinct because of an applied magnetic field, and $z_v$ is the number of neighbor for inter-layer coupling. The factor of 4 appears because there are eight Cr atoms in the magnetic unit cells of the DFT calculations. It follows that the inter-layer exchange coupling constant can be mapped as follow:

$$J_v = (E_{\text{AF}}^{\text{cell}} - E_{\text{FM}}^{\text{cell}})/(8z_v|S|^2).$$

(S2)

To extract the intra-layer exchange interaction parameters, we note that the Heisenberg model energies of the
FIG. S3: Total energy difference $\Delta E$ between the ground state Layer Ferromagnetic (L-FM), AB' of R3 phase and other possible metastable spin and stacking configuration states in C2m phase stacked bi-layer CrI$_3$ obtained within our DFT calculations. The AC stacking corresponds to the bulk high temperature phase structure. The metastable stacking is drawn from the translation of top layer with reference to the most adjacent Iodine (I) atom in the bottom layer. Our DFT calculations carried out for bilayer geometries show that the total energies for FM and AFM phases for the same atomic structure have minimal differences barely visible, where generally the FM phase is favored, except for the AB''' stacking with higher energy than the ground state. The top panel shows the amount of energy per Cr atom is different from the ground state. Layer Ferro (L-FM) and layer anti-Ferro (L-AFM) spin arrangement for possible in-plane magnetic order such as Néel-AF, Zigzag-AF, and Stripy-AF are considered to determine the ground state. The bottom panel shows the top (XY-plane) and side views (XZ-plane) for all possible symmetric stacking arrangements. The red panels show the stacking arrangement from in-plane sliding, and the green panels show the stacking arrangement that arises due to the three-fold rotation symmetry. The ground-state energy calculations are carried out using plane-wave density functional theory as implemented in Quantum Espresso. [S8]

We have used the Rapppe-Rabe-Kaxiras-Joannopoulos ultrasoft (RRKJUS) pseudopotentials for the semi-local Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [S5, S6] together with the VdW-D2 [S7].

magnetic configurations considered (AF, Néel, zigzag, and stripy) are:

\[
\begin{align*}
E_{\text{cell}}^{\text{AF}} &= E_0^{\text{cell}} - 4(3J_{t1} + 6J_{t2} + 3J_{t3})|S|^2 - 4(3J_{b1} + 6J_{b2} + 3J_{b3})|S|^2 + 4z_vJ_v|S|^2 \\
E_{\text{cell}}^{\text{Neel}} &= E_0^{\text{cell}} - 4(-3J_{t1} + 6J_{t2} - 3J_{t3})|S|^2 - 4(3J_{b1} + 6J_{b2} + 3J_{b3})|S|^2 \\
E_{\text{cell}}^{\text{zigzag}} &= E_0^{\text{cell}} - 4(J_{t1} - 2J_{t2} - 3J_{t3})|S|^2 - 4(3J_{b1} + 6J_{b2} + 3J_{b3})|S|^2 \\
E_{\text{cell}}^{\text{stripy}} &= E_0^{\text{cell}} - 4(-J_{t1} - 2J_{t2} + 3J_{t3})|S|^2 - 4(3J_{b1} + 6J_{b2} + 3J_{b3})|S|^2
\end{align*}
\]

The intralayer exchange coupling parameters in the absence of an electric field are therefore:

\[
J_1 = \frac{E_{\text{cell}}^{\text{stripy}} - E_{\text{cell}}^{\text{zigzag}} + E_{\text{cell}}^{\text{Neel}} - E_{\text{cell}}^{\text{AF}}}{32|S|^2} + \frac{z_v}{8}J_v
\]
FIG. S4: **Left panel:** Spin collinear calculations for the total energy difference of FM and AF spins vs. van der Waals gap from the relaxed bilayer with AF bilayer structure for both R3 phase (left) and C2m (right) phases using collinear spin calculations, and no transition from FM to AFM state. The interlayer FM phase is favored even when we compare the total energies obtained fully relaxing the FM atomic coordinates while keeping the same interlayer distance for the Cr atoms. **Right panel:** Non-collinear calculations for the total energy difference of FM and AF spins as a function of van der Waals gap is obtained, from the relaxed AF bilayer structure. The left side panel is for R3 phase, and the right side panel is for C2m. In the case of R3, at almost 1.1 Å interlayer vdW gap separation from the equilibrium interlayer distance there is a transition from FM to AF using VASP. Using Quantum-espresso, with ultra-soft pseudo-potentials, the phase transition from FM to AF is at 1.4 Å. For the C2m phase, within VASP there is a similar phase transition upon the expansion FM to AF for shorter interlayer vdW gap between 0.6 to 0.5 Å from equilibrium interlayer distance compared to the R3 phase.

for the nearest neighbor exchange coupling and

$$J_2 = \frac{E_{\text{cell strip}} - E_{\text{cell zigzag}} - E_{\text{cell Neel}} + E_{\text{cell AF}}}{64|S|^2} + \frac{z_v}{16} J_v$$  \(S5\)

for the second nearest neighbor exchange coupling and

$$J_3 = \frac{-3E_{\text{cell strip}} + 3E_{\text{cell zigzag}} + E_{\text{cell Neel}} - E_{\text{cell AF}}}{96|S|^2} + \frac{z_v}{24} J_v.$$  \(S6\)

Numerical values for the intra-layer and inter-layer exchange interaction parameters are listed in Table II. The intra-layer magnetic exchange interactions obtained in this way were used in the Monte-Carlo calculations for the magnetic and magneto electric properties of CrI$_3$ bilayers reported on in the main paper and later in this supplementary material.

**Stacking dependent interlayer exchange**

The stacking dependence of interlayer exchange interaction is shown as in Fig. S6. The dependence of stacking is sensitive and the difference of AF and FM configuration energy can be varied up to around 6 meV, which is much larger than the observed experimental value (which is around -0.23 meV). It is shown that LDA+U describes the interlayer exchange coupling better than that without U, which is set to be 3 eV in the calculations. Even without relaxations, the stacking may lead to a very large change of inter-layer exchange coupling, if DFT gives reliable predicts, we would expect that twisted vdW magnetic bilayers can be a prospective platform to form ground magnetic Skyrmionic states without external field and Dzyaloshinskii-Moriya interactions.
FIG. S5: Metastable bilayer spin configurations used to calculate the magnetic exchange interaction parameters. In each case the bottom layer is ferromagnetic with spins down. (a) The experimental antiferromagnetic state (AF) in which the top layer bottom layer is also ferromagnetic and has the opposite spin-orientation; (b) Top layer Néel AF, (c) To layer zigzag type AF and (d) top layer stripy AF.

TABLE II: DFT estimates of the exchange constants of R3 phase bilayer CrI$_3$ vs. gate electric field: interlayer $J_v$, intralayer near-neighbor $J_t^{1/b}$, intralayer next neighbor $J_t^{2/b}$, and intralayer third neighbor $J_t^{3/b}$. Here $t/b$ label the top/bottom layer and the electric field point from bottom layer to top layer.

| Electric Field (V/nm) | 0.0  | 0.1  | 0.5  | 1.0  |
|----------------------|------|------|------|------|
| $J_v$ (meV)          | 0.121| 0.121| 0.121| 0.121|
| $J_t^1$ (meV)        | 1.730| 1.729| 1.725| 1.718|
| $J_t^2$ (meV)        | 0.259| 0.258| 0.256| 0.254|
| $J_t^3$ (meV)        | -0.088| -0.088| -0.087| -0.087|
| $J_t^{1/b}$ (meV)    | 1.730| 1.732| 1.738| 1.744|
| $J_t^{2/b}$ (meV)    | 0.259| 0.259| 0.260| 0.262|
| $J_t^{3/b}$ (meV)    | -0.088| -0.088| -0.088| -0.088|

Magnetoelectric response

The low energy degrees of freedom of CrI$_3$ bilayers that are responsible for its magnetism are $S = 3/2$ Cr$^{3+}$ spins. The system’s magnetoelectric response in the absence of carriers is therefore due to the electric field dependence of the spin Hamiltonian. When an electric field is applied along the $\hat{z}$-axis, the $J$ values for the bottom and the top layers are different, but can still be evaluated by mapping the DFT magnetic energy landscape to a Heisenberg model as explained above. The key element of this procedure is the use of spin-configurations in which spin-orientations are varied only within one layer as described in Fig. S5. The response of the magnetic exchange interaction parameters of R3 phase bilayer CrI$_3$ to an electric field has been characterized by considering electric fields up to ± 1 V/nm with a step of 0.1. Structural relaxations were performed at each applied field value. (In the DFT calculation dipole corrections to the potential were implemented to avoid the interaction between the periodically repeated images.) We find that the variation of the vdW gap with applied electric field is negligible (∼ 0.001Å as shown in Fig.S7 for both the FM and AF phases.

The linear variation of the intralayer exchange parameters with electric field expected on symmetry grounds is illustrated in Fig. S8, for the R3 and C2m phase bilayer stacking. The magnetoelectric response is proportional to the slopes of these lines.
FIG. S6: Stacking dependence of interlayer exchange coupling (that is proportional to the energy difference between the AF and FM magnetic configuration between the two layers.)

FIG. S7: The variation of the van der Waals gap as a function of applied electric field for AF and FM states of CrI$_3$ bilayer with R3 phase stacking. It is clear that there is almost zero effect on the interlayer vdW gap between the layers with the applied electric field.

**Magnetic Anisotropy Energy (MAE)**

The magnetic anisotropy energy of CrI$_3$ bilayer for the R3 phase is determined from the total energy difference of given spin configuration to the lowest energy spin configuration. We vary the spin direction from $+\hat{z}$ to $-\hat{z}$ of each Cr atom, i.e., 0 to 180° with the step of 10°. The spin-orbit coupling is included on top of spin collinear self-consistent geometries. The energy difference from the lowest energy spin direction as a function of spin angle is shown in Fig. S9. From the calculation, the easy axis direction for magnetization is out-plane ($\theta = 0^\circ$), and the magnetic anisotropy energy is 659.75µeV per Cr atom.
FIG. S8: The variation of exchange coupling $J$ values for first (top panel), second (middle panel) and third (bottom panel) nearest neighbor Cr atoms as a function of applied electric field up to ±1 V/nm. The top and bottom layer $J$ are having different values at a given electric field, and are same for zero applied field. The case of C2m stacking is calculated with a larger vdW gap at around 7.2 Å, while the case of R3 stacking is calculated at around 6.53 Å.

FIG. S9: Magnetic Anisotropy Energy (MAE) obtained from the total energy difference from the lowest energy spin configuration, where the spin direction varies from $+\hat{z}$ to $-\hat{z}$ of each Cr atom, i.e., 0 to 180° with the step of 10°. The lowest energy is associated for the spins aligned along the z-axis, and the magnetic anisotropy energy is calculated to be 659.75 μeV per Cr atom.

Magnetization and Magnons

Heisenberg Model

CrI$_3$ has a ABC stacked hexagonal lattice structure, let $\mathbf{R}$ the 2D in-plane lattice vector and $i, j$ is the index of the layers, the Heisenberg model is then written as:

$$H = -\frac{1}{2} \sum_{i,\mathbf{R},\mathbf{R}'} J_i (\mathbf{R} - \mathbf{R}') \mathbf{S}_{i\mathbf{R}} \cdot \mathbf{S}_{i\mathbf{R}'} - \frac{1}{2} \sum_{i \neq j} J_{ij} \mathbf{S}_{i\mathbf{R}} \cdot \mathbf{S}_{j\mathbf{R}} - \frac{D}{2} \sum_{i,\mathbf{R}} (S^z_{i\mathbf{R}})^2 - g\mu_B \sum_{i,\mathbf{R}} B S^z_{i\mathbf{R}}$$  \hspace{1cm} (S7)

Define the antiferromagnetic sites as A and B site, its spin operators are $\mathbf{S}_{ai}$ and $\mathbf{S}_{bi}$, then the Hamiltonian can be
written as:

$$H = -\frac{1}{2} \sum_{ij,lm,\mu} J_{ij}^{\mu} S_{\mu i} \cdot S_{\mu j}^m - \frac{1}{2} \sum_{i,lm} J_{ij}^{\mu} S_{\alpha i}^m \cdot S_{\beta i}^m - \frac{D}{2} \sum_{i,lm} (S_{\mu i}^{lz})^2 - g\mu_B B \sum_{i,l,\mu} S_{\mu i}^{lz}$$ (S8)

where \(i, j\) is the index of unit cell, \(l, m = 1, 2\) is the index of atoms per unit cell, \(\mu = a, b\) is the two antiferromagnetic sites.

**Holstein-Primakoff Theory**

Write \(S_i S_j\) as \((S_i^+ S_j^- + S_i^- S_j^+)/2 + S_i^z S_j^z\) and use a Holstein-Primakoff transformation as:

$$S_{ai}^{l+} = \sqrt{2S} S_{\mu i}^l \left( 1 - \frac{a_i^l a_i^{\dagger}}{2S} \right), \quad S_{ai}^{l-} = \sqrt{2S} S_{\mu i}^l \left( 1 - \frac{a_i^l a_i^{\dagger}}{2S} \right), \quad S_{ai}^{lz} = S - a_i^l a_i^{\dagger}$$ (S9)

for A site and

$$S_{bi}^{l+} = \sqrt{2S} b_{i\mu}^l \left( 1 - \frac{b_i^l b_i^{\dagger}}{2S} \right), \quad S_{bi}^{l-} = \sqrt{2S} b_{i\mu}^l \left( 1 - \frac{b_i^l b_i^{\dagger}}{2S} \right), \quad S_{bi}^{lz} = -S + b_i^l b_i^{\dagger}$$ (S10)

for B site, with an expansion in the square root in \(1/S\):

$$\sqrt{1 - \frac{\mu_i^l\mu_j^l}{2S}} = \left[ 1 - \frac{\mu_i^l\mu_j^l}{2S} + o\left(\frac{1}{S^2}\right) \right]$$ (S11)

which is 1 when omitting the magnon-magnon interactions. Then we have:

$$S_{\mu i}^l \cdot S_{\mu j}^m = S^2 + S(\mu_i^l\mu_j^m + \mu_i^l\mu_j^m + \mu_i^m\mu_j^l + \mu_j^m\mu_i^l)$$

for the in-plane term \(\mu = a, b\) and

$$S_{ai}^l \cdot S_{bj}^m = -S^2 + S(a_i^l b_j^m + a_i^l b_j^m + a_i^l a_i^l + b_j^l b_j^l)$$ (S13)

for the inter-plane term. The magnetic anisotropic energy term is:

$$(S_{\mu i}^{lz})^2 = S^2 - 2\mu_i^l \mu_i^l$$ (S14)

and the Zeeman term is:

$$S_{ai}^{lz} = S - a_i^l a_i^{\dagger}, \quad S_{bi}^{lz} = -S + b_i^l b_i^{\dagger}$$ (S15)

In the form of boson operators, the Heisenberg model of antiferromagnets can be then written as follow:

$$H = -\frac{1}{2} \sum_{ij,lm,\mu} J_{ij}^{\mu} \{S^2 + S(\mu_i^l\mu_j^m + \mu_i^l\mu_j^m - \mu_i^l\mu_j^l - \mu_j^m\mu_j^m)\} - \frac{1}{2} \sum_{i,lm} J_{ij}^{\mu} \{-S^2 + S(a_i^l b_j^m + a_i^l b_j^m + a_i^l a_i^l + b_j^l b_j^l)\}$$

$$- \frac{D}{2} \sum_{i,l,\mu} (S^2 - 2\mu_i^l \mu_i^l) + g\mu_B B \sum_{i,l} (a_i^l a_i^{\dagger} - b_i^l b_i^{\dagger})$$ (S16)

the Hamiltonian is then \(H = H_0 + H_1\) with the classical ground energy as:

$$H_0 = -\frac{1}{2} \sum_{ij,lm,\mu} J_{ij}^{\mu} S^2 + \frac{1}{2} \sum_{i,lm} J_{ij}^{\mu} S^2 - \frac{D}{2} \sum_{i,l,\mu} S^2$$ (S17)
and the magnon part as:

\[
H = -\frac{1}{2} \sum_{ij,l,m,\mu} J_{ij}^{\mu} S(\delta_{ij}^{l,m} + \delta_{ij}^{m,l} - \delta_{ij}^{l,m} - \delta_{ij}^{m,l}) - \frac{1}{2} \sum_{i,l,m} J_{i}^{\mu} S(a_{i}^{l+} b_{i}^{m+} + a_{i}^{l-} b_{i}^{m-})
\]

\[
+ DS \sum_{i,l,\mu} \mu_{i}^{l+} \mu_{i}^{l-} + g\mu B S \sum_{i,l} (a_{i}^{l+} a_{i}^{l-} - b_{i}^{l+} b_{i}^{l-})
\]

(S18)

Perform the Fourier transformations as follow:

\[
a_{i}^{l} = \sqrt{2N} \sum_{q} e^{iR_{i}^{l} q_{a}^{l}} a_{q}^{l}, \quad a_{i}^{l} = \sqrt{2N} \sum_{q} e^{-iR_{i}^{l} q_{a}^{l}} a_{q}^{l}, \quad b_{i}^{l} = \sqrt{2N} \sum_{q} e^{iR_{i}^{l} q_{a}^{l}} b_{q}^{l}, \quad b_{i}^{l} = \sqrt{2N} \sum_{q} e^{-iR_{i}^{l} q_{a}^{l}} b_{q}^{l}
\]

(S19)

Define \(\delta^{lm} = R^{l}_{j} - R^{m}_{i}\) and use \(2N^{-1} \sum_{\delta} e^{i(a-q')\cdot\delta^{lm}} = \delta_{qq'}\), then for the inplane part:

\[
\sum_{ij} \mu_{i}^{l} \mu_{j}^{m+} = \sum_{q} (\sum_{\delta} e^{-i\delta\cdot\mu}) \mu_{q}^{l} \mu_{q}^{m+}
\]

\[
\sum_{ij} \mu_{i}^{l} \mu_{j}^{m} = \sum_{q} (\sum_{\delta} e^{i\delta\cdot\mu}) \mu_{q}^{l} \mu_{q}^{m}
\]

\[
\sum_{ij} \mu_{i}^{l} \mu_{j}^{m} = \sum_{q} (\sum_{\delta} \mu_{q}^{l} \mu_{q}^{m}) = \sum_{q} z_{\mu}^{lm} \mu_{q}^{l} \mu_{q}^{m}
\]

(S20)

and for the inter-plane part is:

\[
\sum_{ij} a_{i}^{l} b_{j}^{m} = \sum_{q} (\sum_{\delta} e^{-i\delta\cdot\mu}) a_{q}^{l} b_{q}^{m}, \quad \sum_{ij} a_{i}^{l} b_{j}^{m+} = \sum_{q} (\sum_{\delta} e^{i\delta\cdot\mu}) a_{q}^{l} b_{q}^{m+}
\]

\[
\sum_{i} a_{i}^{l} b_{i}^{m} = \sum_{q} (\sum_{\delta} a_{q}^{l} b_{q}^{m}) = \sum_{q} z_{\nu}^{lm} b_{q}^{l} b_{q}^{m}, \quad \sum_{i} b_{i}^{l} b_{i}^{m+} = \sum_{q} (\sum_{\delta} b_{q}^{l} b_{q}^{m+}) = \sum_{q} z_{\nu}^{lm} b_{q}^{l} b_{q}^{m}
\]

(S21)

The Hamiltonian in q-space is then

\[
H_{1} = \frac{1}{2} \sum_{q, l, m, \mu} J_{l}^{\mu} S(\delta_{q}^{lm} a_{q}^{l} a_{q}^{l} + z_{\mu}^{lm} a_{q}^{l} a_{q}^{m} - \gamma_{\mu}^{lm} a_{q}^{l} a_{q}^{m} - \gamma_{\mu}^{lm} a_{q}^{l} a_{q}^{m})
\]

\[
- \frac{1}{2} \sum_{q, l, m} 2J_{l}^{\nu} S(\delta_{q}^{lm} a_{q}^{l} a_{q}^{l} + z_{\nu}^{lm} a_{q}^{l} a_{q}^{m} + \gamma_{\nu}^{lm} a_{q}^{l} a_{q}^{m} + \gamma_{\nu}^{lm} a_{q}^{l} a_{q}^{m}) + DS \sum_{q, l, \mu} \mu_{q}^{l} \mu_{q}^{l} + g\mu B \sum_{q, l} (a_{q}^{l+} a_{q}^{l-} - b_{q}^{l+} b_{q}^{l-})
\]

(S22)

For the bilayer CrI\(_3\) system, we have \(z_{\nu}^{lm} = 1\) where we only consider the nearest neighbor interactions for the inter-plane coupling, define:

\[
\xi_{l}^{\mu} = \frac{1}{2} \sum_{m} J_{l}^{\mu} S \delta_{l}^{lm} - \frac{1}{2} \sum_{m} J_{l}^{\mu} S(\gamma_{l}^{m} + \gamma_{l}^{m*}) - J_{l} S + DS \pm g\mu B
\]

\[
\lambda_{l}^{\mu} = \frac{1}{2} \sum_{l} e^{-i\delta\cdot\mu}, \quad \lambda_{l}^{\mu*} = \frac{1}{2} \sum_{l} e^{i\delta\cdot\mu}, \quad \lambda_{l}^{\mu} + \lambda_{l}^{\mu*} = 2J_{l} S
\]

(S23)

Then we get a Hamiltonian as:

\[
H_{1} = \sum_{q, \mu, l} \{\xi_{l}^{\mu} \mu_{q}^{l} \mu_{q}^{l} + \sum_{q, \mu, l \neq m} (\lambda_{l}^{\mu} \mu_{q}^{l} \mu_{q}^{m} + h.c.) + \lambda^{\nu} \sum_{q, l, m} (a^{l} b^{m} + h.c.)\}
\]

(S24)

Bogoliubov transformation

Performing Bogoliubov transformation:

\[
\alpha_{q}^{l} = u_{q}^{l} a_{q}^{l} + v_{q}^{l} b_{q}^{l}, \quad \alpha_{q}^{l*} = u_{q}^{l*} a_{q}^{l*} + v_{q}^{l*} b_{q}^{l*}, \quad \beta_{q}^{l} = v_{q}^{l} a_{q}^{l} + u_{q}^{l} b_{q}^{l}, \quad \beta_{q}^{l*} = v_{q}^{l*} a_{q}^{l*} + u_{q}^{l*} b_{q}^{l*}
\]

(S25)
with \( u_q^2 - v_q^2 = 1 \). We can easily get the inverse transformation as

\[
a^q_l = u_q a^q_l - v_q \beta^q_l, \quad d^q_l = u_q d^q_l - v_q \beta^q_l, \quad b^q_l = -v_q a^q_l + u_q \beta^q_l, \quad \bar{b}^q_l = -v_q a^q_l + u_q \beta^q_l
\]  

(S26)

Then the Hamiltonian in the new basis is

\[
H_1(q) = \sum_{l,q}(u^2 q^2 c^a_{ql} + v^2 q^2 c^b_{ql} - 2u_q v_q \lambda^l) \alpha^q_l \alpha^q_l + \sum_{l,q}(u^2 q^2 c^a_{ql} + v^2 q^2 c^a_{ql} - 2u_q v_q \lambda^l) \beta^q_l \beta^q_l + \sum_{l,q}(\lambda^l(u^2 q^2 + v^2 q^2) - 2u_q v_q \lambda^l)(\alpha^q_l \alpha^q_l + \beta^q_l \beta^q_l)
\]  

(S27)

\[
+ \sum_{l,q}(\lambda^l(u^2 q^2 + v^2 q^2) - 2u_q v_q \lambda^l)(\alpha^q_l \beta^q_l + \alpha^q_l \beta^q_l) + \sum_{l,q}(v^2 q^2 - 2u_q v_q \lambda^l)
\]

(S28)

Define :

\[
\xi^l = \frac{\xi^l + \xi^l}{2}, \quad \bar{\xi}^l = \frac{\xi^l - \xi^l}{2}
\]

(S29)

Let the coefficients of \( \alpha^q_l \beta^q_l \) and \( \alpha^q_l \beta^q_l \) to be 0, solve the following equations:

\[
u q^2 - v q^2 = 1
\]

(S30)

\[
2u_q v_q \xi - (u^2 q^2 + v^2 q^2) \lambda^l = 0
\]

it can be seen that

\[
u_q = \cosh \theta_q, \quad v_q = \sinh \theta_q
\]

(S31)

The Hamiltonian is then:

\[
H_1 = \sum_{l,q}(u^2 q^2 + v^2 q^2) \xi^l - 2u_q v_q \lambda^l + \xi^l) \alpha^q_l \alpha^q_l + \sum_{l,q}(u^2 q^2 + v^2 q^2) \lambda^l \beta^q_l \beta^q_l + \sum_{l,q}(\lambda^l(u^2 q^2 + v^2 q^2) - 2u_q v_q \lambda^l)(\alpha^q_l \alpha^q_l + \beta^q_l \beta^q_l)
\]

(S32)

\[
+ \sum_{l,q}(\lambda^l(u^2 q^2 + v^2 q^2) - 2u_q v_q \lambda^l)(\alpha^q_l \beta^q_l + \alpha^q_l \beta^q_l) + \sum_{l,q}(2v^2 q^2 - 2u_q v_q \lambda^l)
\]

use the relations of hyperbolic functions as:

\[
u^2 q = \cosh^2 \theta_q = \frac{\cosh 2\theta_q + 1}{2}, \quad v^2 q = \sinh^2 \theta_q = \frac{\cosh 2\theta_q - 1}{2}, \quad u_q v_q = \sinh \theta_q \cosh \theta_q = \frac{\sinh 2\theta_q}{2}
\]

(S33)

and we also have

\[
tanh 2\theta_q = \eta_q, \quad \sinh 2\theta_q = \sqrt{1 - \tanh^2 2\theta_q} = \frac{\eta_q}{\sqrt{1 - \eta_q^2}}, \quad \cosh 2\theta_q = \frac{1}{\sqrt{1 - \tanh^2 2\theta_q}} = \frac{1}{\sqrt{1 - \eta_q^2}}
\]  

(S34)
then

\[ u_q^2 + v_q^2 = \cosh 2\theta_q = \frac{1}{\sqrt{1 - \eta_q^2}}, \quad 2u_qv_q = \sinh 2\theta_q = \frac{\eta_q}{\sqrt{1 - \eta_q^2}} \]  

(S35)

The final Hamiltonian becomes as:

\[ H_1(q) = \begin{pmatrix} \chi \xi_1^a + \xi_2^a & \kappa^a - \eta \kappa^v & 0 & \kappa^v - \eta \kappa^a \\ \kappa^a - \eta \kappa^v & \chi \xi_2^a + \xi_2^a & \kappa^v - \eta \kappa^a & 0 \\ 0 & \kappa^v - \eta \kappa^a & \chi \xi_1^b + \xi_1^b & \kappa^b - \eta \kappa^v \\ \kappa^v - \eta \kappa^a & 0 & \kappa^b - \eta \kappa^v & \chi \xi_2^b + \xi_2^b \end{pmatrix} \]  

(S36)

with \( \chi = \sqrt{1 - \eta_q^2} \), \( \kappa^a = \lambda^a / \chi \) and \( \kappa^v = \lambda^v / \chi \)

**Correction of Ground Energy**

The ground state satisfies:

\[ \alpha^l_q |0\rangle = \beta^l_q |0\rangle = 0 \]  

(S37)

It follows that the corrected ground state is:

\[ E_0^c = \langle 0 | H_1 | 0 \rangle = \sum_{q,l} (\sqrt{1 - \eta_q^2} - 1) \xi^l \]  

(S38)

**Magnons in CrI\(_3\)**

Because our DFT calculations give an interlayer exchange constant of the wrong sign \((J_v \approx 0.12 \text{ meV})\), we estimate this interaction strength \(z_vJ_v \approx -0.05 \text{ meV}\) from experiment. Combining this with theoretical intralayer exchange constants and using a linearized spin-wave theory, we have evaluated the magnon dispersion relation in bilayer CrI\(_3\). The result in the absence of gate fields, illustrated in Fig. S10(a), has a gap of around 1 meV at \(\Gamma\). Theoretically \(\hbar \omega_{q=0} \approx 2S \sqrt{D(D/4 - z_vJ_v)}\) for the lower energy magnon branch. Since \(D\) and \(z_vJ_v\) are of the same order, the magnon gap at \(\Gamma\) is substantially influenced by both anisotropy and interlayer exchange. The magnon Dirac cone around the K point is expected, given the honeycomb lattice and the close analogy between magnon and one-band tight-binding model electronic dispersions, discussed recently [S12] in the ferromagnetic multilayer case. While for the antiferromagnetic bilayer case a Bogoliubov transformation needs to be performed, and besides the coupling between the intra-plane sublattice coupling, there is also an inter-layer coupling. Two Dirac cones are thus coupled (shown as in the insert of Fig. S10, where red and blue Dirac cones belong to the two layers) at the \(K\) point.

**Metropolis Monte Carlo \(T_c\) calculations**

The Curie temperature \(T_c\) of the anisotropic classical Heisenberg model in a honeycomb lattice is calculated using the Metropolis Monte Carlo method [S13, S14]. In the following we provide a brief description of the anisotropic Heisenberg model and the simulation method to obtain the \(T_c\) values. We begin by noting that the direction of the classical spins are defined through \(\theta\) and \(\phi\) and explicitly given by the spherical polar coordinates

\[ S_x = |S| \sin \theta \cos \phi \]  

(S39)

\[ S_y = |S| \sin \theta \sin \phi \]  

(S40)

\[ S_z = |S| \cos \theta. \]  

(S41)
FIG. S10: Magnons and magnetization: Magnon dispersion of bilayer CrI$_3$, where including interlayer and neighbor and next nearest neighbor intralayer exchange coupling. The insert is the zoomed dispersion at the $K$ point, as shown there are two Dirac cones, belong to the two layers correspondingly and labeled with red and blue color.

**Calculation of Spin Anisotropy ($\Delta$)**

We define the magnetocrystalline anisotropy energy per lattice site as the difference between two directions of spins

$$\text{MAE} = E(0^\circ) - E(90^\circ), \quad (S42)$$

where the MAE can be accounted form through a parameter $\Delta$ in the Heisenberg model Hamiltonian consisting of $J(R_i - R_j)$ exchange coupling model where we retain the contributions from the three nearest neighbors in the Hamiltonian. We obtain the expression for the total energy

$$E = -\frac{1}{2N} \sum_{i,j} J(R_i - R_j) \left( S_i^z S_j^z + (1 - \Delta) (S_i^x S_j^x + S_i^y S_j^y) \right) = \frac{1}{2N} \sum_i E_i \quad (S43)$$

where $E_i$ is the energy of each site $i$ interacting with neighboring atomic sites $j$ and includes an anisotropy term $\Delta$ presented in earlier literature of the anisotropic Heisenberg model [S15], and $N$ is the number of sites in the supercell. The $1/2$ factor accounts for the double counting of the interaction between the sites. Here, the limit of $\Delta = 0$ corresponds to the isotropic Heisenberg Hamiltonian while $\Delta = 1$ represents the pseudo-Ising model, whose difference with the Ising model consists in the larger phase space where the spins are allowed to fluctuate in the $x$-$y$ directions. When $\theta = 0^\circ$ the spins align along the positive $z$ direction, while for $\theta = 90^\circ$ the spins are in the $x$-$y$ plane. We can write for $E_i(\theta = 0^\circ)$ pointing in the $z$ direction for an arbitrary lattice site $i$

$$E_i(\theta = 0^\circ) = -\left( J_{1z} S_i^z + J_{2z} S_i^z + J_{3z} S_i^z \right) \sum_j S_j^z \quad (S44)$$

with three, six and three connecting $j$ neighbor sites for $J_1$, $J_2$ and $J_3$ exchange couplings respectively. Likewise $E(\theta = 90^\circ)$ is written as:

$$E_i(\theta = 90^\circ) = (1 - \Delta) \times -\left( J_{1x} S_i^x + J_{2x} S_i^x + J_{3x} S_i^x \right) \sum_j S_j^x - \left( J_{1y} S_i^y + J_{2y} S_i^y + J_{3y} S_i^y \right) \sum_j S_j^y \quad (S45)$$

Considering the isotropy of the Hamiltonian for $\Delta = 0$ we note that the different $x, y, z$ components of the exchange coupling for every cartesian axis satisfy $J_i = J_{ix} = J_{iy} = J_{iz}$. The $J$ exchange coupling parameters are defined consistently with the magnetic moments using classical spin vectors $|S| = 3\mu_B/2$ represented in units of Bohr magneton. We consider a uniform ferromagnetic magnetization and use the definition in Eq. (S42) to obtain

$$\text{MAE} = -\Delta [3J_1 + 6J_2 + 3J_3] |S|^2/2$$

and we calculate $\Delta$ from the magnetic anisotropy energy

$$\Delta = -\frac{2\text{MAE}}{[3J_1 + 6J_2 + 3J_3]|S|^2}.$$
We obtain the exchange coupling $J$ parameters ($J_1 = 1.730$ meV, $J_2 = 0.258$ meV, $J_3 = -0.0884$ meV) and the MAE from the density functional calculations to obtain:

Monolayer CrI$_3$: MAE = $-0.956$ meV/Cr, then $\Delta = 0.0328$

Bi-Layer CrI$_3$: MAE = $-0.659$ meV/Cr, then $\Delta = 0.0226$.

### Classical Monte Carlo critical temperatures

The Monte Carlo calculations were performed in honeycomb lattice sites with $50 \times 50$ with brick lattice configurations and up to $80 \times 80$ for convergence verification which are large enough to capture total energy differences due to anisotropy with a resolution of $\Delta \gtrsim 1/N^2$ of about one thousandth’s of the largest $J$ coupling parameter due to magnetic anisotropy. The magnetocrystalline anisotropy energies favoring the $z$ axis were obtained for $\text{MAE}_{\text{mono}} = 956.9$ micro-eV and $\text{MAE}_{\text{bi}} = 659.7$ micro-eV per Cr atom from ab initio calculations with fully-relativistic pseudopotentials as implemented in Quantum Espresso. We have typically used 100k Monte Carlo steps for thermalization and 100k for averaging the observables, and up to 400k averaging steps for smoother results when a higher resolution in temperature was required for electric-field induced effects. We use the Landau-Binder spin-flip procedure that satisfies [S15]

$$S'_{i\alpha} = \frac{S_{i\alpha} + \rho^\alpha \delta}{\left[\sum_\alpha (S_{i\alpha} + \rho^\alpha \delta)^2\right]^{1/2}}$$ (S46)

where the $\alpha$ is the Cartesian spin components, $\rho^\alpha$ is a random number between $(-1,1)$ and $\delta$ is a parameter that limits the maximum change allowed in the spin component. We have used $\delta = (Ck_B/J_{\text{max}})T \simeq T$ where the units of $T$ are given in meV/$k_B$. This spin sampling procedure can potentially lead to spurious metastable phases in the limit of $T \to 0$ [S16] but shouldn’t affect the calculation of $T_c$ that take place at higher temperatures.

### Effect of spin anisotropy on Curie Temperature

The role of spin anisotropy ($\Delta$) on Curie temperature $T_c$ is calculated for various anisotropy values starting from 0.0001 to 1.0 meV (pseudo Ising limit) for the case of monolayer and bilayer CrI$_3$. The interlayer exchange parameter for bilayer is $J_v = 0.121$ meV, and the experimental value $J_v = -0.05$ meV. The $J$ values obtained for the zero electric fields are used to capture the interlayer coupling. For the case of the monolayer, the $J$ values of either top or bottom layers are used to estimate the $T_c$. While the $T_c$ shows a clear decrease for $\Delta \to 0$ there is a rather sharp increase in $T_c$ particularly for small values of $\Delta$. for values above less than 0.4 meV, and later the $T_c$ saturated to a constant value as shown in Fig.S11. The drastic decrease in the $T_c$ for lower anisotropy values indicates that the $T_c$ value eventually should be zero for zero anisotropy, i.e., the uniform distribution of spin direction without any anisotropy.

### Effect of interlayer exchange coupling

Magnetic properties, of monolayer and bilayer CrI$_3$ as a function of interlayer coupling $J_v$ parameter are estimated. The anisotropy values for monolayer, $\Delta = 0.0328$ and for bilayer, $\Delta = 0.0226$, and with the $J$ values obtained for zero electric fields are used (see Fig. S12). There is a direct effect in the $T_c$ with the interlayer exchange parameter ($J_v$).

### Scaling of exchange coupling in top layer

In Fig. S12 we can observe how the $T_c$ value is affected by the magnitude of the interlayer exchange $J_v$ and how these are also affected by the intralayer $J$ values. Here, we quantify the $T_c$ values by scaling the exchange parameters of the top layer ($J_t$) up to $\pm 20\%$ for $J_v = \pm 0.05$ meV and $\pm 0.121$ meV. From Fig. S13, it is clearly found that there is a linear dependence of $T_c$ on the change of magnitude of $J_t$ values. Fig. S13, shows the behavior of $T_c$ for relative scaling of the top layer exchange parameters is varied. From the variation of $T_c$ as a function of intralayer $J_t$ versus interlayer $J_v$ we can conclude that the role of intralayer exchange is much stronger than the interlayer exchange.
FIG. S11: The Curie temperatures as a function of $\Delta$ anisotropy are obtained for the mono and bi-layer CrI$_3$. The $T_c$, for monolayer, is always lower compared to the bilayer. Moreover, the $T_c$ values in the bilayer is found to be increased with the interlayer exchange value. A progressive increase of $T_c$ with the $\Delta$ anisotropy is observed in case of monolayer and bilayer of CrI$_3$. $T_c$ are extracted from the maxima of the heat capacity.

**Effect of electric field**

Finally, we compare the $T_c$ variation as a function of applied electric field ($\pm 0.1$, $\pm 0.5$ and $\pm 1$ V/nm) for interlayer exchange parameter $J_v = \pm 0.121$meV and $\pm 0.05$ meV (S14). The variation of $T_c$ is found to be on the order of 2% which is consistent with the similar variations of the exchange coupling values due to the applied electric fields, see Fig. S8. We show that the $T_c$ is dominated by the layer with the largest intralayer exchange coupling parameters and the role of the electric field is directly related with the variations in the exchange parameters introduced by the applied electric fields, and are shown in Fig. S14.

**Mean Field Theory**

The Heisenberg model for the antiferromagnetic CrI$_3$ without magnetic anisotropic energy and external magnetic field is:

$$H = -\frac{1}{2} \sum_{ij} J_{ij}^a S_i^a \cdot S_j^a - \frac{1}{2} \sum_{ij} J_{ij}^b S_i^b \cdot S_j^b - \frac{1}{2} \sum_{ij} J_{ij}^v S_i^a \cdot S_j^b$$ (S47)

where $S_i^{a/b}$ is the spin operators of the $i^{th}$ sites for a/b sublattice, $J_{ij}^{a/b}$ is the exchange coupling in the a/b sublattice plane and $J_{ij}^v$ is the exchange coupling between the two sublattice. With

$$S_i \cdot S_j = S_i \cdot \langle S_j \rangle + \langle S_i \rangle \cdot S_j - \langle S_i \rangle \cdot \langle S_j \rangle (S_j - \langle S_j \rangle)$$ (S48)

here the last term is the fluctuation and will be omitted. The Hamiltonian in the mean field approximation is then:

$$H = -g\mu_B \sum_i B_a \cdot S_i^a - g\mu_B \sum_i B_b \cdot S_i^b + E_{MF}$$ (S49)

with $\mu_B$ the Bohr magneton, and

$$E_{MF} = \frac{1}{2} \sum_{\alpha=a,b} \sum_{k} z_k J_{k}^\alpha (S^\alpha)^2 + \frac{1}{2} z_v J_v (S^a)(S^b)$$ (S50)
FIG. S12: The specific heat and magnetization as a function of temperature for monolayer and bilayer with different interlayers coupling values of $J_v = \pm 0.05$ meV and $\pm 0.121$ meV. The $T_c$ that can be read from the divergence of the heat capacity or the abrupt changes in the magnetization is seen to increase together with the magnitude of interlayer coupling regardless of sign. We notice the onset of antiferromagnetic ground states and vanishing total magnetization when $J_v < 0$.

is the mean field energy, with $z_{k/v}$ the number of neighbors, the effect field of the a/b sublattice is:

$$g\mu_B B_\alpha (\langle S^a \rangle, \langle S^b \rangle) = \frac{1}{2} \left( \sum_k z_k J_k^a \langle S^a \rangle + \frac{1}{2} z_v J^v \langle S^a \rangle \right) \langle S^a \rangle + \frac{1}{2} z_v J^v \langle S^a \rangle$$

(S51)

with $B_{a/s}$ and $B \cdot S_i$ have the relation of $B \cdot S_i = B_{a/s}$. To get the magnetization, we can calculate the partition function as:

$$Z_\alpha = \text{Tr} e^{-\beta H^a} = \sum_{s_i = -S}^S e^{\beta g\mu_B B_\alpha s_i}$$

(S52)

where $\beta = (k_B T)^{-1}$, then we have $Z_\alpha = \prod_{i=1}^{N/2} \sum_{s_i = -S}^S e^{\beta g\mu_B B_\alpha s_i}$. Define $b = g\mu_B B_\alpha$, then :

$$Z_\alpha = \left[ e^{\beta b (S + 1)} + e^{-2S+b} + \cdots + e^{-2S+b} \right]^{N/2}$$

(S53)

Since $\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n$ and sinh $x = \frac{e^x - e^{-x}}{2}$, the partition functions become as $Z_\alpha = \left[ \sinh \beta b (S + \frac{1}{2}) \right]^{N/2}$ From the partition functions, we can get the free energy as $F = \frac{1}{\beta} \ln Z$, the magnetization is then:

$$M_\alpha = \frac{\partial F_\alpha}{\partial B_\alpha} = \frac{N}{2} g\mu_B S B_S (\beta g\mu_B B_\alpha)$$

(S54)

where $B_S(x)$ is Brillouin function as $B_S(x) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} x - \frac{1}{2S} \coth \frac{1}{2S} x$. The magnetization is:

$$M_\alpha = \frac{N}{2} g\mu_B (S^a)$$

(S55)
FIG. S13: The behavior of the specific heat and magnetization when one of the layer $J$ values are uniformly varied and the interlayer exchange parameter $J_v = \pm 0.121, \pm 0.05$ meV are used. We observe enhancement of $T_c$ values for larger intralayer and interlayer $J$ coupling parameters.
FIG. S14: The behavior of the specific heat and magnetization as a function of electric field for interlayer exchange coupling values of $J_v = \pm 0.121$ meV and $J_v = \pm 0.05$ meV. The interlayer coupling is ferromagnetic $J_v > 0$ and antiferromagnetic $J_v < 0$ depending on the sign.
From Eq. S51, S54 and S55, we can get:

\[
\langle S^a \rangle = S_B S(\beta S) \left( \frac{1}{2} \sum_k z_k J_k^a \langle S^a \rangle + \frac{1}{2} z_v J_v \langle S^b \rangle \right)
\]

\[
\langle S^b \rangle = S_B S(\beta S) \left( \frac{1}{2} \sum_k z_k J_k^b \langle S^b \rangle + \frac{1}{2} z_v J_v \langle S^a \rangle \right)
\]

\[\text{(S56)}\]

**Magnetoelectric response**

Define the ferromagnetic order parameters as:

\[
f = S(s_0 - s_1), \quad g = S(s_0 + s_1) \quad \text{(S57)}
\]

where \( s_i \) can be solved from Eq. S56. When including the magnetic field and electric field, then we have \( s_i = B_S(\beta h_i) \) and \( h_i \) is

\[
h_0 = \tilde{J}_F s_0 + \tilde{J}_{AF} s_1 + H + \lambda E s_0
\]

\[
h_1 = \tilde{J}_{AF} s_0 + \tilde{J}_F s_1 - H - \lambda E s_1 \quad \text{(S58)}
\]

with \( H \) have the unit of \( \tilde{J}_F \) which is defined in the main text. Without electric field and magnetic field, the antiferromagnetic order vs temperature is shown in Fig. S15, as we see that the thermodynamical behavior is nearly independent of the interlayer exchange coupling. The magnetic susceptibility which is defined as \( \partial f / \partial H \) at \( E = 0 \) is shown in Fig. S16. It shows a critical divergence in \( \chi \) that would occur at the Néel temperature \( T_N \) if the ground state were ferromagnetic is only weakly truncated in the antiferromagnetic state. The thermal dynamics of magnetoelectric response is shown in Fig. S17, as it shows that in the absent of electric field, there is no ferromagnetic order at all range of temperature. While increasing the temperature up to the critical \( T_c \), a maximum of magnetoelectric response happens close to \( T_c \) at finite electric field. Based on the intra-layer exchange coupling got from DFT (Table II), and the experimental estimated inter-layer exchange coupling, the ferromagnetic order vs. temperature is shown in Fig. S18.
FIG. S18: Mean-field temperature-dependent magnetization under the influence of an electric field using the exchange constants from Table II.
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