

Ab initio methodology for magnetic exchange parameters: Generic four-state energy mapping onto a Heisenberg spin Hamiltonian

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The recent development in the field of two-dimensional magnetic materials urges reliable theoretical methodology for determination of magnetic properties. Among the available methods, *ab initio* four-state energy mapping based on density functional theory stands out as a powerful technique to calculate the magnetic exchange interaction in the Heisenberg spin model. Although the required formulas were explained in earlier works, the considered Hamiltonian in those studies always corresponded to the specific case that the off-diagonal part of J matrix is antisymmetric, which may be misleading in other cases. Therefore, using the most general form of the Heisenberg spin Hamiltonian, we here derive the generic formulas. With a proper choice of four different magnetic states, a single formula governs all elements of the exchange interaction matrix for any considered pair of spin sites.

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I. INTRODUCTION

After the experimental realization of the ferromagnetic monolayer of CrI_3 in 2017 [1], two-dimensional (2D) magnetic materials have been at the very forefront of both theoretical [2–5] and experimental [6–8] investigations. Previously, 2D ferromagnetism was not deemed possible due to the Mermin-Wagner theorem [9], which states that long-range order cannot survive temperature fluctuations in an isotropic system. In monolayer CrI_3 and in different 2D magnetic materials reported later [2,8], the magnetic anisotropy due to the strong spin-orbit coupling removes the Mermin-Wagner restriction and allows the material to retain the magnetization at nonzero temperature.

On the other hand, strong spin-orbit coupling also instigates antisymmetric magnetic exchange interaction between the spin sites, the so-called Dzyaloshinskii-Moriya interaction (DMI) [10,11]. Contrary to the usual magnetic exchange interaction which favors magnetic moments that are parallel or antiparallel, DMI forces the magnetic moments to be orthogonal. DMI is observed in the presence of structural anisotropy in the system at low temperatures and is responsible for the emergence of nontrivial spin textures, such as skyrmionic ones [12,13].

With such prominent recent advances in the field of 2D magnetism and the emerging significance of the microscopic interactions, such as DMI, for the overall magnetic properties, the need for reliable theoretical frameworks is growing rapidly.

The calculation of the microscopic magnetic parameters using methods based on mapping between the quantum many-body Hamiltonian and the simpler, classical spin Hamiltonian is already common [3,4,7,14–19]. Mapping between two spectra can roughly be grouped into two categories. The first

category maps (the first or second) derivatives of the total energies between two Hamiltonians [17–19], where derivatives are taken with respect to the polar and/or azimuthal angles of each spin vector. The second category maps the total energies between two Hamiltonians [3,4,7,14–16]. These methods, in general, rely on obtaining the energies of several alternative magnetic configurations and mapping those energies to the specific Hamiltonian that governs the considered system. Such energy mapping produces a system of equations to be solved by algebraic methods in order to obtain the magnetic exchange parameters. Since algebraic manipulations are, in general, much less demanding than dealing with the derivatives, most recent studies employed methods based on the second type of energy mapping. Among such methods, the four-state methodology (4SM), which was presented by Xiang *et al.* [15,16], stands out as particularly effective [5,7]. One should note, however, that 4SM, although widely used in the analysis of 2D magnetic crystal analysis, is not limited to 2D crystals exclusively. As explained in Refs. [15,16], 4SM can be employed in any magnetic system.

The most important advantage of the 4SM method compared to methods based on density functional theory (DFT) and energy mapping used previously [3,4,14] is that all parameters of the Heisenberg spin Hamiltonian are calculated on an atomic level, i.e., pair- or sitewise, instead of the collective spin-state considerations leading to quasiaveraged values of the microscopic magnetic exchange parameters. Furthermore, Refs. [15,16] also presented the technique to calculate DMI parameters in detail. As a consequence of the recent advance in field of 2D magnetism, the impact of studies involving magnetic chirality is growing rapidly [5,20,21]. However, in both Refs. [15,16], the considered spin Hamiltonian consisted of an exchange interaction matrix where the off-diagonal elements were antisymmetric. In Ref. [22] [Eq. (2c)] and in Ref. [23], one can find that the antisymmetric spin Hamiltonian is considered a general one. This is not correct, and in

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later studies [5,20,21], such a consideration was shown not to be compatible with all materials, although in a subtle way, i.e., without any specific comment on that matter.

To remove any possible ambiguity in the procedure to properly calculate off-diagonal exchange elements and DMI components, here, we rewrite the methodology by considering the truly general Heisenberg spin Hamiltonian, without any constraint. In a general case, one should use the same formulas for all exchange parameters $J_{\alpha\beta}$ (without an extra minus sign in any case) and then calculate DMI components in, e.g., the Cartesian frame of reference as $D_x = \frac{1}{2}(J_{yz} - J_{zy})$, $D_y = \frac{1}{2}(J_{zx} - J_{xz})$, and $D_z = \frac{1}{2}(J_{xy} - J_{yx})$. In addition, we further derive the formulas for single-ion anisotropy (SIA) parameters. We also discuss the formation of the SIA matrix in the presence of rotational symmetry as found in 2D and quasi-2D materials (such as few-layer 2D materials and layered bulk materials), where it is clearly possible to distinguish the in-plane directions from the out-of-plane direction. However, different constraints for the SIA matrix might be imposed by different symmetry operations, even in three-dimensional crystals, such as that considered by Xu *et al.* [20] for the rotation around the (111) direction. Although 2D magnetism was the core motivation for this paper, the formulas presented here are applicable to a magnetic system without *any* structural constraint.

This paper is organized as follows. In Sec. II, starting from the most general form of the spin Hamiltonian, we rederive the formulas that allow one to calculate the exchange parameters between different spin sites, as presented in Sec. II A, as well as the single-ion anisotropy, as presented in Sec. II B. In Sec. III we exemplify the 4SM methodology for the case of monolayer CrI₃, with matrix elements extracted from DFT calculations. We present the results obtained using our derived formulas and the results obtained by blindly following the formulas from Refs. [15,16], and we illustrate in detail how one can get misled in the formalism and obtain erroneous conclusions about the physics of magnetic systems. The summary of our calculations and findings is given in Sec. IV.

II. REDERIVATION OF THE FORMULAS

In this section, we present the derivation of the formulas for exchange J and single-ion anisotropy A parameters, starting from the general quadratic Heisenberg spin Hamiltonian for a magnetic system given as

$$H = H_{EX} + H_{SIA},$$

$$H = \sum_{i<j} \vec{S}_i \cdot J_{ij} \cdot \vec{S}_j + \sum_i \vec{S}_i \cdot A_{ii} \cdot \vec{S}_i. \quad (1)$$

The quadratic spin Hamiltonian is the simplest formalism that successfully captures the magnetic properties of the crystal. Although the terms that include more than two spins can be taken into account, their contribution enters as higher-order perturbations and hence is always smaller than that of quadratic terms. We also note that Hamiltonians with terms higher than quadratic would require a departure from the four-state methodology towards an eight- or sixteen-state one in order to have a sufficient number of equations to be able to reduce them to only the terms of interest, as demonstrated in this paper.

The first term describes the magnetic exchange interaction between the i th and j th spin sites, with J_{ij} being a 3×3 matrix. In this study, spin is considered a classical vector $\vec{S}_i = (S_i^x, S_i^y, S_i^z)$, where x , y , and z are chosen Cartesian coordinates. For instance, the interaction between S_i^y and S_j^z is determined by J_{ij}^{yz} or, equivalently, by J_{ji}^{zy} ($\equiv J_{ij}^{yz}$). The details of the methodology to obtain each element of the exchange matrix are given in Sec. II A.

The second term in the Hamiltonian describes the interaction between the spin components of a single ion. Three-dimensional consideration of spin ensures that A_{ii} is a 3×3 matrix which consists of the elements $A_{ii}^{\alpha\beta}$ (α and β are Cartesian coordinates). The process to determine its elements is explained in Sec. II B.

A. Exchange parameter J

We start with the exchange term. In order to determine the magnetic exchange interaction between two neighboring spins, one needs to calculate all nine parameters (nine elements of the exchange interaction matrix J_{ij}). The exchange part of the general Hamiltonian can be written in the explicit form

$$H_{EX} = \sum_{i<j} \vec{S}_i \cdot J_{ij} \cdot \vec{S}_j$$

$$= \sum_{i<j} [S_i^x \cdot J_{ij}^{xx} \cdot S_j^x + S_i^x \cdot J_{ij}^{xy} \cdot S_j^y + S_i^x \cdot J_{ij}^{xz} \cdot S_j^z$$

$$+ S_i^y \cdot J_{ij}^{yx} \cdot S_j^x + S_i^y \cdot J_{ij}^{yy} \cdot S_j^y + S_i^y \cdot J_{ij}^{yz} \cdot S_j^z$$

$$+ S_i^z \cdot J_{ij}^{zx} \cdot S_j^x + S_i^z \cdot J_{ij}^{zy} \cdot S_j^y + S_i^z \cdot J_{ij}^{zz} \cdot S_j^z]. \quad (2)$$

One should note that in general $J_{ij}^{\alpha\beta} \neq J_{ij}^{\beta\alpha}$ ($\alpha, \beta = x, y, z; \alpha \neq \beta$), although the symmetry of a system might impose equality. Next, we arbitrarily choose two spin sites (labeled $i = 1$ and $j = 2$). The contribution of the chosen pair to the general Hamiltonian can be written as

$$H = \vec{S}_1 \cdot J_{12} \cdot \vec{S}_2 + \sum_{j \neq 2} \vec{S}_1 \cdot J_{1j} \cdot \vec{S}_j + \sum_{i \neq 1} \vec{S}_i \cdot J_{i2} \cdot \vec{S}_2$$

$$+ \sum_{i \neq 1, j \neq 2} \vec{S}_i \cdot J_{ij} \cdot \vec{S}_j + \vec{S}_1 \cdot A_{11} \cdot \vec{S}_1 + \vec{S}_2 \cdot A_{22} \cdot \vec{S}_2$$

$$+ \sum_{i \neq 1, 2} \vec{S}_i \cdot A_{ii} \cdot \vec{S}_i. \quad (3)$$

The decomposition of the matrices into Cartesian components results in

$$H = \sum_{\alpha, \beta} S_1^\alpha \cdot J_{12}^{\alpha\beta} \cdot S_2^\beta + \sum_{j \neq 2} \sum_{\alpha, \beta} S_1^\alpha \cdot J_{1j}^{\alpha\beta} \cdot S_j^\beta$$

$$+ \sum_{i \neq 1} \sum_{\alpha, \beta} S_i^\alpha \cdot J_{i2}^{\alpha\beta} \cdot S_2^\beta + \sum_{i \neq 1, j \neq 2} \sum_{\alpha, \beta} S_i^\alpha \cdot J_{ij}^{\alpha\beta} \cdot S_j^\beta$$

$$+ \sum_{\alpha, \beta} S_1^\alpha \cdot A_{11}^{\alpha\beta} \cdot S_1^\beta + \sum_{\alpha, \beta} S_2^\alpha \cdot A_{22}^{\alpha\beta} \cdot S_2^\beta$$

$$+ \sum_{i \neq 1, 2} \sum_{\alpha, \beta} S_i^\alpha \cdot A_{ii}^{\alpha\beta} \cdot S_i^\beta. \quad (4)$$

Here, the only thing left is to choose which parameter $J_{12}^{\alpha\beta}$ from the 3×3 matrix J_{12} one wants to calculate. Without the loss of generality, we choose α to be x and β to be z . We present the derivation and formula only for the J_{12}^{xz} matrix element, as all other elements can be determined in the same manner. The reason for the particular choice of this matrix element lies in the fact that it is connected to the y component of the DMI vector. In the paper where 4SM was introduced [16], there is an additional minus sign in the formula for the mentioned y component, which is correct for the antisymmetric Hamiltonian considered in that paper, but not for a general Hamiltonian. In order to isolate J_{12}^{xz} , one needs to obtain the energies of four different magnetic states of the lattice as follows:

$$\begin{aligned} \text{State 1 : } \vec{S}_1 &= (+S, 0, 0), & \vec{S}_2 &= (0, 0, +S), \\ \text{State 2 : } \vec{S}_1 &= (+S, 0, 0), & \vec{S}_2 &= (0, 0, -S), \\ \text{State 3 : } \vec{S}_1 &= (-S, 0, 0), & \vec{S}_2 &= (0, 0, +S), \\ \text{State 4 : } \vec{S}_1 &= (-S, 0, 0), & \vec{S}_2 &= (0, 0, -S), \end{aligned}$$

and for all the rest, $\vec{S}_{i \neq 1,2} = (0, +S, 0)$ or $\vec{S}_{i \neq 1,2} = (0, -S, 0)$ for all four states. The four states give four energies:

$$\begin{aligned} E_1 &= S \cdot J_{12}^{xz} \cdot S + \sum_{j \neq 2} S \cdot J_{1j}^{xy} \cdot S + \sum_{i \neq 1} S \cdot J_{i2}^{yz} \cdot S \\ &+ \sum_{i \neq 1, j \neq 2} S \cdot J_{ij}^{yy} \cdot S + S \cdot A_{11}^{xx} \cdot S + S \cdot A_{22}^{zz} \cdot S \\ &+ \sum_{i \neq 1,2} S \cdot A_{ii}^{yy} \cdot S, \end{aligned} \quad (5)$$

$$\begin{aligned} E_2 &= -S \cdot J_{12}^{xz} \cdot S + \sum_{j \neq 2} S \cdot J_{1j}^{xy} \cdot S - \sum_{i \neq 1} S \cdot J_{i2}^{yz} \cdot S \\ &+ \sum_{i \neq 1, j \neq 2} S \cdot J_{ij}^{yy} \cdot S + S \cdot A_{11}^{xx} \cdot S + S \cdot A_{22}^{zz} \cdot S \\ &+ \sum_{i \neq 1,2} S \cdot A_{ii}^{yy} \cdot S, \end{aligned} \quad (6)$$

$$\begin{aligned} E_3 &= -S \cdot J_{12}^{xz} \cdot S - \sum_{j \neq 2} S \cdot J_{1j}^{xy} \cdot S + \sum_{i \neq 1} S \cdot J_{i2}^{yz} \cdot S \\ &+ \sum_{i \neq 1, j \neq 2} S \cdot J_{ij}^{yy} \cdot S + S \cdot A_{11}^{xx} \cdot S + S \cdot A_{22}^{zz} \cdot S \\ &+ \sum_{i \neq 1,2} S \cdot A_{ii}^{yy} \cdot S, \end{aligned} \quad (7)$$

and

$$\begin{aligned} E_4 &= S \cdot J_{12}^{xz} \cdot S - \sum_{j \neq 2} S \cdot J_{1j}^{xy} \cdot S - \sum_{i \neq 1} S \cdot J_{i2}^{yz} \cdot S \\ &+ \sum_{i \neq 1, j \neq 2} S \cdot J_{ij}^{yy} \cdot S + S \cdot A_{11}^{xx} \cdot S + S \cdot A_{22}^{zz} \cdot S \\ &+ \sum_{i \neq 1,2} S \cdot A_{ii}^{yy} \cdot S. \end{aligned} \quad (8)$$

We explicitly write resultant energy expressions in order to show why these four states are necessary and how they serve to determine the sought-for parameter. In order to extract only

the first term one needs to form pairs of equations where the first term has the same sign, i.e., to pair the equations (E_1, E_4) and (E_2, E_3) . Equations within one pair should be summed to cancel out the interaction of each of the two ions of interest with the “sea” of others, while these sums of two pairs of equations should be subtracted from one another in order to cancel out the interactions between and on the other ions. Therefore, it is necessary to combine all four independent configurations as described above to isolate the desired interaction parameter.

After subtracting the energies corresponding to states 2 and 3 from the sum of energies corresponding to states 1 and 4 and canceling all the terms with opposite signs and the same magnitude, the only noncanceled term is proportional to the parameter we intended to extract. This manipulation results in

$$E_1 + E_4 - E_2 - E_3 = 4S^2 \cdot J_{12}^{xz},$$

where it is trivial now to extract J_{12}^{xz} , i.e.,

$$J_{12}^{xz} = \frac{E_1 + E_4 - E_2 - E_3}{4S^2}. \quad (9)$$

It is worth mentioning that in the special case when the off-diagonal elements are antisymmetric, i.e., $J^{\alpha\beta} = -J^{\beta\alpha} = D^\gamma$, where (α, β, γ) are (x, y, z) or (y, z, x) or (z, x, y) , Eq. (9) from this derivation reduces to Eq. (A5) from Ref. [16].

We want to point out that \vec{S}_1 and \vec{S}_2 are alternating in parallel to the x and z directions, respectively, which corresponds to the J_{12}^{xz} element and $\vec{S}_{i \neq 1,2}$ being parallel or antiparallel to the y direction. In the case of the calculation of the diagonal elements, i.e., J_{12}^{xx} , J_{12}^{yy} , or J_{12}^{zz} , both \vec{S}_1 and \vec{S}_2 are chosen to be alternating in parallel to x , y , and z , respectively, and $\vec{S}_{i \neq 1,2}$ are chosen to be perpendicular to them.

B. Single-ion anisotropy A

In order to complete the analysis, we also consider SIA parameters which govern the interaction between the spin components of the single ion. Unlike J_{ij} , SIA matrix A_{ii} has to be symmetric, regardless of the structural symmetry. This is a consequence of the fact that the interaction between, e.g., x and z components is physically the same interaction as between z and x components on the same spin site i . In addition, based on the relation $S_i^2 = S^2 = (S_i^x)^2 + (S_i^y)^2 + (S_i^z)^2$, each component can be represented through the total spin S and two other components. Due to everything stated above, in general case, for the off-diagonal elements of the SIA matrix, one needs to calculate only three upper (or lower) elements. For the diagonal element of the SIA matrix, it is sufficient to obtain two reduced terms for the diagonal part instead of all three elements separately. First of all, we present the SIA Hamiltonian in explicit form:

$$\begin{aligned} H_{\text{SIA}} &= \sum_i \vec{S}_i \cdot A_{ii} \cdot \vec{S}_i \\ &= \sum_i [S_i^x \cdot A_{ii}^{xx} \cdot S_i^x + S_i^x \cdot A_{ii}^{xy} \cdot S_i^y + S_i^x \cdot A_{ii}^{xz} \cdot S_i^z \\ &+ S_i^y \cdot A_{ii}^{yx} \cdot S_i^x + S_i^y \cdot A_{ii}^{yy} \cdot S_i^y + S_i^y \cdot A_{ii}^{yz} \cdot S_i^z \\ &+ S_i^z \cdot A_{ii}^{zx} \cdot S_i^x + S_i^z \cdot A_{ii}^{zy} \cdot S_i^y + S_i^z \cdot A_{ii}^{zz} \cdot S_i^z]. \end{aligned} \quad (10)$$

In order to obtain the elements of the SIA matrix, one can use the same idea as for the exchange matrix elements with small adaptations. The first adaptation is that one needs to choose the spin site, not the pair. The second adaptation is that one should use different procedures to obtain the off-diagonal and diagonal elements.

1. Off-diagonal elements of the SIA matrix

An off-diagonal element of the SIA matrix describes the interaction between different Cartesian components of the spin at the chosen site (we take site $i = 1$ without loss of generality). Namely, the elements are $A_{11}^{xy} = A_{11}^{yx}$, $A_{11}^{xz} = A_{11}^{zx}$, and $A_{11}^{yz} = A_{11}^{zy}$. The spin vector at that site should lie on the plane determined by the Cartesian components whose interaction one wants to investigate, making a 45° angle with the two axes. All the other spins should be chosen along the complementary Cartesian axis. This means that in order to conduct 4SM using the DFT calculation for the A_{11}^{xy} parameter, one should choose the four states in the following form:

$$\begin{aligned} \text{State 1 : } \vec{S}_1 &= (+S\sqrt{2}/2, +S\sqrt{2}/2, 0), \\ \text{State 2 : } \vec{S}_1 &= (+S\sqrt{2}/2, -S\sqrt{2}/2, 0), \\ \text{State 3 : } \vec{S}_1 &= (-S\sqrt{2}/2, +S\sqrt{2}/2, 0), \\ \text{State 4 : } \vec{S}_1 &= (-S\sqrt{2}/2, -S\sqrt{2}/2, 0), \end{aligned}$$

and for all the rest, $\vec{S}_i = (0, 0, +S)$ for all states. As was the case with exchange interaction, all four independent configurations need to be combined in order to extract only the desired parameter. The same paired energies will be summed in order to cancel out interactions of the desired site with the others, and then those sums will be subtracted from each other to cancel out the same additive constant appearing in all four equations.

The four states give four energies:

$$\begin{aligned} E_1 &= \sum_{j>1} S\sqrt{2}/2 \cdot J_{1j}^{xz} \cdot S + \sum_{j>1} S\sqrt{2}/2 \cdot J_{1j}^{yz} \cdot S \\ &+ \sum_{i \neq 1, j > i} S \cdot J_{ij}^{zz} \cdot S + \frac{S^2}{2} \cdot A_{11}^{xx} + \frac{S^2}{2} \cdot A_{11}^{xy} \\ &+ \frac{S^2}{2} \cdot A_{11}^{yx} + \frac{S^2}{2} \cdot A_{11}^{yy} + \sum_{i \neq 1} S \cdot A_{ii}^{zz} \cdot S, \end{aligned} \quad (11)$$

$$\begin{aligned} E_2 &= \sum_{j>1} S\sqrt{2}/2 \cdot J_{1j}^{xz} \cdot S - \sum_{j>1} S\sqrt{2}/2 \cdot J_{1j}^{yz} \cdot S \\ &+ \sum_{i \neq 1, j > i} S \cdot J_{ij}^{zz} \cdot S + \frac{S^2}{2} \cdot A_{11}^{xx} - \frac{S^2}{2} \cdot A_{11}^{xy} \\ &- \frac{S^2}{2} \cdot A_{11}^{yx} + \frac{S^2}{2} \cdot A_{11}^{yy} + \sum_{i \neq 1} S \cdot A_{ii}^{zz} \cdot S, \end{aligned} \quad (12)$$

$$\begin{aligned} E_3 &= - \sum_{j>1} S\sqrt{2}/2 \cdot J_{1j}^{xz} \cdot S + \sum_{j>1} S\sqrt{2}/2 \cdot J_{1j}^{yz} \cdot S \\ &+ \sum_{i \neq 1, j > i} S \cdot J_{ij}^{zz} \cdot S + \frac{S^2}{2} \cdot A_{11}^{xx} - \frac{S^2}{2} \cdot A_{11}^{xy} \end{aligned}$$

$$- \frac{S^2}{2} \cdot A_{11}^{yx} + \frac{S^2}{2} \cdot A_{11}^{yy} + \sum_{i \neq 1} S \cdot A_{ii}^{zz} \cdot S, \quad (13)$$

and

$$\begin{aligned} E_4 &= - \sum_{j>1} S\sqrt{2}/2 \cdot J_{1j}^{xz} \cdot S - \sum_{j>1} S\sqrt{2}/2 \cdot J_{1j}^{yz} \cdot S \\ &+ \sum_{i \neq 1, j > i} S \cdot J_{ij}^{zz} \cdot S + \frac{S^2}{2} \cdot A_{11}^{xx} + \frac{S^2}{2} \cdot A_{11}^{xy} \\ &+ \frac{S^2}{2} \cdot A_{11}^{yx} + \frac{S^2}{2} \cdot A_{11}^{yy} + \sum_{i \neq 1} S \cdot A_{ii}^{zz} \cdot S. \end{aligned} \quad (14)$$

After adding the energies for states 1 and 4 and subtracting from energies corresponding to states 2 and 3, the only term remaining is $A_{11}^{xy} = A_{11}^{yx}$:

$$E_1 + E_4 - E_2 - E_3 = 2S^2 \cdot A_{11}^{xy} + 2S^2 \cdot A_{11}^{yx} = 4S^2 \cdot A_{11}^{xy};$$

hence, the single-ion anisotropy parameter is obtained by the formula

$$A_{11}^{xy} = A_{11}^{yx} = \frac{E_1 + E_4 - E_2 - E_3}{4S^2}. \quad (15)$$

The same equation (with the corresponding energies) can be written for all off-diagonal terms in the SIA matrix.

2. Diagonal elements of the SIA matrix

As we pointed out above, in order to describe the diagonal elements of the SIA matrix, it is sufficient to calculate two reduced terms of the diagonal elements due to the fact that $(S_i^y)^2$ can be written as $(S_i^x)^2 = (S_i)^2 - (S_i^y)^2 - (S_i^z)^2$. According to the relation, the diagonal part of the SIA Hamiltonian can be written as follows:

$$\begin{aligned} H_{\text{SIA}}^{\text{dia}} &= S_1^x A_{11}^{xx} S_1^x + S_1^y A_{11}^{yy} S_1^y + S_1^z A_{11}^{zz} S_1^z \\ &= A_{11}^{xx} S_1^2 + (A_{11}^{yy} - A_{11}^{xx}) (S_1^y)^2 \\ &+ (A_{11}^{zz} - A_{11}^{xx}) (S_1^z)^2. \end{aligned} \quad (16)$$

The term $A_{11}^{xx} S_1^2$ is simply an additive constant. The terms $A_{11}^{yy} - A_{11}^{xx}$ and $A_{11}^{zz} - A_{11}^{xx}$ govern all information of the diagonal part of the SIA matrix. Here, we present the extraction of the parameter $A_{11}^{yy} - A_{11}^{xx}$ as an example in which the same strategy is valid to determine $A_{11}^{zz} - A_{11}^{xx}$ as well. The four states to be obtained are as follows:

$$\begin{aligned} \text{State 1 : } \vec{S}_1 &= (0, +S, 0), \\ \text{State 2 : } \vec{S}_1 &= (0, -S, 0), \\ \text{State 3 : } \vec{S}_1 &= (+S, 0, 0), \\ \text{State 4 : } \vec{S}_1 &= (-S, 0, 0), \end{aligned}$$

and for all the rest, $\vec{S}_{i \neq 1} = (0, 0, +S)$ for all states. The energies corresponding to the chosen states are

$$\begin{aligned} E_1 &= \sum_{j>1} S \cdot J_{1j}^{yz} \cdot S + \sum_{i \neq 1, j > i} S \cdot J_{ij}^{zz} \cdot S \\ &+ S \cdot A_{11}^{yy} \cdot S + \sum_{i \neq 1} S \cdot A_{ii}^{zz} \cdot S, \end{aligned} \quad (17)$$

$$\begin{aligned}
 E_2 = & - \sum_{j>1} S \cdot J_{1j}^{yz} \cdot S + \sum_{i \neq 1, j>i} S \cdot J_{ij}^{zz} \cdot S \\
 & + S \cdot A_{11}^{yy} \cdot S + \sum_{i \neq 1} S \cdot A_{ii}^{zz} \cdot S,
 \end{aligned} \quad (18)$$

$$\begin{aligned}
 E_3 = & \sum_{j>1} S \cdot J_{1j}^{xz} \cdot S + \sum_{i \neq 1, j>i} S \cdot J_{ij}^{zz} \cdot S \\
 & + S \cdot A_{11}^{xx} \cdot S + \sum_{i \neq 1} S \cdot A_{ii}^{zz} \cdot S,
 \end{aligned} \quad (19)$$

and

$$\begin{aligned}
 E_4 = & - \sum_{j>1} S \cdot J_{1j}^{xz} \cdot S + \sum_{i \neq 1, j>i} S \cdot J_{ij}^{zz} \cdot S \\
 & + S \cdot A_{11}^{xx} \cdot S + \sum_{i \neq 1} S \cdot A_{ii}^{zz} \cdot S.
 \end{aligned} \quad (20)$$

Here, the form of equations is different from those in exchange interaction and off-diagonal SIA parameters. Therefore, the pairing of equations needed to extract the sought-for parameter is different, but the reasons are exactly the same: summation of energies within the pair of equations will cancel the interaction of the desired site with the other sites, and subtraction between pair sums of equations will cancel the additive constant originating from the other sites. In this case, the suitable pairs are (E_1, E_2) and (E_3, E_4) . After summing the energies of states 1 and 2 and subtracting those of states 3 and 4, one obtains the relation

$$E_1 + E_2 - E_3 - E_4 = 2S^2 \cdot A_{11}^{yy} - 2S^2 \cdot A_{11}^{xx},$$

which results in the formula

$$A_{11}^{yy} - A_{11}^{xx} = \frac{E_1 + E_2 - E_3 - E_4}{2S^2}. \quad (21)$$

In general material analysis, one needs to find all five elements of all the SIA matrices. Here, we extend our discussion on SIA for 2D and quasi-2D materials which exhibit three-, four-, and sixfold rotation symmetry around the out-of-plane axis. In such a case, SIA of the spin site can be described by a single parameter instead of a matrix.

3. Symmetry-imposed constraint in SIA of 2D and quasi-2D materials

The constraints in the SIA matrix are a direct consequence of the symmetry of the crystal. In the presence of three-, four-, or sixfold rotation symmetry around the out-of-plane axis in a 2D or quasi-2D material, all the elements of each matrix are equal to zero, except $A_{11}^{zz} - A_{11}^{xx}$. Here, we show how the structural symmetry affects SIA of a spin site. The symmetry can be described by the transformation matrix. Let B be the transformation of the form

$$A_{\text{new}} = B \cdot A_{\text{old}} \cdot B^T. \quad (22)$$

Moreover, if the coordinate transformation B is a symmetry operation of the considered system, then $A_{\text{new}} \equiv A_{\text{old}}$.

In this particular section, we discuss coordinate transformation under rotation of the system. This means that matrix B is actually the rotation matrix around the z axis—the axis

orthogonal to the layer(s) of the (quasi-)2D material. We start from the general rotation matrix (any arbitrary angle θ) and later choose only four possible values compatible with the translation symmetry of the crystal systems, i.e., $\pi, \frac{2\pi}{3}, \frac{\pi}{2}, \frac{\pi}{3}$, corresponding to two-, three-, four-, and sixfold rotation symmetries, respectively.

The rotation by angle θ around the z axis is given in its matrix representation as

$$R_z(\theta) = \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}. \quad (23)$$

Now, after using $A = R_z(\theta) \cdot A \cdot R_z^T(\theta)$ on each matrix element, one ends up with three systems of equations. Namely, the matrix elements with indices 11 (22) and 12 (21) yield the following system of equations:

$$\begin{aligned}
 (A_{yy} - A_{xx}) \cdot \sin^2 \theta + 2A_{xy} \cdot \sin \theta \cos \theta &= 0, \\
 (A_{yy} - A_{xx}) \cdot \sin \theta \cos \theta - 2A_{xy} \cdot \sin^2 \theta &= 0.
 \end{aligned} \quad (24)$$

The elements with indices 13 (31) and 23 (32) result in the equations

$$\begin{aligned}
 A_{xz} \cdot (\cos \theta - 1) + A_{yz} \cdot \sin \theta &= 0, \\
 -A_{xz} \cdot \sin \theta - A_{yz} \cdot (\cos \theta - 1) &= 0,
 \end{aligned} \quad (25)$$

while equality of the elements with indices 33 yields the trivial relation $A_{zz} = A_{zz}$.

One can easily obtain determinants of the 2×2 systems 24 and 25, D^* and D^{**} , respectively, as

$$\begin{aligned}
 D^* &= -\sin^2 \theta, \\
 D^{**} &= 2(1 - \cos \theta).
 \end{aligned} \quad (26)$$

It is well known that a homogeneous system has a non-trivial solution if and only if the determinant of the system is equal to zero. It is obvious that in the case of three-, four-, and sixfold rotational symmetry, both determinants are different from zero, resulting in only trivial solutions for the corresponding systems of equations. This means that if three-, four-, or sixfold rotational symmetry around the out-of-plane axis is present in the system, the only element of the SIA matrix allowed to be nonzero is $A_{zz} - A_{xx}$.

This makes the computation of the SIA part of the general spin Hamiltonian parameters five times less demanding in the case of three-, four-, and sixfold symmetry in 2D materials. This is due to the fact that one needs to find only one SIA matrix element, instead of five, as is the case in the most general computation, when none of the mentioned symmetries are *a priori* present.

III. EXAMPLE OF MONOLAYER CrI_3

In this section we present the values obtained for the exchange matrix parameters, as well as the SIA matrix parameters for a pristine monolayer of CrI_3 , using the DFT methodology described in the Appendix, in combination with calculations described in Sec. II. We present results calculated by applying the formulas given in this study, together with the results obtained by directly applying the formulas given in the Ref. [16]. Furthermore, we comment on the differences

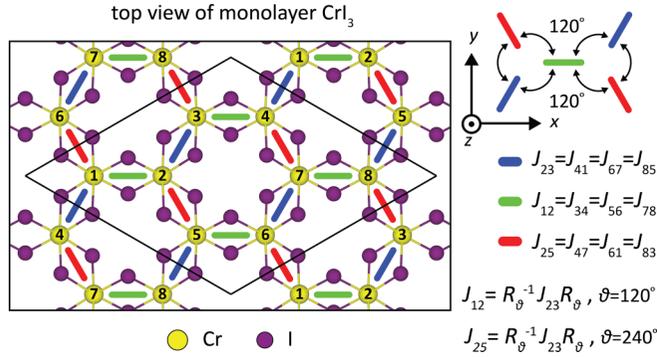


FIG. 1. Pristine monolayer CrI₃ and its $2 \times 2 \times 1$ supercell (black solid line). Magnetic Cr atoms are colored yellow and labeled, while nonmagnetic I atoms are colored purple. Three Cr-Cr bonds connected with the threefold in-plane symmetry are shown as blue, green, and red bars with the respective magnetic exchange matrices.

between the formulas and potential misconceptions that could arise.

We present the values of the exchange parameters between Cr atoms labeled 2 and 3 in Fig. 1. The exchange interaction matrix between any other nearest-neighbor pair in the crystal can be calculated from the results for the mentioned pair 2-3. Atom pairs 4-1, 8-5, and 6-7 are structurally identical to pair 2-3; therefore, the matrix parameters are the same as those of pair 2-3. Exchange matrices for pairs 2-5, 8-3, 4-7, and 6-1, as well as for pairs 1-2, 3-4, 5-6, and 7-8, can be obtained from the matrix characterizing pair 2-3 by applying the threefold rotation (around the out-of-plane axis) operations on the matrix corresponding to pair 2-3. Regarding the single-ion anisotropy, all atoms are described with a single matrix in the case of pristine CrI₃. Moreover, the only nonzero SIA matrix element is $A_{zz} - A_{xx}$ (for details, see Sec. II B 3).

Following the formulas given in this paper, we found all nine elements of the matrix J_{23} . The total magnetic moment of monolayer CrI₃ in its ground state is found to be $3\mu_B$ per Cr atom, which is consistent with previous studies [4,5]. Therefore, we use $S = 3/2$ everywhere in the formulas. The diagonal elements are $J_{23}^{xx} = -4.12$ meV, $J_{23}^{yy} = -4.79$ meV, and $J_{23}^{zz} = -4.63$ meV, and off-diagonal elements are $J_{23}^{xy} = J_{23}^{yx} = -0.58$ meV, $J_{23}^{xz} = J_{23}^{zx} = 0.74$ meV, and $J_{23}^{yz} = J_{23}^{zy} = -0.40$ meV. Obviously, matrix J_{23} is symmetric. Moreover, exchange matrices of all other pairs are symmetric. This means that the antisymmetric exchange interaction, i.e., DMI, between any two nearest-neighbor spin sites is equal to zero. This is in agreement with Ref. [10], which states that if an inversion center is present in the middle between two spin sites, the DMI between them has to be zero. The same conclusion is reached in Ref. [5] as well. Moreover, one notices the qualitative similarity and consistent quantitative difference between parameters calculated in Ref. [5] and the ones reported here. After aligning the global Cartesian coordinate systems from two studies, one realizes that the ratios of the corresponding exchange parameters are consistently between 2 and 2.5, which we believe is mainly the consequence of different exchange-correlation energy functionals.

Although the four-state analysis in Ref. [5] was done by following the main idea of Ref. [16], the correct formula for

the J_{xy} parameter in Ref. [5] is given only in the supplementary material. However, no comment on the generalization of the procedure from Ref. [16] is presented there; on the contrary, it is stated that a detailed analysis is readily given in Ref. [16], and in the supplementary material of Ref. [5] the main idea of the method is briefly introduced. In other words, the ambiguity of the method remained unresolved. To illustrate the impact that direct use of the formulas from Ref. [16] could have, we present below the results obtained in that manner for monolayer CrI₃. Formulas for the off-diagonal elements of the exchange matrix yield $D_{23}^z = -0.58$ meV, $D_{23}^y = -0.74$ meV, and $D_{23}^x = -0.40$ meV. This is in contradiction to the symmetry consideration by Moriya [10]. Furthermore, this error is even more dangerous than it may seem since the approach gives zero average DMI experienced by each site, which is actually correct! For example, focusing on site 2 and calculating D_{12}^z and D_{25}^z using the formulas from Ref. [16], one finds that together with D_{23}^z they add up to zero, i.e., $D_{12}^z + D_{23}^z + D_{25}^z = 0$ (the same as for the x and y components). This leads to an incorrect conclusion that DMI exists on the pair level (between two spin sites) in pristine monolayer CrI₃ but is then canceled out by different pair contributions. The influence of these and similar errors could progressively grow in the future with the strongly increasing number of works on 2D magnetic materials. Misconceptions at the onset of a new and growing field must be avoided, and our above considerations are in service of exactly that.

Regarding the SIA matrix, since spin sites in monolayer CrI₃ exhibit threefold rotation symmetry around the out-of-plane axis, it follows that the only nonzero SIA parameter is $A_{11}^{zz} - A_{11}^{xx}$, and it is equal to -0.08 meV in our case. A negative value implies that the SIA favors the out-of-plane direction instead of the in-plane one.

IV. SUMMARY AND CONCLUSIONS

To summarize, starting from the general Heisenberg spin Hamiltonian, we derived the formulas for diagonal and off-diagonal elements of 3×3 matrices governing the magnetic exchange interaction between two magnetic sites J and single-ion anisotropy of a single magnetic site A . The formulas are based on *ab initio* energetic calculations of the four different magnetic configurations of the magnetic crystal. The formulas as previously derived in Refs. [15,16] are not appropriate for the general case. The generalization provided here is important and timely due to the recent realization of 2D ferromagnetism and the gaining momentum of the *ab initio* approach to magnetic systems. Otherwise, the general use of nongeneralized formulas may result in incorrect conclusions, e.g., about the existence of DMI between the magnetic sites of the perfectly symmetric lattice of CrI₃.

In order to prevent researchers from misusing the formulas, here, we presented the general and complete set of equations that is applicable to any magnetic crystal. The general formula for each element of the exchange matrix J is in the form

$$J_{ij}^{\alpha\beta} = \frac{E_1 + E_4 - E_2 - E_3}{4S^2}, \quad (27)$$

where i and j are indices for different magnetic sites and α and β correspond to two of the three Cartesian coordinates.

E_{1-4} are the energies of the four states corresponding to the spins of the i th and j th sites (S_i and S_j) aligning parallel to the directions of $\pm\alpha$ and $\pm\beta$, combined with the alignment of $S_{\text{others}\neq i,j}$ with the third Cartesian axis ($\neq \alpha, \beta$).

The formulas for the off-diagonal elements ($\alpha \neq \beta$) of A are of the form

$$A_{ii}^{\alpha\beta} = \frac{E_1 + E_4 - E_2 - E_3}{4S^2}, \quad (28)$$

where i is the index of the considered single magnetic site. α and β correspond to two of the three Cartesian coordinates. E_{1-4} are the energies of the four states specified as S_i lying in the $\alpha\beta$ plane and making a 45° angle with $\alpha, \beta; -\alpha, \beta; \alpha, -\beta;$ and $-\alpha, -\beta$. The spins of other sites $S_{\text{other}\neq i}$ point along the third Cartesian axis. For the diagonal elements ($\alpha = \beta$) one needs to calculate their reduced form:

$$A_{ii}^{\alpha\alpha} - A_{ii}^{xx} = \frac{E_1 + E_2 - E_3 - E_4}{2S^2}, \quad (29)$$

where α is either y or z . E_{1-4} are the energies of the four states of S_i pointing along $\pm\alpha$ and $\pm x$, with $S_{\text{other}\neq i}$ being orthogonal to both α and x . In addition to the general assessment of SIA, we present SIA analysis for specifically 2D-like crystals which exhibit three-, four-, or sixfold rotation symmetry. In such cases, there are three possible results: (i) the in-plane anisotropy, where $A_{zz} - A_{xx} > 0$; (ii) out-of-plane anisotropy, where $A_{zz} - A_{xx} < 0$; and (iii) no anisotropy $A_{zz} - A_{xx} = 0$. In the last case, SIA is the zero matrix, i.e., $A_{xx} = A_{yy} = A_{zz} = A$. In terms of the total Heisenberg Hamiltonian, SIA is just an additive constant equal to AS^2 and does not influence the Hamiltonian spectrum.

Finally, the formulas derived here were applied to the pristine crystal of monolayer CrI_3 . The results are given together with those obtained by strictly following Refs. [15,16] in order to illustrate the error one could make if not carefully applying four-state methodology to the system of interest. For example, the general formula presented here results in no DMI between adjacent Cr atoms of monolayer CrI_3 , which is consistent with Moriya's theorem [10], while the direct application of previously established formulas yields finite DMI as an erroneous result.

By clearly stating the complete formalism, we hope to remove any potential doubt or eventual error that might have arisen in the field. Such error is rather likely when estimating the off-diagonal exchange parameters, which correspond to the DMI. In fact the DMI in 2D materials is an entirely

new subject; hence, it is timely and important to clarify and generalize the relevant formulas and thereby avoid erroneous results and conclusions at the onset of this exciting field of research.

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APPENDIX: COMPUTATIONAL DFT METHODOLOGY

For the purposes of applying the formulas derived in this paper to a specific material, we performed DFT-based calculations using the Vienna Ab initio Simulation Package (VASP) [24,25] within the projector augmented-wave [26] method, with spin-orbit coupling always included. The electron exchange and correlation are described as the Perdew-Burke-Ernzerhof [27] form of the generalized gradient approximation due to its documented advantages over the local-density approximation regarding simulations of transition-metal compounds [28]. The $3d^5$ and $4s^1$ electrons of the Cr atom [29] and $5s^2$ and $5p^5$ electrons of the I atom were considered as valence electrons. To construct a 2D crystal structure, we set a vacuum height of 15 \AA . In order to isolate the spin (pair) site from the neighboring unit cell, a $2 \times 2 \times 1$ supercell was considered as the unit cell for the four-state calculation, and a $3 \times 3 \times 1$ k -point sampling was chosen. We have validated that a $2 \times 2 \times 1$ supercell is large enough to (1) isolate the desired pair or ion and (2) exclude the influence of further nearest neighbors, up to the fourth one (i.e., its contribution remains below 0.01 meV). Note that if one needs to calculate any other neighbor interaction, one requires a larger unit cell (e.g., in the case of a second-nearest neighbor one needs at least a $3 \times 3 \times 1$ supercell). The cutoff energy for a plane wave basis set was chosen to be 500 eV . The energy convergence criterion was set to 10^{-5} eV between two successive iterations. The on-site Coulomb repulsion parameter U was taken to be 4 eV for magnetic Cr atoms [30] and zero for I atoms [31]. For the Brillouin zone integration we used Gaussian smearing of 0.01 meV .

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