DFT study of itinerant ferromagnetism in p -doped monolayers of MoS₂Yuqiang Gao,^{1,2,*} Nirmal Ganguli^{1,†} and Paul J. Kelly^{1,3,‡}¹*Faculty of Science and Technology and MESA⁺ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*²*Department of Applied Physics, Northwestern Polytechnical University, Xi'an, China*³*The Center for Advanced Quantum Studies and Department of Physics, Beijing Normal University, 100875 Beijing, China*

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We use density functional theory to explore the possibility of making the semiconducting transition-metal dichalcogenide MoS₂ ferromagnetic by introducing holes into the narrow Mo d band that forms the top of the valence band. In the single impurity limit, the repulsive Coulomb potential of an acceptor atom and intervalley scattering lead to a twofold orbitally degenerate effective-mass-like e' state being formed from Mo $d_{x^2-y^2}$ and d_{xy} states, bound to the K and K' valence band maxima. It also leads to a singly degenerate a'_1 state with Mo $d_{3z^2-r^2}$ character bound to the slightly lower lying valence band maximum at Γ . Within the accuracy of our calculations, these e' and a'_1 states are degenerate for MoS₂ and accommodate the hole that polarizes fully in the local spin density approximation in the impurity limit. With spin-orbit coupling included, we find a single ion magnetic anisotropy of ~ 5 meV favoring out-of-plane orientation of the magnetic moment. Pairs of such hole states introduced by V, Nb, or Ta doping are found to couple ferromagnetically unless the dopant atoms are too close in which case the magnetic moments are quenched by the formation of spin singlets. Combining these exchange interactions with Monte Carlo calculations allows us to estimate ordering temperatures as a function of the dopant concentration x . For $x \sim 9\%$, Curie temperatures as high as 100 K for Nb and Ta and in excess of 160 K for V doping are predicted. Factors limiting the ordering temperature are identified and suggestions made to circumvent these limitations.

DOI: [10.1103/PhysRevB.100.235440](https://doi.org/10.1103/PhysRevB.100.235440)**I. INTRODUCTION**

The discovery of ferromagnetism in (In,Mn)As [1] and (Ga,Mn)As [2] and predictions for achieving room temperature ordering [3] sparked a huge effort to realize a dilute magnetic semiconductor (DMS) that might lead to a semiconductor-based spin electronics (“spintronics”). After 25 years of intensive research, the maximum ordering temperature has stagnated at values too low for extensive applications [4]. The number of material systems being considered has proliferated but it is not clear what the fundamental limit is to the ordering temperature achievable in any particular material system. There are many reasons for the low ordering temperatures [5,6] but the essential dilemma is that the open d shell states of magnetic impurities like Mn are quite localized. While this favors the on-site exchange interaction that is the origin of the Hund’s-rule spin alignment and makes the ionic moment insensitive to temperature, it leads to weaker exchange interactions between pairs of impurity ions that determine the Curie temperature T_C , the ferromagnetic ordering temperature. To increase T_C , the concentration of impurity atoms has to be increased. This is accompanied by

a variety of adverse effects such as a nonuniform distribution of magnetic impurities or the formation of antisite defects that are electron donors which counter the intended increase in the concentration of holes. In many semiconductors, transition metal ions like Mn, Fe, or Co introduce “deep levels,” tightly bound partially occupied states, in the fundamental gap of the semiconductor. At high dopant concentrations, these form deep impurity bands that dominate the (transport) properties of a material that is no longer a semiconductor and from the electronic structure point of view, is an entirely new material.

In a quite different context, it was long believed that long-range magnetic ordering would not be possible in two-dimensional (2D) materials [7,8]. However the observation of ferromagnetism in ultrathin epitaxial layers of, e.g., Fe on Au substrates, demonstrated that the Mermin-Wagner theorem is not watertight, violation of the proof usually being attributed to magnetocrystalline anisotropy [9]. The recent observation of ferromagnetic ordering in two different chromium-based 2D crystalline materials Cr₂Ge₂Te₆ [10] and CrI₃ [11] nonetheless attracted considerable attention [12]. One reason was because of the general interest in 2D materials, triggered by spectacular observations on graphene [13–15]. This interest was reinforced by the realization that the properties of semiconductors like MoS₂ could also be importantly different in few-layer and monolayer form [16–18] and was compounded by the desirability of stacking layers of 2D materials with different properties [19], whereby the lack of a ferromagnetic material in a vast profusion of

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FIG. 1. Non-spin-polarized band structures of monolayers of trigonal prismatic 1H VS₂ (a) and MoS₂ (b). The Fermi level is indicated by a horizontal dashed green line. The MoS₂ valence band maximum (VBM) at the K and K' points has mixed $d_{x^2-y^2}$ and d_{xy} character. The slightly lower-lying valence band maximum at the Γ point has $d_{3z^2-r^2}$ character.

2D materials was a striking lacuna [20]. Because the Curie temperatures of monolayers of the chromium based materials [10,11] is low, $\lesssim 50$ K, the very recent reports that the transition metal dichalcogenide VSe₂ [21] and Fe₃GeTe₂ [22] exhibit ferromagnetism at room temperature acquires huge significance.

The ferromagnetism of VS₂ and VSe₂ was predicted with the aid of density functional theory (DFT) calculations [23]. The driving force behind the magnetic ordering can be understood in terms of the band structure of the nonmagnetic 1H phase shown in Fig. 1(a) that is very similar to that of the isostructural MoS₂ shown in Fig. 1(b) but with one valence electron per formula unit less so that it is metallic with the Fermi level situated in the middle of the solid red band. Bulk multilayered MoS₂ is a nonmagnetic semiconductor with an indirect band gap of about 1 eV. In monolayer form it was predicted to have a larger, direct gap [24] and this was confirmed experimentally where direct gaps of ~ 1.8 eV have been reported [16,17]. In the figure, the “nominal” Mo 4d bands are indicated in red, the black bands are sulfur-derived 3p bands. The interaction of the Mo-*d* and S-*p* states is such that a large covalent bonding-antibonding gap is formed leaving a single Mo-*d* band (solid red line) with mixed $\{d_{x^2-y^2}, d_{xy}, d_{3z^2-r^2}\}$ character in the fundamental band gap [25,26]. For MoX₂ this band is completely filled but for VX₂ it is only half full. The dispersion of only about 1 eV leads to a high average density of states of ~ 2 states/eV and the gain in energy achieved by exchange splitting this narrow band more than offsets the kinetic energy cost. The bandwidth reduction in 2D that leads to larger band gaps is favorable for itinerant ferromagnetism because of the higher average densities of states (DoS) than in three dimensions. Likewise 3d elements are more favorable than 4d and 4d more favorable than 5d because of the greater localization of the *d* electrons and concomitant smaller bandwidth as the principal quantum number decreases.

A number of intrinsic defects have been found to form local moments [27–31] in MX₂ materials and suggestions

FIG. 2. Schematic of the effective-mass acceptor states bound to the valence band maxima (VBM): An e' state bound to the K-K' VBM and an a'_1 state to the Γ VBM. n is the principal quantum number and only $n = 1, 2, 3$ levels of the Rydberg series are sketched at the Γ point.

have been made to make the MX₂ materials magnetic by adsorption of impurity atoms [27,28,32,33], or by substituting M or X atoms with impurity atoms [28,33–51]. Even though the Mermin-Wagner theorem [7,8] tells us that there is no long-range ordering in two dimensions for isotropic Heisenberg exchange, few attempts have been made to determine the exchange coupling between magnetic impurities [33,37,38,40,41,47,51] and it was only very recently that the magnetic anisotropy of a defect was calculated, for an antisite defect in MoS₂ [31]. Replacing some of the M atoms with Hund’s-rule coupled transition metal atoms like Mn or Fe gives rise to deep impurity levels in the semiconductor gap. Where attempts have been made to estimate the Curie temperature, the predicted values are either very low or the concentration of transition metal dopant is so high that the doped material is no longer a semiconductor [35,37,38,40,41,50]. Based upon the electronic structure shown in Fig. 1(b), we explore a different approach to making MoS₂ ferromagnetic in this paper [52].

Group VIB Mo has a $4d^5 5s^1$ electronic configuration and, in a dichalcogenide like MoS₂, is nominally Mo⁴⁺ with one up-spin and one down-spin *d* electron so it is nonmagnetic as seen in Fig. 1(b). When a Mo atom is substituted by a group VB atom like V, Nb, or Ta, then the dopant atom, e.g., V⁴⁺, has a single unpaired *d* electron and a single hole is thereby introduced into the narrow Mo 4*d* band; substitution of a group IVB atom (Ti, Zr, Hf) will introduce two holes per dopant atom. In the impurity limit, the asymptotic Coulomb potential leads to a series of hydrogenic states bound to the top of the valence band; to the maxima at the K and K' points with mixed Mo $d_{x^2-y^2}$ and d_{xy} character and to the slightly lower valence band maximum at the Γ point with Mo $d_{3z^2-r^2}$ character and a large effective mass [53].

The aim of this paper [52] is to determine if there are dopant atoms whose potential is sufficiently similar to that of the host Mo atom that only weakly bound, effective-mass-like states are formed above the valence band edge, Fig. 2. At low concentrations these bound states should polarize and form impurity bands that have such a high density of states that they remain exchange split [54]. At finite temperatures these

polarized bound holes will be excited into the valence band giving rise to a DMS. The key objectives of this paper are to determine (i) whether single acceptor dopant atoms give rise to polarized effective-mass-like states in the MoS_2 host system and to determine the position of these states with respect to the valence band edge. (ii) Whether the interaction between pairs of dopant atoms favors ferromagnetic or antiferromagnetic alignment and to identify the nature of the interaction, Zener p - d type, double exchange etc. [5,6] and understand the factors determining it. (iii) The magnetic anisotropy of single impurities, the so-called single ion anisotropy (SIA). (iv) The ordering temperature and express it in terms of parametrized models that describe the dopant-induced states and their interactions in order to identify the most promising regions of parameter space to realize a room temperature DMS.

To do this we use density functional theory total energy calculations to determine ground state energies of single acceptor impurities. We outline the methods used and give some technical details specific to the present work in Sec. II. Our results are presented in Sec. III beginning with a study of the single impurity limit of a substitutional vanadium atom in Sec. III A including the effects of spin polarization and local atomic relaxation. The binding of pairs of V dopants is considered in Sec. III B and their magnetic “exchange” interaction in Sec. III C with special attention being devoted to understanding the quenching of the magnetic moments of close pairs of impurity ions. In Sec. III D we briefly compare V with Nb and Ta. Section IV is concerned with the question of magnetic ordering and begins with a study of the single ion anisotropy of V impurities in Sec. IV A to justify using an Ising spin model with the exchange interactions from Sec. III C and the Monte Carlo techniques described in Sec. IV B to estimate ordering temperatures in Sec. IV C. A comparison of our findings with other calculations in Sec. V leads us to consider how using the generalized gradient approximation (GGA) would alter our local density approximation (LDA) results. After a brief discussion in Sec. VI some conclusions are drawn in Sec. VII.

II. COMPUTATIONAL DETAILS

Calculations of the total energy and structural optimizations were carried out within the framework of density functional theory (DFT) using the projector augmented wave (PAW) method [55] and a plane-wave basis set with a cut-off energy of 400 eV as implemented in the VASP code [56–58]. Monolayers of MX_2 periodically repeated in the c direction were separated by more than 20 Å of vacuum to avoid spurious interaction.

The equilibrium structural parameters for bulk and monolayer MoS_2 were calculated in both the LDA [61] and GGA [62] and are given in Table I. It can be seen that the GGA slightly overestimates lattice constants and bond lengths compared to experiment [59]. The LDA underestimates them by more than the GGA overestimates them, a result found for many materials. In the present case, the agreement with experiment is still very reasonable for both LDA and GGA. However, we see that for an MoS_2 monolayer the LDA gives a better description of the energy levels near the valence

TABLE I. In-plane lattice constant a , distance between sulfur atoms d_{SS} (thickness of an MoS_2 monolayer), Mo-S bond length d_{MoS} , energy gap $\Delta\epsilon_g$, and energy difference between the valence band maxima (VBM) at the K and Γ points $\Delta_{K\Gamma} = \epsilon_K - \epsilon_\Gamma$ in LDA and GGA for bulk and monolayer (ML) MoS_2 . A van der Waals functional should be used to obtain a reasonable interlayer separation for bulk layered MoS_2 . Because we are only interested in monolayers of MoS_2 in this paper, we have used the experimental value of c to obtain the bulk results shown here.

		a (Å)	d_{SS} (Å)	d_{MoS} (Å)	$\Delta\epsilon_g$ (eV)	$\Delta_{K\Gamma}$
Bulk	GGA	3.183	3.127	2.42	0.885	−0.640
	LDA	3.125	3.115	2.38	0.748	−0.640
	Exp	3.160 ^a	3.172 ^a	2.41 ^a	1.290 ^b	−0.600 ^c
ML	GGA	3.185	3.130	2.42	1.650	0.012
	LDA	3.120	3.115	2.38	1.860	0.150
	Exp	3.160	3.172	2.41	1.900 ^b	0.140 ^c

^aReference [59].

^bReference [17].

^cReference [60].

band maximum (VBM) than does the GGA, in particular the important quantity $\Delta_{K\Gamma} = \epsilon_K - \epsilon_\Gamma$, the position of the VBM at the Γ point ϵ_Γ , relative to the top of the valence band at the K point ϵ_K [60]. To describe acceptor states accurately, it is important to have a good description of the host band structure in the vicinity of the VBM so we will describe exchange and correlation effects in this paper using the local spin density approximation LSDA as parametrized by Perdew and Zunger [61]. Results obtained with the GGA are considered in Sec. V.

We model substitutional impurities and impurity pairs in $N \times N$ in-plane supercells with N as large as 15 using the calculated equilibrium lattice constant for the pure monolayer (ML) host, Fig. 3. Local geometries are first relaxed using $N = 6$ and only a small differential relaxation needs to be performed in the larger supercells. Interactions between pairs of impurities were studied in 12×12 supercells. The atomic positions were relaxed using a $2 \times 2 \times 1$ Γ -centered k -point mesh until the forces on each ion were smaller than 0.01 eV/Å. Spin-polarized calculations were performed with a denser mesh corresponding to 4×4 k points for a 12×12 unit cell.

III. RESULTS

Impurity states in semiconductors are usually described in one of two limits: (i) in effective-mass theory (EMT) where the main emphasis is on the Rydberg series of bound states tied to the conduction band minima or valence band maxima formed in response to a Coulomb potential or (ii) in the tight-binding limit where the main emphasis is on the local chemical binding, atomic relaxation, and impurity states formed deep in the fundamental band gap associated with an impurity potential very different to the host atomic potential [63–65]. Because there is no consensus of how best to combine both aspects [66], we consider the behavior of shallow acceptor states in a periodic supercell geometry in some detail in the following section.

FIG. 3. Sketch of a 12×12 MoS_2 supercell with a substitutional atom at the origin O. Shown is the more symmetric Wigner-Seitz cell. The potential on the Mo atom indicated with a red circle that is furthest from this atom will be used to identify the host valence band maximum (VBM). Mo atoms at various distances from the central atom are labeled A1–A6, B1–B4, C1–C4, D1–D3, and E1 for later reference.

A. Single impurity limit: V in MoS_2

We begin by replacing a single Mo atom in an $N \times N$ MoS_2 supercell with a V atom with one valence electron less, Fig. 3.

To more easily identify the downfolded host bands we choose N to be a multiple of three, whereby the K and K' points fold down to the Γ point of the reduced BZ. The energy bands for this supercell before relaxing the local geometry are shown in Fig. 4 for $N = 3, 6, 9, 12$, and 15 . The repulsive (for electrons; attractive for holes) impurity potential is seen to push not one but three impurity states out of the valence band to form localized states labeled a'_1 and e' under the local D_{3h} symmetry, Fig. 2. By projecting the corresponding wave functions at the Γ point onto spherical harmonics on the V_{Mo} site, we find that the singly degenerate a'_1 state has $V d_{3z^2-r^2}$ character while the e' state that is doubly degenerate at the center of the BZ has $V \{d_{x^2-y^2}, d_{xy}\}$ character. The corresponding partial charge density plots are shown on the left-hand and right-hand sides (lhs, rhs) of Fig. 5, respectively. By fitting the wave functions of the impurity states to a hydrogenic wave function $\psi(r) = A \exp(-r/a_0^*)$, we find effective Bohr radii a_0^* of 4.2 and 8.0 Å for the a'_1 and e' states, respectively in Figs. 5(c) and 5(d).

We identify these a'_1 and e' states with the most tightly bound (effective-mass-like) acceptor states formed when a screened Coulomb potential is introduced by substitution of a Mo atom by V (Nb or Ta). In the single impurity limit, intervalley scattering leads to a twofold orbitally degenerate effective-mass-like state formed from Mo $\{d_{x^2-y^2}, d_{xy}\}$ states bound to the K and K' valence band maxima in Fig. 1 and a singly degenerate state with Mo $d_{3z^2-r^2}$ character bound to the slightly lower lying valence band maximum at Γ in Fig. 1. Within the accuracy of our calculations, these e' and a'_1 states are (accidentally) degenerate for MoS_2 and accommodate the hole that we will see polarizes fully in the local spin density approximation [67]. The shape of the dispersion of the impurity states is essentially independent of the supercell size so the bands can be described with a single effective hopping parameter. The a'_1 state exhibits very little dispersion

FIG. 4. The band structure of an MoS_2 monolayer with a single Mo atom replaced by V without relaxation in 3×3 , 6×6 , 9×9 , 12×12 , and 15×15 supercells (a)–(e) aligned with respect to the valence band maximum determined with respect to semicore level states on the Mo atom furthest from the origin (horizontal black dot-dashed line at energy zero) and of an undoped MoS_2 monolayer (f). The Fermi energy is indicated by the horizontal green dot-dashed line. The contribution from vanadium $d_{3z^2-r^2}$ and $\{d_{x^2-y^2}, d_{xy}\}$ orbitals are shown as open circles and half-filled blue circles, respectively, in (a)–(c) where the symbol size is proportional to the population of the corresponding state.

FIG. 5. Charge density plots for the a_1' (lhs) and e' (rhs) states at the Γ point in Fig. 4(d) in the central [001] plane through the Mo atoms (top view) and [010] plane (side view) for a 12×12 supercell. The isosurface levels are $0.001 e/\text{\AA}^3$. (c) and (d) Circularly averaged charge densities fitted with a Bohr model.

consistent with the out-of-plane $d_{3z^2-r^2}$ orbital character at Γ where the weak dispersion of the host MoS_2 bands is described by a large effective mass [68]. In the language of effective-mass theory (EMT), the binding energy of the a_1' state is dominated by the central cell correction [63].

In the rightmost panel of Fig. 4 we show the band structure of an undoped monolayer calculated in a 15×15 supercell so the K point VBM is downfolded onto Γ . If we compare this with the impurity supercell bands on the left, we see that even for $N = 15$, Fig. 4(e), the interaction of the impurity bands and the VBM still suppresses the VBM quite noticeably, by more than 20 meV.

1. Screened impurity potential

Identifying the valence band maximum (VBM) in an impurity supercell calculation is complicated by the Rydberg series of effective-mass-like states associated with the single impurity whose wave functions will overlap with their periodic images and form bands that overlap and hybridize with the “true” valence band states, Fig. 2. To disentangle those effects, we first determine the position of the VBM with respect to Mo 4s semicore states $\varepsilon_{4s}^{\text{Mo}}$ for an undoped monolayer of MoS_2 ; ε denotes a Kohn-Sham eigenvalue. For a sufficiently large impurity supercell, the position of $\varepsilon_{4s}^{\text{Mo}}$ for the Mo atom furthest from the impurity (indicated with a red circle in Fig. 3) relative to the VBM should be asymptotically

FIG. 6. Dependence of the Mo 4s semicore level on the separation from the V_{Mo} dopant ion. The Coulomb potential of the V dopant is screened by the host valence electrons and by the a_1' hole (upper panel), respectively, by the e' hole (lower panel). The 18 data points refer to the 18 inequivalent Mo atoms labeled in Fig. 3. The asymptotic value $\varepsilon_{\text{core}}(\infty)$ was determined by fitting the calculated data points in the insets to an exponential wave function and using this fit (red and blue curves) to extrapolate to $R = \infty$.

equal to the corresponding energy separation for an undoped monolayer of MoS_2 because the impurity potential far from the dopant center will be completely screened by the bound charge of the neutral impurity in an a_1' or e' bound state. To test this hypothesis quantitatively, we plot $\varepsilon_{4s}^{\text{Mo}}$ with respect to its asymptotic value as a function of the separation of Mo from the impurity V ion in the insets of Fig. 6 for $N = 12$ supercells (symbols). The corresponding results for the S semicore $2s$ state $\varepsilon_{2p}^{\text{S}}$ are shown in Appendix A and yield similar conclusions.

In an impurity supercell calculation, a localized electron in a (semi)core level on a Mo atom a distance R from the impurity atom will see a screened $1/\epsilon_r R$ repulsive potential that is partially compensated by the charge of the bound hole $n_{\text{hole}}(r)$. Here ϵ_r is the relative static dielectric constant. We can “measure” this screened Coulomb potential by studying how Mo (and S) semicore levels behave as a function of their separation from the central V atom. The perturbing electrostatic potential seen by the core electrons has the

form

$$\varepsilon_{\text{core}}(R) - \varepsilon_{\text{core}}(\infty) = \frac{1}{\varepsilon_r R} \left(1 - \int_0^R n_{\text{hole}}(r) 2\pi r dr \right) \quad (1a)$$

$$= \frac{e^{-\frac{2R}{a_0^*}} \left(\frac{2R}{a_0^*} + 1 \right)}{\varepsilon_r R}, \quad (1b)$$

where in 1(a) $n_{\text{hole}}(r) = \int_{-\infty}^{\infty} n_{\text{hole}}(r, z) dz$ and $n_{\text{hole}}(r, z)$ is obtained by integrating $|\psi_i(r, \theta, z)|^2$ over θ for $i = a'_1$ or e' . In 1(b) we assume that $\psi_i(r, \theta, z)$ is the solution of a strictly two-dimensional hydrogenic problem [69]. If we take the natural logarithm of 1(b), the slope is $-2/a_0^*$ for large values of R and we can extract a_0^* from Fig. 6.

In the supercell band structures shown in Fig. 4, the a'_1 and e' derived states overlap and $n_{\text{hole}}(r)$ is a mixture of these two states with different masses m_h . To circumvent this complication, we calculate the electronic structure at the K (or M) point where the lowest unoccupied state has a'_1 character. By using a sufficiently small temperature broadening we can obtain the corresponding charge density and obtain the result shown in Fig. 6 (upper panel). Alternatively, we calculate the electronic structure at the Γ point where the lowest unoccupied state has e' character to obtain Fig. 6 (lower panel). The *ab initio* values of $\varepsilon_{\text{core}}(R)$ and $\ln[\varepsilon_{\text{core}}(R) - \varepsilon_{\text{core}}(\infty)]$ are fit quite well with 1(b) with an effective Bohr radius of $a_0^* \sim 5.4$ Å and $\varepsilon_r = 20$ for the a'_1 hole and $a_0^* \sim 8.7$ Å and $\varepsilon_r = 13$ for the e' hole. The values of ε_r should be compared to recent calculations for the in-plane “macroscopic” dielectric constant where $\varepsilon_r = 15$ was found for monolayers of MoS₂ as well as for bulk MoS₂ with negligible ionic contribution to the screening [70]. The deviation of $\varepsilon_r = 20$ from the macroscopic value is not very surprising in view of the localization of the a'_1 hole that does not “see” many unit cells of MoS₂. The value for the e' hole is reasonable.

At large values of R in Fig. 6, the potential felt by the core states is seen not to decay but to oscillate. We attribute this to the accumulation of the residual hole charge at the supercell boundary that is a consequence of charge neutrality. The data points in Fig. 6 that deviate from the trend line are to be found outside the circle inscribed in the hexagonal WS cell.

In the effective-mass approximation the effective Bohr radius $a_0^* = \varepsilon_r/m_h \times 0.529$ Å and the ground state binding energy with respect to the appropriate VBM is $\varepsilon_b = m_h/\varepsilon_r^2 \times 13.606$ eV. From the band structure in Fig. 1, the effective mass in units of the free electron mass m_0 is $m_h \sim 0.56$ at the K point VBM and 3.42 at the Γ point VBM, consistent with a previous calculation [71]. Combining these masses with $\varepsilon_r = 15$ [70] leads to values of $a_0^* \sim 14$ Å and $\varepsilon_b \sim 34$ meV for e' holes and $a_0^* \sim 2.3$ Å and $\varepsilon_b \sim 207$ meV for a'_1 holes, respectively. At best the EMT is indicative but is clearly not quantitative for the most strongly bound acceptor states—a conclusion that is not especially surprising in view of the expected central cell correction for ground states [63] as well as the strong localization of both states.

The screening of the impurity potential by (i) the MoS₂ valence electrons and (ii) by the bound impurity hole means that the residual perturbation measured by the core states decreases rapidly with R allowing us to estimate the position of the reference core state far from the impurity and therefore

FIG. 7. Dependence on the supercell size N of the (spin-degenerate) a'_1 and e' impurity levels induced by a substitutional vanadium atom V_{Mo} with respect to the valence band maximum. The solid lines are fits to the data points using a model that includes the tail of the Coulomb potential in first order perturbation theory. (Inset) Truncation of the Coulomb potential in a supercell calculation.

of the VBM to an accuracy of a few meV for $N = 12$. This procedure was used to estimate the position of the VBM and of the impurity states with respect to it for each supercell size shown in Fig. 4 (dot-dashed line).

The same results can be obtained more simply by noting that the repulsive potential that binds a Rydberg series to the top of the valence band has little effect on the conduction band edge. Since we know the value of the band gap, the VBM can be determined from the conduction band minimum. We verified that this leads to the same results as the more elaborate procedure discussed in the foregoing.

2. Hydrogenic perturbation model

Now that we have established procedures for determining the position of the VBM, we see that the a'_1 and e' impurity bands in Fig. 4 not only narrow as the supercell size N is increased but rise with respect to the VBM. To make this clearer, we plot their centers of gravity

$$\bar{\varepsilon}_i = \frac{\sum_{n\mathbf{k}} f_{in}(\mathbf{k}) \varepsilon_n(\mathbf{k})}{\sum_{n\mathbf{k}} f_{in}(\mathbf{k})} \quad (2)$$

with respect to the VBM in Fig. 7; both levels are seen to rise as a function of N . The probability $f_{in}(\mathbf{k})$ is the i character of the wave function $\psi_{n\mathbf{k}}$ obtained by projecting $\psi_{n\mathbf{k}}$ onto site centered orbitals β_i and $i \equiv Rlm$ is a composite site, angular momentum index. Here we have chosen i to be the $d_{x^2-y^2}$ and d_{xy} Kubic harmonics on the V_{Mo} atom for the e' state and $d_{3z^2-r^2}$ on V_{Mo} for the a'_1 state and the summation is carried out over the entire Brillouin zone and over the three split-off impurity bands in Fig. 4. Since the position of the impurity levels introduced by V_{Mo} atoms will play an important role in determining the magnetic moment and exchange interaction between impurities, we wish to understand this increase.

A Coulomb potential in a semiconductor gives rise to a Rydberg series of bound states. A finite supercell cannot

describe the asymptotic form of the potential correctly but will truncate it on the supercell boundary. In a self-consistent calculation, the requirement of charge neutrality will lead to the charge in the tail of the hydrogenic state accumulating on the supercell boundary. As the supercell size is increased, more of the “tail” of the (repulsive) Coulomb potential is described correctly, leading to the rise of the impurity levels seen in Figs. 4 and 7.

The effect of truncating the Coulomb potential can be estimated using a simple two-dimensional (2D) hydrogenic [69] model and first order perturbation theory. For simplicity we assume a circular geometry and replace the 2D Wigner-Seitz cell with a circle of radius S with the same area $\pi S^2 = A_{WS}$. The correction to the ground state energy of a hydrogen atom in 2D is

$$\int_S^\infty R^2(r) \frac{e^2}{4\pi\epsilon_r r} 2\pi r dr = \frac{e^2}{2\pi\epsilon_r a_0^*} e^{-2S/a_0^*}, \quad (3)$$

where a_0^* is the effective Bohr radius, ϵ_r is the relative dielectric constant, and $R(r)$ is the radial part of the 2D hydrogenic wave function [69] for a screened Coulomb potential. Taking the top of the valence band ε_{VBM} of an ideal MoS₂ monolayer, as estimated in the previous subsection, to be zero, we fit the *ab initio* calculated data points with the solid curves shown in Fig. 7. The fit is very good and deviations can be attributed to local screening effects in the “real” inhomogeneous crystal as modeled in DFT.

The a_1' and e' impurity levels increase in energy with increasing supercell size and converge to a (coincidentally) common value of ~ 62 meV in the single impurity limit ($N \rightarrow \infty$). From the fitting we obtain another estimate of the effective Bohr radius of 8.3 Å for the e' state, of 5.5 Å for the a_1' state, and of $\epsilon_r \sim 10.0$ for the in-plane dielectric constant. These values should be compared to the EMT predictions of $a_0^* \sim 14$ Å and $\varepsilon_b \sim 34$ meV with respect to the K point VBM for the e' holes and $a_0^* \sim 2.3$ Å and $\varepsilon_b \sim 207$ meV with respect to the Γ point VBM for the a_1' holes. Taking the LDA value of $\Delta_{K\Gamma} \sim 150$ meV from Table I into account, we would expect to find the a_1' ground state at $207 - 150 = 57$ meV above the K point VBM.

According to Fig. 7, the highest e' impurity states emerge from the valence band when the supercell size is larger than 5×5 . This is consistent with the effective Bohr radius of the impurity levels deduced in Fig. 5. For impurity states with higher principal quantum numbers, the Bohr radii are at least twice as large. These states are not sufficiently localized in the Coulomb potential to appear above the valence band maximum for the largest supercells we have studied.

We can also determine effective Bohr radii from the dependence of the widths of the impurity bands, shown in Fig. 4, on the supercell size N because of the dependence of the bandwidth on the overlap of impurity wave functions in neighboring supercells. In Fig. 8 we plot the second moment of the impurity bands

$$\sqrt{\frac{\sum_{\mathbf{nk}} f_{in}(\mathbf{k})(\varepsilon_n(\mathbf{k}) - \bar{\varepsilon}_i)^2}{\sum_{\mathbf{nk}} f_{in}(\mathbf{k})}} \propto e^{-R/a_0^*} \quad (4)$$

as a function of N where a_0^* is the effective Bohr radius and R is the distance between dopants in neighboring supercells.

FIG. 8. Dependence of the bandwidth of (spin-degenerate) impurity bands induced by substitutional V impurities on the supercell size N . The data points calculated using (4) are fit using the hydrogen model discussed in the text.

From the fitting we get effective Bohr radii of 7.8 Å for the e' state and 5.2 Å for the a_1' state which are consistent with our earlier results summarized in Table II.

3. Effect of relaxation

One of the most attractive and useful features of a plane-wave basis is the ease with which Hellmann-Feynman forces can be calculated. This makes it simple to determine how the host MoS₂ crystal relaxes locally in response to substituting a Mo atom with V, Fig. 9. According to the electronic structure Fig. 4(d) for the unrelaxed geometry, shown enlarged in Fig. 10(b), the Fermi level is essentially pinned in the orbitally nondegenerate a_1' state and the system does not undergo a Jahn-Teller (JT) distortion; if we begin geometry optimization from a JT distorted configuration, the system relaxes back to a symmetric one. Consistent with this, we find only symmetry-conserving (“breathing mode”) relaxation about the vanadium ion with the six nearest neighbor sulfur atoms relaxing towards the V atom and the six in-plane neighboring Mo atoms relaxing radially away, shown in Fig. 9. The displacements converge rapidly with supercell size to $\Delta d_{V-S} = 0.060$ Å and $\Delta d_{V-Mo} = 0.008$ Å as seen in Table III. The total energy gain from relaxation is 150 meV.

TABLE II. Summary of the a_1' and e' bound state effective Bohr radii a_0^* (Å) derived in different ways without relaxation.

	V		Nb		Ta	
	$a_1'(\Gamma)$	$e'(K)$	$a_1'(\Gamma)$	$e'(K)$	$a_1'(\Gamma)$	$e'(K)$
Fig. 5	4.2	8.0	5.3	10.0	5.2	10.3
Fig. 6, Eq. 1(b) Mo	5.4	8.7	6.2	9.6	5.8	9.7
Fig. 29, Eq. 1(b) S	6.5	8.8	6.8	10.0	6.5	10.0
Fig. 7, Eq. (3)	5.5	8.3	5.9	10.0	6.2	10.4
Fig. 8, Eq. (4)	5.2	7.8	5.2	9.8	5.4	10.1
EMT ($\epsilon_r = 15$)	2.3	14.0	2.3	14.0	2.3	14.0

FIG. 9. Schematic of the relaxation about a vanadium atom on a substitutional Mo site V_{Mo} in MoS_2 .

The band structures of the unrelaxed and relaxed 12×12 impurity supercells are compared in Figs. 10(b) and 10(d). The band structures are aligned on the VBM, located at the Γ point as seen in Fig. 10(a) for an undoped monolayer, using the $4s$ semicore level shift of the “B4” Mo atom on the boundary of the Wigner-Seitz cell furthest from the dopant V atom, see Fig. 3. The main effect of relaxation is to lift the quasidegeneracy of the a'_1 and e' impurity states, Fig. 10(d). The increased V-Mo bond length leads to a lowering of the center of gravity of the e' state with respect to the a'_1 state that is antibonding with respect to the neighboring S p states. As a consequence, the hole state acquires essentially pure a'_1 character.

4. Spin polarization

The electronic structure of an unpaired spin in an orbitally nondegenerate a'_1 impurity state resembles that of a free hydrogenlike atom and, like a free atom, its total energy can be lowered by allowing the electron to polarize in the local spin density approximation [67,72]. The result of doing so in the dilute limit is shown in Figs. 10(c) and 10(e). Without relaxation, the localized and dispersionless a'_1 state splits by

TABLE III. Relaxation of nearest neighbor S and Mo shells about a substitutional vanadium atom as a function of the $N \times N$ supercell size N . Atomic displacements in Å.

N	3	6	9	12	15
Δd_{V-S}	-0.060	-0.060	-0.060	-0.060	-0.060
Δd_{V-Mo}	0.003	0.005	0.008	0.008	0.008

91 meV leaving the hole with mixed a'_1 - e' character and a magnetic moment of $m = 1 \mu_B$. Expressing the exchange splitting in terms of an effective Stoner parameter I_{xc} as $\Delta\varepsilon = mI_{xc}$ results in a value of I_{xc} of 91 meV that is substantially less than the free atom value of $I_{xc} \sim 0.7$ eV [73]. In the local density approximation, it is the local electron density that drives the exchange splitting and the small exchange splitting can be understood in terms of the much lower spin density of the impurity state compared to that of a free atom. Consistent with this picture is the even smaller exchange splitting of the more delocalized e' state that is only ~ 25 meV. Before relaxation, the partial occupation of a'_1 and e' states allows the e' state to “freeload” on the much more localized a'_1 electron density enhancing its spin polarization and exchange splitting (24.7 meV) which decreases to 15.2 meV after relaxation, Table VI. The mixing of the e' impurity state with what will eventually become the top of the valence band is clearly seen in the 12×12 supercell in terms of the large exchange splitting of the uppermost host valence band state (black solid and dashed bands) at the Γ point. The total energy gain from spin polarization of 13 meV without relaxation or 16 meV with relaxation is dwarfed by the 150 meV energy gain from relaxation.

For smaller supercell sizes, the dispersion of the e' state increases until it overlaps the unoccupied a'_1 level and begins to quench the spin polarization for $N < 8$, Table IV. Reducing the supercell size further increases the quenching

FIG. 10. Effect of relaxation and spin polarization on the electronic structure of a 12×12 supercell for an MoS_2 monolayer with a single Mo atom replaced by V. (a) Reference bands for an undoped MoS_2 monolayer, energy bands for a single substitutional V impurity (b) without relaxation, (c) with spin polarization (SP) and without relaxation, (d) with relaxation, without spin polarization, and (e) spin polarized and relaxed. The a'_1 level is red, the e' states are blue. In (c) and (e) the solid (dashed) lines indicate minority (majority) spin states. The energy gain with respect to the unrelaxed case is given in each panel in meV. The zero of energy is the VBM and the Fermi level is indicated by a green dot-dashed line.

TABLE IV. Calculated magnetic moment (in μ_B) for an MoS₂ monolayer supercell doped with V, Nb, and Ta as a function of the $N \times N$ supercell size without (Un) and with (Re) relaxation. For V the effect of an on-site Coulomb repulsion parameter $U = 1$ eV was examined for the relaxed case. The reciprocal space sampling density is constant.

N		3	4	5	6	7	8	9	10	11	12
V	Un	0.00	0.00	0.61	0.82	0.97	1.00	1.00	1.00	1.00	1.00
	Re	0.00	0.00	0.81	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	U	0.54	0.68	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Nb	Un	0.00	0.00	0.00	0.34	0.54	0.68	0.87	0.93	1.00	1.00
	Re	0.00	0.00	0.00	0.66	0.75	0.89	1.00	1.00	1.00	1.00
Ta	Un	0.00	0.00	0.00	0.32	0.42	0.57	0.86	0.95	1.00	1.00
	Re	0.00	0.00	0.00	0.68	0.83	0.92	1.00	1.00	1.00	1.00

and when, in addition, the impurity potential fails to pull the impurity levels above the VBM for supercell sizes smaller than 5×5 , the magnetic moment disappears. Relaxation enhances the magnetic moment by reducing the overlap of the a'_1 and e' states in spite of the unfavorable increase of the e' state dispersion. Even a very small value of the Coulomb repulsion parameter $U = 1$ eV [74] can lead to a 3×3 supercell becoming polarized. Most of the discrepancies in the literature can be explained in terms of the supercell size, k -point sampling, exchange-correlation potential, U , etc. [28,33,36,39,42,44,49,50,75].

5. Formation energies

The formation energy of a substitutional dopant X_{Mo} is defined as

$$E_{\text{form}}[X_{Mo}] = E_{\text{tot}}[\text{MoS}_2:X] - E_{\text{tot}}[\text{MoS}_2] + \mu_{Mo} - \mu_X, \quad (5)$$

where $E_{\text{tot}}[\text{MoS}_2:X]$ is the total energy of an MoS₂ monolayer with one Mo atom replaced by one X atom, $E_{\text{tot}}[\text{MoS}_2]$ is the total energy of a pristine MoS₂ monolayer, and μ_{Mo} and μ_X are the total energies per atom of Mo and X in their bulk metallic bcc phases, respectively. Taking the (spin-polarized) S₂ molecule as the reference chemical potential for S, the heat of formation of a MoS₂ monolayer $E_{\text{form}}[\text{MoS}_2]$ was calculated to be -5.31 eV/formula unit. The formation energy of V_{Mo} is small and those of Nb_{Mo} and Ta_{Mo} actually become negative when relaxed indicating that doping MoS₂ with these group V elements should be experimentally feasible, Table V.

B. Binding of V impurity pairs

Two substitutional dopant V atoms will have a negligible interaction energy when sufficiently far apart. This energy can be calculated as follows. First define a reference energy E_V^N

TABLE V. Formation energies in eV of substitutional V, Nb, and Ta impurities in an MoS₂ monolayer for a 12×12 supercell.

	V	Nb	Ta
Unrelaxed	0.40	0.01	-0.12
Relaxed	0.25	-0.15	-0.23

FIG. 11. $E_b^N(R_{\text{max}})$ as a function of the supercell size N for spin-polarized unrelaxed (open red circles) and relaxed (filled red squares) geometries. The red lines are a guide for the eye.

for a single V dopant atom substituting a Mo atom in MoS₂ as

$$E_V^N = E_{\text{tot}}^N[V_{Mo}] - E_{\text{tot}}^N[\text{MoS}_2], \quad (6)$$

where $E_{\text{tot}}^N[\text{MoS}_2]$ is the total energy of an $N \times N$ supercell of MoS₂ in equilibrium and $E_{\text{tot}}^N[V_{Mo}]$ is the total energy of the same supercell with one Mo atom replaced with a V atom. To calculate absolute formation energies, suitable chemical potentials would need to be included to take account of where the V atom came from and where the Mo atom went to; we will not be concerned with those here. The binding energy E_b is then

$$E_b^N(R) = E_{\text{tot}}^N[V_2(R)] - E_{\text{tot}}^N[\text{MoS}_2] - 2E_V^N, \quad (7)$$

where $E_{\text{tot}}^N[V_2(R)]$ is the total energy of a supercell with two Mo atoms a distance R apart substituted with V atoms and the last two terms on the right do not depend on R . We consider the two cases where relaxation is (Re) and is not (Un) included.

For supercells containing two substitutional V atoms as far apart as possible (R_{max}), with one V atom at the origin and the second at the corner site in Fig. 3, the binding energy $E_b^N(R_{\text{max}})$ is shown as a function of the supercell size N in Fig. 11 with spin polarization included. Although $E_b^N(R_{\text{max}})$ does not change much for $N \geq 12$, there is still a surprisingly large binding energy of ~ 8 meV for $N = 15$ in the unrelaxed case. We can trace this to the near degeneracy of the minority-spin e' and a'_1 related bands shown in Fig. 10(c) for the unrelaxed V_{Mo} as well as the relatively long range of the e' holes. When relaxation is included, the hole becomes localized in the dispersionless minority-spin a'_1 band, Fig. 10(e), it becomes much easier to converge the total energy (with respect to BZ sampling and self-consistency) and $E_b^{12}(R_{\text{max}})$ decreases fast to ~ 2 meV for $N = 12$. In general, when there is a gap between occupied and unoccupied states, total energies can be converged better. Since the problem has to do with the (separation independent) reference energy E_V^N , it turns out to

FIG. 12. Red symbols: interaction energies of dopant V_{Mo} atoms in a 12×12 MoS_2 supercell as a function of their separation. The binding energy was calculated using (8) for unrelaxed (open red circles) and relaxed (filled red squares) geometries. The lines are a guide to the eye. Black symbols: Total energy differences between parallel and antiparallel aligned spins on the V dopant atoms without (open black circles) and with (filled black squares) relaxation. The lines are fits to an exponentially decaying function. The dashed black line extrapolates the relaxed exchange interaction to separations where it is found to be quenched. The labels along the top of the figure indicate the sites in Fig. 3 and the large symbols refer to the A3 configuration discussed in the text and Fig. 16.

be better to consider

$$E_b^N(R) = E_{tot}^N[V_2(R)] - E_{tot}^N[V_2(R = \infty)] \quad (8)$$

and approximate $E_{tot}^N[V_2(R = \infty)] \sim E_{tot}^N[V_2(R_{max})]$.

Using a 12×12 supercell and (8) we explore the pair binding energy $E_b^{12}(R)$ for V_{Mo} dopants as a function of their separation R in Fig. 12 where one dopant atom is assumed at the site marked 0 in Fig. 3. Without relaxation, the (absolute value of the) binding energy decreases monotonically from a value of ~ 220 meV for V atoms on neighboring Mo sites to a value of ~ 0 meV at the maximum separation in a 12×12 supercell (open red circles, left axis). Because these energies are so small, we will later assume that dopant atoms are randomly distributed in real materials that are not in full thermodynamic equilibrium.

With relaxation (filled symbols), the magnitude of the binding energy increases for separations R smaller than a critical separation $R_c \sim 8.5$ Å, and does not change for separations larger than this. This behavior is intimately related to quenching of the magnetic moments for V dopant atoms closer than R_c and for these separations, $R < R_c$, an exchange interaction cannot be determined. We proceed to consider the magnetic interactions.

C. Magnetic interaction of impurity pairs

We estimate the exchange interaction $\Delta E(R)$ between pairs of dopant atoms as the energy difference between configurations with the V magnetic moments aligned parallel (“ferromagnetically”, FM) and antiparallel (“antiferromagnetically”,

AFM)

$$\Delta E(R) = E_{tot}[V_2^{AFM}(R)] - E_{tot}[V_2^{FM}(R)] \quad (9)$$

in 12×12 supercells so that the interaction between periodic images is acceptably small. Because the spin-polarized calculations are computationally expensive, care is taken to construct suitable starting V_2^{FM} configurations using “superpositions” of relaxed, spin-polarized local atomic configurations for single V_{Mo} . Starting V_2^{AFM} configurations are constructed from relaxed V_2^{FM} configurations so only the much smaller differential relaxation needs to be calculated.

The energy difference between antiferromagnetic and ferromagnetic ordering without (open black circles) and with (filled black squares) relaxation is shown on the right axis of Fig. 12. Before relaxation, neighboring V dopant atoms show FM coupling with a total moment of $2 \mu_B$ or $1 \mu_B$ per V for all separations. The interaction decreases monotonically and exponentially from a maximum of ~ 33 meV for nearest neighbors with a decay length of ~ 5.3 Å. With relaxation included the magnetic moments are quenched for separations R smaller than a critical separation $R_c \sim 8.5$ Å, and for these separations an exchange interaction cannot be determined. For separations $R > R_c$, the coupling remains ferromagnetic and is enhanced. Because the maximum value of the magnetic ordering temperature will depend strongly on this relaxation-induced behavior, we need to understand its origin.

1. Quenching of moments for $R < R_c$

To do so, we consider a 12×12 supercell for an MoS_2 monolayer with a pair of Mo atoms on neighboring sites substituted with V. The unpolarized supercell electronic structures and DoS are shown in Fig. 13 without (left) and with relaxation (right). The corresponding band structures for a single V impurity are included in the left panels for reference. In the spirit of a defect molecule model, Figs. 13(a)–13(c) suggests that the e' orbitals form σ bonding-antibonding $e-e^*$ pairs scarcely lifting the degeneracy of the e states while the a'_1 states interact less strongly to form a π bonding-antibonding $a-a^*$ pair. Without relaxation, the strength of the π bond between the a'_1 orbitals is not strong enough to raise the a^* level above the e^* level and the two holes reside on the fourfold orbitally and spin degenerate e^* states as sketched in Fig. 13(g). This leads to a DoS peak at the Fermi level that is unstable with respect to exchange splitting.

Relaxation results in a structure where the neighboring S atoms move closer to the V atoms, the two V atoms move apart and the a'_1 levels on individual V_{Mo} atoms are lifted clear of the e' levels. The reduced V-S separation strengthens the π bond [Fig. 14(a) versus Fig. 14(c)] through hybridization between vanadium $d_{3z^2-r^2}$ and sulfur p_x and p_y orbitals, while the σ bonds formed by vanadium $\{d_{xy}, d_{x^2-y^2}\}$ orbitals are weakened by the increased V-V separation [Fig. 14(b) versus Fig. 14(d)]. This makes the π bond the dominant bonding interaction between dopants. The $a-a^*$ splitting is increased so much by relaxation that the a^* level is lifted well above the e^* level and the two holes are accommodated in an orbitally nondegenerate state (rhs of Fig. 13).

To demonstrate how competition between bonding and exchange interactions of the V $d_{3z^2-r^2}$ orbitals leads to the

FIG. 13. Spin unpolarized electronic structure (bands and DoS) for a 12×12 MoS₂ supercell with two V atoms in an A1 configuration on nearest neighbor Mo sites (b), (c), (e), and (f) and, for comparison, for a single V_{Mo} atom (a) and (d) corresponding to Figs. 10(b) and 10(d). Without (a), (b), (c), and (g) and with (d), (e), (f), and (h) atomic relaxation. Schematic of the coupling mechanism between two V dopants with two holes without (g) and with (h) atomic relaxation. Impurity bands are highlighted in red and blue. The K point VBM is set to be zero (dot-dashed black line) and the Fermi level is shown as a dashed green line.

quenching of the magnetic moments, we examine how these interactions depend on the separation between the dopant atoms. We define the bond strength Δ_π of the π bond to be the a^*-a bonding-antibonding splitting. Figure 15 shows how Δ_π depends on the impurity separation R with (filled black squares) and without (open black circles) structural relaxation. As R increases, Δ_π decreases because of the decreasing wave function overlap. Without relaxation (open circles), Δ_π is smaller than the exchange splitting (red triangles, dashed red line) for all separations and a triplet state would form as indicated in the rhs inset of Fig. 15. With relaxation (filled squares), Δ_π is larger and exceeds the exchange splitting at distances smaller than ~ 7 Å. A singlet state is formed to gain bonding energy, as sketched in the lhs inset of Fig. 15, and this leads to the quenching of the magnetic moment. The critical quenching separation is twice the effective Bohr radius $a_0^* = 4.2$ Å for the a_1' state, implying the formation of a π bond. In general, to quench the magnetic moment, the π bonding interaction should be strong enough to make the a^* state the highest lying state.

Lastly, we note a significant enhancement of the exchange splitting when two vanadium atoms are close, Fig. 15. From a value of 92 meV for single V dopants, the increase in hole density at short separations doubles the exchange splitting to ~ 180 meV for (unrelaxed) V dopants on neighboring Mo sites.

2. Enhancement of exchange interaction for $R > R_c$

For separations greater than R_c , the exchange interaction is strongly enhanced by relaxation before decaying more strongly than the unrelaxed case till it eventually becomes smaller when $R \sim 13$ Å, Fig. 12. We can understand the enhancement by considering in Fig. 16 the defect levels associated with the A3 configuration, Fig. 3. For the unrelaxed structure (lhs), the breaking of the local D_{3h} symmetry is negligible and the bonding e and antibonding e^* states remain doubly degenerate. At this separation of 9.55 Å, the bonding interaction of the a_1' states is much less than that of the e' states so that the e^* level is the lowest unoccupied level to which both holes gravitate. Because it is degenerate, the e^* level can exchange split with both holes aligned to form a triplet spin state. The exchange splitting is weak because of the delocalisation of the e levels.

Relaxation reduces the V-S bond length while increasing the V-V bond length and breaks the local D_{3h} symmetry leading to a significant splitting of the degenerate e and e^* levels as well as a small increase in the bonding interaction between the a_1' levels (Fig. 16, rhs). The net result is that the a^* level and highest e^* level become degenerate and accommodate the two holes. Because of the greater localization of the a levels, this leads to an enhancement of the exchange splitting for the parallel (FM) configuration of the two V_{Mo}

FIG. 14. Side view of the partial charge distributions of the π bond (left panels) and top view of the σ bond (right panels) without (a) and (b) and with (c) and (d) atomic relaxation. The corresponding atomic structures are shown in (e) and (f).

dopants (compared to the unrelaxed case) and a reduction for the antiparallel (AFM) configuration with a corresponding increase of the $E_{\text{AFM}} - E_{\text{FM}}$ energy difference (large symbols in Fig. 12). To a good approximation the interaction strength only depends on the separation and decays exponentially more rapidly than the unrelaxed case with a much reduced decay length of 3.6 Å reflecting the greater localization of the a'_1 holes.

D. Nb and Ta in MoS₂

We expect Nb and Ta to more closely resemble Mo than V with a weaker central cell potential leading to less localized impurity states than in the case of V. Nb and Ta will turn out to have very similar effective Bohr radii and binding energies that lead to virtually indistinguishable magnetic properties.

1. Single impurity limit: Nb and Ta in MoS₂

For an unrelaxed Nb (Ta) substitutional impurity, we find an effective Bohr radius of 10.0 (10.3) Å for the e' state and 5.3 (5.2) Å for the a'_1 state by fitting the circularly averaged wave function in a 12×12 supercell to be compared to values of 8 and 4.2 Å, respectively, for V found in Sec. III A, Table II. The binding energies of these e' and a'_1 states converge to a common value of ~ 45 meV in the large supercell, single impurity limit Fig. 17; the results for Nb and Ta are virtually indistinguishable and only those for Nb are shown. The smaller binding energies and larger effective Bohr radii make the Nb (Ta) impurity states more sensitive to the supercell

FIG. 15. Unpolarized a - a^* level separation with (filled black squares) and without (open black circles) atomic relaxation plotted as a function of the separation between the substitutional dopant atoms in a 12×12 MoS₂ supercell. The a^* exchange splitting for different (unrelaxed) configurations is indicated by red triangles. The insets show the energy level schemes with spin polarization included for relaxed configurations with impurity separations below (lhs) and above (rhs) the critical separation of 8.5 Å, respectively.

truncation of the impurity potential compared to V. Increasing delocalization of the holes from V $\rightarrow$ Ta leads to a reduction of the exchange splittings, Table VI, and a magnetic moment is found to develop only when $N > 5$. Total polarization only occurs for $N > 10$, see Table IV.

After relaxation, the Nb-Mo (Ta-Mo) bond length increases by 0.040 (0.036) Å, leading to a lowering of the e' state. The hole then goes into the a'_1 state whose exchange splitting increases while that of the e' state decreases because of the reduced overlap in space of the e' and a'_1 partial electron densities. As we already saw for V in Table IV, relaxation enhances the magnetic moments.

FIG. 16. Defect level structure calculated without spin polarization for an A3 configuration of two V_{Mo} atoms: (lhs) unrelaxed and (rhs) relaxed. The levels are calculated from the appropriate weighted average of the Γ , K/K' , and M eigenvalues of the corresponding bands. a and a^* (red), e and e^* (blue) levels originate in the a'_1 and e' levels for single V_{Mo} dopants. The zero of energy is the Fermi level indicated by a black dashed horizontal line.

FIG. 17. Same as Fig. 7 but for Nb instead of V. The corresponding results for Ta are virtually indistinguishable.

2. Interaction of Nb (Ta) impurity pairs

Because of the smaller bound state energies and weaker spin polarization, the exchange interaction between pairs of Nb (Ta) dopant atoms is weaker than that between pairs of V atoms, Fig. 12, and decays more slowly with increasing separation, Fig. 18. To a good approximation the interaction strength only depends on the separation R and decays exponentially with R with a decay length of 5.2 (5.8) Å versus 3.6 for V when relaxation is included.

The exchange splitting of the a'_1 and e' levels and their relative hole occupations determine the strength of their different exchange interactions. Relaxation raises the a^* level to become degenerate with the upper e^* level, enhancing the exchange splitting of the a level while reducing that of the e level (see Table VI) and changes the character of the holes from e -like to $a + e$ -like. This increases the strength of the exchange interaction but leads to a faster decay as we saw in Fig. 12 for vanadium and in Fig. 18.

In summary, before relaxation, the long-range weak e' ferromagnetic interaction dominates while the strong short-range

FIG. 18. Same as Fig. 12 but for Nb instead of V. The corresponding results for Ta are virtually indistinguishable.

TABLE VI. Summary of the exchange splitting Δ_{ex} in meV of a'_1 and e' bound states in unrelaxed (Un) and relaxed (Re) structures in 12×12 supercells.

	V		Nb		Ta	
Δ_{ex}	$a'_1(\Gamma)$	$e'(K)$	$a'_1(\Gamma)$	$e'(K)$	$a'_1(\Gamma)$	$e'(K)$
Un	91.3	24.7	32.4	10.9	35.6	10.8
Re	96.1	15.2	53.2	9.8	52.0	9.7

a'_1 interaction dominates after relaxation, the near degeneracy of the upper e^* and a^* levels making it possible to form a triplet without violating the Pauli exclusion principle.

IV. MAGNETIC ORDERING

The Ising spin model in two dimensions undergoes a phase transition to long-range magnetic order at a finite temperature [76,77]. For a Heisenberg model with isotropic exchange interactions, thermal fluctuations destroy long-range magnetic ordering in two dimensions at any finite temperature [7,8]. The Ising spin model, with spin dimensionality $n = 1$, is recovered by assuming a generalized Heisenberg spin Hamiltonian with isotropic exchange and strong perpendicular anisotropy. Though the predictions of such generalized Heisenberg models are not identical to those of the Ising spin model, the consensus is that for ferromagnetism to exist in two-dimensional systems, magnetic anisotropy is essential. We therefore begin this section on magnetic ordering by studying the magnetic anisotropy of a single substitutional dopant, the so-called single ion anisotropy (SIA).

A. Single ion anisotropy

Microscopically, magnetic anisotropy arises when spin and orbital degrees of freedom are coupled by the spin-orbit interaction so that the total energy depends on the spatial orientation of the magnetic moment. According to the “force theorem” [78,79], *changes* to the total energy δE that result from a small perturbation can be related to changes in the sum of the single-particle eigenstates of the Kohn-Sham equations [80] of DFT, $\delta E \sim \delta \sum_i^{\text{occ}} \varepsilon_i$, which should not be iterated to self-consistency. The force theorem has been applied to the calculation of the magnetic anisotropy energy (MAE) where the perturbation is the spin-orbit coupling (SOC) [81] and comparison with explicit total energy calculations yields essentially perfect agreement for Fe, Co, and Ni [82]. The advantage of the force-theorem approach is that it allows the MAE to be directly related to (changes to) the electronic structure [83,84] which are shown for the relaxed configuration of a single V atom in a 6×6 supercell of MoS₂ in Fig. 19.

In the context of Fig. 10(e), we already discussed the exchange splitting of the a'_1 and e' levels. In a 6×6 supercell, the increased band dispersion leads to a smaller exchange splitting. With (without) relaxation, these splittings averaged over the Brillouin zone are, respectively, 66 (64) meV and 20 (22) meV [Fig. 19(b)]. Because MX₂ monolayers do not have inversion symmetry, SOC leads to a substantial splitting of the spin degenerate states at K and K' with $\{d_{xy}, d_{x^2-y^2}\}$ character

FIG. 19. The band structure of a single V dopant in a 6×6 supercell including relaxation. (a) Non-spin-polarized (NSP), (b) spin polarized (SP), (c) only spin-orbit coupling (SOC). Including SOC and SP with the magnetization in-plane ($\mathbf{M} \parallel a$) (d) and perpendicular to the monolayer plane ($\mathbf{M} \parallel c$) (e). Because SOC does not mix the e' ($m_l = \pm 2$) and a'_1 ($m_l = 0$) states strongly, we can continue to label these blue and red. In (b), the solid and dashed lines represent spin-up and spin-down states, respectively. The Fermi level shown as a horizontal green dashed line is chosen to be zero.

($l = 2, m = \pm 2$) [85]. In Fig. 19(c) we see that SOC splits the e' level at Γ by 130 meV while the a'_1 level with $d_{3z^2-r^2}$ character ($l = 2, m = 0$) is not affected. For a larger (12×12) supercell, the effect of SOC on the bands shown in Fig. 10(d) is to split the upper e' level so that the topmost level lies above the unaffected a'_1 level and accommodates the hole.

To understand the energy levels obtained with SOC and spin polarization (exchange splitting) in the single impurity limit, it is instructive to consider the model Hamiltonian

$$H = H_0 + \Delta \mathbf{m} \cdot \mathbf{s} + \xi \mathbf{l} \cdot \mathbf{s}, \quad (10)$$

where H_0 is the spin-independent part of the Hamiltonian, $\Delta \mathbf{m}$ is the exchange field that leads to an exchange splitting Δ , and $\mathbf{m}$ is a unit vector in the direction of the magnetization $\mathbf{m} \equiv \mathbf{M}/|\mathbf{M}|$. In the subspace of the $l = 2, m_l = \pm 2$ orbitals

$$\xi \mathbf{l} \cdot \mathbf{s} = \frac{\xi}{2} \begin{pmatrix} l_z & l_- \\ l_+ & -l_z \end{pmatrix} = \begin{pmatrix} \xi & 0 \\ 0 & -\xi \end{pmatrix}, \quad (11)$$

where we use Hartree atomic units with $\hbar = 1$. For $\mathbf{M} \parallel c$,

$$\Delta \mathbf{m} \cdot \mathbf{s} = \begin{pmatrix} \frac{\Delta}{2} & 0 \\ 0 & -\frac{\Delta}{2} \end{pmatrix} \quad (12)$$

and the SOC Hamiltonian can be written as

$$H = H_0 + \begin{pmatrix} \xi + \frac{\Delta}{2} & 0 & 0 & 0 \\ 0 & -\xi - \frac{\Delta}{2} & 0 & 0 \\ 0 & 0 & -\xi + \frac{\Delta}{2} & 0 \\ 0 & 0 & 0 & \xi - \frac{\Delta}{2} \end{pmatrix}. \quad (13)$$

For $\mathbf{M} \parallel a$ we have

$$H = H_0 + \begin{pmatrix} \xi & \frac{\Delta}{2} & 0 & 0 \\ \frac{\Delta}{2} & -\xi & 0 & 0 \\ 0 & 0 & -\xi & \frac{\Delta}{2} \\ 0 & 0 & \frac{\Delta}{2} & \xi \end{pmatrix}. \quad (14)$$

Diagonalizing H results in the energy level scheme sketched in Fig. 20. The magnetic anisotropy energy is

$E_{\text{MAE}} = E_a - E_c$, where E_a and E_c are the total energies when $\mathbf{M} \parallel a$ and $\mathbf{M} \parallel c$, respectively. Using the force theorem, the energy change on including SOC is given by the change in the sum of single-particle eigenvalues. The reference energy (without SOC) cancels when the difference is taken for the two magnetization directions and, for occupancy with a single hole, E_{MAE} can be estimated to be

$$E_{\text{MAE}} = E_a - E_c = \xi + \frac{\Delta}{2} - \sqrt{\xi^2 + \frac{\Delta^2}{4}}, \quad (15)$$

where we make use of the fact that the sum over all single particle eigenvalues is zero to express the sum over occupied states in terms of the sum over unoccupied states that is simply the energy of the hole. In this simple model, it is clear that for single acceptors the energy is lower when the magnetization is out of plane. In the limit that $\Delta \ll \xi$, $E_{\text{MAE}} \sim \frac{\Delta}{2}(1 - \frac{\Delta}{4\xi})$.

To determine the MAE using the VASP code [86] we adopt a two step procedure. We first perform a well-converged self-consistent spin-polarized calculation for the minimum energy geometry without SOC. The output from that calculation is used as input to the second step where SOC is added and the Kohn-Sham equation is solved non-self-consistently yielding

FIG. 20. Schematic of the e' energy levels with spin orientation in-plane ($\mathbf{M} \parallel a$) and out-of-plane ($\mathbf{M} \parallel c$). The solid blue lines are spin degenerate.

FIG. 21. Convergence of the anisotropy energy of a relaxed substitutional V_{Mo} atom in a monolayer of MoS_2 for 6×6 (black), 9×9 (blue), and 12×12 (red) supercells as a function of the area s of the triangular surface element used to perform the two-dimensional BZ integral, given as a fraction of the total area of the 2D BZ, S_{BZ} , for a 1×1 unit cell. The number of divisions of the reciprocal lattice vectors corresponding to each surface element is indicated for each supercell.

a new eigenvalue spectrum, Fermi energy and wave functions from which a total energy can be determined; to use the force theorem, we will just make use of the eigenvalue-sum part of the total-energy output. When adding the SOC, an orientation for the exchange field (magnetization direction) needs to be chosen and this will yield an orientation dependent eigenvalue spectrum, Fermi energy etc. To determine the MAE, we need to perform two calculations with the magnetization chosen (i) perpendicular to the plane and (ii) in-plane. The MAE will be expressed as the difference. To calculate the single particle eigenvalue sum for the electronic structure shown in Fig. 19 requires a careful BZ summation [81,83,87] for which we use the improved tetrahedron method [88]. The results obtained using the force theorem for a 6×6 supercell and 4, 8, and 12 divisions of the reciprocal lattice vectors are shown in Fig. 21 as a function of the BZ area element ($2s$) normalized to the area S_{BZ} of the BZ for a 1×1 primitive unit cell (black squares). An integral is defined as the limit where $s \rightarrow 0$ for an infinite number of sampling k points and from the figure we expect a value of $\sim 0.8 \pm 0.2$ meV.

When the supercell size is increased and the dispersion of the e' and a'_1 states becomes smaller, we might expect the BZ summation to converge faster but the situation is complicated by the near degeneracy of the e' and a'_1 bands. Figure 21 includes results for 9×9 and 12×12 supercells indicating a strong increase in the size of the E_{MAE} in the single impurity limit. The strong dependence of the MAE on the supercell size can be understood in terms of the reduced dispersion of the impurity levels and the contribution to the MAE from states near the Fermi level whose degeneracy is lifted when the magnetization direction is rotated from in-plane with $\mathbf{M} \parallel a$ to out-of-plane with $\mathbf{M} \parallel c$ as illustrated by Figs. 19(d), 19(e) and 20. For a 12×12 supercell, we can extrapolate the results obtained using a 2×2 and 4×4 k -point

sampling to estimate a converged MAE of 4.2 meV. The exchange-splitting Δ is 15.2 meV for the e' level and using this value of Δ and $2\xi = 130$ meV in (15) yields a value of $E_{MAE} \sim 7.2$ meV that is still larger than the 4.2 meV estimate from the full calculation. We can extrapolate the results for the three sizes of supercell to $s = 0$ and then plot the results as a function of the inverse supercell size (inset) to estimate the SIA in the infinite supercell limit to be 4.5 ± 0.5 meV per V ion. This is much larger than the value reported for 2D CrI_3 [89] that exhibits Ising behavior [11]. The dipole-dipole interactions that play an important role in determining whether or not the magnetization of thin magnetic layers and magnetic multilayers is in-plane or out-of-plane are orders of magnitude smaller in the present case and can be safely neglected [81,83,87].

B. Monte Carlo calculations

Very strong single-ion anisotropy combined with isotropic Heisenberg exchange results in Ising-like behavior [90] which automatically gives a magnetically ordered phase at finite temperature [76,77]. We map the energy differences calculated between FM and AFM oriented spins onto an isotropic Heisenberg exchange interaction and then model the V-doped MoS_2 monolayer as an Ising spin system for which all odd moments disappear in zero field by symmetry. Monte Carlo calculations are used to determine the Curie temperature T_C using Binder's cumulant method [91,92] where the fourth order cumulant of the magnetization $\mathbf{M}$ simplifies to $U_4(T, L) = 1 - \langle M^4 \rangle / 3 \langle M^2 \rangle^2$. As the system size $L \rightarrow \infty$, $U_4 \rightarrow 0$ for $T > T_C$ and $U_4 \rightarrow 2/3$ for $T < T_C$. For large enough lattice size, $U_4(T, L)$ curves for different values of L cross as a function of temperature at a "fixed point" value U^* and the location of the crossing fixed point is the critical point [92].

At a given temperature and doping concentration, we establish thermodynamic equilibrium in 10^5 Monte Carlo (MC) thermalization steps and then average over 48 different random dopant configurations to obtain $\langle M^2 \rangle$ and $\langle M^4 \rangle$. Three different lattice sizes with $L = 50, 75, 100$ are used to calculate U_4 as a function of the temperature T with doping concentrations from 1% to 11%. An example of the results is shown in Fig. 22 where the fitting curve for the unrelaxed case in Fig. 12 is used to describe the exchange interactions for a doping concentration of 9%. The temperature corresponding to the size independent universal fixed point U^* where the $U_4(L, T)$ curves for different lattice sizes L intersect yields an estimate for T_C . For the largest supercell size $L = 100$, we calculated the magnetic susceptibility $\chi = [\langle M^2 \rangle - \langle |M| \rangle^2] / Nk_B T$ which diverges at the critical temperature in the thermodynamic limit [92]. An example is shown in Fig. 23 in which the Curie temperature obtained from the position of the magnetic susceptibility peak is in good agreement with that obtained from the fourth order cumulant.

C. Curie temperature

The ordering temperatures we calculate are shown in Fig. 24 for V doping concentrations x in the range from 1%

FIG. 22. Variation of the fourth order cumulant for three different supercell sizes $L = 50, 75, 100$ as a function of temperature.

to 11%. Without relaxation, $T_C(x)$ increases monotonically with doping concentration and reaches room temperature for a concentration of $\sim 11\%$. With relaxation, the ferromagnetic exchange interaction is quenched for close dopant pairs and $T_C(x)$ exhibits a maximum of ~ 165 K for 9% doping. If we extrapolate the exchange interaction for relaxed dopant pairs to separations smaller than the critical separation where quenching occurs (dashed line in Fig. 12), the Curie temperature increases rapidly and monotonically with doping concentration and exceeds room temperature for dopant concentrations larger than 9%. Because the maximum value of $T_C(x)$ we obtain would be higher but for the quenching of the magnetic moments of closely separated relaxed dopants, it becomes important to consider how to suppress the quenching to obtain higher Curie temperatures. This will be discussed in Sec. VI.

FIG. 23. Variation of the magnetic susceptibility as a function of temperature for 9% unrelaxed V dopant concentration with $L = 100$.

FIG. 24. Variation of the Curie temperature as a function of the doping concentration calculated using Binder's cumulant method and the exchange interactions shown in Fig. 12 for an MoS_2 monolayer doped with V. The dashed curve was calculated by extrapolating the exchange interaction for relaxed dopant pairs to separations shorter than the critical separations where quenching occurs.

V. COMPARISON WITH OTHER WORK

Table VII summarizes earlier computational work on doping MoS_2 monolayers with V, Nb, or Ta. Because much of it was concerned with doping rather than with magnetic ordering, no attempts were made to calculate the magnetic anisotropy. Most of the calculations were done using small supercells and the separation dependence of the exchange interaction was not studied systematically, if at all. We noted in Sec. II that the GGA positions the Γ -point VBM too high with respect to the K -point VBM by comparison with experiment [60] and we therefore used the LDA that yields better agreement with experiment in this regard. Because most of the calculations referred to in Table VII were performed with the GGA exchange-correlation potential, we examine the effect of using the GGA rather than the LDA.

A. GGA versus LDA

If we use atomic configurations whose geometry was optimized using the LDA and repeat the electronic structure calculations using the GGA, we qualitatively reproduce the LDA results for the exchange interaction between V dopant atoms. The significant differences that will be documented below therefore have their origin in the only slightly different minimum-energy geometries predicted by the GGA.

Our starting point is an MoS_2 monolayer whose lattice constant $a_{\text{GGA}} = 3.185$ Å minimizes the GGA total energy, Table I. The GGA overestimate of the position of the Γ -point VBM with respect to the K/K' VBM makes the a'_1 level much higher than the e' levels as shown in Fig. 25 where these levels are plotted as a function of supercell size. The asymptotic values are ~ 76 and ~ 20 meV for the a'_1 and e' states, respectively, compared to ~ 62 meV for both in the LDA case, Fig. 7. Compared to the LDA estimate of a Bohr radius of 4.2 Å from the radial extent of the partial charge density in Fig. 5, with the GGA we find a slightly larger

TABLE VII. Computational studies of single acceptor dopants in MoS₂. SC: Supercell. XC: Exchange-correlation functional. MAE: Magnetic anisotropy energy. US-PP: Ultrasoft pseudopotential [93]. NC-PP: Norm-conserving pseudopotential [94]. PAW: Projector augmented wave [55]. LDA: Local density approximation [61]. CA: Ceperley-Alder [95]. GGA: Generalized gradient approximation. PBE: Perdew-Burke-Ernzerhof [62]. HSE: Heyd-Scuseria-Ernzerhof [96]. QE: QUANTUM ESPRESSO [97]. VASP: Vienna *ab initio* simulation package [57,58]. WIEN2K [98]. SIESTA [99].

SC size (No. atoms)		Vac.					Exchange			
Default	Max/test	Dopant	Method	XC	U (eV)	(Å)	Code	MAE	Int. $J(d)$	Reference
4 × 4		V, Nb, Ta	US-PP	GGA/PBE	0	10	QE	No	No	Cheng PRB13 [35]
4 × 4		V	PAW	GGA/PBE	0	12	VASP	No	No	Yue PLA13 [36]
5 × 5	6 × 6	Nb	NC-PP	LDA/CA	0	15	SIESTA	No	No	Dolui PRB13 [33]
		Nb	PAW	HSE	0		VASP	No	No	Dolui PRB13 [33]
5 × 5		V	PAW	GGA/PBE	0	15	VASP	No	No	Yun PCCP14 [39]
8 × 8		V	PAW	GGA/PBE	5.5		VASP	No	No	Andriotis PRB14 [42]
5 × 5	7 × 7	V, Nb, Ta	US-PP	GGA/PBE	0	12	QE	No	No	Lu NRL14 [28]
4 × 4		V	PAW	GGA/PBE	0	15	VASP	No	No	Miao JMS16 [44]
5 × 5		V	PAW	GGA/PBE	3	15	VASP	No	Yes	Fan NRL16 [47]
6 × 6		Cr, V	PAW	GGA/PBE	0	20	VASP	No	No	Robertson ACSN16 [48]
4 × 4	4 × 4	V, Cr	FLAPW	GGA	2.5	15	WIEN2K	No	No	Singh AM17 [49]
	8 × 5	V	PAW	GGA/PBE	0	16	VASP	No	Yes	Miao ASS18 [50]
6 × 6		Nb, Ta	PAW	HSE	0	17	VASP	No	No	Choi PRAP [100]
3 × 3	4 × 4	V	US-PP	GGA	3	20	QE	No	Yes	Mekonnen IJMPB18 [51]
12 × 12	15 × 15	V, Nb, Ta	PAW	LDA(GGA)	–	20	VASP	Yes	Yes	This work

value of 4.7 Å for the a'_1 state. By analogy with a hydrogen atom where the extent of the $1s$ orbital increases greatly for the H^- ion compared to the neutral atom, we attribute the slightly larger radial extent for the more strongly bound hole in the GGA case to its greater a'_1 (hole) occupancy. In the GGA, the doped system is fully spin polarized for the smallest 3×3 supercell we considered and the a'_1 exchange splitting of 142 meV is much larger than the 91 meV we found in the unrelaxed LDA case. (The LDA predicts an exchange splitting of $\Delta\epsilon_{1s} = \epsilon_{1s}^\uparrow - \epsilon_{1s}^\downarrow = 0.35$ Ry for a hydrogen atom compared to 0.55 Ry for the GGA; see Table IX in Appendix B.)

Figure 26 shows the exchange interaction calculated with the GGA for pairs of unrelaxed V_{Mo} dopants as a function

of the distance between them. We observe an oscillatory behavior with FM coupling for neighboring pairs (“A1” configuration, see Fig. 3) that switches to AFM for B1, A2, C1, and A3 configurations after which it is essentially zero reflecting the small effective Bohr radius of the a'_1 level ($a_0^* \sim 4.7$ Å). The relatively large separation in energy of the a'_1 and e' levels means that for separations larger than ~ 9 Å, both holes are to be found in the antibonding a^* level because the bonding-antibonding interaction is too weak to lead to hole occupancy of the e^* level. Because both holes must of necessity occupy the a^* level, their spins must be opposite and FM ordering is energetically unfavorable (though the energy difference is very small).

FIG. 25. Dependence on the supercell size N of the a'_1 and e' impurity levels induced by an unrelaxed substitutional vanadium atom V_{Mo} with respect to the valence band maximum in the GGA.

FIG. 26. The total energy difference between parallel and antiparallel aligned spins on the V dopants without relaxation within GGA.

FIG. 27. Energy diagrams for unrelaxed dopant pairs in A1 and A2 configurations (Fig. 3) with and without spin polarization calculated in GGA. The levels are calculated from the appropriate weighted average of the Γ , K/K' , and M eigenvalues as in Figs. 13 and 16. The Fermi level is indicated as a black dashed horizontal line. The spin-up and spin-down states are represented as dashed and solid lines, respectively.

To understand the oscillation for small separations, we consider the electronic structures of the a'_1 and e' derived a - a^* and e - e^* bonding and antibonding states for the A1 and A2 configurations in Fig. 27 with and without spin polarization. We begin with the A1 configuration. Compared to the LDA case that was shown in Fig. 13(b), we see that the unpolarized a and a^* levels (lhs of Fig. 27) are higher than the e - e^* levels reflecting the corresponding feature for a single substitutional dopant and that the a - a^* bonding-antibonding interaction is larger because the Bohr radius of the a'_1 states is larger in the GGA. On the rhs of the A1 panel, we see that the exchange splitting of the a^* levels is approximately doubled to ~ 300 meV for the A1 configuration compared to the single V_{M_0} case because of the overlapping hole densities; the same doubling occurs in the LSDA, where the exchange splitting of 92 meV for a single substitutional V is enhanced to 180 meV for neighboring V pairs, see Fig. 15. The exchange splitting is so large that the down-spin a^* level moves below the (approximately doubly) degenerate up-spin e^* level with the result that the hole can flip its spin and the Fermi level is pinned in the half-filled up-spin e^* state. By having one hole in an a^* state and the other in an e^* state it is possible for their spins to be parallel and to simultaneously gain spin polarization and bonding energy.

As the separation between the V_{M_0} atoms is increased, the exchange splitting and bonding interaction decrease rapidly for the a states and a FM triplet state is only formed at the expense of having one hole occupying a bonding a state (rhs of A2 panel); spin-polarization energy gain is offset by loss of bonding energy. Antiparallel alignment of the holes allowing gain of both spin polarization and bonding energy becomes more favorable.

The effect of relaxation is to push the a'_1 level up in energy and increase the a - a^* bonding-antibonding splitting so that the unpolarized electronic structure resembles that of Fig. 13(e) with both holes in the a^* level. For dopant separations less

TABLE VIII. Effect of SOC on the band gap $\Delta\varepsilon_g$ and valence band alignment for an MoS_2 monolayer in the LDA and GGA. $\Delta_{K\Gamma} = \varepsilon_K - \varepsilon_\Gamma$ is the energy difference between the valence band maximum (VBM) at the K and Γ points.

	No SOC		Including SOC	
	$\Delta\varepsilon_g$ (eV)	$\Delta_{K\Gamma}$	$\Delta\varepsilon_g$ (eV)	$\Delta_{K\Gamma}$
GGA	1.650	0.012	1.586	0.088
LDA	1.860	0.150	1.787	0.216
Expt.			1.900 ^a	0.140 ^b

^aReference [17].

^bReference [60].

than ~ 10 Å this leads to quenching of the magnetism. For separations larger than this, the a'_1 levels ($a'_0 \sim 4.7$ Å) interact only weakly with each other leading to very small energy differences $E_{\text{AFM}} - E_{\text{FM}}$ and negligible exchange interaction because the e' related levels are too low in energy to be occupied.

As anticipated at the beginning of this section, we can trace the large difference between the GGA and LDA descriptions of the exchange interaction between pairs of V_{M_0} dopants to the 2% difference between the LDA and GGA lattice constants. If we use the experimental lattice parameters listed in Table I, the differences between LDA and GGA disappear and we find that near-degenerate e' and a'_1 impurity levels with binding energies of 56 meV in a direct band gap of 1.78 eV couple ferromagnetically for all separations. The different orbital character of the e' and a'_1 levels means that they are very sensitive to the in-plane lattice constant a and out-of-plane d_{SS} , respectively, whose ratio determines their relative positions. From Table I, we see that the LDA ratio of 1.001 is much closer to the experimental value of 0.996 than the GGA ratio of 1.018 and argue that the LDA provides a more reasonable description of the relative position of the impurity levels.

When SOC is taken into consideration, the energy difference $\Delta_{K\Gamma}$ between the K/K' and Γ -point valence band maxima increases from 150 to 216 meV for LDA and from 12 to 88 meV for GGA, respectively, because of the large spin-orbit splitting at the K/K' point, Table VIII. The experimental value, 140 meV, is just in between making it unclear what will actually happen. To resolve this issue, experiment should focus on determining the position of the a'_1 level with respect to the top of the valence band in the single impurity limit.

Because the relative position of the impurity states determines the exchange interaction between dopant atoms, we have performed exploratory calculations to tune the relative positions of the K/K' and Γ valence band maxima and consequently of the a'_1 and e' levels with strain. For GGA, a 1% compressive strain ($\Delta a < 0$) is found to lower the a'_1 levels to be degenerate with the e' levels and we find FM coupling for all separations. 2% tensile strain ($\Delta a > 0$) lifts the a'_1 levels far above the e' levels stabilizing the magnetic moment of single impurities but favoring singlet formation of impurity pairs and AFM coupling. So while tensile strain reduces the formation energies of Nb_{M_0} and Ta_{M_0} and facilitates p doping of MoS_2 [100], it is detrimental for ferromagnetic ordering.

If the exchange interactions are so sensitive to the lattice constant and the ratio of a to d_{SS} , it might be useful to consider

tuning this ratio by modifying $\Delta_{K\Gamma}$ either using strain or by alloying, $\text{Mo}(\text{S}/\text{Se}/\text{Te})_2$. In the MoSe_2 , MoTe_2 , and WSe_2 systems, the a'_1 level lies so much lower than the e' level that using GGA or LDA with their different lattice parameters has little effect; the coupling is dominated by the long range of the e' levels.

B. LDA+ U

Two of the studies cited in Table VII use a finite value of U to better describe on-site Coulomb repulsion between electrons in localized d orbitals [42,49]. We find that LDA+ U [74] with modest values of U makes the local magnetic moment more localized and enhances it. The (more localized) a'_1 level is more sensitive to U than the e' level.

A small value of U (less than 1 eV) increases the exchange splitting of the a'_1 level and increases the FM exchange interaction which would yield a larger T_C compared to calculations without U . A larger value of U (larger than 3 eV) causes the hole to become even more localized and fully polarized even at very high concentrations (25%). As a consequence, the exchange interaction decays more rapidly and the separation below which quenching occurs decreases because the bonding interaction decays more rapidly. Compared to LDA calculations, the Curie temperature would be lower at low dopant concentration but enhanced at high concentration.

In our LDA calculations, we find that the shallow vanadium $3d$ orbitals hybridize strongly with S- $3p$ and Mo- $4d$ orbitals delocalizing the holes. We expect the Coulomb U in our system to be small and with a small U , the Curie temperature should be enhanced. Our LDA results should thus represent a lower bound on the exchange interaction and ordering temperature.

VI. DISCUSSION

According to the Zener p - d model used to interpret magnetic coupling in $\text{Ga}(\text{Mn})\text{As}$ dilute magnetic semiconductors [4], holes in As (p) bonding states mediate the exchange interaction between strong local (d^5) magnetic moments on Mn^{2+} dopant ions. In the present case, the magnetic moments that we find come from unpaired (d^1) spins in gap states that are only weakly bound by the Coulomb potential of the dopant ions, Fig. 2. The large Bohr radii we find for these states, Table II, allows them to overlap to form narrow bands and suggests that on-site Coulomb interactions may play a minor role and a model of itinerant ferromagnetism may be more appropriate than the various localized models used to study the $\text{Ga}(\text{Mn})\text{As}$ and related systems [5,6]. Compared to the transition metal dopants Mn, Fe, and Co that form deep impurity levels 0.4–0.9 eV below the bottom of the conduction band with effective Bohr radii of ~ 2 Å, the much larger radii of the group VB dopants (see Table II) give rise to longer-range exchange interactions. For a low concentration of dopant atoms, higher ordering temperatures should be attainable with group VB dopants than with n -type transition metals while maintaining the semiconducting electronic structure of the host. When the holes are in orbitally nondegenerate a'_1 levels, AFM coupling is favored to satisfy Pauli's exclusion principle; when they are in the degenerate e' levels, FM coupling is preferred to minimize the

FIG. 28. Schematic of the relative position of VBM at K and Γ points and corresponding impurity levels for MX_2 .

Coulomb interaction. For MoS_2 , the (accidental) near degeneracy of the a'_1 and e' hole states leads to them competing to determine the magnetic properties, whereby the strength of the exchange interaction is related to the exchange splitting of the impurity band and will be affected by the band dispersion for high doping concentrations.

In the low doping limit, the impurity states have no dispersion and are fully polarized. As the impurity concentration is increased, the impurity levels overlap to form narrow bands that broaden and eventually overlap the narrow Mo band that forms the top of the valence band. As seen in Fig. 8, the impurity bandwidth increases exponentially with increasing doping concentration. For the 9% V dopant concentration for which we find T_C to be a maximum, the e' impurity bandwidth is ~ 400 meV. The a'_1 band is narrower, only about a third as wide. Both bandwidths exceed the 91 meV exchange splitting we find for single V impurities in Fig. 10 that would imply partial quenching of the magnetic moments. For the ordered V dopants studied in Table IV, this quenching occurs as the concentration is increased above 3% and is complete by 6%. For itinerant electrons occupying narrow bands, it has been argued that the effective interaction predicted by the Stoner criterion will not be reduced by correlation effects or spin wave excitations [54]. In contrast to traditional dilute magnetic semiconductors with large local moments that do not contribute to the spin stiffness, the completely spin-polarized carriers in narrow impurity bands lead to a large spin stiffness and develop ferromagnetic ordering by their mutual interaction.

The quenching of ferromagnetic pairing for close impurity pairs can be avoided by considering instead of MoS_2 as host semiconductor, MoSe_2 or MoTe_2 (WSe_2 or WTe_2) for which the Γ point VBM drops with respect to the K/K' VBM as $\text{S} \rightarrow \text{Se} \rightarrow \text{Te}$ (sketched in Fig. 28). Preliminary calculations show that the a'_1 defect levels do indeed follow the Γ point VBM leaving the holes in the orbitally degenerate e' derived impurity bands. The increased lattice constant makes the e' states more localized and enhances the spin polarization in MoSe_2 and MoTe_2 . Very recently there have been reports of long-range and/or room temperature ferromagnetism occurring in V-doped WSe_2 monolayers [101], in MoSe_2 and MoTe_2 [102], in V- and Ta-doped MoTe_2 [103,104] and in MoS_2 [105], whereby the interaction with anion vacancies would appear to play an important role. These systems clearly warrant closer study.

We might expect double acceptors to have larger magnetic moments and exchange interactions. However, when MoS_2 is

doped with Ti, Zr, or Hf on the Mo site, the a'_1 level is lifted far above the e' levels and accommodates both holes so such substitutional impurities are nonmagnetic in the single impurity limit. Only when dopant pairs are sufficiently close (~ 6 Å) does strong π bonding lift the e^* antibonding level above the a bonding level so all four holes occupy antibonding states. The two holes in the e^* states can become ferromagnetic with a total magnetic moment of $2 \mu_B$ but this does not represent an improvement on the single acceptor case.

In MoSe₂ or MoTe₂ (WSe₂ or WTe₂) monolayers where the Γ point VBM lies well below the K/K' VBM, the two holes introduced by double acceptors occupy e' states that can accommodate four holes. Half-filling of these degenerate levels leads to a competition between Jahn-Teller distortion and exchange splitting. If the Jahn-Teller distortion is sufficiently strong, the magnetic moment will be quenched and we do not expect double acceptors to be magnetic for low doping concentrations.

VII. SUMMARY AND CONCLUSIONS

We have used *ab initio* calculations to explore the possibility of inducing ferromagnetism in an MoS₂ monolayer by substitutionally doping it with V, Nb, or Ta on Mo sites. In the single impurity limit, the resulting repulsive Coulomb potential leads to a doubly degenerate $\{d_{xy}, d_{x^2-y^2}\}$ state with e' symmetry bound to the K/K' valence band maxima and a singly degenerate a'_1 state with $d_{3z^2-r^2}$ character bound to the slightly lower-lying Γ -point valence band maximum that are accidentally degenerate. The exchange interaction between two such hole states depends on whether the holes have a'_1 or e' character, the former being quite localized, the latter quite extended in space. The magnetic moments of the spin $\frac{1}{2}$ acceptor states couple ferromagnetically at low concentrations but if the dopants are closer than the effective Bohr radius of the $d_{3z^2-r^2}$ orbital, the magnetic moments quench in order to profit from the bonding interaction. The details of the exchange interaction depend sensitively on the equilibrium structure of the undoped monolayer that in turn depends on the (approximate) exchange-correlation functional used. We argue that the LDA is preferable to the GGA because it describes the ordering of the K/K' and Γ valence band maxima better compared to experiment.

When spin-orbit coupling is included, we calculate a large magnetic anisotropy energy for acceptors with a preference for out-of-plane orientation and argue that this large single ion anisotropy justifies using an Ising spin model to study the ferromagnetic ordering. We estimate the ordering temperature by combining our (isotropic) separation-dependent exchange interactions with Monte Carlo calculations using Binder's cumulant method. For an MoS₂ monolayer doped with V (Nb or Ta), we estimate ferromagnetic Curie temperatures as a function of the dopant concentration and find a maximum T_C of ~ 170 K (~ 100 K) at around 9% dopant concentration. At sufficiently high concentrations of impurity states, the acceptor states form bands and magnetism is quenched when the bandwidth exceeds a critical value; this critical value depends sensitively on the exchange-correlation functional used.

Although the maximum calculated T_C is below room temperature, our work demonstrates that shallow impurities in MX₂ monolayers that bind weakly but have long-range interactions are promising dopants to explore with a view to realizing room temperature ferromagnetism.

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APPENDIX A: SULFUR REFERENCE ATOM

The impurity potential of a vanadium acceptor screened by a hole in the a'_1 and e' states as felt by S atoms is plotted in the insets to Fig. 29. The effective Bohr radii of these impurity

FIG. 29. Dependence of the S 2s semicore levels on the separation from the V_{Mo} dopant ion. The (screened) Coulomb potential of the V dopant is screened by the a'_1 hole (upper panel), respectively, by the e' hole (lower panel). The asymptotic value $\epsilon_{core}(\infty)$ was determined by fitting the calculated data points in the insets to an exponential wave function and using this fit (red curves) to extrapolate to $R = \infty$.

states determined by fitting to Eq. 1(b) are 8.8 Å for screening by the e' state and 6.5 Å for screening by the a'_1 state. For the e' level, this effective Bohr radius is consistent with the other estimates summarized in Table II. For the a'_1 level, however, the value of 6.5 Å yielded by the S atom probes is larger than the value of 5.4 Å yielded by using Mo atoms as probes. We already saw more scatter in the estimate of the a'_1 radius and in view of its very small value and the importance of the central cell potential and local screening effects on this length scale, it is not surprising to see this type of variation measured by probes at different radial distances.

APPENDIX B: HYDROGEN ATOM IN LDA/GGA

In the local density approximation (LDA), the total energy of a neutral hydrogen atom is not -1 Rydberg but its absolute value is about 10% smaller, ~ -0.89 Rydberg and the Kohn-Sham eigenvalue for the $1s$ state is $\varepsilon_{1s} = -0.46$ [67]. It has been shown that the discrepancy can be substantially reduced by using the spin-polarized (SP) version of the LDA, the local spin density approximation (LSDA) [67]. Using the

TABLE IX. Comparison of total energies (E) and Kohn-Sham (KS) eigenvalues (ε) for a hydrogen atom as described by the LDA and the LSDA, the non-spin-polarized (NSP)-GGA and spin-polarized (SP)-GGA in Rydberg units (13.606 eV).

	LDA		GGA	
	NSP	SP	NSP	SP
E	-0.89	-0.97	-0.92	-0.99
$\varepsilon_{1s}^\uparrow$	-0.46	-0.18	-0.47	0.00
$\varepsilon_{1s}^\downarrow$	-0.46	-0.53	-0.47	-0.55
$\Delta\varepsilon_{1s}$	0.00	0.35	0.00	0.55

Perdew-Zunger [61] parametrization of L(S)DA, we obtain total energies (E) and KS eigenvalues (ε) of $E = -0.89$ Ry, $\varepsilon = -0.46$ Ry (LDA), and $E = -0.97$ Ry (LSDA) and an exchange splitting of the Kohn-Sham $1s$ eigenvalues of -0.35 Ry. If instead of the L(S)DA, we use the Perdew-Burke-Ernzerhof [62] GGA, we obtain energies of -0.92 Ry (GGA) and -0.99 Ry (SP-GGA) and an exchange splitting of -0.55 Ry, see Table IX.

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