

Polaron-mediated anisotropic exchange in two-dimensional magnets

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Two-dimensional (2D) magnets offer a rich platform for exploring emergent spin phenomena due to their unique and diverse magnetic properties. Beyond intrinsic magnetism, external manipulation—such as defect engineering, molecular adsorption, or charge doping—offers powerful routes to control their magnetic behavior. In this work, we demonstrate that localized electron polarons provide an effective means to modulate magnetism in 2D magnets. Using first-principles calculations, we investigate polaron formation in monolayer MnPS₃ and compute the resulting changes in magnetic exchange interactions. Our results reveal that polarons can locally break magnetic symmetry and induce anisotropic exchange couplings, highlighting an alternative mechanism for tuning magnetic textures. This insight opens promising pathways for designing atomic-scale control of magnetism, with potential impact on spintronic technologies.

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I. INTRODUCTION

2D magnetic materials have attracted significant attention in recent years, as their wide range of behaviors opens possibilities for the development of efficient and controllable next-generation magnetic devices. Notable examples include transition-metal halides and chalcogenides such as CrI₃, VI₃, Fe₃GeTe₂, and NiPS₃, among many others [1–3]. This interest is largely driven by the variety of intrinsic properties that emerge in 2D systems, including a broad spectrum of electronic phases—from semiconducting to metallic—alongside spin-orbit coupling effects, topological states, and complex magnetic textures that can markedly differ from their bulk counterparts due to reduced dimensionality and enhanced quantum confinement [4–9].

Further promoting this rapid development are recent advances in the fabrication of 2D magnets, such as mechanical exfoliation, molecular beam epitaxy, and chemical vapor deposition [10,11], which have made it possible to isolate atomically thin magnetic layers. Crucially, the demonstration of long-range magnetic order at finite temperatures—enabled by magnetocrystalline anisotropy—has challenged the limitations imposed by the Mermin–Wagner theorem [12], thereby allowing stable magnetism in 2D systems.

While intrinsic magnetism in 2D materials is already rich and complex, an additional route to manipulate and control their magnetic properties is through external means—such as the introduction of defects [13–15], adatoms [16–18],

or adsorbed molecules [19–21]. In MnPS₃ monolayers, it has been shown that molecular adsorption breaks spatial inversion symmetry, leading to the emergence of a finite Dzyaloshinskii–Moriya interaction [22]. In addition to symmetry breaking, adsorption induces significant structural and electronic modifications that alter the Mn–S–Mn superexchange interactions. These changes, in turn, affect both the magnetocrystalline anisotropy and the isotropic exchange interactions.

An alternative approach to controlling magnetic properties is charge doping, which can induce or modify magnetic ordering and tune the strength of magnetic interactions, as recently demonstrated in CrI₃ [23]. A particularly remarkable consequence of charge doping is the formation of polarons—composite quasiparticles arising from the interaction between excess charge carriers and the phonon field [24,25], which have also been observed in atomically thin crystals [26–29]. Since polarons are accompanied by anisotropic lattice distortions, it is plausible that their formation could significantly modify magnetic interactions through the associated structural and electronic rearrangements.

While polarons have been extensively studied in bulk polarizable crystals [24], including magnetic systems [30–33], their role in 2D magnetic materials remains relatively unexplored. Only a few studies have begun to address this emerging field. For instance, in monolayer CoCl₂, single electron polarons were created by injecting electrons using a scanning tunneling microscope (STM) through a voltage pulse [27,28]. It was shown that polarons in the system can be also actively created, erased, and repositioned by the electric field generated by the STM tip. However, the impact of these localized charges on the magnetic properties of the system was not addressed.

In this work, we aim to fill this gap by studying how localized electron polarons affect magnetic exchange interactions in MnPS₃, an experimentally exfoliable [34] 2D antiferro-

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magnet (AFM) proposed as a candidate for spin current generation via the spin photogalvanic effect [35]. Our findings reveal a clear connection between polaron formation and the emergence of anisotropic magnetic coupling, pointing toward alternative directions for functional control of magnetism at the atomic scale. As a consequence, self-trapped charges in 2D magnets can locally alter the magnetic texture, potentially giving rise to noncollinear magnetic configurations with promising implications for spintronic and magnetoelectric applications [36–39].

MnPS₃ features a monolayer structure composed of a hexagonal lattice of Mn²⁺ cations, each octahedrally coordinated by sulfur atoms. Positioned at the center of each Mn hexagon is a [P₂S₆]^{4−} bipyramidal unit, oriented perpendicular to the plane. This arrangement gives rise to a primitive unit cell containing two Mn atoms, two P atoms, and six S atoms. As a result of this structural configuration, MnPS₃ behaves as an AFM semiconductor, with a magnetic ground state characterized by Néel-type ordering [22,40–42].

II. THEORETICAL METHODS AND COMPUTATIONAL SETUP

We have addressed the problem by means of first principles calculations within the spin noncollinear DFT + *U* framework using the VIENNA AB INITIO SIMULATION PACKAGE (VASP) [43]. A 3 × 3 × 1 supercell (total of 90 atoms) is employed to model the MnPS₃ monolayer both in its pristine form and in the presence of a localized polaron. The calculations employ the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [44], with a plane-wave energy cutoff of 600 eV and a 3 × 3 × 1 *k*-point mesh used for the self-consistent field calculations.

Within the DFT + *U* approach with a Hubbard parameter of *U* = 5 eV applied to the Mn 3*d* states, the band gap of MnPS₃ has been reported as *E_g* = 2.34 eV [40], *E_g* = 2.40 eV [22], and *E_g* = 2.50 eV in [42], with the latter also reporting a higher value of 3.25 eV obtained from calculations using the HSE06 hybrid functional. This range of band gap values provides a sufficiently wide energy window to support the formation and stabilization of a localized polaronic state. Thus, to account for the strong on-site Coulomb interactions of the Mn 3*d* electrons, we use a Hubbard *U* parameter of 5 eV following the Dudarev approach [45]. With this setup, we determined the lattice constant of the relaxed unit cell to be 6.14 Å and a magnetic moment of *m_s* = 4.6 μ_B on the Mn atoms.

To extract the magnetic exchange interactions, the energy mapping four-states method is employed [46–48]. In this method, each component (*a*, *b*) of the exchange interaction tensor *J_{ij}*, associated with a specific atomic pair (*i*, *j*), is calculated using the expression

$$J_{ij}^{ab} = \frac{E_{ij,\uparrow\uparrow}^{ab} + E_{ij,\downarrow\downarrow}^{ab} - E_{ij,\uparrow\downarrow}^{ab} - E_{ij,\downarrow\uparrow}^{ab}}{4S^2}, \quad (1)$$

where (*a*, *b*) denote the Cartesian components (*x*, *y*, *z*) and *S* is the magnitude of the spin moment on sites *i* and *j*. The quantities *E_{ij}^{ab}* represent the total energies computed for the four distinct spin configurations of the pair: parallel (↑↑, ↓↓) and antiparallel (↑↓, ↓↑). All total energy calculations used

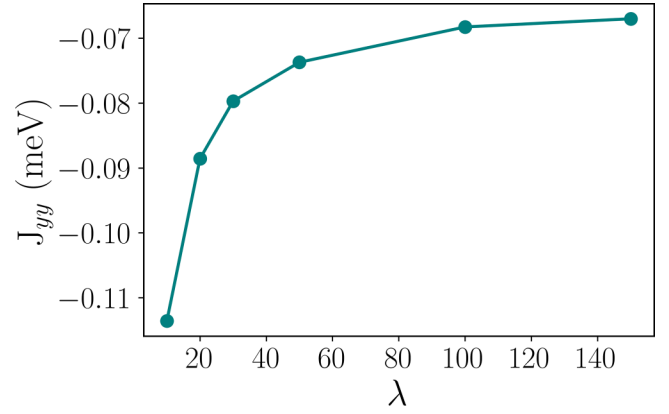


FIG. 1. Convergence of the J_{12}^{yy} component of the polaronic system with the penalty parameter λ .

to extract *J_{ij}* were performed in an AFM background with spins aligned along the *x* direction, including the spins on the polaronic sites, which were initialized in the up-spin state. The Cartesian reference frame is defined by the fixed global axes, with *x* = (100), *y* = (010), and *z* = (001), in which the lattice vectors of the simulation cell are expressed.

To determine the energies *E_{ij}^{ab}*, we constrained both the direction and sign of the magnetic moments. The total energy in this approach is given by

$$E = E_0 + \sum_I \lambda (|\vec{M}_I| - \hat{M}_I^0 \cdot \vec{M}_I), \quad (2)$$

where *E₀* is the DFT energy, and the second term represents a penalty energy. Here, $\vec{M}_I$ is the magnetic moment obtained by integration over a sphere of specified volume at site *I*, and $\hat{M}_I^0$ is the target magnetic moment at the same site. The parameter λ determines the weight of the penalty term in the total energy and can be adjusted as needed. Since the magnitude of the smallest exchange component is on the order of 10^{−5} eV, we performed a convergence test of this component with respect to the penalty parameter (Fig. 1). A value of $\lambda = 100$ was chosen to enforce the rotation of the magnetic moments, as the exchange tensor component J_{12}^{yy} in the polaronic case was observed to converge around this value. For the polaronic system, we also recalculated the *J_{2,3}* tensor including spin-orbit coupling and found that it did not lead to any noticeable difference.

III. RESULTS AND DISCUSSION

A. Polaron formation

To assess the stability of a polaron within the system, we calculated its formation energy, which is defined as the energy difference between a localized polaronic state and a delocalized charge state. Specifically, it is calculated by subtracting the total energy of the polaronic configuration, where the excess electron occupies a localized in-gap state accompanied by a lattice distortion, from the total energy of the delocalized configuration, in which the excess charge is spread across the conduction band minimum without significant atomic rearrangement [49]. This energy difference captures both the electronic stabilization due to charge

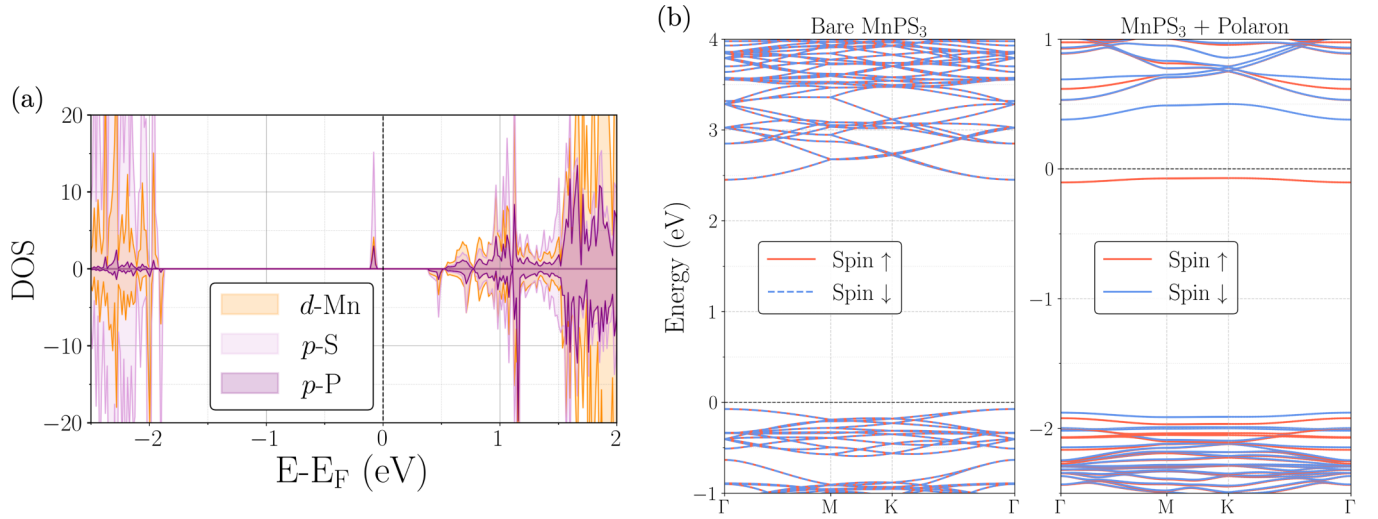


FIG. 2. (a) Spin-polarized projected DOS of MnPS₃ monolayer, showing Mn *d* states (orange), P *p* states (purple), and S *p* states (pink). The upper panel (DOS > 0) represents the spin-up channel, while the lower panel (DOS < 0) corresponds to the spin-down channel. (b) Spin-polarized band structure of the bare, undoped 3 × 3 × 1 MnPS₃ monolayer and of the polaronic solution. The spin-up and spin-down channels are shown in red and blue, respectively. Note that the two band structures span different energy ranges.

localization and the elastic energy cost associated with the accompanying lattice deformation.

To obtain the polaronic solution, we employ a two-step procedure. First, a spin-polarized ionic relaxation is performed by adding one extra electron to the system, introducing small initial distortions in the atomic positions, and applying a large Hubbard *U* value to promote electron localization. In the second step, the Hubbard *U* is removed and the structure is further relaxed. To preserve overall charge neutrality in the periodic supercell calculations, a homogeneous compensating background charge is introduced. We modeled the polaron using the approach described above, initializing the excess charge on a P atom, and present the corresponding results below. Initialization on an S or Mn atom leads to the same polaronic configuration.

The polaron formation energy is estimated to be $E_{\text{pol}} = -0.4$ eV, indicating that the localized polaronic state is energetically favorable and thus stable within the MnPS₃ monolayer. Figure 2(a) shows the spin-polarized projected density of states (DOS) for the polaronic MnPS₃ supercell. The Mn *d* states are depicted in orange, while the *p* states of P and S are shown in purple and pink, respectively. The DOS exhibits a localized peak within the energy gap, which can be attributed to the additional polaronic charge. This peak receives contributions from all three types of orbital characters, with the *p*-S orbitals contributing the most significantly. The spin-polarized DOS for the delocalized solution is shown in Appendix A, displaying the occupation of the lower conduction states by the additional electron.

Figure 2(b) displays a comparison between the spin-polarized band structure of the pristine neutral MnPS₃ monolayer and the one corresponding to the polaronic MnPS₃ monolayer. In the neutral case, the AFM configuration exhibits spin degeneracy and an energy gap of approximately 2.5 eV. Upon adding an extra localized charge, a state that originally belonged to the conduction band becomes occupied and is shifted below the Fermi energy, giving rise to a flat band

in the spin-up channel, corresponding to the localized peak in Fig. 2(a). It can also be observed that the presence of the polaron partially lifts the antiferromagnetic spin degeneracy. This effect originates from its unpaired magnetic moment of about $m_s = 0.6 \mu_B$, delocalized over the three elements, which induces ferromagnetic exchange among the states lying closest in energy to the polaronic state, i.e., the highest occupied and lowest unoccupied states. Figure 3 shows the charge density associated with the polaronic state, revealing its orbital character atop the atomic structure. The polaronic charge is localized within a small region of the material yet extends over several atoms; centered on a P atom, it exhibits trigonal symmetry, with lobes oriented along the P-S bonds and terminating between alternating Mn-Mn distances. Therefore, the presence of the polaron locally breaks the hexagonal symmetry of the magnetic Mn sublattice.

B. Polaron concentration

To evaluate the concentration dependence of polaron stability, we examined additional configurations by varying both the supercell size and the number of polarons within the same supercell, spanning concentrations from 11.1% to 50%. Our results indicate that polarons remain stable up to a concentration of 33.3%. Figure 4 summarizes the investigated cases: 11.1%, 22.2%, 25%, and 33.3%. At higher concentration (50%, corresponding to one polaron in a 1 × 2 supercell, not shown), the localized solution becomes unstable and the excess charge delocalizes. Notably, in all cases where localization occurs, both the orbital occupation and the geometry of the polarons remain consistent with those of the isolated polaron.

C. Exchange tensor

To assess the effect of the diluted polaron (i.e., 11.1% concentration) on the magnetic interactions, we compute the

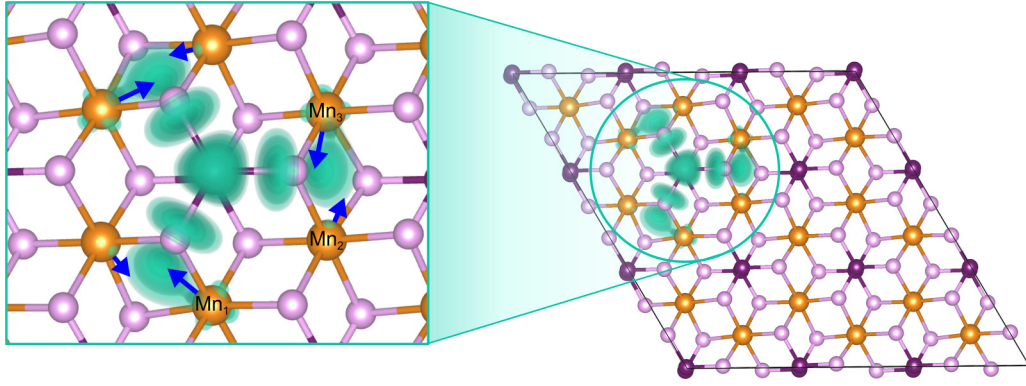


FIG. 3. Crystal lattice of $3 \times 3 \times 1$ MnPS_3 monolayer with a polaron, visualized as the torquiose charge-density cloud corresponding to the in-gap peak in Fig. 2. The displacement of Mn atoms induced by the polaron is indicated by blue arrows in the close-up figure. The Mn atoms that were used for the calculation of the nearest-neighbor exchange matrices J_{ij} are labeled. Visualization done using VESTA [50].

exchange tensor both with and without the the polaronic extra charge. For the pristine material, the four-states method was applied by selecting the central pair of magnetic Mn atoms within the supercell, as all Mn sites are symmetrically equivalent. Throughout the calculations, the magnetic background was kept in the AFM configuration, and we used a spin moment $S = 5/2$ for the Mn atoms.

1. Exchange tensor of bare MnPS_3 monolayer

We first discuss the results for the pristine MnPS_3 monolayer without a polaron. The diagonal elements of

the J_{ij} tensor, $J^{xx} = 0.92$ meV, $J^{yy} = 0.94$ meV, and $J^{zz} = 0.93$ meV, differ by less than 3%, confirming that the exchange interaction is almost perfectly isotropic. Consequently, the nearest-neighbor (NN) exchange interaction is given by $J_1 = \frac{1}{3}\text{Tr}(J_{ij}) = 0.93$ meV. Within the standard Heisenberg spin Hamiltonian, the positive value of sign of J_1 corresponds to an AFM coupling between NN Mn atoms. This result is consistent with recent reports, from which we infer $J_1 \sim -0.96$ meV based on the reported value of $J_1 S^2$ for $U = 5$ eV [51], noting that the opposite sign convention for the Heisenberg Hamiltonian is adopted in the literature. Moreover, we investigate the second-

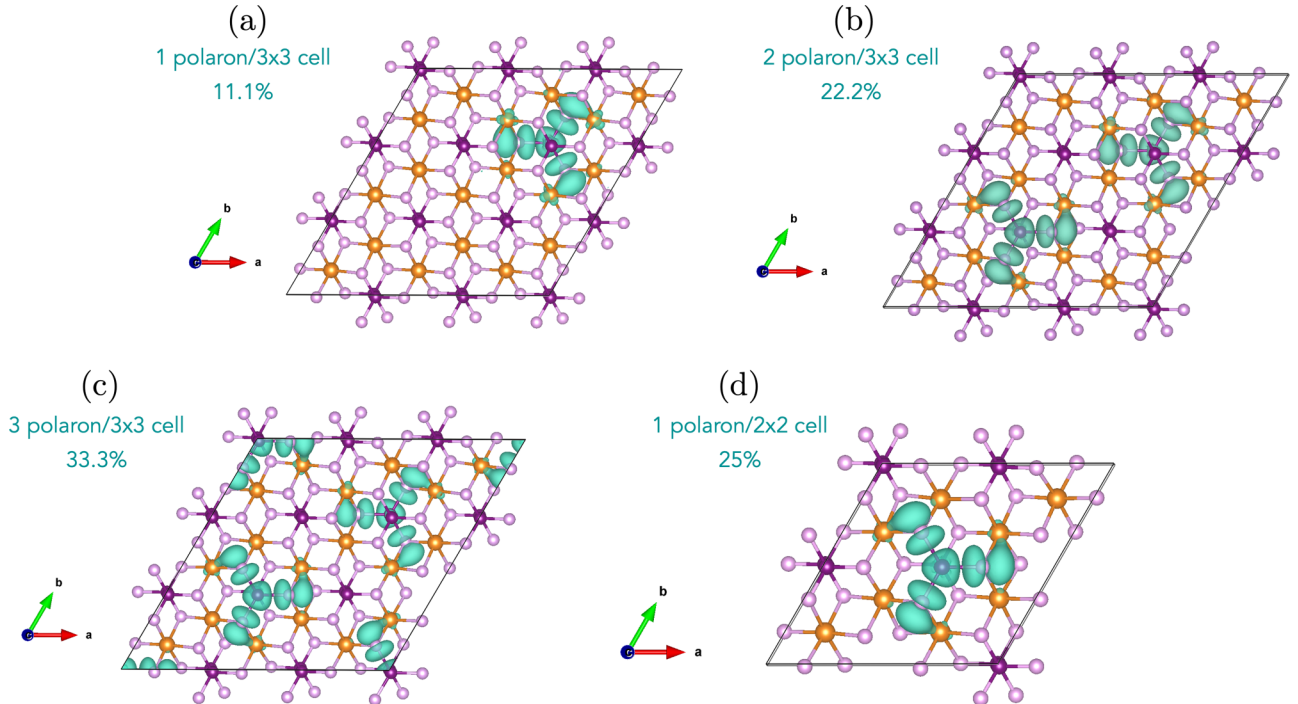


FIG. 4. Polarons in MnPS_3 monolayer at different concentrations. (a) One polaron in a 3×3 supercell, corresponding to an 11.1% concentration; (b) two polarons in the same 3×3 supercell, yielding a 22.2% concentration; (c) three polarons in the 3×3 supercell, corresponding to 33.3%, and (d) one polaron in a smaller 2×2 supercell, corresponding to a 25% concentration.

TABLE I. Mn–Mn distances and NN exchange parameters for nonpolaronic, polaronic, and distorted MnPS₃. Distances in Å, exchange interactions in meV. The corresponding computed total energies used in the four-states method are provided in Tables III–V in Appendix B.

System	Mn pair	Distance	J^{xx}	J^{yy}	J^{zz}
Nonpolaronic (undistorted)	Mn–Mn	3.548	0.92	0.94	0.93
Polaronic (distorted)	Mn ₁ –Mn ₂	3.587	0.61	−0.07	−0.07
	Mn ₂ –Mn ₃	3.475	1.07	0.44	0.44
Nonpolaronic (distorted)	Mn ₁ –Mn ₂	3.587	0.84	0.86	0.86
	Mn ₂ –Mn ₃	3.475	1.27	1.29	1.30

NN and third-NN interactions, which also yield isotropic exchange tensors with $J_2 = 0.05$ meV and $J_3 = 0.33$ meV, respectively, in reasonable agreement with previous reports [52,53].

2. Exchange tensor of polaronic MnPS₃ monolayer

The introduction of a polaron into the material causes a local distortion of the lattice, altering the distance between Mn atoms and generating symmetry-inequivalent pairs. The displacement directions of the Mn atoms is indicated in Fig. 3 by blue arrows, whose lengths are proportional to the corresponding displacement magnitudes, ≈ 0.05 Å. The computed interatomic distances for the investigated cases are given in Table I.

To assess the effect of the polaron on the exchange tensor we repeated the noncollinear calculations by selecting two Mn pairs, Mn₁–Mn₂ and Mn₂–Mn₃, which become symmetry-inequivalent due to the presence of the trigonal-symmetric localized polaronic charge, as illustrated in Fig. 3. The resulting exchange tensors remain diagonal, with the first pair exhibiting components $J_{1,2}^{xx} = 0.61$ meV and $J_{1,2}^{yy} = J_{1,2}^{zz} = -0.07$ meV, while the second pair shows $J_{2,3}^{xx} = 1.07$ meV and $J_{2,3}^{yy} = J_{2,3}^{zz} = 0.44$ meV. These results indicate that the presence of the polaron not only modifies the magnitude of the exchange tensor components but also introduces anisotropy in the exchange interaction, as evidenced by the disparity between the xx component and the $yy = zz$ components. Moreover, the $J_{1,2}$ exchange further exhibits a polaron-induced sign change in the yy and zz components, indicating a weak ferromagnetic interaction. Nevertheless, these components remain significantly smaller than the dominant xx term; consequently, for both Mn pairs, the overall exchange interaction is governed primarily by an AFM coupling. A closer inspection of Table IV reveals that total energy calculations within the four-states method identify the $\downarrow\downarrow$ configuration for the J_{xx} component as the ground state for both Mn pairs. In contrast, without the additional localized electron (pristine and distorted cases), the antiparallel spin configurations are always energetically preferred. This behavior suggests that the polaron induces a spin flip, thereby modifying the local magnetic configuration. Thus, although the pure magnetic exchange intrinsically favors AFM coupling, additional polaron-related effects act to destabilize this configuration

and promote spin flipping. A more detailed analysis of the microscopic origin of these competing interactions will be the subject of future investigations.

To better understand the origin of the asymmetric exchange, we decoupled the two primary effects introduced by the polaron: the excess electronic charge and the associated crystal field distortions. This was achieved by performing additional noncollinear calculations of the J_{ij} tensor on the polaron-distorted structure, but in the absence of the extra electron. The computed values are $J_{1,2}^{xx} = 0.84$ meV, $J_{1,2}^{yy} = 0.86$ meV, and $J_{1,2}^{zz} = 0.86$ meV, as well as $J_{2,3}^{xx} = 1.27$ meV, $J_{2,3}^{yy} = 1.29$ meV, and $J_{2,3}^{zz} = 1.30$ meV. Since these components differ by less than 3% of the average value, this confirms a restored isotropic exchange interactions and demonstrates that the magnetic anisotropy observed in the polaronic system vanishes in the absence of the excess charge. This restored isotropy indicates that the anisotropic exchange arises primarily from the presence of the localized polaronic charge rather than from lattice distortions alone. Nevertheless, the distortions still affect the magnitude of the exchange interactions: J_1 for the Mn₁–Mn₂ pair is slightly reduced compared to the pristine MnPS₃ monolayer, while J_1 for the Mn₂–Mn₃ pair is enhanced—correlating with the previously discussed changes in Mn–Mn bond lengths. Table I summarizes the exchange interactions and bond lengths for the Mn pairs in the three configurations considered: pristine MnPS₃, polaronic (including the extra charge and lattice distortions), and lattice-distorted without the excess charge.

Finally, we computed the second- and third-NN exchange tensors in the polaronic Mn hexagon, as illustrated in Fig. 5(a). Each type of interaction is denoted by a distinct color, whereas in the pristine case only a single type of J_1 interaction is present. The corresponding values are reported in Table II, which also summarizes the Mn–Mn distances associated with each interaction. Compared to the pristine material, we find that the anisotropic character is preserved for both J_2 and J_3 . In particular, the yy and zz components favor ferromagnetic coupling. It is also noteworthy that the J_2 interaction is locally significantly enhanced in the presence of the polaron.

3. Exchange tensor with distance from the polaron

To analyze the effect of the polaron upon distance, we inspected the NN J_1 exchange tensor at increasing distance from the polaronic site. Specifically, we choose one Mn–Mn pair at $d_1 = 3.80$ Å from the center of the polaronic site and one at $d_2 = 9.56$ Å, as shown in Fig. 5(b). The corresponding total energies used within the four-states method are summarized in Table VIII of Appendix B. Our results indicate that, with increasing distance from the polaron, the exchange anisotropy is progressively reduced, with the xx , yy , and zz components tending toward more isotropic values and approaching those of the nonpolaronic system. In particular, for d_1 we obtain $J_{xx} = 0.60$ meV and $J_{yy} = J_{zz} = 0.55$ meV. For d_2 , we find $J_{xx} = 0.90$ meV and $J_{yy} = J_{zz} = 0.91$. These findings demonstrate that the polaron-induced perturbation is strongly localized, affecting only a limited region, and suggest its potential for atomic-scale control of magnetic interactions.

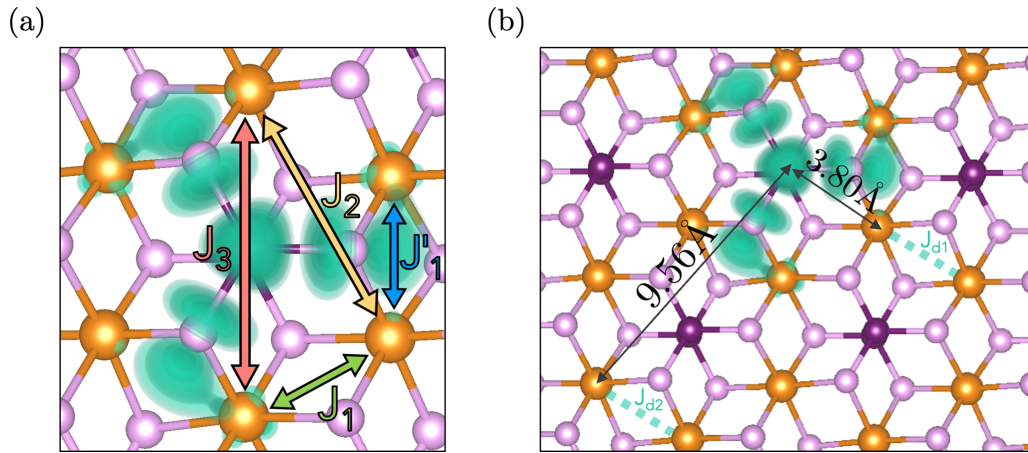


FIG. 5. (a) Calculated exchange interactions between nearest neighbors (J_1), second-nearest neighbors (J_2), and third-nearest neighbors (J_3). (b) Schematic showing the two pairs of Mn atoms located at increasing distances from the polaronic site, for which the exchange interactions J_{d1} and J_{d2} are analyzed.

IV. CONCLUSIONS

In conclusion, we have shown that a single electron polaron can energetically stabilize in a monolayer of the semiconducting antiferromagnet MnPS₃, resulting in a localized in-gap state. The polaron exhibits a complex orbital character, centered on a P atom with a trigonal symmetry that extends over neighboring S and Mn atoms. To assess its influence on magnetic properties, we computed the magnetic exchange interactions in full tensorial form J_{ij} . Our results reveal that the presence of the polaron locally breaks the symmetry of the pristine antiferromagnetic configuration, introducing anisotropy into the exchange coupling. Importantly, this anisotropic behavior is primarily driven by the excess localized electronic charge, whereas the associated lattice distortions mainly modulate the magnitude of the isotropic exchange terms.

We further investigated the spatial dependence of this perturbation and found that the polaron-induced modifications of the exchange interactions rapidly decay with increasing distance from the localization center. This demonstrates that the influence of the polaron is highly localized, with both the anisotropy and the changes in exchange strength. These findings highlight a promising strategy for local control of magnetism in 2D systems: by exploiting polarons as agents for magnetic modification. Furthermore, the polaron-induced

anisotropy in the exchange interactions is expected to influence the magnon spectrum, potentially modifying spin-wave energies and dispersions in ways that could be probed in neutron scattering experiments, thereby demonstrating a direct link between localized charge, lattice distortions, and collective spin excitations. This underlines the importance for further exploration of polaronic 2D magnets as potential platforms for spintronic device applications.

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DATA AVAILABILITY

The data supporting the findings are available within the manuscript.

TABLE II. Mn–Mn distances, second-NN, and third-NN exchange parameters for nonpolaronic and polaronic MnPS₃. Distances in Å, exchange interactions in meV. The corresponding computed total energies used in the four-states method are provided in Tables VI and VII in Appendix B.

System	Distance J_2	Distance J_3	J_2^{xx}	J_2^{yy}	J_2^{zz}	J_3^{xx}	J_3^{yy}	J_3^{zz}
Nonpolaronic (undistorted)	6.144	7.095	0.05	0.05	0.05	0.33	0.34	0.34
Polaronic (distorted)	6.135	7.058	0.21	−0.36	−0.36	0.42	−0.26	−0.26

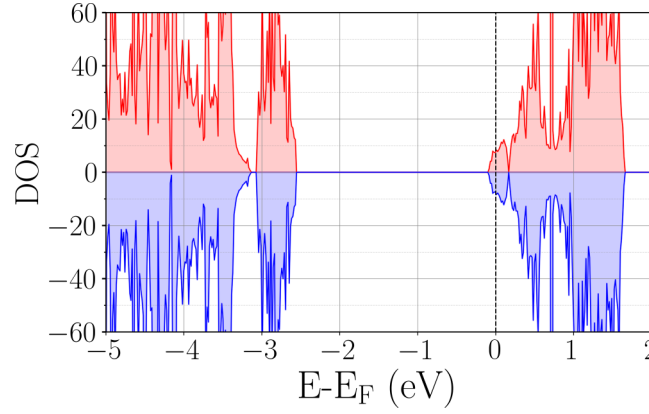


FIG. 6. Spin-polarized DOS of the doped $3 \times 3 \times 1$ MnPS₃ monolayer in the delocalized charge configuration. The upper panel displays the majority spin channel (red), while the lower panel corresponds to the minority spin channel (blue).

APPENDIX A: DENSITY OF STATES WITH A DELOCALIZED EXTRA CHARGE

The total DOS of the delocalized solution is calculated in the MnPS₃ $3 \times 3 \times 1$ supercell with an extra electron, which occupies the lowest conduction band states (see Fig. 6).

APPENDIX B: TOTAL ENERGY VALUES FOR THE FOUR-STATES METHOD

In the following, we summarize the total energies computed for the different investigated systems within the spin configurations required for the four-states method. Each table reports the four energies corresponding to the $\uparrow\uparrow$, $\downarrow\downarrow$, $\uparrow\downarrow$, and $\downarrow\uparrow$ spin arrangements for each component of the J_{ij} tensor.

Specifically, Table III presents the results for pristine MnPS₃, where symmetry reduces the problem to a single Mn–Mn pair. Tables IV and V collect the results for the polaronic MnPS₃ and the non-polaronic distorted case, considering the Mn₁–Mn₂ and Mn₂–Mn₃ pairs. Tables VI and VII report the data for J_2 and J_3 in both pristine MnPS₃ and the polaronic system, respectively. Finally, Table VIII provides the total energy values for J_1 evaluated at distances d_1 and d_2 from the polaronic center as shown in Fig. 5(b).

TABLE III. Total energies (eV) of pristine MnPS₃ for the Mn₁–Mn₂ pair, for each J_{ij}^{ab} component.

ab	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$
xx	−493.2407	−493.2407	−493.2842	−493.2202
xy	−493.2600	−493.2279	−493.2600	−493.2279
xz	−493.2600	−493.2279	−493.2599	−493.2279
yx	−493.2279	−493.2600	−493.2600	−493.2279
yy	−493.2371	−493.2371	−493.2488	−493.2488
yz	−493.2425	−493.2425	−493.2425	−493.2422
zx	−493.2280	−493.2601	−493.2602	−493.2279
zy	−493.2426	−493.2425	−493.2425	−493.2425
zz	−493.2374	−493.2374	−493.2490	−493.2491

TABLE IV. Total energies (eV) of polaronic MnPS₃ for the Mn₁–Mn₂ and Mn₂–Mn₃ pairs, for each J_{ij}^{ab} component.

ab	Mn ₁ –Mn ₂				Mn ₂ –Mn ₃			
	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$
xx	−494.1799	−494.2971	−494.2773	−494.2149	−494.1787	−494.2971	−494.2773	−494.2253
xy	−494.2258	−494.2531	−494.2258	−494.2531	−494.2253	−494.2577	−494.2253	−494.2577
xz	−494.2258	−494.2531	−494.2258	−494.2531	−494.2253	−494.2577	−494.2253	−494.2577
yx	−494.1933	−494.2829	−494.2829	−494.1933	−494.1985	−494.2829	−494.2829	−494.1985
yy	−494.2377	−494.2377	−494.2369	−494.2369	−494.2372	−494.2372	−494.2426	−494.2426
yz	−494.2364	−494.2365	−494.2365	−494.2365	−494.2390	−494.2389	−494.2390	−494.2390
zx	−494.1933	−494.2829	−494.2829	−494.1933	−494.1985	−494.2829	−494.2829	−494.1985
zy	−494.2364	−494.2364	−494.2365	−494.2364	−494.2390	−494.2390	−494.2390	−494.2390
zz	−494.2378	−494.2378	−494.2369	−494.2369	−494.2372	−494.2372	−494.2426	−494.2426

TABLE V. Total energies (eV) in distorted MnPS₃ for the Mn₁–Mn₂ and Mn₂–Mn₃ pairs, for each J_{ij}^{ab} component.

ab	Mn ₁ –Mn ₂				Mn ₂ –Mn ₃			
	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$
xx	–492.3477	–492.3456	–492.3932	–492.3210	–492.3470	–492.3456	–492.3932	–492.3311
xy	–492.3678	–492.3306	–492.3678	–492.3306	–492.3674	–492.3357	–492.3674	–492.3357
xz	–492.3677	–492.3306	–492.3678	–492.3306	–492.3674	–492.3357	–492.3674	–492.3357
yx	–492.3315	–492.3667	–492.3667	–492.3315	–492.3363	–492.3668	–492.3668	–492.3363
yy	–492.3425	–492.3425	–492.3532	–492.3532	–492.3428	–492.3428	–492.3590	–492.3590
yz	–492.3472	–492.3472	–492.3472	–492.3472	–492.3499	–492.3499	–492.3499	–492.3499
zx	–492.3316	–492.3667	–492.3668	–492.3315	–492.3363	–492.3667	–492.3667	–492.3363
zy	–492.3472	–492.3472	–492.3472	–492.3472	–492.3499	–492.3499	–492.3499	–492.3499
zz	–492.3425	–492.3425	–492.3532	–492.3532	–492.3428	–492.3428	–492.3590	–492.3590

TABLE VI. Total energies (eV) of pristine MnPS₃ for second- and third-NN exchange interaction (J_2 and J_3).

ab	J_2				J_3			
	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$
xx	–493.2842	–493.1960	–493.2407	–493.2408	–493.2407	–493.2408	–493.2842	–493.2055
xy	–493.2600	–493.2159	–493.2600	–493.2159	–493.2600	–493.2206	–493.2600	–493.2206
xz	–493.2600	–493.2159	–493.2600	–493.2159	–493.2600	–493.2206	–493.2600	–493.2206
yx	–493.2600	–493.2159	–493.2159	–493.2599	–493.2206	–493.2600	–493.2600	–493.2206
yy	–493.2352	–493.2352	–493.2358	–493.2358	–493.2359	–493.2359	–493.2401	–493.2401
yz	–493.2355	–493.2355	–493.2355	–493.2355	–493.2379	–493.2379	–493.2379	–493.2379
zx	–493.2600	–493.2159	–493.2159	–493.2600	–493.2206	–493.2600	–493.2600	–493.2206
zy	–493.2355	–493.2355	–493.2355	–493.2355	–493.2379	–493.2379	–493.2379	–493.2379
zz	–493.2352	–493.2352	–493.2358	–493.2358	–493.2359	–493.2359	–493.2401	–493.2401

TABLE VII. Total energies (eV) of polaronic MnPS₃ for second- and third-NN exchange interaction (J_2 and J_3).

ab	J_2				J_3			
	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$
xx	–494.2773	–494.3125	–494.2980	–494.2971	–494.1778	–494.2972	–494.2773	–494.2081
xy	–494.2834	–494.3006	–494.2834	–494.3006	–494.2249	–494.2496	–494.2249	–494.2496
xz	–494.2834	–494.3006	–494.2834	–494.3006	–494.2249	–494.2496	–494.2249	–494.2496
yx	–494.2829	–494.3010	–494.3009	–494.2829	–494.1888	–494.2829	–494.2829	–494.1888
yy	–494.2906	–494.2906	–494.2862	–494.2862	–494.2355	–494.2355	–494.2323	–494.2323
yz	–494.2882	–494.2882	–494.2882	–494.2882	–494.2336	–494.2336	–494.2336	–494.2336
zx	–494.2829	–494.3009	–494.3009	–494.2829	–494.1888	–494.2829	–494.2829	–494.1889
zy	–494.2882	–494.2882	–494.2882	–494.2882	–494.2336	–494.2337	–494.2336	–494.2336
zz	–494.2906	–494.2906	–494.2861	–494.2861	–494.2355	–494.2355	–494.2323	–494.2323

TABLE VIII. Total energies (eV) in polaronic MnPS₃ at $d_1 = 3.80$ Å and $d_2 = 9.56$ Å for each J_{ij}^{ab} component.

ab	$d_1 = 3.80$ Å				$d_2 = 9.56$ Å			
	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$	$\uparrow\uparrow$	$\downarrow\downarrow$	$\uparrow\downarrow$	$\downarrow\uparrow$
xx	–494.2352	–494.2971	–494.2773	–494.2670	–494.2355	–494.2378	–494.2773	–494.2185
xy	–494.2539	–494.2812	–494.2539	–494.2812	–494.2540	–494.2257	–494.2540	–494.2257
xz	–494.2538	–494.2812	–494.2539	–494.2812	–494.2541	–494.2258	–494.2540	–494.2257
yx	–494.2489	–494.2830	–494.2829	–494.2489	–494.2245	–494.2551	–494.2551	–494.2246
yy	–494.2615	–494.2615	–494.2683	–494.2683	–494.2332	–494.2333	–494.2446	–494.2447
yz	–494.2643	–494.2643	–494.2642	–494.2642	–494.2382	–494.2382	–494.2382	–494.2382
zx	–494.2489	–494.2829	–494.2829	–494.2489	–494.2246	–494.2551	–494.2551	–494.2246
zy	–494.2643	–494.2643	–494.2642	–494.2643	–494.2383	–494.2382	–494.2382	–494.2382
zz	–494.2615	–494.2615	–494.2684	–494.2683	–494.2332	–494.2332	–494.2446	–494.2446

- [1] M. Gibertini, M. Koperski, A. F. Morpurgo, and K. S. Novoselov, Magnetic 2D materials and heterostructures, *Nat. Nanotechnol.* **14**, 408 (2019).
- [2] S. Kumari, D. K. Pradhan, N. R. Pradhan, and P. D. Rack, Recent developments on 2D magnetic materials: Challenges and opportunities, *Emergent Mater.* **4**, 827 (2021).
- [3] Q. H. Wang, A. Bedoya-Pinto, M. Blei, A. H. Dismukes, A. Hamo, S. Jenkins, M. Koperski, Y. Liu, Q.-C. Sun, E. J. Telford, *et al.*, The magnetic genome of two-dimensional van der Waals materials, *ACS Nano* **16**, 6960 (2022).
- [4] K. S. Novoselov, A. Mishchenko, A. Carvalho, and A. Castro Neto, 2D materials and van der Waals heterostructures, *Science* **353**, aac9439 (2016).
- [5] E. C. Ahn, 2D materials for spintronic devices, *npj 2D Mater. Appl.* **4**, 17 (2020).
- [6] S. Wei, X. Liao, C. Wang, J. Li, H. Zhang, Y.-J. Zeng, J. Linghu, H. Jin, and Y. Wei, Emerging intrinsic magnetism in two-dimensional materials: Theory and applications, *2D Mater.* **8**, 012005 (2021).
- [7] D. Culcer, A. C. Keser, Y. Li, and G. Tkachov, Transport in two-dimensional topological materials: Recent developments in experiment and theory, *2D Mater.* **7**, 022007 (2020).
- [8] K. Premasiri and X. P. Gao, Tuning spin-orbit coupling in 2D materials for spintronics: A topical review, *J. Phys.: Condens. Matter* **31**, 193001 (2019).
- [9] N. C. Frey, H. Kumar, B. Anasori, Y. Gogotsi, and V. B. Shenoy, Tuning noncollinear spin structure and anisotropy in ferromagnetic nitride MXenes, *ACS Nano* **12**, 6319 (2018).
- [10] S. Rahman, J. F. Torres, A. R. Khan, and Y. Lu, Recent developments in van der Waals antiferromagnetic 2D materials: Synthesis, characterization, and device implementation, *ACS Nano* **15**, 17175 (2021).
- [11] M. Hossain, B. Qin, B. Li, and X. Duan, Synthesis, characterization, properties and applications of two-dimensional magnetic materials, *Nano Today* **42**, 101338 (2022).
- [12] N. D. Mermin and H. Wagner, Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg models, *Phys. Rev. Lett.* **17**, 1133 (1966).
- [13] H. Cheng, J. Zhou, M. Yang, L. Shen, J. Linghu, Q. Wu, P. Qian, and Y. P. Feng, Robust two-dimensional bipolar magnetic semiconductors by defect engineering, *J. Mater. Chem. C* **6**, 8435 (2018).
- [14] D. A. Mayoh, G. D. Wood, S. J. Holt, G. Beckett, E. J. Dekker, M. R. Lees, and G. Balakrishnan, Effects of Fe deficiency and Co substitution in polycrystalline and single crystals of Fe_3GeTe_2 , *Crystal Growth Design* **21**, 6786 (2021).
- [15] Y. Zhao, L. Lin, Q. Zhou, Y. Li, S. Yuan, Q. Chen, S. Dong, and J. Wang, Surface vacancy-induced switchable electric polarization and enhanced ferromagnetism in monolayer metal trihalides, *Nano Lett.* **18**, 2943 (2018).
- [16] J. Kim, K.-W. Kim, B. Kim, C.-J. Kang, D. Shin, S.-H. Lee, B.-C. Min, and N. Park, Exploitable magnetic anisotropy of the two-dimensional magnet CrI_3 , *Nano Lett.* **20**, 929 (2020).
- [17] C. Song, W. Xiao, L. Li, Y. Lu, P. Jiang, C. Li, A. Chen, and Z. Zhong, Tunable band gap and enhanced ferromagnetism by surface adsorption in monolayer $\text{Cr}_2\text{Ge}_2\text{Te}_6$, *Phys. Rev. B* **99**, 214435 (2019).
- [18] Y. Guo, S. Yuan, B. Wang, L. Shi, and J. Wang, Half-metallicity and enhanced ferromagnetism in Li-adsorbed ultrathin chromium triiodide, *J. Mater. Chem. C* **6**, 5716 (2018).
- [19] C. Tang, L. Zhang, and A. Du, Tunable magnetic anisotropy in 2D magnets via molecular adsorption, *J. Mater. Chem. C* **8**, 14948 (2020).
- [20] J. He, G. Ding, C. Zhong, S. Li, D. Li, and G. Zhang, Remarkably enhanced ferromagnetism in a super-exchange governed $\text{Cr}_2\text{Ge}_2\text{Te}_6$ monolayer via molecular adsorption, *J. Mater. Chem. C* **7**, 5084 (2019).
- [21] M. Rassekh, J. He, S. F. Shayesteh, and J. J. Palacios, Remarkably enhanced Curie temperature in monolayer CrI_3 by hydrogen and oxygen adsorption: A first-principles calculation, *Comput. Mater. Sci.* **183**, 109820 (2020).
- [22] K. Wang, K. Ren, Y. Cheng, S. Chen, and G. Zhang, The impacts of molecular adsorption on antiferromagnetic MnPS_3 monolayers: Enhanced magnetic anisotropy and intralayer Dzyaloshinskii-Moriya interaction, *Mater. Horiz.* **9**, 2384 (2022).
- [23] M. Orozović, B. N. Šoškić, S. Picozzi, Ž. Šljivančanin, and S. Stavić, Hole doping as an efficient route to increase the Curie temperature in monolayer CrI_3 , *2D Mater.* **12**, 045025 (2025).
- [24] C. Franchini, M. Reticcioli, M. Setvin, and U. Diebold, Polarons in materials, *Nat. Rev. Mater.* **6**, 560 (2021).
- [25] D. Emin, *Polarons* (Cambridge University Press, Cambridge, UK, 2013).
- [26] W. H. Sio and F. Giustino, Polarons in two-dimensional atomic crystals, *Nat. Phys.* **19**, 629 (2023).
- [27] H. Liu, A. Wang, P. Zhang, C. Ma, C. Chen, Z. Liu, Y.-Q. Zhang, B. Feng, P. Cheng, J. Zhao, *et al.*, Atomic-scale manipulation of single-polaron in a two-dimensional semiconductor, *Nat. Commun.* **14**, 3690 (2023).
- [28] M. Cai, M.-P. Miao, Y. Liang, Z. Jiang, Z.-Y. Liu, W.-H. Zhang, X. Liao, L.-F. Zhu, D. West, S. Zhang, *et al.*, Manipulating single excess electrons in monolayer transition metal dihalide, *Nat. Commun.* **14**, 3691 (2023).
- [29] L. Yao, A. Wang, Q. Zheng, and J. Zhao, Small polaron dynamics in a two-dimensional magnetic material, *Phys. Rev. B* **110**, 054305 (2024).
- [30] H. Rho, C. S. Snow, S. L. Cooper, Z. Fisk, A. Comment, and J.-P. Ansermet, Evolution of magnetic polarons and spin-carrier interactions through the metal-insulator transition in $\text{Eu}_{1-x}\text{Gd}_x\text{O}$, *Phys. Rev. Lett.* **88**, 127401 (2002).
- [31] L. Celiberti, D. Fiore Mosca, G. Allodi, L. V. Pourovskii, A. Tasseti, P. C. Forino, R. Cong, E. Garcia, P. M. Tran, R. De Renzi, *et al.*, Spin-orbital Jahn-Teller bipolarons, *Nat. Commun.* **15**, 2429 (2024).
- [32] J. Redondo, M. Reticcioli, V. Gabriel, D. Wrana, F. Ellinger, M. Riva, G. Franceschi, E. Rheinfrank, I. Sokolović, Z. Jakub, *et al.*, Real-space investigation of polarons in hematite Fe_2O_3 , *Sci. Adv.* **10**, eadp7833 (2024).
- [33] D. F. Mosca, L. Celiberti, L. V. Pourovskii, and C. Franchini, Polaron-driven switching of octupolar order in doped $5d^2$ double perovskite, *arXiv:2603.18155*.
- [34] S. N. Neal, H.-S. Kim, K. A. Smith, A. V. Haglund, D. G. Mandrus, H. A. Bechtel, G. L. Carr, K. Haule, D. Vanderbilt, and J. L. Musfeldt, Near-field infrared spectroscopy of monolayer MnPS_3 , *Phys. Rev. B* **100**, 075428 (2019).
- [35] R.-C. Xiao, D.-F. Shao, Y.-H. Li, and H. Jiang, Spin photogalvanic effect in two-dimensional collinear antiferromagnets, *npj Quantum Mater.* **6**, 35 (2021).

- [36] C. Liu, W. Ren, and S. Picozzi, Spin-chirality-driven multi-ferroicity in van der Waals monolayers, *Phys. Rev. Lett.* **132**, 086802 (2024).
- [37] B. H. Rimmler, B. Pal, and S. S. Parkin, Non-collinear antiferromagnetic spintronics, *Nat. Rev. Mater.* **10**, 109 (2025).
- [38] P.-X. Qin, H. Yan, X.-N. Wang, Z.-X. Feng, H.-X. Guo, X.-R. Zhou, H.-J. Wu, X. Zhang, Z.-G.-G. Leng, H.-Y. Chen, *et al.*, Noncollinear spintronics and electric-field control: A review, *Rare Metals* **39**, 95 (2020).
- [39] T. Jungwirth, J. Sinova, A. Manchon, X. Marti, J. Wunderlich, and C. Felser, The multiple directions of antiferromagnetic spintronics, *Nat. Phys.* **14**, 200 (2018).
- [40] Y. Gao, X. Jiang, Z. Qiu, and J. Zhao, Photoexcitation induced magnetic phase transition and spin dynamics in antiferromagnetic MnPS₃ monolayer, *npj Comput. Mater.* **9**, 107 (2023).
- [41] R. Samal, G. Sanyal, B. Chakraborty, and C. S. Rout, Two-dimensional transition metal phosphorous trichalcogenides (MPX₃): A review on emerging trends, current state and future perspectives, *J. Mater. Chem. A* **9**, 2560 (2021).
- [42] J. Yang, Y. Zhou, Q. Guo, Y. Dedkov, and E. Voloshina, Electronic, magnetic and optical properties of MnPX₃ (X = S, Se) monolayers with and without chalcogen defects: A first-principles study, *RSC Adv.* **10**, 851 (2020).
- [43] G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54**, 11169 (1996).
- [44] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [45] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+*U* study, *Phys. Rev. B* **57**, 1505 (1998).
- [46] S. Picozzi, Spin-orbit coupling in quantum materials: Emergent phenomena, their modelling and examples from two-dimensional magnets, *Riv. Nuovo Cimento* **47**, 609 (2024).
- [47] X. Li, H. Yu, F. Lou, J. Feng, M.-H. Whangbo, and H. Xiang, Spin Hamiltonians in magnets: Theories and computations, *Molecules* **26**, 803 (2021).
- [48] H. J. Xiang, E. J. Kan, S.-H. Wei, M.-H. Whangbo, and X. G. Gong, Predicting the spin-lattice order of frustrated systems from first principles, *Phys. Rev. B* **84**, 224429 (2011).
- [49] M. Reticcioli, U. Diebold, G. Kresse, and C. Franchini, Small polarons in transition metal oxides, in *Handbook of Materials Modeling* (Springer, Cham, 2020), pp. 1–39.
- [50] K. Momma and F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Crystallogr.* **44**, 1272 (2011).
- [51] T. Olsen, Magnetic anisotropy and exchange interactions of two-dimensional FePS₃, NiPS₃ and MnPS₃ from first principles calculations, *J. Phys. D* **54**, 314001 (2021).
- [52] R. Basnet, K. M. Kotur, M. Rybak, C. Stephenson, S. Bishop, C. Autieri, M. Birowska, and J. Hu, Controlling magnetic exchange and anisotropy by nonmagnetic ligand substitution in layered MPX₃ (M = Ni, Mn; X = S, Se), *Phys. Rev. Res.* **4**, 023256 (2022).
- [53] J.-T. Yang, C.-J. Xu, H.-J. Wang, Q. Min, S.-J. Luo, Y.-C. Xiong, W. Ren, and C. Jing, Stable antiferromagnetic property and tunable electronic structure of two-dimensional MnPX₃ (X = S and Se) from pristine structure to Janus phase, *J. Phys.: Condens. Matter* **35**, 395501 (2023).