Electronic properties of transition metal atoms on Cu$_2$N/Cu(100)

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We study the nature of spin excitations of individual transition metal atoms (Ti, V, Cr, Mn, Fe, Co and Ni) deposited on a Cu$_2$N/Cu(100) surface using both spin-polarized density functional theory (DFT) and exact diagonalization of an Anderson model derived from DFT. We use DFT to compare the structural, electronic and magnetic properties of different transition metal adatoms on the surface. We find that the average occupation of the transition metal $d$ shell, main contributor to the magnetic moment, is not quantized, in contrast with the quantized spin in the model Hamiltonians that successfully describe spin excitations in this system. In order to reconcile these two pictures, we build a multi-orbital Anderson Hamiltonian for the $d$ shell of the transition metal hybridized with the $p$ orbitals of the adjacent Nitrogen atoms, by means of maximally localized Wannier function representation of the DFT Hamiltonian. The exact solutions of this model have quantized total spin, without quantized charge at the $d$ shell. We propose that the quantized spin of the models actually belongs to many-body states with different charge configurations in the $d$ shell, hybridized with the $p$ orbital of the adjacent Nitrogen atoms. This scenario implies that the measured spin excitations are not fully localized at the transition metal.

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I. INTRODUCTION

The Cu(100) surface coated with a Cu$_2$N monolayer has turned out to be a remarkable system\textsuperscript{1,11} to probe and engineer the electronic properties of individual transition metal atoms using scanning tunneling microscopy (STM) and inelastic electron tunneling spectroscopy (IETS). A variety of breakthroughs have been reported on this system, such as the first measurement of the magnetic anisotropy of an individual quantized spin by means of IETS\textsuperscript{2} the demonstration of single atom spin torque\textsuperscript{2} the fabrication of nano engineered chains both with antiferromagnetism\textsuperscript{2} and ferromagnetism\textsuperscript{2} broken symmetry ground states, probed by means of spin-polarized STM, the measurement of spin excitations in spin chains with strong quantum fluctuations that prevent spin symmetry breaking\textsuperscript{18,19}, the measurement of single spin relaxation time by means of voltage pulse pump-probe technique\textsuperscript{20} the observation of renormalization of magnetic anisotropy due to Kondo exchange interactions\textsuperscript{21} and the imaging of spin wave modes with atomic scale resolution\textsuperscript{21}.

The system has been studied from the theoretical standpoint, using a variety of approaches\textsuperscript{21,23}. Importantly, both the spin excitation spectra of individual atoms\textsuperscript{2,13,14} and multi-atom structures\textsuperscript{1,4,7,9,11,13} as well as their spin relaxation dynamics have been successfully described using model Hamiltonians\textsuperscript{18,20} where quantized spins interact with each other via Heisenberg coupling\textsuperscript{1,11,18,20} and are Kondo coupled both to the tunneling electrons\textsuperscript{18,19} and to the substrate\textsuperscript{9,22,23}. Treating Kondo coupling up to second order in perturbation theory accounts for spin relaxation\textsuperscript{22,24} and magnetic anisotropy renormalization\textsuperscript{2,24}. Furthermore, calculations\textsuperscript{25,26} up to third order are also able to account for non-trivial IETS line shapes, including Kondo peaks. Numerical renormalization group non-perturbative calculations for the anisotropic spin Kondo model also provide very good description for both the finite energy spin excitations and the zero bias Kondo peak in these systems\textsuperscript{21,42,43}. The origin of the Kondo couplings in these systems can be traced down to a multi-orbital Anderson model for these $S > 1/2$ systems\textsuperscript{21,22} in line with the very well known results for the mapping\textsuperscript{14,26} of the single orbital Anderson model\textsuperscript{47} to the Kondo model.

In spite of the success of quantized spin Hamiltonians to describe many experiments of transition metals on Cu$_2$N, there is a problem of principle that we address in this paper. Density functional theory (DFT) calculations, most of them\textsuperscript{21,22,23,24} dealing with Ti, Mn, Fe and Co adatoms on Cu$_2$N/Cu(100), show that nor the charge, neither the magnetic moment of these magnetic atoms are quantized.

Here we provide a comprehensive and comparative study of the electronic and structural properties of the entire series of 3$d$ transition metals (Ti, V, Cr, Mn, Fe, Co and Ni). To the best of our knowledge, no DFT calculations have been reported for V and Ni on Cu$_2$N/Cu(100). Our calculations confirm the fractional nature of the average occupation of the $d$ levels in these systems, which is not surprising given their conducting nature, but it poses an apparent contradiction with the quantized spin model description. In the second part of the manuscript we provide a solution to this apparent conflict. We build a multi-orbital Anderson model, using as starting point the representation of the DFT Kohn-Sham Hamiltonian...
in a basis of maximally localized Wannier functions. The Anderson model includes spin-orbit interactions, crystal field interactions, on-site Coulomb repulsion and hybridization of the $d$ shell of the transition metal with its Nitrogen neighbors. We solve the model by exact numerical diagonalization within a restricted Hilbert space that includes both $d^n$ configurations with $d^{n+1}p^m$ configurations, where $n$ stands for the number of electrons in the $d$ shell and $m$ stands for the number of electrons in the Nitrogen $p$ orbitals. Our numerics show that the low energy excitations of the model can be mapped into quantized spin Hamiltonians. Within this picture, it is apparent that this quantized spin $S$ describes the quantum number of many-body wave functions that mix states with $n$ and $n+1$ electrons in the $d$ shell, and have thereby non-integer average occupation.

The paper is organized as follows. In Sec. II we describe DFT calculations for different TM atoms at Cu$_2$N paying particular attention to the structural properties, electronic properties and magnetic properties. In Sec. III we build the multi-orbital Anderson model, using as starting point the DFT calculations and we analyze the connection with the Spin Models. Finally, Sec. IV contains a summary and a discussion our most important findings.

II. DENSITY FUNCTIONAL CALCULATIONS

A. Methods

Most of our DFT calculations of 3$d$ transition metal adatoms adsorbed on Cu$_2$N/Cu(100) were done using the generalized-gradient approximation (GGA) and GGA+U for exchange-correlation energy sets and Projector Augmented-Wave (PAW) as implemented in QUANTUM ESPRESSO (QE) code. Additionally, in some particular cases we have performed complementary calculations using Local Spin Density Approximation (LSDA) for exchange-correlation energy, using all-electron full-potential linearised augmented-plane wave (FP-LAPW) as implemented in ELK.

In order to test the size convergence, we have used two super cells with different sizes. Both cells have 4 slabs of Cu(100), separated by a vacuum region of 15 Å. The smaller cell has 37 atoms (1 TM, 4 N and 32 Cu) and a bigger supercell, has 82 atoms (1 TM, 9 N and 72 Cu). The corresponding structures are shown in Fig. 1. In the smallest structure, the intercell distance between TM atoms along the N direction is 7.2 Å, while in the bigger one this distance is 10.8 Å.

QE calculations are done in two stages, structural relaxation and electronic structure calculation. In the relaxation stage, the mesh in $k$ space for the small and big cells were $6 \times 6 \times 1$ and $4 \times 4 \times 1$ respectively. In both cases the relaxation was performed until the forces acting on atoms were smaller than $10^{-3} \text{a.u.}$. In the second stage, the meshes used were $8 \times 8 \times 1$ for the small supercell and $6 \times 6 \times 1$ for the big one. In all the calculations we used a smearing with a broadening parameter of $0.01 - 0.02 \text{Ry}$, in line with previous work, and we fixed the cutoff energies for the wave function and charge density at 40-80 Ry and 400-800 Ry respectively. For the Elk calculations, we started from the relaxed structures obtained with QE. In this case the mesh in $k$ space was $4 \times 4 \times 1$, the product of the muffin-tin radius and the momentum cutoff is $R_{MT} k_{max} = 6$ and we employed Local Spin Density Approximation (LSDA) for exchange-correlation and DFT+U with Yukawa screening.

In the case of Fe and Co we have also obtained the so called maximally localized Wannier functions (MLWF) associated to the Bloch states of the DFT calculation, using the package Wannier90. The Wannier functions form an orthogonal and complete basis set that we can use to describe our system. Importantly, the representation of the Kohn-Sham Hamiltonian in the DFT basis provides an effective tight-binding model to describe the electronic states of the system, that we use as a starting point to build a multi-orbital Anderson model, as described in Sec. III.

B. Structural properties

We now discuss the structural properties of a single 3$d$ TM atom bonded to the Cu site of the Cu$_2$N/Cu(100) surface. This is the binding site most frequently reported in the literature. In order to refer to the different TM atoms we shall use indistinctly their chemical formula (Ti, V, Cr, Mn, Fe, Co, Ni) or the nominal charge on the $d$ shell $g_d = 2, 3, 4, 5, 6, 7, 8$.

Cu$_2$N is known to form a weakly buckled square lattice on top of the Cu(100), consistent with our DFT calculations. In all cases considered, the adsorption of
FIG. 2. (Color online) Schematic diagram of the Cu$_2$N (Cu atoms in brown, N atoms in blue) surface with the TM atom (green). $d_N$ is the distance from the TM atom to the nearest neighbors N atoms, $d_{Cu}$ refers to the distance from the TM atom to the Cu atom lying just below the magnetic atom, $\theta$ is the angle formed by the N-TM-N trimer and the red arrow shows the position of the Cu atom used to define the surface.

the TM introduces a local distortion on the Cu$_2$N lattice, shown in Fig. 2 the underneath Cu atom is pushed towards the bulk, and the N atoms are pulled out. These results are in line with previous works.$^{21,33,59}$ In order to characterize this structural distortion, we introduce 3 distances: the TM-N distance ($d_N$), the TM-Cu distance ($d_{Cu}$) and the TM-surface vertical displacement, $z$, that we take as the $z$ component of the vector that joins the TM with the farthest Cu surface atom, marked with an arrow in Fig. 2. In addition we also introduce the angle formed by the N-TM-N trimer ($\theta$).

Our calculations, performed both for the small and large supercell (see Fig. 1) show how these structural values are similar for different TM atoms, but with clear and systematic variations as a function of the number of $d$ electrons. Whereas both the TM-N and the TM-Cu distances undergo minor variations across the TM series, the $\theta$ angle has a much more marked change, going from structures where the TM is clearly a protrusion and the N atoms are weakly detached from surface, for small $q_d$, to structures where TM is almost collinear with the N atoms, for Co and Ni. The tendency to form collinear N-TM-N structures is particularly clear in the case of Co and Ni chains (small cells). In the case of Co, the marked difference between the small and big cells suggests that there is a cooperative distortion in the case of Cobalt chains along the N direction also visible for Ni, and clearly absent in the case of the lighter TM, such as Fe, for which these chains have been studied experimentally.$^{22}$

C. Electronic Properties

We now discuss the electronic properties of the adsorbed TM on the Cu site of Cu$_2$N/Cu(100). Our calculations for the pristine surface show that the Cu and N atoms in the Cu$_2$N layer have charge $q_{Cu} = +0.2$ and $q_{N} = -0.4$. The adsorption of the TM atom results in a charge transfer mostly from the TM $s$ orbitals to the N ligands, increasing their negative charge. The TM atoms lose practically all the 4$s$-electrons. The outermost electrons are thereby in the $d$ shell.

A naive interpretation of the picture that arises from the use of quantized spin models to describe these systems would lead to conclude that the charge in the $d$ shell of the TM is quantized. Our calculations show that this is not the case. A hint of this can be already seen by inspection of the spin-resolved density of states projected over the $d$ orbitals of the adsorbed TM atoms, shown in Fig. 3 obtained with QE, for the small cell. For instance, the occupancy of the majority spins (left-panel) is not 5 for Ni and Co. The presence of very broad peaks indicates strong hybridization of some of the $d$ orbitals with the rest of the system, as we show below.

In Fig. 4 we show the integrated density of states up to the Fermi energy, that gives the occupation of the $d$-shell for the different TM atoms, using both GGA and GGA+$U$, for several values of $U$. The results are plotted together with the charge of the isolated atom. In all instances we find that the $d$ shell is more charged than in the free atom case.

The difference between the computed charge and isolated charge, $\Delta q$, is shown in the inset for $U = 0$ and $U = 5$eV. Expectedly, increasing $U$ reduces $\Delta q$. Interestingly, $\Delta q$ increases as we move away from half filling (the Mn atom). Varying $U$ does not yield large changes...
D. Magnetic Properties

We now discuss the evolution of the magnetic moments, $\mu$, of the series of 3d TM adsorbed atoms. In Fig. 6 we show the magnetic moment of the free atoms, $\mu_{\text{free}}$, as given by Hund’s. The largest free atom moment is $\mu = 5\mu_B$, for the half-filled shell (Mn) and goes down as we move away from half filling. The upper panel of Fig. 6 shows the GGA+U calculation of the magnetic moment of the TM atoms. With the only exception of Cr, the magnetic moment for the adsorbed TM is always smaller than the free atom case. The deviations become particularly severe as we move away from half filling. For instance, the magnetic moment of adsorbed Ni is half the value of the free atom case. In contrast with the case of $\Delta q$, the value of the magnetic moment depends more strongly on the value of $U$, yet, the atomic limit is only reached in the case of Cr for $U = 5\text{eV}$.

Whereas most of the spin is localized on the magnetic atoms, a substantial amount of the spin density is not located at the $d$-levels of the atom. Therefore, we also plot the cell magnetic moment and compared them with the free atom case (see Fig. 6b). It is apparent that, in the case of the cell moment, the deviations from the free case are very small for V, Cr, Mn and Fe. In the case of Ti and Ni, the deviation from the free case is still a factor of two. The overall trend is that, close to half-filling, the DFT results are closer to the free case.

Fig. 7 shows the Spin polarization of the different $d$ orbitals as a function of the TM atom. Whereas at half filling the magnetic moment has to be evenly distributed in the 5 $d$ orbitals, away from half filling this is no longer the case. The orbital composition of the magnetization is interesting because it affects the magnetic anisotropy
and because only one of the $d$ orbitals, the $d_z^2$, couples to the $s$ orbital of the last atom in STM tip. This results particularly interesting in the case of Ti, Co and Ni where we can appreciate that the $d_z^2$ orbital has a very small spin polarization. These calculations were performed for the small cell, then we should expect interesting features in STM experiments when dealing with Co and Ni chains.

The difference between the atomic and the cell magnetization, summarized in Table I implies that the surrounding atoms gain some magnetic moment as well. Our results, shown in Fig. 8 also show that their alignment with the N atoms can be both ferromagnetic (FM) or antiferromagnetic (AFM) depending on the TM. In particular, the correlation is AFM below half-filling and FM above half-filling. At half filling the results depend on the value of $U$. Below we provide an explanation to this sign, based on a multi-orbital Anderson model.

Finally, calculations for Co atoms were performed using ELK for different values of $U$ in order to check the magnetic properties obtained with QE. The results obtaining with both codes were in very good agreement.

| Atom | $d$-shell | TM atom | Cell | Free atom |
|------|-----------|---------|------|-----------|
| Ti   | 0.62      | 0.71    | 0.6  | 1         |
| V    | 1.32      | 1.45    | 1.41 | 1.5       |
| Cr   | 1.98      | 2.10    | 1.97 | 2         |
| Mn   | 2.25      | 2.36    | 2.47 | 2.5       |
| Fe   | 1.62      | 1.75    | 1.91 | 2         |
| Co   | 1.05      | 1.1     | 1.25 | 1.5       |
| Ni   | 0.46      | 0.47    | 0.57 | 1         |

TABLE I. DFT calculation of the spin polarization for ($U = 5$ eV).

FIG. 8. (Color online) GGA+$U$ calculation of the magnetic moment of the nearest neighbor N atom as a function of the TM atom, for different values of $U$.

III. CONNECTION WITH THE SPIN MODELS

The DFT results of the previous section clearly show that the charge and spin of the $d$ shells are not quantized. There is thus an apparent conflict between the DFT calculations and the use of spin Hamiltonian models with quantized spins [12,13]. In this section we address this important topic and provide a solution for this conundrum. First, we build a multi-orbital Anderson model starting from the DFT results. The Anderson model describes the $d$ orbitals of the TM atom, their hybridization to their neighbors, the crystal field splitting due to electrostatic interactions, intra-shell Coulomb repulsion, and the spin-orbit coupling. Most of these parameters are obtained from the DFT calculations, as we discuss below. Second, we solve the Anderson model exactly within a restricted multi-particle Hilbert space that includes both $d^n p^l$ and $d^{n+1} p^l$ configurations, where $d^n$ stands for $n$ electrons in the $d$ shell of the TM and the $p^l$ stands for $m$ electrons in the $p$ shell of the Nitrogen first neighbors (without charge transfer there are 6 electrons in each $p$-shell of the N atoms). Charge fluctuations were shown to be important in the case of Cobalt adatoms on MgO/Ag. Including charge fluctuations in the Anderson model gives rise to a non-integer occupation of the $d$ shell but still preserves many-body states with a quantized spin $S$, that is identified with the spin of the quantum spin Hamiltonians.

A. Maximally localized Wannier functions as atomic like basis set

The derivation of an effective Anderson model starting from the DFT calculations requires a representation of the Khon-Sham Hamiltonian in a basis set that contains atomic-like $d$ states localized around the transition metal atom. Our DFT calculations are performed with a plane-wave basis whereas the multi-orbital Anderson Hamiltonian demands a local basis. Thus, to go from plane wave to a local basis, we represent the DFT Kohn-Sham Hamiltonian in the basis of maximally localized Wannier functions (MLWF) [24-26] computed using the code Wannier90, as described in reference [57].

The computation of the MLWF is implemented as follows. First, we select a group of Bloch bands from a spin unpolarized [26] calculation for a given TM/Cu$_2$N system. An energy window of 16eV around the Fermi energy is taken, and the band disentanglement procedure is performed. The selected Bloch bands are initially projected over the $s$, $p$ and $d$ orbitals of both the TM atom and the copper atoms and over the $p$ and $s$ orbitals of the nitrogen atoms. The total number of states involved in this procedure is 313, corresponding to the 4 Nitrogen atoms (4 orbitals each), 32 Copper atoms and the TM atom (9 orbitals each).

An iterative procedure yields a total of 313 MLWF including 3 $p$-like and 5 $d$-like MLWFs localized around the...
the Nitrogen atoms and the TM atom respectively. They are shown in Fig. 9 and Fig. 10 where two different iso-surfaces of the MLWF with $y$ and $x^2 - y^2$, for Fe and Co, are represented. In the case of iso-surfaces with larger value, corresponding to the wave-function close to atomic cores, these MLWF have the same symmetry as the real spherical harmonics with $L = 1$ and $L = 2$. In comparison, the iso-surfaces with small value do not show the symmetry of the Cartesian atomic orbitals.

The Anderson model is build in a basis of single particle states that involves the 5 $d$ orbitals of the TM and the 6 $p$ orbitals of the two first neighbor nitrogen atoms. The representation of the Khon-Sham Hamiltonian $H_{KS}$ in this basis can be written as:

$$H_{CF} + H_{hyb} = \begin{pmatrix} H_{dd} & H_{dp} \\ H_{dp} & H_{pp} \end{pmatrix} \tag{1}$$

where we identify the crystal field Hamiltonian for the $d$ orbitals $H_{CF} = H_{dd}$ and the $pd$ hybridization Hamiltonian with the off-diagonal blocks $H_{dp}$ and $H_{pd}$. Importantly, Fig. 9 and Fig. 10 show how the MLWF for Cobalt are more extended than those of Fe, both for the $x^2 - y^2$ and $y$ orbitals. This accounts for the fact that the hybridization between the TM $d$ orbitals and Nitrogen $p$ orbitals is larger for Co than for Fe. In particular, the matrix element $\langle x^2 - y^2 | H_{KS} | y \rangle$ is twice as large for Co than for Fe.

### B. Multi-orbital Anderson model

We now introduce the multi-orbital Anderson model for the TM on the Cu$_2$N substrate describing the electrons in the 5 $d$ orbitals hybridized with the $p$ orbitals of the two adjacent $N$ atoms. The Hamiltonian is the sum of 4 terms, the Kohn-Sham Hamiltonian of the previous section, plus the Coulomb repulsion of the electrons in the $d$ shell, the Coulomb attraction of the $d$ levels with the TM nucleus, and their spin-orbit coupling:

$$H = H_{KS} + H_{\text{Coul}} + H_Z + H_{\text{SO}} \tag{2}$$

In the following we label the five $d$-like MLWF of the TM with the index $m$, and 6 $p$-like MLWF of the two Nitrogen atoms with the index $n$. The second quantization representation of the first term reads:

$$H_{KS} + H_{Z} = \sum_{m,m',\sigma} \langle \psi | H_{KS} | \psi' \rangle + E_d \delta_{m,m'} d_{m\sigma}^\dagger d_{m'\sigma} +$$

$$+ \sum_{n,n',\sigma} \langle \psi | H_{KS} | \psi' \rangle + E_d \delta_{n,n'} p_{n\sigma}^\dagger p_{n'\sigma} +$$

$$+ \sum_{n,m,\sigma} \langle \psi | H_{KS} | \psi' \rangle + E_d \delta_{n,m} p_{n\sigma}^\dagger p_{m\sigma} + \text{h.c.} \tag{3}$$

The matrix $H_{dd} = \sum_{n,m,\sigma} \langle m | H_{KS} | n \rangle d_{m\sigma}^\dagger d_{m\sigma}$ describes the crystal field. The $E_d$ energy scale accounts for the Coulomb interaction with the positive charge in the nucleus and has to be included to offset the excess in Coulomb repulsion in the configurations $d^{n+1}$ with an extra electron. The matrix $H_{pp} = \langle n | H_{KS} | n \rangle$ describes
the single-particle $p$ levels of the first neighbor nitrogen atoms and $H_{dp} = \langle n | H_{KS} | n \rangle$ describes their hybridization with the $d$ levels, responsible of the charge fluctuation. $H_{dd}$, $H_{pp}$ and $H_{pd}$ are obtained from the DFT Hamiltonian using the wannierization procedure described above.

The electron-electron Coulomb repulsion in the $d$ shell reads:

$$H_{\text{Coul}} = \frac{1}{2} \sum_{m_{\ell},m'_{\ell},m''_{\ell}} V_{mm'm''m'} \sum_{\sigma \sigma'} d_{m\sigma}^\dagger d_{m'\sigma'}^\dagger d_{m''\sigma} d_{m'\sigma'},$$

For the evaluation of the Coulomb integrals $V_{mm'm''m''}$, we transform the angular part to a basis of eigenstates of $\ell = 2$. For the radial part we take an effective radial hydrogen-like function (with effective charge $Z$ and an effective Bohr radius $a_0$) to avoid the otherwise cumbersome numerical integration of the actual Wannier functions. In the basis of eigenstates of $\ell = 2$, all the Coulomb integrals scale linearly with the value of $V_{6000} \equiv U_{dd}$. Although the numerical evaluation of $U$ in terms of the parameters $Z$ and $a_0$ is straightforward, for the sake of generality, $U$ will be considered a parameter, taken to satisfy the atomic Hund’s rule. For a given choice of $U$, $E_d$ is adjusted so that the average charge in the ground state of the many-body calculation described below equals the charge obtained in the DFT calculations.

The spin-orbit term in the TM reads:

$$H_{\text{SO}} = \lambda_{\text{SO}} \sum_{mm',\sigma\sigma'} \langle m | \hat{\ell} \cdot \hat{S} | m' \sigma' \rangle d_{m\sigma}^\dagger d_{m'\sigma'},$$

where $\lambda_{\text{SO}}$ is the atomic spin-orbit coupling of the $d$-electrons. This term is the only one that does not commute with the total spin operator and is the ultimate responsible of the lifting of the $2S + 1$ degeneracy of the spin multiplets.

In the following we shall show results for the case of Fe on Cu$_3$N. Given the small size of the single particle basis ($5$ d orbitals and $6$ p orbitals) and the fact that we restrict the Hilbert space to the configurations $d^n p^{12}$ and $d^{n+1} p^{11}$, with $n = 6$ for Fe, with a total of 1650 multi-electron states, the multi-orbital Anderson model can be solved by exact numerical diagonalization.

### C. Effective spin model

In the seminal work of Hirjibehedin et al., the spin excitations measured with STM-IETS were found to be described with the following spin Hamiltonian:

$$H = D \left( \vec{e}_1 \cdot \vec{S} \right)^2 + E \left[ \left( \vec{e}_2 \cdot \vec{S} \right)^2 - \left( \vec{e}_3 \cdot \vec{S} \right)^2 \right]$$

with $S = 2$ and $\vec{e}_1 = (0,1,0)$ along the Nitrogen direction, and $\vec{e}_2$ and $\vec{e}_3$ are the off-plane and the hollow directions. The experimental results could be fitted with $D = -1.55$ meV and $E = 0.31$ meV. Thus, the wave function of the ground state and first excited state would be given by linear combinations of the rates of $\{2, ±2\}$, with a small mixing with the state $\{2, 0\}$ in the case of the ground state. The height of the inelastic steps was found to be related to the matrix elements of the spin operators, giving additional support to the notion that the quantized spin Hamiltonian provides a quite good description of the spin excitations of iron on this surface. Recent experiments with a detailed study of the IETS of single Fe/Cu$_3$N as a function of the three components of the magnetic field show that the addition of extra terms in the Hamiltonian yields an even better agreement with the experiment. Spin chains formed with Fe atoms in this system can also be modeled successfully with this Hamiltonian and the addition of interatomic Heisenberg coupling. Altogether, these results support the notion that Fe can be described with a quantized anisotropic spin $S = 2$.

### D. Adiabatic continuity and spin conservation argument

We now address the crucial question: given that according to DFT, both charge and spin of the $d$ electrons in the transition metal are not quantized, what is the origin of the quantized spin in the model Hamiltonian? We now show that the quantized spin belongs to the many-body wave function that combines configurations with different charge states in the $d$ shell. In the case of Fe, these would be configurations $d^6 p^{12}$ with $S(d) = 2$ and configurations with $d^7 p^{11}$ and $S(d) = \frac{3}{2}$, where $S(d)$ is the spin of the $d$ electrons. These many-body states yield non-integer charge and magnetic moment in the TM, in agreement with DFT, but they have a well defined total quantized spin, in agreement with the spin quantized models. This is strictly true in the absence of spin-orbit interactions, and remains true when spin-orbit splittings are much smaller than the energy gap between different multiplets, which we show to be the case in a wide range of parameters.

In order to understand the results of our numerical calculations, it is convenient to remind that atomic iron, with 6 $d$ electrons, has a ground state with $S = 2$ and $L = 2$, and a total degeneracy of $(2L + 1)(2S + 1) = 25$. The former ground state is captured by the multi-orbital Anderson model when switch off the $H_{dd}$ crystal field, the $H_{pd}$ hybridization, the SOC, considering configurations with 6 electrons. The crystal field $H_{pd}$ quenches the orbital moment, so that in the absence of spin-orbit coupling, the ground state of the model has $S = 2$ and no orbital degeneracy. This multiplet is separated from the next higher energy multiplets, also with $S = 2$, by a gap of at least 300 meV, although this number depends on $U$.

We now discuss the effect of mixing configurations with a different number of electrons in the $d$ shell. On one
hand, the relative weight of the configurations \(d^6p^{12}\) and \(d^7p^{11}\) depends on \(U\), which is taken to be \(U = 5.5\) eV. On the other hand, \(H_{pp}, H_{dd}, H_{pd}\), are obtained from DFT and \(E_d\) remains as the only adjustable parameter in the calculation. We start with a value of \(E_d\) so that the charge at Fe is \(q = 6\) and ramp up \(E_d\), so that \(q\) increases, as shown in Fig. 11(a). In Fig. 11(c) we plot the evolution of the excitation energies as a function of \(E_d\). For \(q = 6\) the ground state has a multiplicity of 5. The next multiplet lies 300 meV above. As we ramp up \(q\), these two multiplets remain well separated in energy, quite beyond the point where \(q = 6.4\), the value obtained from DFT. We thus see that the ground state multiplet at \(q = 6.4\) is adiabatically connected to the ground state multiplet at \(q = 6\). The effect of spin-orbit coupling, that we discuss in detail below, is to create a small splitting and to mix different states within the multiplet as \(E_d\) is varied, implying a change in the magnetic anisotropy tensor.

The total spin is preserved as we ramp \(E_d\). However, by changing the relative weight of \(d^6p^{12}\) and \(d^7p^{11}\) configurations, the magnetic moment in the \(d\) levels is expected to be reduced, moving from \(S(d) = 2\) towards \(S(d) = 3/2\). This is reflected in our calculations (see Fig. 11(b)), taking \(\lambda_{SO} = 0\) and a finite magnetic field \(B\) that lifts the \(2S + 1\) degeneracy. As \(E_d\) is increased, the expectation value of the operator describing the spin of the \(d\) electrons along the \(y\) axis, \(S_y^{(d)}\), calculated with the 5 lowest energy states, evolves from the eigenstates of \(S_y\) for \(S = 2\) to non-quantized values, in agreement with DFT results.

Further increase of \(E_d\) yields that the mixing between \(d^6p^{12}\) and \(d^7p^{11}\) is so large that the splitting between the ground state \(S = 2\) multiplet and the first excited multiplet vanishes. When such regime is reached, the spin of the ground state changes, breaking the adiabatic connection with the state with \(S = 2\) and quantized charge. In our calculations this happens for \(q \approx 6.8\), larger than the DFT charge, \(q > 6.4\). Thus, the model captures the crossover from the weak coupling limit, where the ground state adiabatically connected with the \(q = 6, S = 2\) state, to the strong coupling limit in which the spin of the ground state multiplet changes and the adiabatic connection is lost.

E. TM-Nitrogen spin correlation

The fact that the quantized spin corresponds to configurations with two charge states involving both \(d\) electrons in the TM and \(p\) electrons in the first neighbor Nitrogen atoms has implications on the spin correlation of the TM and N magnetic moments. Since both \(d^6p^{12}\) and \(d^{n+1}p^{11}\) have the same total spin, we have \(S(d^6) = S_T = S(d^{n+1}) = 5/2\). The sign, and thereby the spin-correlation between the unpaired electron in the ligand and the magnetic moment of the atom, depends on whether \(S(d^n)\) is larger or smaller than \(S(d^{n+1})\). Thus, for Fe we have that \(S(d^6) = 2\) and \(S(d^7) = 3/2\), so that the unpaired fermion must couple ferromagnetically with the \(S = 3/2\) of the \(d^7\) configuration, to keep \(S = 2\). In contrast, for Cr we have \(S(d^5) = 2\) mixing with \(S(d^6) = 5/2\) configurations, to bring up the charge, so that the unpaired fermion in the Nitrogen must couple antiferromagnetically with the atomic magnetic moment.

This argument accounts for the trend obtained in our DFT calculations, shown in Fig. 11(d), where the small magnetization of the first-neighbor nitrogen atoms is antiparallel to the TM magnetic moment for Ti, V, and Cr, and is ferromagnetic in the case of Fe, Co and Ni. In the case of Mn we obtain both signs, depending on \(U\). From the argument of the previous paragraph we would expect a ferromagnetic coupling. Incidentally, the same argument can be applied to the conventional Anderson model with \(S = 1/2\), predicting correctly the well known antiferromagnetic interaction between the local moment and the adjacent electrons.
and Fig. 6 the electron at the E obtained from the exact diagonalization for two values of with well defined total be written as linear combinations of configuration states the eigenstates obtained from DFT. For that matter, we use the fact that the fine structure within the lowest energy multiplet can be atributed, even in the presence of spin-orbit coupling. However, the splittings between the different multiplets are still much larger than the energy can come from the interplay between the crystal field term in the Hamiltonian, $H_{dd}$ and the spin-orbit coupling. Interestingly, when $E_q$ is ramped so that $q$ increases, the content of the wave functions evolves and for $q = 6.4$ the wave functions (Fig. 2, Fig. 3 and Fig. 4(a)) are in good agreement with those obtained from the spin model in which the Nitrogen direction is the easy axis in the problem $(\vec{e}_1 = (0,1,0)$ and $D > 0$ in Eq. (6)). In particular, we note that the five lowest energy states of the Anderson model have wave-functions with strong overlap with those of the effective spin Hamiltonian. We thus see that the ligand field contribution, coming from the $dp$ hybridization, changes qualitatively the magnetic anisotropy tensor. Interestingly, in the case of Fe/Cu$_2$N we find that the inclusion of charge fluctuations is essential to capture the correct easy axis within the multi-orbital Anderson model.

We finally analyze the low energy excitation spectrum,
of the charge in the 2
for the fourth excited state as a function of the charge in the

tained from our calculation are a 25 percent smaller than
those observed in the experiment. So, whereas the model
proposed . This behavior can be understood
in terms of degenerate perturbation theory, where spin-
orbit coupling only splits the states in the lowest energy
multiplet through virtual transitions to the higher state
multiplets. We note that the spin excitation energies ob-
tained from our calculation are a 25 percent smaller than
those observed in the experiment. So, whereas the model
captures the right symmetry, it can only give a rough de-
scription of the excitation energies, which is probably due
to the approximations in the model, such as the restric-
tions taken in the many-body Hilbert space.

IV. CONCLUSIONS

In this work we have undertaken a systematic study
of the electronic properties of the 3d transition metals
on the Cu$_2$N surface. We systematically find that the
charge and spin of the d electrons are not quantized,
and are thereby different from the one in isolated atoms,
which is expected given the conducting nature of the sub-
strate. We have then addressed the issue of how to recon-
cile these results with the fact that quantized spin mod-
els account for the spin excitations of Mn, Fe and Co
ad-atoms. For that matter we propose a multi-orbital
Anderson model in which many-body states that mixes
configurations with two charge states in the d shell are
considered. Importantly, even if the charge is not well de-
finite in the d shell, these multi-electron wave functions
have a well defined total spin $S$. We find that the states
with a quantized charge in the d shell are adiabatically
connected with the actual many-body states that mix
configurations $d^n p^2$ and $d^{n+1} p^1$ in the sense that both
have the same total spin $S$ and there is no mixing with
higher energy multiplets as the addition energy is varied
numerically.

We thus conclude that quantized spin $S$ of the model
actually refers to the spin of these many-body states that
include both the d electrons and the ligand electrons. It
is thus fair to say that the magnetism in this system
is not strictly atomic, which connects with previous re-
sults in the case of magnetic atoms on metallic surfaces, for
which sophisticated theoretical treatments have been
proposed. Our picture provides a natural explana-
tion to the sign of the spin correlation between the TM
and the nitrogen atoms obtained in the DFT calcula-
tions and reconciles the use of quantized spin Hamil-
tonians with the results of DFT calculations. Our Ander-
son model calculations for Fe/Cu$_2$N also indicate that a
charge fluctuations in the Fe d shell, due to the hybridiza-
tion to the ligands, are essential to capture both the sym-
metry and the magnitude of the magnetic anisotropy ob-
erved in the experiment.

Finally, we expect that our analysis should also be ap-
plicable to other systems with magnetic adatoms and
molecules deposited in conducting surfaces whose spin
excitations can be described in terms of quantized spin
models.

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