Induced Magnetism of the MoS$_2$ Monolayer during the Transition Metal (Fe/Ni) Bombardment Process: A Nonadiabatic Ab Initio Collision Dynamics Investigation

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ABSTRACT: The source of induced magnetism in the MoS$_2$ monolayer induced by transition metal (Fe/Ni) collision is investigated using nonadiabatic ab initio molecular dynamics simulations that take into account high-spin and low-spin energy states during trajectory integration. By considering various metal firing angles, a strong interaction between the Fe/Ni atom and the MoS$_2$ surface can be observed because of enormous increase in the kinetic energy of the metal atom. When firing along the Mo–S bond, the Fe bullet is pulled more strongly than when firing along the S–Mo–S bisector. Spin polarization of MoS$_2$ is gradually induced when Fe approaches the surface and eliminated when Fe roams around a potential energy trap on the MoS$_2$ layer. We observe that there is charge transfer between Fe and Mo atoms, which enhances the probability of electron pairing and leads to instantaneous vanishing of total magnetization. The Ni–MoS$_2$ system is found to establish a total magnetization of 1.5–4 $\mu_B$ when Ni is 2.0 Å above the surface. Interestingly, the strong bonding attachment of Ni suppresses the band gap to at least 40%.

1. INTRODUCTION

Quasi-two-dimensional (Q2D) materials have attracted a great deal of interest over the past 2 decades because of their notable mechanical and electronic properties. To date, the poplar Q2D family of materials consists of graphene, hexagonal boron nitride, silicon, phosphorene, and transition metal dichalcogenides (TMDC). Graphene and TMDCs, particularly molybdenum disulfide (MoS$_2$), have been considered as potential candidates for a wide range of applications in reaction catalysis, lithium-ion batteries, phototransistors, and nanoelectronics because of their appropriate band gap. In the multilayer form, MoS$_2$ was shown to establish a band gap of 1.2 eV, while the single-layer form had a wider gap of 1.8 eV. Besides, MoS$_2$ has had a long history of traditional use in the manufacturing industry as a lubricant because of its weak van der Waals interaction on the layer surface.

The typical characteristics of a semiconducting nonmagnet was also reported using various optical spectroscopy techniques. It was confirmed that the bulk form had an indirect band gap of 1.3 eV, while the two-dimensional layer exhibited a similar band gap as discussed above. Recently, many studies have been performed to innovate new effective methodology to induce magnetism onto the MoS$_2$ layer at room temperature, with the objective to expand the range of applications in spintronics and quantum information devices. To our knowledge, there are several methods such as adatom absorption, impurity doping, external strain, and defects. Among these methods, transition metal adsorption on the MoS$_2$ monolayer seems to be an effective and promising approach to induce magnetism because of the hybridization between metal 3d/4d and S 3p orbitals. In several previous studies, the magnetism was observed for Fe, Ni, Mn, Co, Cu, and so forth. However, the magnetism induced by metal adsorption is hard to control and monitor because the induced magnetism strongly depends on absorption configurations and the number of adatoms.

In the current study, we attempt to investigate the adsorption and collision processes of two transition-metal atoms (Fe, Ni) on the MoS$_2$ monolayer by performing nonadiabatic ab initio molecular dynamics (MD) simulations to explore the full interacting scheme leading to magnetic evolution. We choose two distinct magnetic elements to study the distinctive effects of inducing magnetism on MoS$_2$, which potentially establish coordination interactions with the 3p shell of S and potentially the 4d shell of Mo. Previously, the decoration of Fe on MoS$_2$ was shown to exhibit half-metallic magnetism, while experimental observations supplied evidence of paramagnetic Fe–Mo configurations based on their bonding characteristics. The Ni–MoS$_2$ defect-engineered monolayer was synthesized with interesting catalytic activity for hydrogen evolution in a recent study.

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other hand, Ni tends to exhibit less significant magnetism on the TMDC monolayer, but it is worth to investigate the spin evolution process. In our MD investigations, the induced magnetism of MoS$_2$ is monitored along with the interacting course with Fe/Ni, and the mechanism is explained from detailed electronic structure analysis.

2. COMPUTATIONAL METHODS

Our main objective is to investigate the effects of induced magnetism of MoS$_2$ through a single Fe/Ni atom firing toward and colliding with the MoS$_2$ monolayer. In this study, we adopt our in-house MD driver to execute nonadiabatic trajectory integration. The preparation process consists of three primary steps, as described below in detail

(i) Collect randomized configurations of the pure MoS$_2$ surface without metal atoms from a thermal vibration trajectory at 300 K (discussed in Section 2.1).
(ii) Perform ab initio MD simulations for the collision between metal atom X (Fe/Ni) and the MoS$_2$ system to examine the bonding interaction of X with respect to MoS$_2$ (discussed in Section 2.2).
(iii) Investigate and analyze the electronic properties of the interesting configurations obtained from the trajectories using higher qualitative self-consistent calculations (discussed in Section 2.3).

2.1. Randomizing Configurations for the Pure MoS$_2$ Surface at 300 K. Initially, the primitive cell of a two-dimensional MoS$_2$ monolayer is fully optimized to obtain the most relaxed configuration. The so-obtained lattice parameter of 3.19 Å is in reasonable agreement with the experimental value of 3.16 Å. We construct a (3 × 3) supercell consisting of 27 atoms (9 Mo and 18 S atoms) and subsequently allow it to undergo thermal vibration at room temperature (300 K), as shown in Figure 1. The in-plane lattice parameter for the supercell is 9.59 Å, while the vacuum thickness of 15 Å is adopted to optimize the spurious interaction between neighboring slabs in the z direction. In previous studies, the variation of lattice constant was observed to change insignificantly during the collision process. Thus, the defined lattice parameter is held constant during the entire MD investigation to reduce computational effort.

After the optimization process, the Born–Oppenheimer MD method implemented in Vienna ab initio simulation package (VASP) is deployed to simulate the fluctuation of the MoS$_2$ system at room temperature (300 K) to sample experimental reality. The cut-off energy is chosen to be 400 eV, and Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional is employed to execute electronic structure calculations for the MoS$_2$ system. The randomized geometry and velocity configurations obtained from the process are stored and used to prepare configurations for the next collision dynamic step.

2.2. Performing Direct Ab Initio MD for the X–MoS$_2$ (X = Fe/Ni) System. After constructing the database for thermally equilibrated configurations, we insert a single metal atom (Fe/Ni) onto the MoS$_2$ system. The distance between two adjacent metal atoms is 9.59 Å. In fact, such a chosen distance between two metal atoms can be considered sufficiently large to neglect bonding interaction in the periodic cell. The metal atom is located 8 Å away from the approximated plane of the MoS$_2$ surface where its projection image lies on the top of an Mo atom. A distance of 8 Å is sufficient to prevent initial contact. For verification of further distances (e.g. 9 and 10 Å), we also perform additional Fe–MoS$_2$ trajectories and check the evolution of magnetism in the metal–MoS$_2$ system with respect to those initial distances. The results show a magnetic behavior similar to the corresponding case having a distance of 8 Å. The trajectories for the 9 and 10 Å cases are included in the uploaded data in the Supporting Information. For each metal case study with an initial distance of 8 Å, we investigate 21 collision cases; in each case, the metal is fired at different striking angles (from 0 to 135°) at a kinetic energy level of 0.5 eV. More specifically, the striking angle can be described as follows

(i) In the first case, the metal atom is set to collide perpendicularly to the MoS$_2$ surface. In other words, the velocity vector is set to aim toward one of the Mo atoms (denoted as the direct D case).
(ii) In cases 2−11, the metal atom is set to strike 10 different spots of destination on a projected-to-plane Mo–S ionic linkage (denoted as C cases).
(iii) For cases 12−21, the metal atom is fired with an initial velocity vector aiming toward 10 different spots residing on the bisecting vector of two chosen Mo–S bonds (B cases).

In Figure 1, we denote radius $R$ as the projected distance of an approximate equilibrium Mo–S bond. The spots of destination are chosen at the point $x^2R$ (Å) along radius $R$, where $x$ holds a value in the range of [0, 1] with a discrete step of 0.1. The probability of locating the destination point on a circular surface (considered as a cross section) of radius $R$ is proportional to $x^2$, which was described in a theoretical work by Kuppermann and Greene. For convenience, we name D as the case X being fired perpendicularly to the surface; C1, C2, ..., C10 and B1, B2, ..., B10 as the cases in which X is aimed toward the so-defined B or C spots on the projected Mo–S vector and the bisecting vector of two Mo–S bonds, respectively. In total, 42 trajectories of X–MoS$_2$ (X = Fe/Ni) collision are investigated in this study.

The MD trajectories are simulated by employing our MD external driver with the implemented velocity Verlet

![Figure 1. Top and side projection representations of the X–MoS$_2$ (X = Fe/Ni) system with a description for initializing the velocity vector to aim at various destination spots in the B and C cases.](https://dx.doi.org/10.1021/acsomega.0c01740)
algorithm, which was described in the previous studies, to investigate the collision process. A fixed time step of 10 time units in the Hartree atomic unit (0.24 fs) is used to integrate the equations of motion. The equations of atomic motions are simultaneously integrated with atomic forces extracted directly from spin-polarized self-consistent calculations executed using the VASP. The projector-augmented wave method is utilized to assemble the electronic wave function for the system, while the PBE functional is adopted to associate exchange-correlation with total electronic energy calculations. We use a cut-off energy of 400 eV with a k-point mesh of (3 × 3 × 1) to ensure the numerical accuracy during the MD process. For each case, a maximum number of 2700 MD steps (653.4 fs) are monitored to examine Fe landing on the MoS₂ surface, while a maximum number of 1700 MD steps (411.4 fs) are used for the Ni cases. In this nonadiabatic process, the overall potential energy surface (PES) is constructed by considering the high-spin and low-spin PES’s. The total electronic energy of a certain configuration is given by the ab initio energy of the most stable spin state. Therefore, for each configuration in every MD trajectory, we evaluate both low-spin and high-spin energies to select the most stable spin configuration. Atomic gradients given by the more stable spin state will be utilized for Verlet integration of the MD trajectory.

2.3. Investigating the Electronic Structure for the Chosen X–MoS₂ (X = Fe/Ni) Systems. After MD simulations, several interacting configurations are chosen to study the effects of the X atom on the induced magnetism of the X–MoS₂ system. These configurations consist of structures at different simulation time events: (1) the X–MoS₂ system at the initial state, (2) X starting to feel the attraction by MoS₂, (3) X collides most strongly with the MoS₂ surface, (4) X penetrating deeply into the surface, and (5) X settles on the surface with a stable ionic bond. The qualitative calculations with a k-point mesh of 12 × 12 × 1 are performed to explore the spin density and partial density of states (PDOS) of the system.

3. RESULTS AND DISCUSSION

3.1. Collision Process of a Single Metal Atom X (X = Fe/Ni) on MoS₂. Setting up the collision with an initialized kinetic energy of 0.5 eV, our purpose is to investigate a slow adsorption process of a single metal atom on MoS₂. To find the settlement of the metal atom on the MoS₂ surface, the velocity vector is aimed to drive a single metal atom toward the surface with a chosen destination defined by the targeting factor x at a distance of 8 Å away from the MoS₂ surface. During the MD process, the X atom is observed to be attracted by long-range interaction with the MoS₂ surface. At an early stage, the kinetic energy gradually increases until it reaches the maximum. We observe that for the Fe cases, the maximum kinetic energy is achieved up to 2.30 eV, while it may even reach 5.00 eV in the Ni cases, which is much higher than the initial kinetic energy of 0.5 eV. This shows an enormous attraction from the TMDC layer that pulls the metal atom strongly. In the previous studies, the MoS₂ vibration is observed to play an important role in the movement of the metal atom toward MoS₂. The up and down motion of MoS₂ is due to internal vibration, which can be regarded as the “breathing” behavior, which attracts the metal atom and partially evokes the enhancement of kinetic energy. At an initial temperature of 300 K, the approximate period for thermal vibration of MoS₂ is about 28 fs. However, periodicity is almost unchanged even when the metal successfully establishes the bonding with MoS₂. At a distance of 1 Å from the surface, the repulsive force rises dramatically and breaks the movement of X until it collides with MoS₂. With the amount of remaining kinetic energy, the metal atom in fact subsides deeply into MoS₂ and bounces “inside” the layer several times, while at the same time interacting closely with an Mo atom. This phenomenon looks like a X–Mo distance fluctuation. After that, the metal atom is ejected and settles on the surface. At this point, no further penetration could be observed because the kinetic energy is not enough to overcome the repulsive force from the MoS₂ surface. Table 1 shows shooting angles, required time for the collision, the maximum achieved kinetic energy, and the maximum induced magnetic moment of the Fe–MoS₂ system.

| case | shooting angle (deg) | required time for collision (fs) | maximum kinetic energy (eV) | maximum magnetization on MoS₂ (μB) |
|------|---------------------|---------------------------------|-----------------------------|-----------------------------------|
| D    | 0.00                | 263.3                           | 3.62                        | 1.69                              |
| C1   | 0.11                | 253.6                           | 3.91                        | 3.83                              |
| C2   | 0.45                | 261.1                           | 3.64                        | 1.72                              |
| C3   | 1.01                | 248.3                           | 3.84                        | 3.32                              |
| C4   | 1.82                | 425.9                           | 2.01                        | 0.80                              |
| C5   | 2.88                | 379.2                           | 1.85                        | 2.21                              |
| C6   | 4.22                | 415.8                           | 2.17                        | 1.70                              |
| C7   | 5.87                | 384.1                           | 1.68                        | 1.00                              |
| C8   | 7.85                | 467.5                           | 1.77                        | 1.11                              |
| C9   | 10.21               | 430.8                           | 1.67                        | 0.78                              |
| C10  | 12.99               | 418.9                           | 1.44                        | 1.56                              |
| B1   | 0.07                | 394.7                           | 2.16                        | 1.08                              |
| B2   | 0.30                | 405.1                           | 2.26                        | 2.68                              |
| B3   | 0.68                | 370.0                           | 2.08                        | 2.50                              |
| B4   | 1.22                | 383.3                           | 2.10                        | 1.19                              |
| B5   | 1.85                | 378.7                           | 2.11                        | 2.17                              |
| B6   | 2.88                | 402.9                           | 2.41                        | 1.58                              |
| B7   | 4.04                | 425.2                           | 1.83                        | 1.09                              |
| B8   | 5.46                | 392.5                           | 1.90                        | 0.89                              |
| B9   | 7.21                | 424.7                           | 1.52                        | 1.21                              |
| B10  | 9.34                | 397.1                           | 1.60                        | 0.86                              |

average: 377.3 ± 64.1
Obviously, the interacting time of Fe is about 250 fs in cases C1–C3, which is significantly smaller than those recorded in the B cases (over 400 fs). Meanwhile, the period for the remaining B cases (B4–B10) is quite longer (approximately 400 fs). There is a remarkable distinction between small (C1–C3) and large (C4–C10) firing angles which shows that higher kinetic energy of Fe results in earlier interaction time for the collision of Fe–MoS2. We observe that the kinetic energy of small firing angles (cases C1–C3) can reach up to 3.91 eV, while all remaining cases (cases C4–C10) are around twice smaller (under 2.1 eV). This means that firing along the Mo–S bond will cause more attractive interaction than firing toward the bisector region. Because the splitting window of shooting angles is quite small, it can be predicted that the strongest attraction field along the Mo–S bonds is between 0.02 and 0.14 Å corresponding to the firing cases C1 to C3. On the other hand, there is no significant fluctuation in kinetic energy of all firing angles in the B cases (1.60–2.16 eV) compared to all C cases (1.44–3.91 eV). The above comparison clearly indicates various colliding characteristics between small C and large C firing angles. Besides, the kinetic energy of vertical firing (case D) is only 3.62 eV with an interaction time of 260 fs. In all B, C, and D cases, most kinetic energy of Fe is transferred to the MoS2 layer, which can be observed by a sudden increase in the kinetic energy of the monolayer after collision. For several shooting angles in both B and C cases, Fe is capable of penetrating deeply into the MoS2 layer (Figure 2).

During the collision, the phase–space plot could display the evolution of induced magnetism in the Fe–MoS2 system. In the phase–space plot in Figure S1 (see Supporting Information), we show the scaled total electronic energy ΔE with respect to the average distance between Fe and MoS2 surface for the D case. From 8 to 4 Å, the breathing behavior and long-range interaction of MoS2 with the Fe atom leads to the energy fluctuation. A total magnetic moment of 4–5 μB originates from the Fe atom in this period. At a distance of 4 Å, ΔE suddenly decreases, implying the bonding of Fe and MoS2. At this moment, the magnetic moments drop to 2 μB. With the remaining kinetic energy (3.62 eV), Fe continuously subsides deeply into the MoS2 layer. During the Fe-layer distance fluctuation in 0.5–2 Å, while Fe bounces several times, ΔE and the magnetic moment continue to fluctuate. Finally, ΔE increases as a result of ejection of Fe from the surface, and the bonding between Fe and MoS2 becomes weak.

3.1.2. Ni Cases. The required time for Ni to collide with the MoS2 layer is around 200–220 fs for all firing angle of all B, C and D cases (see Table 2). There seem to be no significant difference between the bisector and edge firing cases (C and B) for the Ni trajectories. Considering the collision process as a slow adsorption process, the large kinetic energy of Ni at the

![Figure 2. X–MoS2 distances and kinetic energy with respect to time for cases D, B5, B10, C5, and C10 of the (a) Fe–MoS2 (upper panel) and (b) Ni–MoS2 (lower panel) systems.](https://dx.doi.org/10.1021/acsomega.0c01740)

### Table 2. Shooting Angle, Required Time for Collision, Maximum Kinetic Energy, and Maximum Induced Magnetic Moment of the Ni–MoS2 System

| case | shooting angle (deg) | required time for collision (fs) | maximum kinetic energy (eV) | maximum magnetization on MoS2 (μB) |
|------|----------------------|---------------------------------|-----------------------------|-------------------------------------|
| D    | 0.00                 | 223.9                           | 5.37                        | 0.81                                |
| C1   | 0.11                 | 217.6                           | 4.95                        | 0.49                                |
| C2   | 0.44                 | 222.3                           | 5.53                        | 0.95                                |
| C3   | 1.01                 | 232.2                           | 4.46                        | 0.65                                |
| C4   | 1.82                 | 219.5                           | 5.03                        | 0.52                                |
| C5   | 2.87                 | 212.7                           | 5.85                        | 0.96                                |
| C6   | 4.20                 | 228.4                           | 4.83                        | 0.79                                |
| C7   | 5.87                 | 219.9                           | 4.95                        | 0.78                                |
| C8   | 7.85                 | 220.2                           | 4.65                        | 0.79                                |
| C9   | 10.22                | 232.6                           | 3.88                        | 0.64                                |
| C10  | 12.99                | 231.4                           | 4.03                        | 0.75                                |
| B1   | 0.07                 | 225.3                           | 4.95                        | 0.75                                |
| B2   | 0.30                 | 224.8                           | 4.82                        | 0.64                                |
| B3   | 0.68                 | 212.2                           | 5.95                        | 1.16                                |
| B4   | 1.22                 | 220.5                           | 5.61                        | 0.86                                |
| B5   | 1.94                 | 222.2                           | 5.46                        | 0.98                                |
| B6   | 2.85                 | 230.6                           | 5.17                        | 0.68                                |
| B7   | 4.04                 | 226.9                           | 4.54                        | 0.64                                |
| B8   | 5.44                 | 220.2                           | 5.23                        | 0.61                                |
| B9   | 7.21                 | 227.5                           | 4.65                        | 0.56                                |
| B10  | 9.27                 | 227.7                           | 4.90                        | 0.78                                |
| average |                    | 223.8 ± 5.9                    |                             |                                     |
later stage corresponds to a strong ionic interaction between Ni and S. Actually, our results indicate that the maximum kinetic energy of Ni on MoS$_2$ is dramatically higher than that of Fe (Figure 2b). Noticably, the average kinetic energies of Ni are over 5.00 eV for B, C, and D cases, which are quite greater than the average kinetic energy of Fe (2.30 eV). Presumably, this is due to the atomic mass of Ni, which has a strong effect on the kinetic energy. The distinction between large and small firing angles in the B and C cases cannot be observed clearly in terms of interaction between Ni and MoS$_2$, when the difference of the maximum value of kinetic energy among cases is rather small.

In addition, the electronic affinity has a vital role in the adsorption interaction between metals (Fe and Ni) and the MoS$_2$ film. We consider retention time as the period the metal stays on MoS$_2$ until it starts to take off from the film. Interestingly, the recorded retention time of Ni is about 20−30 fs, which is approximately 9 times smaller compared to the values of Fe (from 180 to 200 fs), and Fe possesses an enormous tendency to fluctuate up and down within the potential trap of MoS$_2$. This further indicates that each metal atom (Ni or Fe) would have different interactive bonding effects with the MoS$_2$ film.

3.2. Influence of Metal Adsorption on Induced Magnetism of MoS$_2$. The magnetic behavior of the Fe−MoS$_2$ system can be observed in Figure 3. Overall, MD simulation processes for different firing angles for the C and B cases exhibit similar magnetic characteristic variation with respect to time. Let us split a typical MD process into three different time frames

(i) Frame 1: the total magnetic moment of the Fe−MoS$_2$ system is mostly contributed by atomic Fe. In other words, the Fe atom has not yet induced magnetism on MoS$_2$. At this time, the polarization of the electronic structure solely originates from the Fe atom.

(ii) Frame 2: the Fe atom starts to establish bonding interaction and thus induce magnetism on the MoS$_2$ monolayer, which enhances the total magnetic moment of the whole system. The interaction between Fe and MoS$_2$ leads to resistance to spin polarization of the layer.

(iii) Frame 3: Fe gets closer to MoS$_2$ and the total magnetic moment of the system dramatically drops to 2 μ$_B$. After the Fe−MoS$_2$ collision, there is a strong electronic structure alteration in this period, which shows magnetic moment exchange between Fe and MoS$_2$. The bonding scheme established by Fe then comes to stabilization on the MoS$_2$ surface, and the magnetic moment fluctuation is almost eliminated.

Initially, in frame 1, the magnetic moment of the Fe atom is approximately 5 μ$_B$; meanwhile, MoS$_2$ is nonmagnetic. In the extended calculations with a dense k-point mesh of (12×12×1), the magnetism attains a better magnetism result (4 μ$_B$). This magnetism is a result of four unpaired electrons in the 3d orbitals (d$_{x^2−y^2}$, d$_{xy}$, d$_{yz}$, and d$_{z^2}$). Considering various firing angles, we observe that the small firing angle cases of C (including D) can induce magnetism on the MoS$_2$ earlier than in the remaining cases. For example, the collision times from C1 to C3 are about half compared to other cases (125 vs 250 fs). On the other hand, the distances between Fe and MoS$_2$ exhibiting magnetism for small firing angles (C1−C3) are also larger than those for the remaining cases (4.5 vs 3.5 Å).

Different firing angles impart different magnetic characteristics to MoS$_2$. Especially, small firing angle cases show that the metal atom establishes high magnetic moment and kinetic energy, which induces magnetism in the monolayer from a further distance compared to the remaining cases.

Frame 2 is the period when the magnetic effect is induced on MoS$_2$, which is proved by the change in the electronic structure of the Fe−MoS$_2$ system (Figure 4). We can see that...
Figure 5. Difference in charge density for cases C1 and C7 of the Fe−MoS$_2$ system with yellow and cyan regions indicating increasing and decreasing charge density, respectively.

Figure 6. Difference in charge density of the B5 and B10 cases of the Fe−MoS$_2$ system, with yellow and cyan regions indicating increasing and decreasing charge density, respectively.
exchange of magnetic moments compared to that in the cases with $x = 0.6$–1.0.

In fact, the magnetic moment of MoS$_2$ originates from the spin polarization of the Mo atom evolving directly from the interactions between Fe and Mo, which was also verified experimentally in a previous study. Therefore, small firing angles allow Fe to have stronger interaction with Mo atoms than large firing angles, which depicts stronger magnetic moment exchange. Besides, magnetism is induced less in the B cases than in the C cases. For the B cases, the metal atom moves to connect to two S atoms, while only one S atom establishes bonding in the C cases. This means that the S atoms on the surface tend to be less polarized. Especially, we found that the B10 and C7 cases show compensated magnetic moment in frame 3 (100–150 fs). After this period of time, both cases show a comeback of the total magnetism (2 $\mu_B$). This phenomenon arises from the probability of forming new chemical bonds between the Fe–S pairs, thus establishing new nonpaired electrons. On the other hand, the magnetic compensation of the total system is only momentary and does not retain for the long trajectory period. To clarify the magnetic behavior in firing cases, we examined the electronic structure to understand its changes during the MD process.

To study the origin of fluctuation in magnetic alignment with respect to various firing angles, we analyze the electronic structure of several typical cases. Four cases have been verified to monitor the changes in electronic structure: B5, B10, C1, and C7, which clearly show the characteristics of magnetism of the Fe–MoS$_2$ system. The B5 case exhibits a magnetic “oscillation” in frame 3. The C1 case is chosen because the largest induced magnetic moment on MoS$_2$ is recorded. For the B10 and C7 cases, the magnetic moment compensation mostly happens in frame 3. First, we verify polarization from the electronic structure to find the root of magnetism. Figure 4 describes spin polarization in three frames of each MD process (randomly chosen for each stage). It can be seen that the Fe atom does not only invoke spin polarization for Mo but also for the S atoms. However, spin polarization of S is quite small compared to that of Mo. Therefore, we focus on analyzing spin polarization contributed by the Fe and Mo atoms, which shows clear contributions to the overall magnetic alignment of the system.

In the C1 case, the firing angle is almost vertical. There are obvious changes in the electronic structure and spin polarization with respect to time. Spin polarization (magnetic moment) of the system in frame 1 (25 fs) is almost cultivated by Fe 3d. In frame 2 (200 fs), the induced magnetic moment of the MoS$_2$ layer arises as a consequence of the interaction between Fe and MoS$_2$. The polarization of Mo can be observed from Mo 4d, which can be clearly observed in an energy range of $-2$ to 0 eV (Figure 4) in the highest occupied states. However, the polarization of Fe is larger than that of Mo, where the polarized state density of Fe 3d is more dominant. The initial stage of frame 3 (250 fs) shows spin polarization generated by Mo 4d, which is predominant over Fe 3d. When the fired atom moves deeper into the film (350 fs), the polarization of the film is greater than that of the metal.

In the case of B5, the firing angle increases along the bisector line. In comparison with the C1 case, frame 2 (270 fs) of the B5 case is found to form a very small polarization contributed by Mo 4d. Figures 5 and 6 show the difference in charge density for cases C1 and C7 and B5 and B10 of the Fe–MoS$_2$ system, with yellow and cyan regions indicating increasing and decreasing charge density, respectively. The smaller firing angle (nearly vertical) leads to the capacity of Fe influencing the strong magnetic moment of MoS$_2$. The beginning of frame 3 (360 fs) shows a clear polarization of Mo 4d. The spin polarization of Mo 4d grows when the metal atom penetrates deeper into the MoS$_2$ layer (480 fs). There seems to be an overlap (hybridization) between the D orbital of Mo and Fe at this time.

The periods at 25 fs of the C7 and B10 cases are found to establish similar results in spin polarization of the system compared to the previous two cases, while the polarization of the system originates from Fe 3d alone. Frame 1 of the four firing angles is examined, and the obtained results are consistent in terms of magnetism. The magnetism of the system is contributed by spin polarization of Fe alone. Frame 2 (270 fs) of C7 has a result similar to the B5 cases when spin polarization of the MoS$_2$ layer is quite small. Meanwhile, the B10 case shows that spin polarization contributed by Mo 4d is larger than that in the C7 case. However, the spin polarization of Mo 4d is smaller than the polarization of Fe, similar to case C1. The resultant polarization indicates that total magnetism of the system in frame 2 is contributed mainly from the magnetic moment of Fe and a minority of MoS$_2$. The occurrence of layer magnetization induced by the metal has contributed to increase in the total magnetism of the system, which reveals long interaction between Fe and MoS$_2$. In the beginning of frame 3 (350 and 360 fs, respectively, for cases C7 and B10), a clear polarization of the layer is observed. This result is similar to the previous two cases of firing angles (C1 and B5) when the polarization of Mo 4d seems to be greater than that of Fe 3d. When Fe moves deeper into the MoS$_2$ layer, a special event of magnetism occurs when the total magnetism vanishes for both cases C7 and B10.

We carry out the PDOS analysis for the 3d orbitals of Fe to predict the selection rule of magnetic alignment according to the Fe–MoS$_2$ interaction at various bonding distances. Figure S2 shows the electronic occupation inferred from the PDOS analysis. In addition, the spin density with respect to various Fe-layer distances is shown in the same figure. In the strong bonding configuration (Fe-layer distance = 2 Å), the majority of spin density resides around the Fe site and a minor part resides around the three S sites and Mo sites. When the interacting distance is greater (cases of 4 and 6 Å), spin density mainly locates around the Fe site. Having four unpaired electrons, the 3d occupation diagram in the cases of 6 and 4 Å are distinctive. More specifically, $d_{xy}$ is doubly occupied in the 4 Å case, while $d_{x^2}$ is doubly occupied in the 6 Å case. The magnetic moment of 4 $\mu_B$ comes from the single occupation of four remaining 3d subshells in those two cases. In the bonding configuration (2 Å), both $d_{xz}$ and $d_{yz}$ are doubly occupied, while $d_{xy}$ and $d_{x^2-y^2}$ are singly occupied, which leads to a magnetism of 2 $\mu_B$ for the Fe site. Besides, the spin density distribution also reveals that the overall magnetic alignment is nonlocal as the spin tends to spread to three surrounding S sites and the nearest Mo site in the bonding configuration.

An analysis of charge density is performed to validate charge transfer of the system at the time when the magnetism of the system vanishes (450 and 480 fs corresponding to cases C7 and B10, respectively). In order to clarify the origin of magnetism, we also verify charge density difference at 350 and 480 fs of cases C1 and B5, respectively. The results of cases C7 and B10 show that the Fe atom not only exchanges charge with the nearest Mo atom but also with two neighboring Mo atoms.
Meanwhile, Fe in the case of C1 (Figure 5) and B5 (Figure 6) only exchanges charge with a single Mo atom. Therefore, the compensated magnetism does not show up during frame 3; however, there is a reappearance of magnetic moment at the end of the period. This behavior can be used to predict that the magnetic suppression of the system in cases C7 and B10 is due to the fact that Fe has a charge exchange with more Mo atoms to form the Mo–Fe interaction than in the other cases. The process of exchanging charges with multiple Mo atoms gives a higher probability of spin misalignment compared to those cases involving less Fe–Mo interaction. When the Fe atom returns to the MoS₂ surface, the bonding of Fe with the neighboring Mo atom is no longer established, leading to the reappearance of magnetism in the system. In addition, the electronic structure of such instances in cases C7 and B10 (Figure 4) is found to have a band gap of about 0.2 eV. Thus, it can be asserted that the electrons of C7 and B10 cases are completely coupled, leading to the narrowing of a band gap in the electronic structure. It is the pairing of electrons that makes the system nonpolarized, which causes the magnetism of the system to vanish.

For the Ni cases, there is no significant difference in the change in induced magnetism for the C and B cases (Figure 7a). During the collision process, the total magnetic moment is observed to vary from 1.5 to 4.0 μ_B when the distance between Ni and the MoS₂ surface is larger than 2 Å. Otherwise, the magnetism of Ni–MoS₂ vanishes when the distance is smaller than 2 Å. The magnetic moment is observed to reappear when Ni bounces on the surface (for the small firing factor x < 0.5). Overall, the magnetic contribution mostly comes from Ni. The induced magnetic moments of MoS₂ can be observed, but it is negligible. To investigate the electronic behavior, we analyze DOS with respect to the distance between Ni and the MoS₂ surface (6, 4, 2, and 0 Å) for cases D, C10, and B10 as shown in Figure 7b. Figure 7b depicts the strong polarization of the 3d orbital of Ni. The total magnetic moments mostly come from the Ni atom when the atom–surface distance is larger than 2 Å. For a metal–surface distance around 2 Å, a strong interaction between Ni and MoS₂ is also observed, as shown in Figure 7b. In the strong ionic bonding state, the 3d orbitals of Ni become fully occupied, leading to the pairing of electrons and thus suppressing the magnetic alignment of Ni. The hybridization between 3d–4d orbitals of Ni and Mo and the 3p orbital of S has an effect to suppress the band gap of the system. Particularly, the highest occupied state is constituted by the 3d orbital of Ni, while the lowest unoccupied state comes from the 4d orbitals of Mo. The system band gap can be reduced up to 40% (1.0–0.6 eV) compared to pure MoS₂. This band gap implies the strong coupling of electrons, leading to the vanishing of magnetism of Ni.

4. CONCLUSIONS

In this study, we have investigated the induced magnetism in the MoS₂ monolayer during a transition metal (Fe/Ni) bombardment process using systematic nonadiabatic ab initio MD. The metal atom (Fe/Ni) is fired toward the Mo–S linkage (C cases) or the bisecting vector of a Mo–S bond (B cases) with an initial kinetic energy of 0.5 eV. In total, the trajectories of 42 collision cases are monitored for Fe and Ni. During the MD process, we observe that there is a strong interaction between Fe/Ni and the MoS₂ surface at various bonding distances, leading to large kinetic energy enhancement (4 eV for Fe, 5 eV for Ni). The thermal vibration of MoS₂ plays an important role in imposing enormous attraction on the metal atom, thus accelerating its rapid movement toward MoS₂. Besides, the strength of interaction depends on the firing factor x and the projected direction (Mo–S linkage or bisector of two Mo–S bonds). For those Fe cases involving firing along a Mo–S bond, the metal bullet is observed to be more attracted than for the cases firing Fe along the bisector of two Mo–S bonds. Meanwhile, there seems to be no significant difference for the Ni trajectory samples in terms of the magnetic alignment. Remarkably, with the firing factor x < 4, the firing cases possess a shorter collision time and a higher kinetic energy.
rate of kinetic energy enhancement, which implies that there is stronger interaction between the metal bullet and Mo with small firing angles.

In the last section, the induced magnetic behavior of MoS2 is examined by analyzing the electronic structure of the metal–MoS2 interacting configurations. For the Fe cases, magnetism of MoS2 is gradually induced when Fe moves closer to the surface. After collision, magnetic moment exchange between Fe and MoS2 is observed. Then, the magnetic fluctuation is almost eliminated when Fe finds a better stabilization location on the MoS2 surface. The magnetic moment exchange behavior is caused by the polarization of Fe 3d and Mo 4d. Interestingly, this magnetic behavior strongly depends on interacting configuration. The electronic structure results reveal that there is the charge transfer between Fe and Mo atoms, which can cause the high probability of electron pairing and lead to nonmagnetism. The Ni−MoS2 system is found to exhibit a lower magnitude of magnetization of 1.5−4 μB. Interestingly, such a level of magnetism is found when Ni is 2.0 Å above the surface. In addition, the strong bonding attachment of Ni reduces the band gap by at least 40%.

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