Comparative study of electronic and magnetic properties of iron and cobalt phthalocyanine molecules physisorbed on two-dimensional MoS₂ and graphene

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In this paper, we have done a comparative theoretical study of electronic and magnetic properties of iron phthalocyanine (FePc) and cobalt phthalocyanine (CoPc) molecules physisorbed on a monolayer of MoS₂ and graphene by density functional theory. Various types of physisorption sites have been considered for both surfaces. The lowest energy structure for both metal phthalocyanine (*MPc*) molecules physisorbed on MoS₂ is a sulfur-top position, i.e., when the metal center of the molecule is on top of a sulfur atom. However, on graphene, the lowest energy structure for the FePc molecule is when a metal atom is on top of a bridge position. In contrast to this, the CoPc molecule prefers a carbon-top position. The adsorption of *MPc* molecules is stronger on the MoS₂ surface than on graphene (~ 2.5 eV higher physisorption energy). In these systems, spin dipole moments of the metal centers are antiparallel to the spin moments and hence a huge reduction of effective spin moment can be seen. The calculations of magnetic anisotropy energies using both variational and second-order perturbation approaches indicate no significant changes after physisorption. In case of the FePc and CoPc physisorption, respectively, an out-of-plane and an in-plane easy axis of magnetization can be observed. Our calculations indicate a reduction of MoS₂ work function ~ 1 eV due to physisorption of *MPc* molecules while it does not change significantly in the case of graphene.

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I. INTRODUCTION

Over the past two decades, the research fields of molecular electronics and spintronics have achieved a significant advancement with a remarkable progress in nanoscience, particularly the development of experimental techniques such as scanning tunneling microscopy, mechanically controlled break junctions, and electromigration break junctions, which has made it possible to detect, manipulate, and utilize intrinsic single molecular properties for electronic and spintronic device fabrication. Integrability of a molecule in a device without compromising its intrinsic properties is a key challenge on this front and sets the current trend of research in molecular electronics and spintronics. Metal-organic complexes are particularly potent from these aspects, as extended organic complex plays a major role in device integrability while the central ionic complex carries out the key molecular features. However, to achieve the functionalities of electronic (spintronic) device, molecules are required to express multiple conformations, be it structural or electronic, that can be accessed externally. Metal-porphyrin(*MP*) and -phthalocyanine(*MPc*) molecules hold an immense potential

in this regard, as they offer conformation switching based on structural [1], charge [2], and spin degrees [3] of freedom. *MP* and *MPc* molecules containing magnetic core are of particular interest for spin-based molecular devices. The molecules often respond to the external manipulations, such as temperature, light, or mechanical strain, and exhibit spin-crossover or change in magnetic anisotropy [4]. Both these properties are extremely crucial for molecule-based spin valve or magnetic storage devices. In addition, these molecules possess planar structures, which improve significantly the feasibility of adsorption on different surfaces and are found to have long-range structural ordering [5]. These features pave the way to exploit the interface properties of molecules and substrates to control the molecular properties for desired applications. Several fundamental approaches based on magnetic properties of *MP* and *MPc* have been explored both experimentally and theoretically. The manipulation of the spin state with surface-controlled ligand field [6,7], molecule-surface magnetic exchange coupling with surface modification [8,9] and additional ligation of functional groups [10], or emergence of Kondo resonance [11] have been reported, emphasizing the accessibility of the magnetic states in these molecules.

However, the choice of adsorbent surface is equally crucial for controlling the molecular properties as it dictates the interface properties. Atomically thin layers are particularly appealing from this aspect with their exotic surface properties and also from the point of view in finding applications in nanoscale devices. The absorption properties of ultrathin graphene, graphene-BN layers, have been explored extensively [12–14], which combined with intrinsic molecular properties [6] raise the potential for the designing of devices.

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Two-dimensional (2D) MoS₂ is an ultrathin semiconductor with unique electronic and optical properties, that has potential applications in optoelectronics, fluorescence imaging, photo catalysis, solar cells, valley electronics or as photodynamic, photo thermal materials and even in biomedicine as antibacterial agents [15–21]. Monolayer MoS₂ has a direct band gap of 1.9 eV, which is suitable to absorb visible light [22,23]. The multifunctionalities of MoS₂ have opened up many new routes to encompass the interface manipulations. Tuning of electronic and optical properties of MoS₂ by means of molecular charge transfer using organic molecules adsorption has also been reported in recent theoretical studies [24]. Effects of CuPc and TiOPc physisorption on the optical properties of 2D MoS₂ have also been investigated recently [25].

In this paper, we have explored extensively the physisorption properties of MPc molecules on single free-standing layers of MoS₂ and graphene and their impact on the electronic and specifically the magnetic properties of the molecule, aiming at their applications in spintronic devices. FePc and CoPc molecules were chosen as the representatives of metal phthalocyanine molecules, owing to the subtle balance between spin-pairing energy and ligand field that gives rise to exotic electronic and magnetic properties in the molecules. Our calculations indicate a stronger adsorption of MPc on MoS₂ surface compared to that on a graphene layer, along with different favored adsorption sites. With the aid of density functional theory, incorporating static electron correlation (DFT+U), we've performed a detailed analysis of molecular adsorption scenario, surface work functions, and the impact of the interface properties on the electronic and magnetic structures of the molecules. The plan of the paper is as follows. In the next section, we will present the computational details followed by Results and Discussions in Sec. III. In the Results and Discussions section, we will first discuss the structural properties (Sec. III A), and then it will be followed by the discussion of electronic structure (Sec. III B), spin dipole contributions (Sec. III B 2), magnetic anisotropy (Sec. III B 3), and work function (Sec. III B 4). The conclusions are presented in Sec. IV.

II. COMPUTATIONAL DETAILS

All the calculations have been performed with supercells of monolayer MoS₂ and graphene. The supercells of MoS₂ and graphene are generated by repeating the primitive cells by 9 and 12 times, respectively, in both *a* and *b* directions. The MPc (*M* = Fe, Co) molecules are placed on top of these surfaces. A vacuum of 20 Å is included to avoid the interaction with periodic images. All the calculations have been performed using plane-wave-based density functional code VASP [26] within the projector augmented wave method (PAW) for describing electron-ion interactions. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) has been used for the exchange-correlation potential [27,28]. All the structures have been fully relaxed using the conjugate gradient method with the forces calculated using the Hellman-Feynman theorem. We have used the energy and the Hellman-Feynman force thresholds of 10⁻⁴ eV and 10⁻² eV/Å, respectively. We have used 500 eV cutoff energy to truncate the plane waves. A 3 × 3 × 1 Monkhorst-

Pack *k*-grid was used for all our calculations. To address the problem of electron correlation effect in the narrow *d* states of metal atoms (Fe, Co), we have used GGA+U approach following the formalism proposed by Dudarev *et al.* [29] A Coulomb interaction term is added according to the mean field Hubbard U formalism [29–31]. For the exchange parameter, *J*, we have used a value of 1.0 eV. We have used 4.0 eV and 6.0 eV as the Coulomb parameter, *U*, values for FePc and CoPc, respectively [32,33]. These values are taken as they correctly reproduce the electronic structures and magnetic properties of FePc and CoPc in gas phase.

The van der Waals (vdW) interaction between the MPc molecules and the MoS₂ or graphene layer originates due to the fluctuating charge distribution and hence cannot be described by PBE functionals alone. Hence for all the calculations, we have included the vdW effect by adding a correction to the conventional Kohn-Sham DFT energy through a pair wise force field following the method proposed by Tkatchenko-Scheffler [34].

The physisorption energy, *E_a*, for metal phthalocyanine molecule physisorbed on MoS₂ or graphene is defined as follows:

$$E_a = [E_{\text{layer}} + E_{\text{MPc}}] - E_{\text{layer+MPc}}, \quad (1)$$

where

- (i) *E_{layer}* is the total energy of either MoS₂ or graphene supercell.
- (ii) *E_{MPc}* is the total energy of the MPc molecules in the gas phase.
- (iii) *E_{layer+MPc}* is the total energy of MPc physisorbed on MoS₂ or graphene supercell system.

These total energies are taken after the structures are fully relaxed, according to the force convergence criterion. Hence, they include the energy contributions due to any kind of structural deformations.

III. RESULTS AND DISCUSSIONS

A. Structural properties

We will begin our discussion of results from the analyses of structural properties and the energetics of the systems studied. We will first discuss the results of MPc physisorption on MoS₂ followed by the results of physisorption on graphene.

To find out the most energetically favorable physisorbed position, we have considered different possible positions of the MPc molecules on the 2D surfaces. These different positions of the molecules can be distinguished by the position of the metal atom center with respect to the underlying surface layer of MoS₂ or graphene. For MoS₂, there are four possible positions, which are (i) S-Top—when the metal atom center is at the top of an S atom, (ii) Mo-Top—when the metal atom center is at the top of a Mo atom of the second atomic layer, (iii) Bridge—when the metal atom center is at the bridge position of two S atoms belonging to the top layer of MoS₂, and (iv) Hex – when the metal atom center is on top of the center of a hexagon, created by Mo and S. In Fig. 1, we have shown the representations of these four positions for FePc molecule on MoS₂ only. However, these different geometry positions are also applicable for the CoPc molecule. In the case of graphene, however, only three positions are

FIG. 1. Representative figure of various optimized geometries considered for *MPc* molecules on MoS_2 in our calculations to obtain energetically most favorable positions for physisorption. These geometry positions are S-Top, Bridge, Hexagonal, and M-Top (from left to right, respectively). We have taken FePc molecule on MoS_2 as the representative to show these positions. The upper panel of the figure shows a closeup top view of these four structural positions. The lower panel shows the side view for the same along with the vertical distance from Fe atom to the top S layer. See Sec. III A for detailed discussions.

possible. Following the above terminology, these positions are (i) C-Top, (ii) Bridge, and (iii) Hex. In our calculations, *MPc* molecules are placed on the surfaces with a particular xy position and then we have relaxed the atomic positions completely without any constraint until the force convergence was achieved.

In Table I, we have shown the physisorption energies (E_a) and the vertical distances (D_h) between the metal center and the MoS_2 layer for all of the four FePc and CoPc physisorbed structures as described before. The analyses of geometries reveal that for both molecules, all four bond-lengths between the metal and the nitrogen atoms are identical—1.95 Å for FePc and 1.94 Å for CoPc, maintaining a D_{4h} symmetry of the molecule. For S-Top configuration, the vertical heights from the MoS_2 layer are different for the two molecules. The vertical distances between the metal center of the molecules and the MoS_2 layer are 3.18 Å and 3.21 Å for FePc and CoPc, respectively. Interestingly, the vertical separations between the molecule and the MoS_2 layer for the other geometry positions are almost identical. A close inspection reveals that the molecules are slightly concave upward and downward for S-Top and Bridge configurations, respectively. However,

the molecules remain flat for the other two configurations. The physisorption energies for S-Top geometry configurations for both FePc and CoPc are at least ~ 0.14 eV higher as compared to that of the other configurations (see Table I). The lowest physisorption energies can be observed for Mo-Top configurations. These are mainly because S atom is more electronegative as compared to that of Mo atom and interacts with the metal atom center of the *MPc* molecule more strongly. This fact is also evident from the concave and flat molecular structure of *MPc* molecules in S-Top and M-top configurations, respectively. Hence, we can conclude that the S-Top configuration is energetically the most favorable physisorption structure for the *MPc* molecules physisorbed on MoS_2 .

We have also calculated the physisorption of the *MPc* molecules on graphene to compare the same on MoS_2 . To find out the most energetically favorable physisorption sites, we have optimized three different geometry configurations of *MPc* molecules physisorbed on graphene.

The calculated physisorption energies (E_a) and vertical distances between the metal center and graphene layer (D_h) are tabulated in Table II. The analyses of physisorption energies show that for graphene, the most favorable site for FePc molecule physisorption is when the Fe metal center resides at the bridge position (figure not shown). This is quite different

TABLE I. Physisorption energies (E_a) [see Eq. (1)] and vertical distances of *M* atom (D_h) from top S layer of MoS_2 for *MPc* physisorbed on MoS_2 . The most stable structure with highest E_a is written in bold. On MoS_2 , the vdW energy contributions for FePc and CoPc physisorptions are around three times larger than that on graphene.

FePc@ MoS_2	E_a (eV)	D_h (Å)	CoPc@ MoS_2	E_a (eV)	D_h (Å)
S-Top	6.21	3.18	S-Top	6.18	3.21
Bridge	6.06	3.42	Bridge	6.05	3.42
Hex	6.03	3.37	Hex	6.01	3.38
Mo-Top	5.98	3.39	Mo-Top	5.96	3.40

TABLE II. Physisorption energies (E_a) [see Eq. (1)] and vertical distances of *M* atom (D_h) from graphene layer for *MPc* physisorbed on graphene. The most stable structure with highest E_a is written in bold.

FePc@ Gr	E_a (eV)	D_h (Å)	CoPc@ Gr	E_a (eV)	D_h (Å)
Top	3.38	3.37	Top	3.39	3.39
Bridge	3.40	3.34	Bridge	3.38	3.34
Hex	3.36	3.43	Hex	3.35	3.43

from the physisorption of iron porphyrin (FeP) molecule on graphene, where the energetically favorable physisorption position is on the top of C atom [8]. This can be attributed to the larger macrocycle in FePc as compared to that of in FeP and, hence, stronger vdW interaction. However, for CoPc, the most stable physisorption site on graphene is the top site, where the metal atom is on top of a C atom. This is similar to cobalt porphyrin (CoP) physisorption on graphene/Ni observed previously [35]. However, for both the physisorbed molecules, the difference in physisorption energies for different configurations is quite small (see Table II).

A comparison of results listed in Table I and Table II shows an interesting contrast between the two cases of physisorption of the *MPc* molecules on the MoS_2 and the graphene. It can be clearly observed that the energies of the *MPc* physisorption are quite high for the MoS_2 as compared to that of the graphene. These are due to a strong interaction between the metal d_π states with the S p_z states of MoS_2 (see detailed discussions on density of states in Sec. III B). On graphene, the interaction between metal d_π states and C p_z states is relatively weak and hence the physisorption energies are much lower. The different strengths of interactions are also reflected on the vertical distances of *MPc* molecules from the MoS_2 and graphene surface. For energetically most favorable physisorption position, the vertical distances between the molecule metal centers and graphene are ~ 0.20 Å higher as compared to that of the vertical distances between the molecule metal center and the MoS_2 . The analyses of the structures also show that, unlike the MoS_2 , the physisorbed molecules on the graphene remain flat.

It is also interesting to note that the physisorption energy differences between different positions of the *MPc* molecules on the graphene are quite small (~ 0.02 eV). However, on the MoS_2 , the physisorption energy difference between the most stable physisorption site and the next probable site is substantially higher as compared to that of the graphene (~ 0.14 eV). These are due to the fact that the graphene is planar and hence the interaction of the graphene with the physisorbed molecules will not change drastically. However, in the MoS_2 surface, S and Mo atoms are in different layers and, S being more electronegative, interacts strongly with the physisorbed molecules.

Our analyses of the structural properties and physisorption energies conclude that the *MPc* molecules have weaker interaction with graphene surface, but they will be strongly physisorbed on MoS_2 surface.

B. Electronic structure

In this subsection, we will discuss the electronic properties of the *MPc* molecules physisorbed on MoS_2 and graphene. We have used total, site, and m_l projected density of states and charge densities for our analysis.

In the two panels of Figs. 2(a) and 2(b), respectively, we have shown the m_l decomposed d states of the Fe atom of the FePc molecule physisorbed on MoS_2 and graphene. For comparison, m_l decomposed d states of the Fe atom from the gas phase FePc molecule are plotted in Fig. 2(c). In Fig. 2(a), we have also plotted the projected density of states of p_z orbitals of S atoms of MoS_2 beneath the FePc molecule.

FIG. 2. Density of states plots for- (a) Fe d orbitals of FePc physisorbed on MoS_2 along with the p_z orbitals of the S atoms beneath the molecule, (b) Fe d orbitals of FePc physisorbed on graphene along with the p_z orbitals of the C atoms beneath the molecule, and (c) Fe d orbitals of gas phase FePc. The white and the grey areas represent the spin-up and spin-down channels of the DOS, respectively.

The p_z orbitals of the C atoms of graphene below the FePc molecule are also plotted in Fig. 2(b). In Figs. 3(a)–3(c), we have plotted the similar quantities as described for Fig. 2, but for Co atom of the CoPc molecule.

From the analyses of projected density of states, it can be seen that the out-of-plane d orbitals of the Fe atom become broadened after physisorption of the FePc molecule on MoS_2 as compared to that of the gas phase [see Fig. 2(a)]. These are mainly seen on the occupied out-of-plane d_{z^2} orbital as well as d_π orbitals. These broadening of orbitals are mainly due to the strong interactions between out-of-plane d orbitals of the physisorbed molecule and the p_z orbitals of top layer S atoms of MoS_2 . In case of graphene, a similar broadening can also be seen [see Fig. 2(b)]. However, the interactions are relatively weak, which are evident from the smaller physisorption energies and larger vertical distances (cf. Tables I and II). Similar broadening of d_π orbitals can also be observed for Co atom of CoPc molecule physisorbed on MoS_2 and graphene [see Figs. 3(a)–3(b)]. However, for CoPc physisorption, the broadening of d_{z^2} orbital of Co atom is significantly less as compared to that of the FePc physisorption.

FIG. 3. Density of states plots for- (a) Co d orbitals of CoPc physisorbed on MoS₂ along with the p_z orbitals of the S atoms beneath the molecule, (b) Co d orbitals of CoPc physisorbed on graphene along with the p_z orbitals of the C atoms beneath the molecule, and (c) Co d orbitals of gas phase CoPc. The white and the grey areas represent the spin-up and spin-down channels of the DOS, respectively.

The total magnetic moments after physisorption on MoS₂ and graphene are $2.0 \mu_B$ and $1.0 \mu_B$, respectively, for FePc and CoPc. For both molecules, the major part of the magnetic moments originate from the d_{z^2} orbital of the metal atom. The physisorbed FePc has a spin configuration of $S = 1$. This results from $b_{2g}^2, e_g^3, a_{1g}^1$ electronic configurations where $b_{2g}(d_{xy})$ orbital has an occupancy 2, $e_g(d_\pi)$ orbital has an occupancy 3 and $a_{1g}(d_{z^2})$ orbital has an occupancy 1. However, for CoPc, the spin configuration is $S = 1/2$, which results from $b_{2g}^2, e_g^4, a_{1g}^1$ electronic configuration where $b_{2g}(d_{xy})$ orbital has an occupancy 2, $e_g(d_\pi)$ orbital has an occupancy 4 and $a_{1g}(d_{z^2})$ orbital has an occupancy 1. The Bader charge analysis indicates that ~ 0.09 electrons are transferred per MPc molecule physisorbed on graphene. For physisorption on MoS₂, the amounts of charge transfer are ~ 0.004 and ~ 0.01 electrons for FePc and CoPc molecule, respectively. These very small values indicate that there are hardly any charge transfers occur after the physisorption. Our calculations for the gas phase molecules show that the magnetic moments and the electronic configurations of MPc molecules in the physisorbed situation do not change from the

gas phase values. These are because the d_π and d_{z^2} orbitals are energetically positioned far below the Fermi energy. Thus, there is no significant hybridization with the surface, hence almost no transfer of electrons occurs. The m_l - projected density of states corresponding to free molecule and molecule on surface differs slightly, but the orbital resolved occupations (and hence the magnetic moment) remain the same. The effect of the surface molecular interaction in molecular electronic structure is, hence, revealed in energy-resolved projected DOS but not in the quantities like orbital projected occupations or magnetic moment, which are energy integrated.

1. Analysis of charge density difference

To find out the charge accumulations due to the electronic interactions between the molecules and the surface, we have computed and analyzed the charge density differences for the composite MPc molecules physisorbed on MoS₂/graphene systems with respect to the isolated MPc molecules and pristine MoS₂/graphene surface. We have used the following formula for the calculation:

$$\Delta\rho = \rho_{\text{MPc@MoS}_2/\text{graphene}} - (\rho_{\text{MoS}_2/\text{graphene}} + \rho_{\text{MPc}}). \quad (2)$$

Here, $\rho_{\text{MPc@MoS}_2/\text{graphene}}$, $\rho_{\text{MoS}_2/\text{graphene}}$, and ρ_{MPc} are the total charge densities of the composite physisorbed system, isolated MoS₂/graphene, and isolated MPc molecules, respectively. For the isolated systems, we have fixed the geometries obtained from the optimized composite systems. In Figs. 4 and 5, we have shown these charge density difference plots for FePc and CoPc physisorbed systems, respectively (see Supplemental Material [36] for top and 360° views of the charge density differences). From the analyses of the charge density difference plots, we see that a significant amount of charge accumulates on the whole MoS₂ surface for the MPc physisorption. These observations are consistent with charge density difference observed for physisorption of copper phthalocyanine molecule on mono layer MoS₂ [25]. However, in the case of graphene, the accumulated charges are localized at the vicinity of the MPc molecules only. This large amount of charge accumulation on the MoS₂ surface also indicates that there are strong vdW interactions (~ 0.13 eV/atom higher vdW energy contribution) between the MPc molecules and the MoS₂ surface as compared to that of the vdW interactions between the MPc molecules and the graphene.

2. Spin dipole contribution

For a low symmetry structure, deformations in the spin densities are expected to be large. These deformed spin densities lead to a large value of spin dipole moment $7\langle T \rangle$. The spin dipole moments are relevant for the XMCD measurements, where the measured effective moments contain both spin and spin-dipole moments. The spin dipole operator, T , is defined as follows [37]:

$$T = \sum_i Q^{(i)} s^{(i)}, \quad (3)$$

where, $Q^{(i)}$ is the quadrupolar tensor and can be described as

$$Q_{\alpha\beta}^{(i)} = \delta_{\alpha\beta} - 3\hat{r}_\alpha^{(i)}\hat{r}_\beta^{(i)}. \quad (4)$$

FIG. 4. Charge density difference plots between the MoS₂/graphene surface and FePc for the composite FePc on MoS₂ (top panel) and FePc on graphene (bottom panel) system. The isosurfaces are plotted with one-tenth of the maximum isosurface values. Red (blue) colors denote positive (negative) charge density values. The FePc molecule is made transparent for easier viewing of the charge density difference in the molecule.

The components of T can be written in the second quantized form as

$$T_{\pm} = T_x \pm iT_y = \sum_{\gamma\gamma'} T_{\gamma\gamma'}^{\pm} a_{\gamma}^{\dagger} a_{\gamma'}, \quad (5)$$

$$T_z = \sum_{\gamma\gamma'} T_{\gamma\gamma'}^z a_{\gamma}^{\dagger} a_{\gamma'}, \quad (6)$$

where $a_{\gamma} (a_{\gamma}^{\dagger})$ are the annihilation (creation) operators. The matrix elements of $T_{\pm}$ and T_z are as follows:

$$T_{\gamma\gamma'}^{\pm} = \langle \gamma | c_0^2 s_{\pm} - \sqrt{6} c_{\pm 2}^2 s_{\mp} \pm \sqrt{6} c_{\pm 1}^2 s_z | \gamma' \rangle, \quad (7)$$

$$T_{\gamma\gamma'}^z = \langle \gamma | -\sqrt{\frac{3}{2}} c_{-1}^2 s_{+} + \sqrt{\frac{3}{2}} c_1^2 s_{-} - 2c_0^2 s_z | \gamma' \rangle, \quad (8)$$

where, $|\gamma\rangle = |lm, \sigma\rangle$.

To calculate the spin dipole moments in MPc, we have followed the method prescribed by Freeman *et al.* [38] and performed density functional theory calculations including all

the above-discussed effects of surface molecular interactions. The results of calculated spin dipole moments for the MPc gas phase molecules and the MPc molecules physisorbed on the MoS₂ and the graphene are tabulated in Table III. For the MPc molecules with transition metal atom center, the z component of the spin dipole moment will be considered. As seen from the table, the calculated values of the z component of the spin dipole moments ($7\langle T_z \rangle$) are $-2.09 \mu_B$ and $-1.69 \mu_B$ for the FePc and the CoPc physisorbed on the monolayer MoS₂, respectively. On the graphene, the values are $-2.05 \mu_B$ and $-1.70 \mu_B$ for the FePc and the CoPc, respectively. From our calculations, it is clear that the values of the spin dipole moments ($7\langle T_z \rangle$) are very strong and they are opposite to the spin moment ($2\langle S_z \rangle$). Hence, the effective spin moment defined as $S_{\text{eff}} = 2\langle S_z \rangle + 7\langle T_z \rangle$, will be reduced by a significant amount.

Our calculations also indicate that the comparative values of the spin dipole moments do not change significantly for both MPc molecules after physisorption on MoS₂ or graphene as compared to that of the gas phase. The values of the spin

FIG. 5. Charge density difference plots between the MoS₂/graphene surface and CoPc for the composite CoPc on MoS₂ (top panel) and CoPc on graphene (bottom panel) system. The isosurfaces are plotted with one-tenth of the maximum isosurface values. Red (blue) colors denote positive (negative) charge density values. The CoPc molecule is made transparent for easier viewing of the charge density difference in the molecule.

TABLE III. Total spin magnetic moments ($2\langle S_z \rangle$), z component of spin dipole moments ($7\langle T_z \rangle$), and effective spin moments ($S_{\text{eff}} = 2\langle S_z \rangle + 7\langle T_z \rangle$) in the units of μ_B for MPc molecules physisorbed on monolayer MoS_2 (top two rows), graphene (middle two rows), and gas phase MPc (bottom two rows).

System	$2\langle S_z \rangle$	$7\langle T_z \rangle$	S_{eff}
FePc@ MoS_2	2.0	-2.09	-0.09
CoPc@ MoS_2	1.0	-1.69	-0.69
FePc@graphene	2.0	-2.05	-0.05
CoPc@graphene	1.0	-1.70	-0.70
FePc	2.0	-1.99	0.01
CoPc	1.0	-1.70	-0.70

dipole moments depend mainly on the electronic occupations of the d orbitals of the metal atom center of MPc molecules. The analyses of density matrices show that the integrated quantities, such as the electronic occupations of the d orbitals, do not change significantly due to the molecular physisorption situation as compared to that of the gas phase. Hence the changes in spin dipole moments from the gas phase are minimal.

3. Orbital moments and magnetic anisotropy

We have incorporated the spin-orbit coupling in the Hamiltonian of our DFT calculations to calculate orbital moments and magnetocrystalline anisotropy energy (MCA). We have used two different approaches to calculate the MCA (i) variational approach as implemented in VASP code and (ii) second-order perturbation approach where the required energy eigenvalues and the corresponding orbital characters are obtained from scalar-relativistic Kohn-Sham DFT calculations. The MCA originates from the coupling between orbital and spin degrees of freedom. It can be expressed as follows:

$$H_{SO} = \xi \mathbf{L} \cdot \mathbf{S} = \xi (L_x S_x + L_y S_y + L_z S_z), \quad (9)$$

where H_{SO} is the spin-orbit coupling Hamiltonian and ξ , the spin orbit coupling constant, is the radial average of $\xi(r)$ over the $3d$ orbitals which can be defined as follows:

$$\xi = \langle \xi(r) \rangle = \int R_{3d}^2(r) \xi(r) r^2 dr, \quad (10)$$

where $R_{3d}(r)$ is the radial part of the $3d$ wave function. Using the second order perturbation theory, one can write the spin-orbit contribution to the energy as follows:

$$E_{SO} = -\xi^2 \sum_{u,o} \frac{[\langle u | \mathbf{L} \cdot \mathbf{S} | o \rangle \langle o | \mathbf{L} \cdot \mathbf{S} | u \rangle]}{E_u - E_o}. \quad (11)$$

In the above equation, $|o\rangle$ and $|u\rangle$ represent the weighted occupied and unoccupied states of Fe/Co $3d$ orbitals. These occupied and unoccupied states are weighted by the occupations of respective $3d$ orbitals, $|o/u\rangle = |lm, \sigma\rangle$. The orbital and spin operators are denoted by $\mathbf{L}$ and $\mathbf{S}$. E_o and E_u represent, respectively, the eigenvalues of occupied and unoccupied states which have been taken from the *ab initio* calculations. The values of ξ have been taken as 49.6 meV and 63.8 meV for Fe^{2+} and Co^{2+} , respectively [39].

TABLE IV. MCA data within the second variation approach as implemented in VASP code, MCA ($\Delta E = E^{\text{hard}} - E^{\text{easy}}$), and orbital moment (μ_{orb}) for MPc molecules physisorbed on monolayer MoS_2 (top table), on graphene (middle table), and gas phase MPc (bottom table).

System	μ_{orb}	ΔE (μeV)	Easy axis
FePc@ MoS_2	0.012	52	Out-of-plane
CoPc@ MoS_2	0.036	75	In-plane
System	μ_{orb}	ΔE (μeV)	Easy axis
FePc@graphene	0.012	48.5	Out-of-plane
CoPc@graphene	0.037	76	In-plane
System	μ_{orb}	ΔE (μeV)	Easy axis
FePc	0.012	30	Out-of-plane
CoPc	0.037	78	In-plane

From Eq. (11), it is clear that the spin-orbit coupling energy contribution increases when $E_u - E_o$ decreases. Therefore, the relative placement of the $3d$ orbitals of the Fe/Co will dictate the energy contribution to the spin-orbit coupling. The relative arrangement of the $3d$ orbitals can be affected by the physisorption site of the MPc on MoS_2 or graphene. It is worth pointing out that the orbital angular momentum, via the term $\mathbf{L} \cdot \mathbf{S}$, lowers the spherical symmetry of the spin, and hence the geometric anisotropy also affects the magnetic anisotropy. However, the effects of geometrical symmetry lowering (owing to the surface molecular interaction) will be reflected in the nature and energy position of the molecular levels. The relative contributions of different transition metal d orbitals and ligand p orbitals in a molecular level will change if the symmetry is changed. These effects are already incorporated in our calculations by considering the projected occupations, which appear in the numerator along with the change in energy positions in the denominator of Eq. (11) for calculating energy using second-order perturbation theory. A chemisorbed situation can induce such significant changes, e. g., enhancement of metal-N bond length, spin-state change, etc. [7,8]. However, due to weak interactions in the case of physisorption, these effects are quite small.

We have tabulated the results obtained using the variational approach and the second-order perturbation approach in Tables IV and V, respectively. We have reported the orbital

TABLE V. MCA data within the second order perturbation approach, magnetic anisotropy energy ($\Delta E = E^{\text{hard}} - E^{\text{easy}}$), and orbital moment (μ_{orb}) for MPc molecules physisorbed on monolayer MoS_2 (top table), on graphene (middle table), and gas phase MPc (bottom table).

System	μ_{orb}	ΔE (μeV)	Easy axis
FePc@ MoS_2	0.019	103	Out-of-plane
CoPc@ MoS_2	0.028	58	In-plane
System	μ_{orb}	ΔE (μeV)	Easy axis
FePc@graphene	0.024	107.8	Out-of-plane
CoPc@graphene	0.030	60.2	In-plane
System	μ_{orb}	ΔE (μeV)	Easy axis
FePc	0.026	98	Out-of-plane
CoPc	0.028	60	In-plane

magnetic moments, magnetic anisotropy energies along with the information about the easy axis in Tables IV and V. Both approaches mentioned before give similar qualitative results. As seen from Table IV, the orbital moments do not change significantly in the physisorbed systems. The analyses of m_l projected density of states (see Figs. 2–3) indicate that, although the d orbitals below the Fermi levels are broadened in the physisorbed system compared to the gas phase, the band centers remain the same. Hence the orbital moments remain almost similar. The relative positions of d orbitals of the metal center in the MPc molecules do not change significantly from gas phase into the physisorbed phase. Therefore, the transition matrices are similar and hence the MCAs are similar in values. Our results indicate that while for CoPc, the easy axis of magnetization is in-plane, the easy axis is out-of-plane for FePc. However, it is important to note that the DFT+U calculations with static correlations lack correct estimation of MCA and one would require further advanced approaches beyond DFT to incorporate many body effects with dynamical correlations for correct estimations of MCA [40].

4. Work function

One of the important features of adsorption is the change of work function of the substrates. In the present context, this can be achieved by the decoration of the 2D substrates by the molecules, which may be useful for designing nano devices. To investigate possible changes in work functions (Φ) of the MoS₂ and graphene due to the MPc physisorption, we have calculated the work functions of the pristine monolayer MoS₂, graphene, and MPc physisorbed on MoS₂ and graphene. The work function Φ is defined as the minimum energy required to remove an electron from a material to the vacuum. Hence, Φ can be defined as follows:

$$\Phi = V(\infty) - E_f, \quad (12)$$

where, $V(\infty)$ is the self-consistent electrostatic potential in the vacuum far from the surface and E_f is the Fermi energy, which is calculated from a ground-state self-consistent calculation. Here, the top of the valence band has been taken as the Fermi energy. The surface work functions were calculated by applying the Neugebauer-Scheffler dipole correction [41] for the direction perpendicular to the surface. The electrostatic potential is obtained as a function of z ($V(z)$) by averaging the self-consistent potential parallel to the surface, i.e., in the xy plane. Then the potential $V(\infty)$ is approximated as the value of potential at the vacuum layer, where $V(z)$ is reaching its asymptotic limit.

In Table VI, we have tabulated the calculated values of Φ for the above-mentioned cases. The value of Φ for monolayer

graphene is 4.23 eV. This value is quite consistent with previous published result [42]. For MoS₂, the computed value of Φ is 5.94 eV, which is also quite similar to earlier published result [43]. It is evident from our calculations that the values of Φ do not change significantly after MPc physisorptions on graphene. However, the work function values decrease substantially (~ 1 eV for FePc and ~ 0.8 eV for CoPc) due to MPc physisorptions on MoS₂. Therefore, we conclude that it may be possible to tune the Φ of MoS₂ by MPc physisorption, which opens up the possibility of using these materials in electronic and optoelectronic devices for applications in fluorescence imaging, solar cells, and photocatalysis.

IV. CONCLUSIONS

In conclusion, we have performed detailed investigations of electronic and magnetic properties of MPc ($M = \text{Fe, Co}$) physisorption on MoS₂ and graphene using density functional theory along with Coulomb correlation for the metal d electrons. We have considered various possible physisorption sites both on MoS₂ and on graphene to find out energetically most favorable configurations. We have found that MPc molecules are physisorbed strongly on the MoS₂ as compared to that of the graphene. The most stable physisorption site on MoS₂ is when the metal atom center of a MPc molecule resides on top of a S atom. The other physisorption sites have much higher energy (~ 0.14 eV). However, on graphene, the physisorption energies are very similar for different physisorption sites. The out-of-plane d orbitals of the metal centers interacts more strongly with the out-of-plane orbitals from the MoS₂ as compared to that of the graphene. The magnetic moment arises from d_{z^2} orbital of the metal atom center of the molecules. The MPc physisorptions on the MoS₂ reduce the work function by ~ 1 eV whereas it does not change much in the case of physisorption on the graphene. The MPc physisorptions cause the large spin dipole moments opposite to the spin moments causing huge reduction of the effective moments, which can be measured by XMCD experiments. Our calculations of magnetic anisotropy energies using both variational and second-order perturbation approaches indicate no significant changes in the magnetic anisotropy energy values after physisorption of the MPc molecules. An out-of-plane magnetic anisotropy can be observed in the case of FePc whereas for CoPc, it is in-plane. In summary, our theoretical predictions indicate that the hybrid organic-inorganic interfaces consisting of metal centered phthalocyanine molecules and 2D MoS₂ are very interesting choices of system for useful applications.

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TABLE VI. Comparison of work function (Φ) values for monolayer MoS₂, graphene and MPc molecules physisorbed on MoS₂ and graphene.

System	Φ (eV)	System	Φ (eV)
MoS ₂ (1L)	5.94	Graphene (1L)	4.23
FePc@MoS ₂	4.94	FePc@Graphene	4.25
CoPc@MoS ₂	5.17	CoPc@Graphene	4.25

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