

Orbital-driven superexchange engineering at molecule/antiferromagnetic-oxide interfaces

Shuangying Ma[✉], Marco Marino^{✉,*}, and Guido Fratesi^{✉,†}*Physics Department Aldo Pontremoli, University of Milan, via Celoria 16, Milano 20133, MI, Italy*

(Received 12 December 2025; revised 17 April 2026; accepted 23 April 2026; published 1 June 2026)

Antiferromagnetic transition-metal oxides provide robust platforms for spintronic and magnonic applications, where control of magnetic exchange interactions is essential for tailoring spin dynamics. Molecular adsorption at organic/inorganic interfaces offers a promising route to chemically engineer these interactions. We investigate how molecular adsorption modifies surface superexchange interactions in antiferromagnetic transition-metal oxides. Using density functional theory+ U calculations, we study prototypical interfaces formed by C_{60} and cobalt-tetraphenylporphyrin (CoTPP) adsorbed on NiO(001) and CoO(001) and extract exchange coupling constants J from broken-symmetry total-energy calculations mapped onto a Heisenberg model. For clean surfaces, we obtain $J \approx -30$ meV for NiO(001) and $J \approx -21$ meV for CoO(001). Upon molecular adsorption, the magnitude of J increases to $-31/-32$ meV for NiO and to $-27/-30$ meV for CoO, corresponding to enhancements up to 9 meV for CoTPP/CoO(001). Orbital-resolved analysis reveals that the strengthening of superexchange correlates with a directional redistribution of charge within the transition-metal d manifold, characterized by a redistribution of charge involving enhanced occupation of in-plane σ and out-of-plane π -type orbitals aligned with the TM–O–TM and TM–molecule–TM superexchange pathways, accompanied by depletion of out-of-plane σ and in-plane π orbitals. While only two representative molecules and two oxides are considered here, the consistency of the observed trends across chemically distinct systems suggests that the proposed orbital-repopulation mechanism may apply more broadly to related organic/antiferromagnetic-oxide interfaces.

DOI: [10.1103/33f3-z6rd](https://doi.org/10.1103/33f3-z6rd)

I. INTRODUCTION

The concept of spinterface was first proposed to characterize the organic/ferromagnetic (organic/FM) interface, a central theme in molecular spintronics research [1–5]. Initial interest in molecular systems for spintronics stemmed from their exceptional spin coherence characteristics—notably suppressed spin-orbit coupling and hyperfine interactions—which enable prolonged spin lifetimes [6–8]. This prompted the development of early organic spintronic devices including spin valves [7,9,10], magnetic tunnel junctions, and novel device designing [1,4,11–13]. Subsequent investigations uncovered a more dynamic picture: molecular chemisorption at the interface creates spin-polarized hybrid states [11,14–17], fundamentally altering the behavior of the system. These interfacial states not only impart spin polarization to the organic layer [18–20] but also modify the magnetic signature of the ferromagnetic surface [21,22] and even induce spin effects in nonmagnetic materials [23].

Extensive exploration has created diverse spinterfaces by combining various molecules and substrates together.

Much foundational work leverages small and commonly known molecules that can be easily vapor-deposited, such as fullerenes [24–27], porphyrins [19,28,29], and phthalocyanines [30–32]. Additionally, in the attempt to activate the spinterfaces through external stimuli, more particular molecules, such as chiral molecules [33,34] and spin-crossover molecules [35–39] have also been considered.

On the inorganic side, the toolbox has expanded well beyond classic ferromagnets, now incorporating platforms such as graphene-on-metal structures [40,41], 2D materials [42,43], and antiferromagnetic (AFM) materials. In detail, the vanishing net magnetization, the insensitivity to external magnetic field, and the capacity to support high-frequency (THz) spin dynamics, of the latter ones, offered the prospect to conjugate spinterface properties to the promising field of magnonic-based devices [44,45].

Antiferromagnetic transition metal oxides (AFM-TMOs), such as nickel oxide (NiO) [46,47] and cobalt oxide (CoO) [48], exhibit robust long-range order due to the strong oxygen-mediated super-exchange interactions between transition metal (TM) cations. Their high Néel temperatures (~ 523 K for NiO [46,47], ~ 291 K for CoO [48]) ensure thermal stability at ambient conditions, and their chemical robustness and atomically well-defined (001) surfaces make AFM-TMOs highly suitable substrates for the deposition of organic molecules [19,24–39].

Recent investigations of organic molecules adsorbed on AFM-TMO surfaces demonstrate remarkable potential for tuning interfacial electronic and magnetic properties. We mention a few representative examples from the literature:

*Present address: TU Dortmund University, Otto-Hahn-Straße 4, 44227 Dortmund, Germany.

†Contact author: guido.fratesi@unimi.it

Fe-phthalocyanine (FePc) on NiO(001), increasing Ni–O–Ni exchange by 7.7% and hardening surface magnons by ≈ 10 meV [49], whereas on Cr₂O₃(0001) it redistributes Cr 3*d* occupancy and renormalizes optical gaps [50]; C₆₀ on Fe₃O₄(001), altering Fe₂₊/Fe₃₊ ratios and inducing spin-polarized molecular states [51], whereas on CoO(001) it enhances Co–O–Co exchange interactions and boosts exchange bias fields elevating blocking temperatures above 420 K [24]; CoPc molecules on CoO(111), where adsorption induces charge donation at the interface and enhances the molecular spin moment, evidencing a direct magnetic interaction with the oxide surface [52]; FePc molecules on MnO/TiO_x films, demonstrating how the electronic structure of the oxide substrate strongly affects molecule-oxide hybridization and adsorption properties [53]; copper(II) meso-tetrakis(4-carboxyphenyl)porphyrin (Cu-TCPP) molecules on NiO(001), where a net hole transfer from the macrocycle to the NiO valence band highlights substantial interfacial charge redistribution [54]; Co-5,15-diphenylporphyrin (Co-DPP) molecules on ultrathin CoO(111) layers, forming ordered assemblies that remain largely electronically decoupled from the oxide lattice [55]; and free-base 5,10,15,20-tetrakis(p-cyanophenyl)porphyrin (2H-TCNPP), which thermally self-metalates on CoO surfaces to form Co-porphyrins bound to the substrate and introduces in-gap frontier orbitals in the oxide electronic structure [56].

Generally, these studies have mainly addressed interfacial charge transfer, spin polarization, or macroscopic magnetic effects. A detailed microscopic picture of how molecular adsorption modifies the TM–O–TM superexchange pathways in three-dimensional (3D) antiferromagnetic oxides—particularly at the level of orbital-resolved electronic redistribution—has remained largely missing. Bridging this gap is necessary to establish predictive strategies for exchange engineering at organic/AFM-oxide interfaces. (A notable exception is a study of the mechanisms for donor/acceptor molecules modulating magnetic exchange in 2D CrSBr monolayers via combined charge transfer and bond-angle distortions [42].)

To address this fundamental question, we systematically investigate C₆₀ and cobalt tetraphenylporphyrin (CoTPP) [57] on NiO(001) and CoO(001) surfaces. These systems are not arbitrary choices but represent prototypical platforms in molecular spintronics and oxide magnetism. C₆₀ is one of the most extensively studied molecules in spin-interface research, serving as a benchmark acceptor system at both metallic and insulating interfaces [23,24,58–60]. Metal-tetraphenylporphyrins constitute a paradigmatic class of functional molecules used to engineer magnetic and electronic properties at surfaces [19,28–32,61,62]. On the inorganic side, NiO and CoO are canonical antiferromagnetic transition-metal oxides, long-standing model systems for superexchange interactions, exchange bias, and surface magnetism [24,62–69]. The combination of these prototypical molecular and oxide components provides an ideal testbed to extract general microscopic mechanisms governing molecule-induced modifications of superexchange. For these systems, we determine (i) stable adsorption configurations and adsorption energies, (ii) electronic properties including studying the charge transfer and electronic structures, (iii) the

orbital-specific occupancy changes in Ni/Co 3*d* and O 2*p* states, and (iv) resultant modification in the magnetic couplings *J*. We aim to identify transferable orbital-level trends linking interfacial charge redistribution to changes in magnetic exchange. Rather than focusing on system-specific effects, our objective is to elucidate general principles for orbital-driven engineering of superexchange at organic/antiferromagnetic-oxide interfaces, beyond prior phenomenological reports [54–56,70].

II. COMPUTATIONAL DETAILS

Based on density functional theory (DFT), we performed first-principles calculations using the QUANTUM ESPRESSO code (v7.2) [71,72] to study the equilibrium adsorption structures, electronic, and magnetic properties of the (001) surface of NiO and CoO crystals upon CoTPP or C₆₀ molecule adsorption. The numerical framework is the same as in our previous studies for C₆₀/CoO(001) [24] and CoTPP/NiO(001) [62]. The main aspects are summarized here. We consider van der Waals dispersion corrections between molecules and substrates, using the vdW-DF-C09 exchange and correlation functional [73]. The on-site correlation effects of the *d* orbitals of Ni and Co atoms are described through an effective Hubbard *U* of 4.0 eV [74] for the 3*d* orbitals. Also for the CoTPP molecule, a Hubbard *U* = 3 eV parameter was applied to the Co atom, as described in Refs. [75–77]. The ultrasoft pseudopotentials, generated starting from scalar-relativistic all-electron calculations and including non-linear core corrections, have been considered with a plane-wave cutoff of 45 Ry for the wave functions and of 270 Ry for the charge density. The calculated lattice constants of bulk NiO and CoO crystals are 4.168 and 4.256 Å, respectively, which are very close to the experimental values (4.17 Å for NiO [78] and 4.26 Å for CoO [79]). We considered slabs with three layers of NiO(001) or CoO(001) to perform structural relaxations and to select the most stable adsorption configuration. The molecules and the topmost surface layer of each slab were fully relaxed until the forces reached a maximum of 0.001 Ry/Bohr, while the other layers were fixed to their bulk positions. The electronic and magnetic properties of the stable adsorption configurations were subsequently calculated using a thicker slab with five atomic layers. For all the adsorbed structures, we included a vacuum space of about 12 Å. Input and output files of the most stable configurations studied are available online, together with the adopted pseudopotentials [80].

We adopt a simplified Heisenberg model involving the metal atoms of the surface coupled through superexchange (TM–O–TM) interactions that represent the strongest among the TM–TM interactions [81,82]. This is described by the Hamiltonian $H = -J \sum_{i<j} \hat{S}_i \hat{S}_j$, where $\hat{S}_i = \pm 1$ indicates the direction of the spin of metal atom *i* and the sum runs over unique next-nearest-neighbor pairs. In a broken-symmetry approach, we perform total energy calculations where one metal spin is flipped at a time, reversing the sign of four in-plane and one out-of-plane superexchange interaction: correspondingly, *J* is evaluated as $-1/10$ the total energy difference from the ground state, $J = -\Delta E_{\text{tot}}/10$. We then average the results across the surface atoms.

Since we adopt two different surface supercells for the adsorption of the two molecules (see Sec. III below), we checked that the obtained value of J for the clean surface does not depend (within 1 meV) on the surface periodicity adopted. We further remark that, for consistency with the previous studies, the surface Brillouin zone was sampled by a 4×4 and 1×1 Monkhorst-Pack [83] k -point mesh for the (4×2) and $\begin{pmatrix} 2 & 2 \\ -1 & 4 \end{pmatrix}$ unit cells used for C_{60} and CoTPP adsorption, respectively. However, we checked that resulting J values are not affected by this choice, as variations in CoTPP results are no larger than 1 meV upon increasing the k -mesh to 4×4 . Additionally, we also verified independence of the results upon lowering the plane wave cutoffs for wavefunctions and charge density to 40 Ry and 200 Ry, respectively. The robustness of the extracted exchange parameters was further assessed with respect to slab thickness by analyzing thicker slabs of clean NiO(001) consisting of 7, 9, and 12 atomic layers: the value of J , obtained from a surface spin flip, changes by less than 1 meV across all cases.

We remark that beyond numerical convergence, these meV-scale values depend moderately on the chosen simulation protocol (pseudopotentials, exchange-correlation functional, value of the Hubbard correction U), as discussed in the Supplemental Material Sec. S6 [84]. In particular, we observed in our tests variations of the absolute values of J of the order of 10% for NiO(001). Most importantly, such dependence is expected to cancel out when comparing the clean surfaces and the adsorbed systems, as suggested by test calculations for $C_{60}/\text{NiO}(001)$ where we varied U by ± 1 eV: these showed J variations of ± 4 meV, but adsorption induced modifications (adsorbed – clean) affected by only ~ 0.1 meV. In the context of the present work, which focuses on identifying consistent trends and underlying physical mechanisms rather than on a strictly quantitative determination of J , these variations, quantified for the NiO(001) reference system, are not expected to modify the overall physical interpretation.

III. RESULTS AND DISCUSSION

A. Adsorption configurations

To identify adsorption geometries on which to study the electronic and magnetic properties, we follow different strategies for CoTPP and C_{60} molecules. In all cases, the adsorption energy is evaluated as $E_{\text{ads}} = E_{\text{molecule/surface}}^{\text{tot}} - E_{\text{molecule}}^{\text{tot}} - E_{\text{surface}}^{\text{tot}}$, where E^{tot} indicates the total energy of the corresponding system.

For CoTPP, we can exploit the recent experimental (diffraction and microscopy) and theoretical study of CoTPP/NiO(001) [62]. There, molecules form a $p(2\sqrt{5} \times 2\sqrt{5})R26.6^\circ$ superstructure of the (001) surface, that corresponds to a $\begin{pmatrix} 4 & 2 \\ -2 & 4 \end{pmatrix}$ epitaxy matrix in terms of the 1×1 Ni square lattice with 20 atoms. More properly, considering the alternated magnetization of the surface Ni atoms, the clean surface unit cell is a 2×1 rectangle, in terms of which the epitaxy matrix of the molecular overlayer can be expressed as $\begin{pmatrix} 2 & 2 \\ -1 & 4 \end{pmatrix}$. Four initial adsorption structures are studied, differing in adsorption site (O or Ni) and in the angle formed between N-Co-N axis and [100] (0° and 36°),

TABLE I. Characteristics of most stable adsorption configurations. Height of molecules over the TMO surfaces (Δz), defined as the difference in vertical coordinate between the lowest C atom of C_{60} or the Co atom in CoTPP, and the TMO topmost layer. Adsorption energy (E_{ads}), charge transfer ΔN_e , and variation in Löwdin charges ΔQ , per TMO formula unit in the surface layer. Positive values represent the flow of electrons from the molecule to the interface.

	Δz (Å)	E_{ads} (eV)	ΔN_e (e^-)/ TMO (e^-)	$\Delta Q/\text{TMO}$ (e^-)
C_{60}/NiO	2.47	−1.83	0.0073	0.030
CoTPP/NiO	3.00	−5.00	0.0170	0.055
C_{60}/CoO	2.71	−2.16	0.0084	0.030
CoTPP/CoO	3.19	−4.82	0.0170	0.057

and hence named as $R0^\circ @ O$, $R36^\circ @ O$, $R0^\circ @ \text{Ni}$, $R36^\circ @ \text{Ni}$. As an additional degree of freedom, the spin polarization of the Co atom in the molecule can be set parallel or antiparallel to that of Ni underneath (in case of $@ O$ configurations, this is a Ni in the second surface layer). Out of those eight cases, the most stable was identified as $R^\circ @ \text{Ni}$ with antiparallel spins [62], with $E_{\text{ads}} = -5.00$ eV. Considering the similar lattice constant of the NiO and CoO substrates, we assume the same superstructure periodicity and evaluate the adsorption energy for the eight cases. The results of the various cases are reported in Table S2 [84] and confirm the same adsorption site as on NiO: $R0^\circ @ \text{Co}$ with antiparallel molecule-substrate spins and $E_{\text{ads}} = -4.82$ eV.

For C_{60} , we build upon a previous study for $C_{60}/\text{CoO}(001)$ [24]. There, no experimental information on the adsorption superstructure was given whereas simulations investigated a total of ten different adsorption configurations (depending on site and angles) in a 4×4 square surface unit cell [more properly, $p(4 \times 2)$ in terms of the magnetic supercell] that allows C_{60} to rotate. This identified C_{60} with an hexagonal face adsorbed on an oxygen atom as the most stable configuration, for which we computed $E_{\text{ads}} = -2.16$ eV. To discuss $C_{60}/\text{NiO}(001)$, we perform the structural optimization of the same structures, finding again the hexagon/oxygen as the most stable case with $E_{\text{ads}} = -1.83$ eV. The results of the other cases are reported in Table S1 [84].

We hereby focus on the four most energetically stable configurations that will be named for simplicity just C_{60}/NiO , CoTPP/NiO, C_{60}/CoO , and CoTPP/CoO. The structures are reported in Fig. 1 for the NiO(001) substrate: Adsorption on the CoO(001) substrate results in very similar configurations and is shown in Fig. S1 [84]. Their adsorption energy E_{ads} and distance from the surface (Δz) is given in Table I. Besides structures (see in particular the distance Δz), also the adsorption energies of C_{60} (CoTPP) on NiO(001) and CoO(001) surfaces are very similar, suggesting similar adsorption properties.

We note that two of the four molecule–substrate combinations considered here [$C_{60}/\text{CoO}(001)$ and CoTPP/NiO(001)] have been previously investigated in combined experimental and theoretical studies (Refs. [24,62]). In particular, for CoTPP/NiO(001), diffraction and microscopy measure-

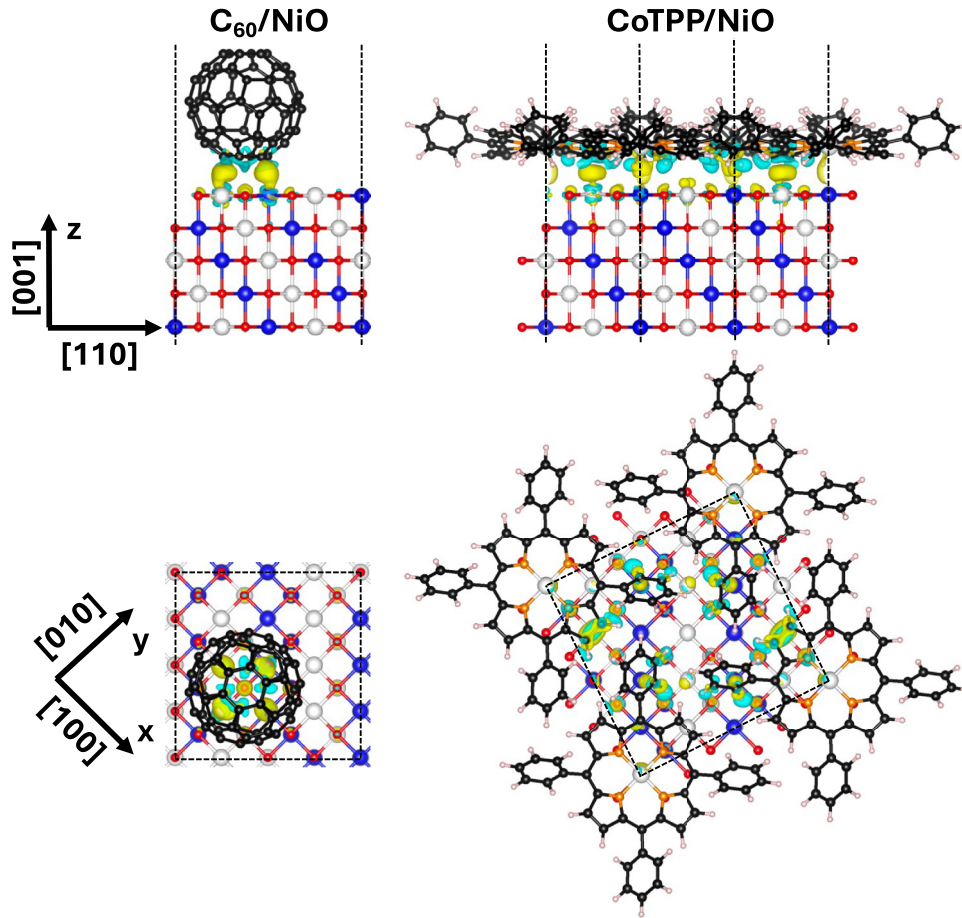


FIG. 1. The most stable adsorption structures of C_{60} and CoTPP molecules adsorbing on the $\text{NiO}(001)$ surface, $\text{CoO}(001)$ case being very similar (see the Supplemental Material Fig. S1 [84]). Spheres in black, blue, orange, pink, red color stand for C, Ni, N, H and O atoms. Spheres in white color stand for Ni atoms in the surface slabs with opposite orientation of their magnetic moments. The figure also shows electron density variation upon adsorption, $\Delta\rho$ (definition within the text). Yellow and green color indicates electron density increase and decrease, with an isovalue of $0.01 \text{ e}/\text{\AA}^3$.

ments provided the adsorption geometry and surface unit cell employed in the present simulations. For $\text{C}_{60}/\text{CoO}(001)$, the experimentally observed magnetic hardening has been associated with an increase in the computed exchange couplings. These benchmarks support the reliability of the adopted structural models and computational description, while possible deviations from ideality in real systems are not expected to qualitatively alter the physical picture discussed below.

B. Electronic properties

To discuss the interface charge modification upon adsorption, the electron density difference for the four stable adsorption structures was calculated following $\Delta\rho = \rho_{\text{molecule/surface}} - \rho_{\text{molecule}} - \rho_{\text{surface}}$, where $\rho_{\text{molecule/surface}}$ is the total electron density of the adsorbed structures, and ρ_{molecule} and ρ_{surface} those of the molecule and free surface, respectively, frozen at the optimized coordinates of the full system.

The results, reported in Fig. 1, indicate that electron density accumulates at the interface region. This is also evident by a planar integral of the charge density difference, as reported in the Supplemental Material (Fig. S5) [84], showing

a polarization of the molecular charge toward the surface: the integral $\int \Delta\rho(x, y, z) dx dy$ as a function of z is used to quantify the electron transfer across a plane at height z . This procedure indicates that around $0.008 \text{ e}^-/\text{TMO}$ in the surface layer ($0.125 \text{ e}^-/\text{molecule}$) accumulate at the interface in the presence of C_{60} , and twice as much, $0.017 \text{ e}^-/\text{TMO}$ for CoTPP ($0.340 \text{ e}^-/\text{molecule}$). These values represent interfacial charge polarization rather than a net molecular charging, which would neither be expected for a type-II interface with the molecular LUMO within the substrate gap (see below); indeed, Bader charge analysis results in nearly vanishing charge transfers ($<0.01 \text{ e}^-$) and is unable to capture the subtleties of the electron density redistribution at the interface, especially when different orbitals at the same atom are involved. In Table I, we further give the variation in Löwdin charges (ΔQ) on the first substrate layer, amounting to about 0.03 e^- per TMO formula unit on both surfaces for C_{60} , and to about twice as much, 0.06 e^- per TMO formula unit, for CoTPP. The calculated adsorption energies and the values of ΔQ indicate that the CoTPP rather than C_{60} molecule has a much larger interaction with the TMO (001) surfaces.

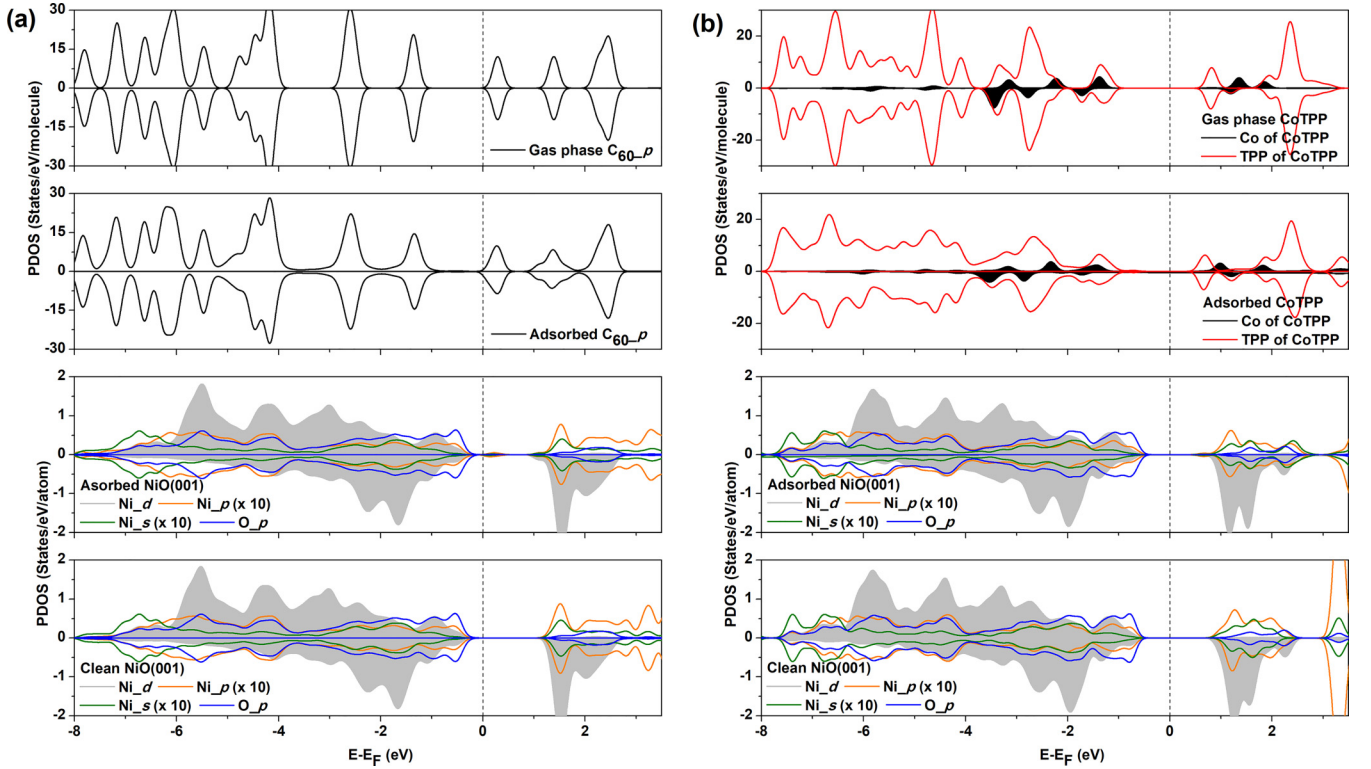


FIG. 2. Projected density of states (PDOS) for (a) $C_{60}/\text{NiO}(001)$ and (b) $\text{CoTPP}/\text{NiO}(001)$. On both sides, from top to bottom: gas phase molecule, molecule in the adsorbed configuration, substrate in the adsorbed configuration, and clean substrate. The minority-spin PDOS is plotted inverted for clarity. The $\times 10$ label denotes a tenfold intensity scaling for selected features.

The projected density of states (PDOS) of the adsorbed systems is compared with the one of the pristine components (clean substrates and free molecules) in Figs. 2(a) and 2(b) for C_{60} and CoTPP on NiO(001). The case of CoO(001) is reported in the Supplemental Material (Fig. S2) [84]. Given the arbitrary position of the Fermi energy within the energy gap for nonmetallic systems, we align deep states. For the transition metal atoms in the substrate, we report only the average of those with positive magnetic moments (the other case being reversed, with differences that are not appreciable on the scale of the plot). The electronic structure of the two surfaces is weakly influenced by the molecular adsorption. Note there is a small reduction of the conduction-valence gaps of the substrate-projected states and a spin asymmetry at Fermi surface with the minority d orbitals majorly contributing. For the full systems, the valence band maximum (VBM) in their PDOS is of a substrate nature (hybridizing the $O-2p$ and TMO- $3d$ orbitals), while the conduction band maximum (CBM) is of molecular LUMO nature. The HOMO and LUMO orbitals show minor effects, as broadening and shifting. In detail, the HOMO of CoTPP hybridizes with the Co surface atom, while the LUMO preserves its TPP nature. The effects on C_{60} are less remarkable. In all cases, the LUMO states of the two molecules lie in the energy gap of the substrates, forming a type-II interface further reducing the VBM-CBM gap of the substrate. We also compute a small acquisition of spin-polarized character in C_{60} ($0.004 \mu_B$ and $0.018 \mu_B$ for NiO and CoO) and a little change in the spin polarization of CoTPP (whose absolute value increases by $0.040 \mu_B$ and $0.033 \mu_B$). Correspondingly, the magnetic moment

of the substrate atoms also vary; we obtain a small decrease, on average, of the TM spin polarization, from $1.555 \mu_B$ and $2.603 \mu_B$ for clean NiO(001) and CoO(001) surface atoms, to, respectively $1.539 \mu_B$ and $2.597 \mu_B$ in the case of C_{60} adsorption and to $1.528 \mu_B$ and $2.569 \mu_B$ in the case of CoTPP.

C. Magnetic properties

We evaluate the exchange couplings J by reversing the magnetic moment at each symmetry-nonequivalent surface atom (see Sec. II) and by performing a weighted average (where multiplicity is taken into account). By comparing with the corresponding J value we evaluate for the clean surface, we could thus obtain the change in exchange coupling parameters between TM atoms on TMO(001) surface before and after adsorbing C_{60} and CoTPP molecules. The J values for the clean surfaces and with the molecules are shown in Table II. The calculated average value of J for Co-Co coupling on the CoO(001) surface is -21 meV, which strengthens to -27 meV after C_{60} adsorption [24] and to

TABLE II. Exchange coupling J between the next nearest TM atoms before and after adsorbing C_{60} or CoTPP molecules. Values in meV.

	Clean TMO(001)	C_{60}	CoTPP
NiO(001)	-30	-31	-32
CoO(001)	-21	-27	-30

–30 meV after CoTPP molecule adsorption. For the NiO(001) surface, the calculated J for Ni-Ni coupling is –30 meV for the clean surface, in good agreement with the value of –24 meV from a previous calculation [85], which enhances slightly to –31 meV after C_{60} adsorption and to –32 meV after CoTPP molecule adsorption. Overall, the enhancement of the exchange coupling is more pronounced for CoO(001) than for NiO(001). In particular, a more pronounced effect of CoTPP compared with C_{60} is observed for CoO(001). This effect is not due to the presence of the metallic center in the first molecule: Indeed, this major effect of CoTPP on the substrate couplings of CoO(001) is still present also when excluding the metallic center contribution from the average over the substrate couplings, obtaining –29 meV in that case.

Although the absolute variations of the exchange coupling range from 1–2 meV for NiO(001) to 6–9 meV for CoO(001) are apparently small (significantly exceeding the estimated computational accuracy from convergence tests reported in Sec. II), their physical relevance should be evaluated in relation to the surface exchange energy scale itself ($|J| \approx 21$ –30 meV) and to typical magnon energies in antiferromagnetic transition-metal oxides. In particular, for CoO(001) the enhancement from –21 meV to –30 meV corresponds to an increase of approximately 40% in the magnitude of the surface exchange interaction (several meV in zone-boundary magnon energies within linear spin-wave theory [86], $\omega \approx zJS$). Such variations are therefore not negligible, especially in the context of interfacial and surface-sensitive magnetic phenomena. Consistently, in the case of C_{60} /CoO(001), the computed enhancement of exchange interactions has been experimentally correlated with sizable increases in blocking temperature, exchange bias field, and coercivity [24]. These observations support the physical significance of molecule-induced exchange tuning at AFM-oxide surfaces.

We now focus on the understanding of the variations observed in the magnitude of magnetic couplings ($\Delta|J|$). It is worth noticing first that one cannot relate the enhancement of J to variations in the TM magnetic moments as these are in fact slightly reduced, as discussed in Sec. III B. We have computed the PDOS projected onto the exchange-relevant d orbitals in the surface layer (Fig. S6 [84]). However, adsorption-induced PDOS variations are subtle and spread over a broad energy window. Instead, we look in detail at the integrated orbital occupations which provide a more sensitive and quantitative measure of the underlying charge redistribution. In particular, we analyze the redistribution of electronic occupation among the TM d orbitals participating in the TM–O–TM superexchange pathway. A schematic representation of the relevant orbital orientations relative to the exchange geometry is shown in Fig. 3. In the chosen surface orientation, the in-plane $d_{x^2-y^2}$ orbitals are aligned along the TM–O–TM direction, whereas the d_{xy} orbitals are oriented at 45° with respect to it. Among the out-of-plane states, the d_{z^2} orbital has significant σ -type overlap along the surface normal, while the (d_{xz}, d_{yz}) pair contributes to π -type hopping channels involving oxygen p states.

We first consider the in-plane manifold. Here, spin-majority orbitals are completely filled and their variations amount to less than $0.001 e^-$, so only the average

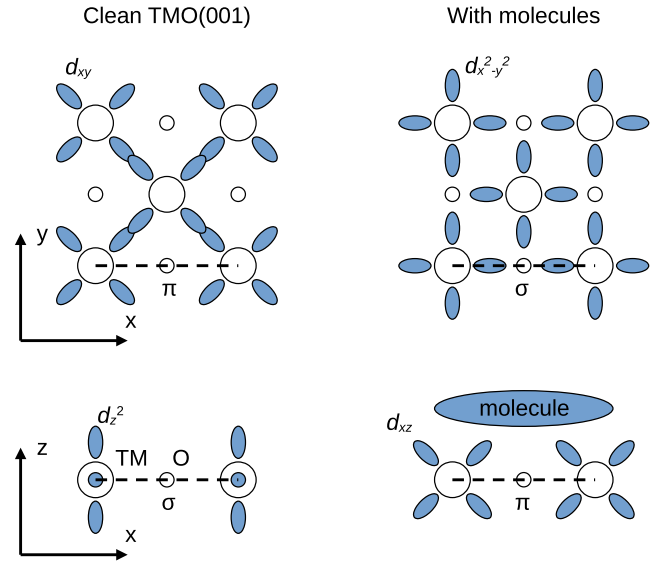


FIG. 3. Schematic of the TM–O–TM superexchange pathway at the TMO(001) surface. Left: Clean surface with in-plane π (top panel) and out-of-plane σ (bottom panel) hopping channels. Right: molecular adsorption redistributes charge among exchange-active d orbitals, enhancing hopping along the TM–O–TM and TM–molecule–TM pathways and strengthening the surface exchange especially for CoO.

spin-minority variations are given in Table III. The enhancement of $|J|$ correlates with a small but systematic increase in the occupation of $d_{x^2-y^2}$ orbitals and a concomitant reduction in d_{xy} occupation. Because the $d_{x^2-y^2}$ orbitals are geometrically aligned with the TM–O–TM direction, they maximize overlap with the intervening O $2p$ states and directly contribute to the dominant hopping amplitude mediating superexchange. In contrast, d_{xy} orbitals are less efficiently aligned with this pathway. A redistribution of charge toward $d_{x^2-y^2}$ therefore favors an increase in the effective TM–O–TM hopping parameter, which in turn influences J to the second power [87].

A complementary trend emerges in the out-of-plane manifold (Table IV). In particular, for CoO(001), where the largest enhancement of $|J|$ is observed, electrons are partially depleted from d_{z^2} and accumulate in the (d_{xz}, d_{yz}) pair. This redistribution is consistent with a modification of the available hopping channels involving oxygen p orbitals further promoting charge alignment along directions that efficiently

TABLE III. $\Delta|J|$: Average change in exchange coupling between the next-nearest Ni (Co) atoms on the first layer of NiO (CoO) (001). TM- $d_{x^2-y^2}$ and TM- d_{xy} : changes in the occupation of spin-minority $d_{x^2-y^2}$ and d_{xy} orbitals in surface TM atoms upon adsorption.

	$\Delta J $ (meV)	TM- $d_{x^2-y^2}$	TM- d_{xy}
C_{60} /NiO	1	0.0013	–0.0003
CoTPP/NiO	2	0.0011	–0.0003
C_{60} /CoO	6	0.0023	–0.0222
CoTPP/CoO	9	0.0027	–0.0250

TABLE IV. TM_ d_{z^2} , TM_ $d_{xz} + d_{yz}$: Average occupation change per TM atom on specified orbitals upon adsorption. TM_ $d_{z^2} + d_{xz} + d_{yz}$: their sum.

	TM_ d_{z^2}	TM_ $d_{xz} + d_{yz}$	TM_ $d_{z^2} + d_{xz} + d_{yz}$
C ₆₀ /NiO	0.0096	-0.0028	0.0069
CoTPP/NiO	0.0120	-0.0035	0.0084
C ₆₀ /CoO	-0.0001	0.0235	0.0234
CoTPP/CoO	-0.0039	0.0341	0.0302

mediate TM–O–TM superexchange, and potentially also enabling exchange pathways through hybrid interface states [40]. Although the absolute occupation changes are small, of the order of a few hundredths of an electron per orbital, they are systematic and correlate with the magnitude of $\Delta|J|$ across the investigated systems.

Overall, the results indicate a directional reshuffling of electronic charge within the TM d manifold: molecular adsorption induces a redistribution toward orbitals that are geometrically aligned with the TM–O–TM and TM–molecule–TM superexchange pathway. This reorganization enhances the effective oxygen-mediated hopping processes and consistently strengthens the surface exchange interaction. The effect is particularly pronounced for CoO(001), explaining the larger exchange enhancement compared to NiO(001).

Further charge analysis shows that the redistributed charge at the interface accumulates mainly on the first layer of TMO, more precisely on the $4p$ orbitals of TM atoms (Table V). Although these channels account for a large fraction of the charge rearrangement, their variations do not display a direct mechanistic relation with the exchange enhancement comparable to that identified for the d -orbital occupations discussed above. We therefore report them mainly for completeness, as they provide a broader description of the interfacial charge redistribution. In addition, part of the transferred charge originates from O $2p$ states, whose occupation correspondingly decreases. We observe that across the four interfaces, the increase in $\Delta|J|$ tends to correlate with the net electron flow from the O $2p$ orbitals toward the transition-metal centers, and ultimately into the exchange-active d orbitals. While these trends are consistent with the mechanism described above, they should be regarded as correlational indicators, whereas the d -orbital descriptors provide the most direct connection to the microscopic origin of the exchange enhancement. The contribution of the p orbitals of the TM atoms is further decomposed into the different axes and spin components in Table VI. Accordingly, we observe that all three p channels of TM atoms grow with $\Delta|J|$, although the correlation is weaker than that observed for the d -orbital descriptors from

Tables III and IV. It is, however, interesting to note that the p_z carries $\approx 60\%$ of the transferred p charge, whereas p_x and p_y share the remainder almost equally, which is qualitatively consistent with the relevance of the π -type channels discussed above. Finally, unlike the nearly filled d orbitals, the p states exhibit appreciable changes in both minority and majority spin components.

Summarizing the results of the above analysis, the rise of $\Delta|J|$ is consistently linked to a directional reshuffle of electrons within the TM center. Electron density from the molecule and O atoms accumulates mostly in TM p , and a small but decisive fraction migrates to and within the TM d orbitals. In the plane, $\Delta|J|$ grows when d_{xy} is depopulated and $d_{x^2-y^2}$ is slightly filled; out of plane, the strongest enhancement occurs on CoO, where d_{z^2} is emptied and the $(d_{xz} + d_{yz})$ pair gains electrons. Thus in-plane σ -channel filling plus π -channel depletion and out-of-plane π -channel filling plus σ -channel depletion widen O-mediated superexchange paths, while the p -shell acts mainly as a charge reservoir. This unified picture explains the modest $\Delta|J|$ gain on NiO (1 to 2 meV) versus the much larger increase on CoO (6 meV to 9 meV) and suggests a roadmap: engineer strain or ligands that favor in-plane σ population and π depopulation and out of plane π population and σ depopulation, to maximize exchange.

IV. CONCLUSIONS

Through *ab initio* DFT+ U calculations, we have investigated how molecular adsorption modifies the surface superexchange interactions of NiO(001) and CoO(001). By mapping total-energy differences onto an effective Heisenberg Hamiltonian, we quantified the exchange coupling between transition-metal atoms before and after adsorption of C₆₀ and CoTPP molecules. For the clean surfaces, we obtain $J \approx -30$ meV for NiO(001) and $J \approx -21$ meV for CoO(001). Molecular adsorption strengthens the exchange interaction in all cases, with enhancements up to 9 meV for CoO(001), corresponding to an increase of approximately 40% in the surface exchange magnitude. The effect is more pronounced for CoO than for NiO, reflecting a stronger interfacial orbital redistribution. The enhancement of $|J|$ correlates with a directional reshaping of the transition-metal d -orbital occupations: molecular adsorption induces a redistribution of charge toward orbitals geometrically aligned with the TM–O–TM exchange pathway, thereby increasing the effective hopping amplitude that mediates superexchange. Although the occupation changes are small in absolute value, their systematic character across chemically distinct molecules and oxides

TABLE V. Average variations in atomic orbital occupations upon adsorption, summed over the surface TMO layer (as in Table I), TM atoms, this one decomposed into $d/s/p$ states, and O atoms.

	TMO	TM	TM_ d	TM_ s	TM_ p	O
C ₆₀ /NiO	0.0301	0.0352	0.0033	-0.0008	0.0326	-0.0051
CoTPP/NiO	0.0555	0.0643	0.0056	-0.0004	0.0590	-0.0088
C ₆₀ /CoO	0.0300	0.0326	-0.0001	0.0005	0.0322	-0.0026
CoTPP/CoO	0.0570	0.0661	0.0078	0.0003	0.0580	-0.0090

TABLE VI. Average variations in the occupations of TM_ p orbitals upon adsorption, averaged among first-layer atoms, resolving out-of-plane (TM_ p_z) and in-plane (TM_ $p_x + p_y$) states and spin orientation (minority/majority according to the direction of the magnetic moment of each TM atom).

	TM_ p_z _min	TM_ p_z _maj	TM_ $p_x + p_y$ _min	TM_ $p_x + p_y$ _maj
C ₆₀ /NiO	0.0121	0.0102	0.0049	0.0055
CoTPP/NiO	0.0199	0.0174	0.0103	0.0129
C ₆₀ /CoO	0.0102	0.0105	0.0058	0.0057
CoTPP/CoO	0.0168	0.0174	0.0123	0.0115

supports a consistent orbital-level mechanism. The meV-scale but relatively large enhancement of surface exchange interactions indicates that orbital-driven interfacial engineering may provide a viable route for tuning magnetic exchange at antiferromagnetic oxide surfaces. More generally, our results offer a microscopic perspective on how molecular adsorption may influence super-xchange in AFM transition-metal oxides, contributing to the understanding of exchange control at organic/oxide interfaces.

ACKNOWLEDGMENTS

This work was supported by the European Union's Horizon 2020 Research and Innovation program under Grant Agreement No. 964396 FET-Open SINFONIA (Selectively

activated INFORMATION technology by hybrid Organic Interfaces). We acknowledge ISCRA for awarding this project access to the LEONARDO supercomputer, owned by the EuroHPC Joint Undertaking, hosted by CINECA (Italy).

S.M. performed the calculations and the numerical analysis, assisted by M.M. and G.F., and drafted the manuscript. M.M. contributed analysis tools. G.F. conceptualized the study. All authors elaborated the theoretical interpretation of numerical results and reviewed and edited the manuscript.

DATA AVAILABILITY

The data that support the findings of this article are openly available [80]; embargo periods may apply.

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