IOP Publishing Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **26** (2014) 176003 (8pp) doi:10.1088/0953-8984/26/17/176003

Electric-field-modulated exchange coupling within and between magnetic clusters on metal surfaces: Mn dimers on Cu(1 1 1)

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Received 29 January 2014, revised
Accepted for publication 27 February 2014
Published 11 April 2014

Abstract

The effects of external electric fields (EFs) on the magnetic state and substrate-mediated magnetic coupling between Mn dimers on Cu(1 1 1) have been studied using a first-principles theoretical method. The calculations show that a change in the ground-state magnetic order, from antiferromagnetic (AF) to ferromagnetic (FM), can be induced within an isolated Mn_2 on Cu(1 1 1) by applying a moderately strong EF of about 1 V Å^{-1}. The magnetic exchange coupling between pairs of dimers displays Ruderman–Kittel–Kasuya–Yosida-like oscillations as a function of the interdimer distance, which depend significantly on the magnetic order within the dimers (FM or AF) and on their relative orientation on the surface. Moreover, it is observed that applying EFs allows modulation of the exchange coupling within and between the clusters as a function of the intercluster distance. At short distances, AF order within the dimers is favoured even in the presence of EFs, while for large distances the EF can induce a FM order. EFs pointing outwards and inwards with respect to the surface favour parallel and antiparallel magnetic alignment between the dimers, resspectively. The dependence of the substrate-mediated interaction on the magnetic state of Mn_2 is qualitatively interpreted in terms of the differences in the scattering of spin-polarized surface electrons.

Keywords: magnetic clusters, electric field, magnetic coupling, magnetic order

(Some figures may appear in colour only in the online journal)

1. Introduction

Understanding and controlling magnetic phenomena in nanoscale materials constitutes a major current challenge in basic and applied science. Recently, external electric fields (EFs) have been used in this context as a potential tool for tuning the basic magnetic properties of low-dimensional metallic systems [1–11]. It is well known that EFs are effectively screened by the conduction electrons within the topmost monolayer of metal surfaces. However, at interfaces and low-dimensional systems, where the surface-to-volume ratio is large, the rearrangements of charge density caused by EFs can strongly modify the electronic structure of the system. In particular, in the case of transition metals, the EF-induced redistribution of electronic density concerns spin polarized 3*d*-states close to the Fermi level, which are responsible for itinerant magnetism. Consequently, the spin-dependent screening of EFs can lead to significant changes in magnetic properties [2–4, 12, 13].

The use of EFs in order to induce and control the magnetic order of surface nanostructures has good prospects for application in magnetic storage media and spintronic devices [14–16]. Following this perspective, Gerhard *et al* showed that a switching between the ferromagnetic (FM) and antiferromagnetic (AF) phases of ultrathin Fe layers can be triggered by applying an external EF [4]. This remarkable effect is achieved by profiting from the structural instability between the AF face-centred cubic (FCC) and FM body-centered cubic (BCC) phases of Fe thin films [4]. Another noteworthy example of electrically induced magnetic switching has been

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demonstrated by Loth *et al* [5]. Applying a spin-polarized tunnelling current, they managed to switch between the two Néel states of antiferromagnetic Fe nanochains deposited on Cu_2N/Cu(1 0 0) [5]. From a theoretical perspective, Negulyaev *et al* investigated how EFs can induce a switching between the different magnetic states of an isolated Mn dimer on Ag(0 0 1) and Ni(0 0 1) [6]. In this case, the small energy difference between the FM and AF states of Mn_2 renders the substrate density distribution crucial for determining the ground-state magnetic order [6, 17–19]. This work also shows that the EF effects are at least twofold. On the one hand, the EF modifies the electronic structure of the dimer and, on the other hand, it affects the electronic coupling between the cluster and the substrate.

Although the previous studies have provided most useful information about the consequences of applying external EFs on the magnetic properties of isolated particles [20–22], very little is still known about the possibility of tuning the exchange interactions between magnetic clusters on surfaces. In fact, the EF-induced displacements of electronic density at metal surfaces should allow us to control the magnetic coupling between two or more supported nanoparticles, for example, by driving changes in the dispersion of the electronic surface states [23, 24]. This is important, since surface states are responsible for the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction [25–30], which gives rise to a long-range exchange coupling between deposited atoms and magnetic nanoparticles [31–37]. The experimental determination of the magnetic coupling between individual adatoms on surfaces has been recently demonstrated by recording atomically detailed maps of surface nanostructures using scanning tunnelling spectroscopy with a spin-polarized tip [32–34]. In addition, it has been shown that the displacement of electronic density at metal surfaces modifies and eventually reverses the substrate-mediated interactions between magnetic impurities at relatively large distances [38]. More recent experiments show that an external EF perpendicular to the surface can induce a uniaxial anisotropy which favours in-plane or out-of-plane magnetization, depending on its sign [11]. Therefore, external EFs offer most interesting possibilities to manipulate the magnetic behaviour of TM nanostructures.

The purpose of this paper is to investigate the magnetic couplings within and between deposited clusters as a function of applied EFs, and to quantify the possibility of manipulating them by this means. The case of Mn dimers on Cu(1 1 1) is particularly interesting in this context since the exchange couplings are expected to depend significantly on the magnetic state of the particles (i.e. FM or AF). Moreover, the magnetic multistability of Mn_2, already observed on other surfaces, suggests the use of EFs to reverse the coupling (i.e. the relative magnetic orientation) between two neighbouring dimers either by inducing a switching of the magnetic state of the dimers or by directly affecting the substrate-mediated interaction [6, 38].

The remainder of the paper is organized as follows. In the following section we review the theoretical and computational method used in the present study, and provide the main details of the calculations. Section 3 presents and discusses the obtained results. It is divided into three parts. First, we analyze the effect of EFs on the magnetic state of a single isolated Mn dimer on Cu(1 1 1). Second, we consider dimer-dimer exchange interactions at short distances. Emphasis is given here to the interplay between the magnetic order within and between the dimers as a function of the applied EF. The third part deals with the substrate-mediated magnetic exchange interaction at larger distances, and with the modifications induced by the external field. Finally, section 4 summarizes the main conclusions and gives a brief overview of some possible future research directions.

2. Theoretical method

The results reported in this study have been obtained from *ab initio* density-functional calculations using the Green\textquoterights function Korringa–Kohn–Rostoker (GF–KKR) method [39, 40]. Electronic exchange and correlation effects have been treated in the local spin-density approximation (LSDA) [41]. The GF–KKR method divides the space into atomic regions where the atoms are represented by spherical scattering potentials in an otherwise potential-free space. The scattering problem, formulated in terms of the GFs, is solved inside the atomic region. In a second step, the single-site solutions are matched by using the multiple scattering formalism [39, 40]. The electronic structure corresponds to the self-consistent solution of the Kohn–Sham (KS) equations. The local electronic density of states $\rho\ (\mathbf{r},\ \varepsilon) = -1/\pi\ \mathrm{Im}\ G\ (\mathbf{r},\ \mathbf{r},\ \varepsilon)$ is obtained from the imaginary part of the locator $G\,(\mathbf{r}, \mathbf{r}, \varepsilon)$. Once the GF G_0 of the periodic solid corresponding to the substrate (in the present case Cu) is obtained, the surface is regarded as an infinite two-dimensional perturbation of the bulk. The GF of the surface $G_s(\varepsilon)$ is computed from G_0 by solving the Dyson equation $G_s = G_0 + G_0 V G_s$, where V is the perturbation potential describing the vacuum. The effects of surface impurities or deposited clusters are incorporated in a real space representation as additional perturbations to the clean surface. The self-consistent solution of the KS equations is found by solving a new Dyson equation, where the GF of the clean surface takes the role of the unperturbed GF and the perturbation V describes the adclusters. This method is particularly appropriate for describing truly semi-infinite systems lacking in-plane translational symmetry. It therefore allows an accurate calculation of the interaction between particles at low coverage [30].

The effect of applied external EFs can be treated within the KKR perturbation approach to metallic surfaces [23]. In this case the surface is modelled by replacing a slab of bulk crystal potentials with vacuum spheres. This configuration results in two half-infinite crystals and a vacuum region bounded by two metallic surfaces. A homogeneous EF is simulated by introducing a two-dimensional layer of point charges q inside the vacuum slab, placed a few layers above the surface. In such an arrangement, the resulting EF is effectively screened at both metal surfaces, and is therefore confined to a finite perturbation region. Positive and negative values of charge q correspond, respectively, to inward and outwards directions of the EF with respect to the crystal surface. Notice that the largest possible $q > 0$ (or inward field strength) is limited by the work

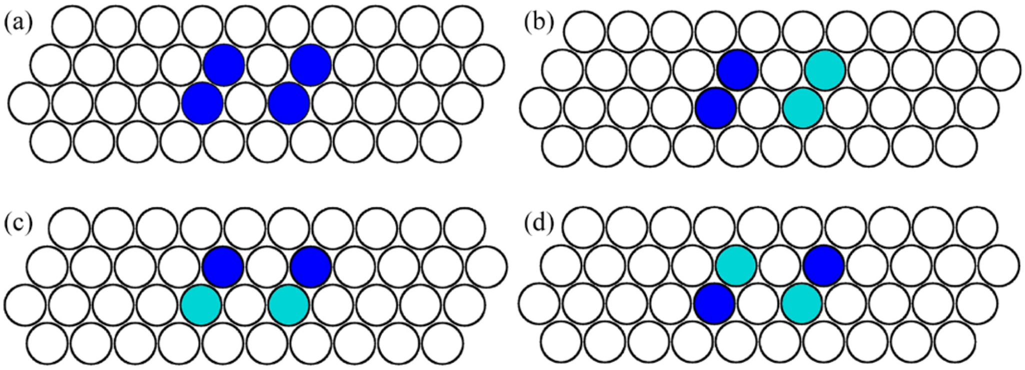

Figure 1. Illustration of the magnetic arrangements of a pair of dimers at second NN positions along the $[1\bar{1}0]$ direction of the (1 1 1) FCC surface. Dark (light)-coloured circles indicate atoms having up (down) magnetic moments. The subfigures (*a*) and (*b*) illustrate the parallel and antiparallel coupling between FM dimers, while (*c*) and (*d*) correspond to the parallel and antiparallel coupling between AF dimers.

function of the metal surface. Further details about the implementation of this approach are available in [23].

For the present study, the Cu(1 1 1) surface has been modelled by replacing a six-layer-thick slab of Cu-bulk potentials with vacuum spheres. The experimental Cu lattice constant a = 3.615 Å is used, and the corresponding atomic positions of the substrate are kept fixed for all considered configurations of the adclusters. Our previous studies have demonstrated that atomic relaxations caused by the EF are small, and that the substrate-mediated interactions should not be essentially affected by them [6, 9, 23, 38]. The layer of point charges q generating the EF is located inside the vacuum slab, specifically, at the atomic positions corresponding to the third layer above the surface. The vertical distance between the charges and the crystal surface is then about 6.3 Å. Values of q in the range $|q/e| < 0.08$ have been considered, which correspond to EF strengths $|E| < 1.5$ V Å^{-1} [23][3].

The Mn dimers are located at Cu lattice positions on top of the surface. The magnetic exchange interactions have been determined by performing electronic self-consistent calculations for different magnetic arrangements of two deposited dimers in the FM and AF states. For each magnetic state of the dimers (FM or AF), the dimer–dimer exchange interaction energy is given by $\Delta E = E_{\mathrm{P}}\,\mathrm{w}{-}E_{\mathrm{AP}}$, where the total energies E_{P} and E_{AP} correspond to the parallel (P) and antiparallel (AP) alignment of the magnetic moments of the two dimers (See figure 1). The values of ΔE have been calculated for interdimer separations corresponding to up to the eighth-nearest neighbours (NNs) along the $[1\,\bar{1}\,0]$ and $[\bar{1}\,\bar{1}\,2]$ directions of the Cu(1 1 1) surface.

3. Results and discussion

In what follows, we first consider the problem of an isolated Mn_2 on Cu(1 1 1) under the effect of external EFs. This provides the basis for discussing the dimer–dimer interactions at small and large distances.

3.1. Mn_2 on Cu(1 1 1)

Before discussing the nature of the interactions between clusters, it is important to consider the effect of an external EF on the ground-state magnetic order of a single Mn dimer. In the absence of EF, the AF configuration is the most stable one. The FM state lies about 30 meV higher in energy. This result contrasts with the FM ground-state found by Negulyaev *et al* for Mn_2/Ag(0 0 1) [6]. Such differences are not surprising, since the behaviour of magnetic impurities on metallic environments is known to depend critically on the properties of the host, particularly on the density of states at the Fermi energy and on the strength of the 3*d*-metal hybridizations [42]. Moreover, the bond length can play an important role in the stability of the magnetic order of Mn_2. In the present study, the Mn atoms are located at perfect Cu lattice positions. Therefore the Mn_2 bond length is the Cu NN distance $d \approx 2.55$ Å, which can favour the stability of the AF state [6, 17, 19, 43, 44]. Taking this into account, it is important to consider both FM and AF dimer configurations in order to asses the dependence of the magnetic interactions between clusters on the local magnetic order[4].

The Mn dimers deposited on Cu(1 1 1) show saturated local spin moments of about 4.1 μ_{B}, irrespective of their internal magnetic configuration (FM or AF). These remain essentially unchanged under the considered applied EF ($|E| < 1.5$ V Å^{-1}). However, as shown in figure 2(*a*), the exchange energy $E_x = E_{FM}$ - E_{AF} strongly increases for positive q (i.e., inwards EF), while it decreases and eventually changes sign for a sufficiently strong negative q (i.e., outward EF). Let us consider the case of $|q/e| = 0.05$ ($|E| \simeq 1$ V Å^{-1}). For an inward EF ($q > 0$) E_x grows up to 70 meV, while for the outward EF

[3] Modeling the electric field sources by point charges at ideal lattice positions is not equivalent to the homogeneous fields typically applied in ultrahigh vacuum experiments. A priori our modelization corresponds more closely to the situation found when electrolytes or ionic liquids are used to generate EFs at surfaces [2, 7]. Nevertheless, it has been shown that the EF effects on the surface states of Cu(1 1 1) are similar in both models [23, 24].

[4] The gas phase (free standing) Mn dimer has been investigated in [43] and found to be a weakly bonded van der Waals molecule. The calculated values of the binding energy depend sensitively on the choice of the basis set and the exchange and correlation potential. In contrast the deposited Mn dimer is strongly bonded with significant overlap between the 3d orbitals. One concludes that the role of the substrate is very important indeed.

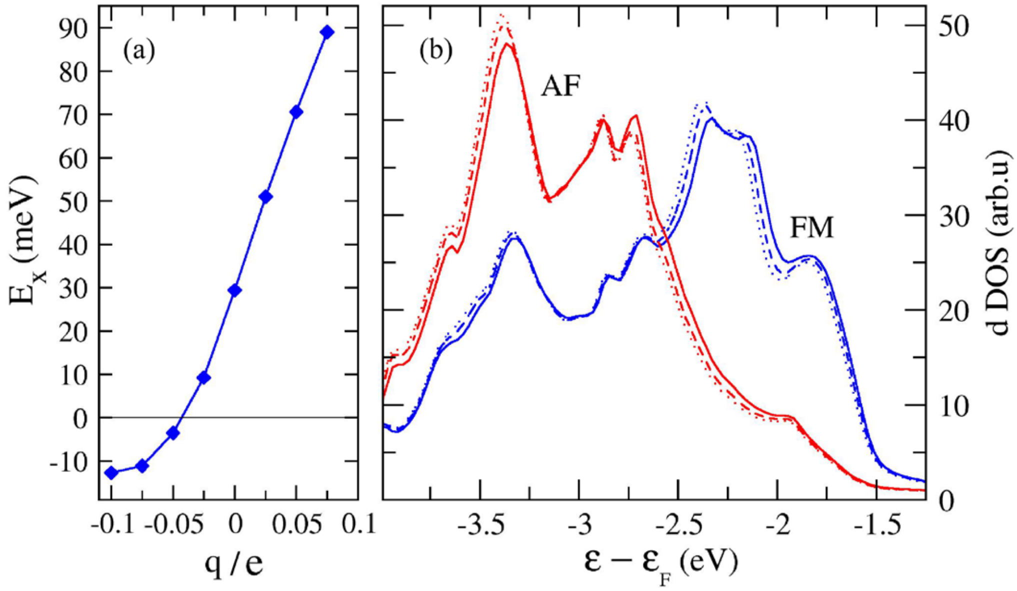

Figure 2. (*a*) Exchange energy difference $E_x = E_{FM} - E_{AF}$ between the FM and AF state of Mn_2 on Cu(1 1 1) as a function of the EF source charge q. Positive and negative values of E_x correspond to AF and FM ground-states, respectively. (*b*) Local density of the majority-spin 3*d*-states at a Mn atom in FM (blue online) and AF (red online) Mn_2. Full, dashed and dotted curves correspond to source charges $q/e = +0.05$, -0.05 and 0.0, respectively. The average EF strength corresponding to $|q| = 0.05$ is approximately 1 V Å^{-1}.

($q < 0$) E_x decreases and changes its sign. This implies that the FM state becomes the ground state. Still, relative stability with respect to the AF configuration remains rather weak ($E_x = -0.35$ meV). Only stronger outward fields enhance the stability of the FM state (see figure 2(*a*)). This trend is in agreement with the behaviour found for Mn_2/Ag(0 0 1) [6]. Notice, moreover, that E_x tends to level off for large negative q after a rapid decrease in the range $-0.05 \leqslant q \leqslant 0.0$. These contrasting behaviours for outward and inward fields reflect the different types of charge redistributions occurring at the metal surface and deposited dimer. For outward EFs, the electronic density is shifted into the bulk, tending to positively charge the deposited Mn_2 and its environment. In contrast, inward fields enhance the density of surface electrons around the dimer, which favours an AF order. It is amusing to observe that the enhanced stability of FM order in Mn_2 with reduced electronic density is consistent with the results obtained for free Mn_2^+, which is found to be FM [43]. In general, the precise asymmetric behaviour of the response of the system to the EF is a consequence of the electronic coupling between adcluster and surface. It is therefore expected to be substrate-dependent.

The nearly saturated values of the local moments imply that the minority-spin states of the Mn atoms lie mostly above the Fermi energy ε_F. Therefore, their contribution to the EF response is not expected to be significant. Figure 2(*b*) shows the local density of the majority-spin *d*-states at a Mn atom in the FM and AF configuration of the dimer. One observes that the bandwidth in the FM state is larger than in the AF case, indicating that the 3*d* electrons are less localized in a FM state and probably extend farther into the vacuum [6]. Therefore, the FM dimer may be more sensitive to the EF. An outgoing EF ($q < 0$) shifts the curves of both states to slightly lower energies. A somewhat larger change in the density of states is observed near the peak, located at about −2.2 eV for the FM configuration. The stability of the FM ground state may be related to these small differences in the field-induced level shifts [6].

3.2. Magnetic state and coupling between dimers at short distances

In order to quantify the magnetic interaction between a pair of dimers, we examine the magnetic arrangements shown in figure 1. For each state of Mn_2 (FM or AF), one considers the parallel (P) and the antiparallel (AP) alignment of the magnetic moments of one dimer with respect to the other. The energy difference $\Delta E = E_P - E_{AP}$ between these two configurations represents the dimer–dimer exchange coupling. Figure 3 shows ΔE for two Mn_2 dimers on Cu(1 1 1) as a function of the interdimer distance r. Notice that different scales are used for the first NN dimer separation (left scale) and for the second, third and fourth NN dimer separations (right scale). First of all, one observes that ΔE strongly depends on the magnetic state of the dimers. At several distances, even the sign of ΔE is different for FM and AF orders, which implies a different relative alignment between the dimers. For example, along the $[\bar{1}\bar{1}2]$ direction at distances beyond first NNs, we find that, in the absence of EF, AF dimers align antiparallel to each other ($\Delta E > 0$) while FM dimers favour parallel alignment ($\Delta E < 0$) (see figure 3, right column for $q = 0$). The behaviour is sensitive to the strength and direction of the external field, since $q/e = -0.05$ follows qualitatively the same trend as $q = 0$, while for $q/e = 0.05$ the opposite is found.

Comparison between the results for dimers along the $[\bar{1}\bar{1}2]$ and $[1\bar{1}0]$ directions enables quantification of the

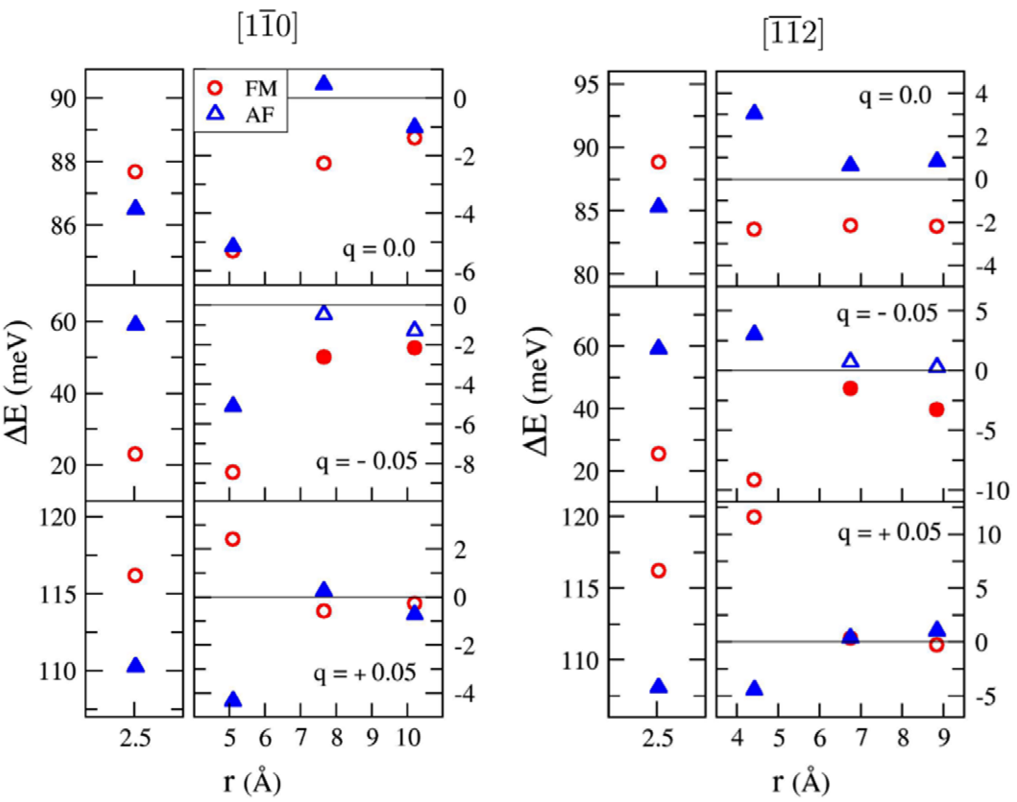

Figure 3. Exchange coupling energy $\Delta E = E_P – E_{AP}$ between two Mn dimers as a function of the interdimer distance r. Both the FM state (circles) and the AF state (triangles) of the dimers are considered (see figure 1). Full symbols indicate the ground-state magnetic order within Mn_2. Results are given for $q/e = 0$, -0.05 and 0.05. The left-side and right-side figures correspond to dimers along the $[1\bar{1}0]$ and $[\bar{1}\bar{1}2]$ directions of Cu(1 1 1), respectively.

dependence of the magnetic couplings on the orientation of the dimers on the surface. The changes in ΔE as a function of magnetic state and relative orientation remain significant even at large distances ($r > 10$ Å). These properties are specific to interacting clusters, but not to adatoms. They are central to the analysis of the EF effect on the interparticle magnetic coupling. Let us now discuss how the interparticle coupling and the EF affect the internal ground state magnetic order of Mn_2. In the absence of EFs ($q = 0$), the AF state remains the ground-state magnetic order within Mn_2 for all considered values of r (full triangles in the top panels of figure 3). In the presence of an outgoing EF ($q = -0.05$) the FM order within Mn_2, which was found to be the ground-state of an isolated dimer, is no longer stable for a pair of dimers at short separations (see figure 3). An AF order within Mn_2 is found for first and second NN distances. This holds for the two considered directions on Cu(1 1 1). In order to analyze this result further, we show in figure 4 the results for ΔE as a function of q for a pair of Mn dimers along the $[1\bar{1}0]$ direction of Cu(1 1 1). One observes that the changes in ΔE also depend on the magnetic state of Mn_2. In general, the EF-effects are stronger for pairs of FM dimers (see figure 4). For NN dimers (figure 4(*a*)), inward and outward EFs cause an increase and decrease, respectively, of ΔE for both FM and AF pairs. Notice that the AF Mn_2 is always more stable than the FM Mn_2, even for $q < 0$, in which case the isolated dimer is FM.

Dimers at first NN distance are in fact diamond-shaped tetramers on Cu(1 1 1). In this case, the antiparallel alignment between AF Mn_2 (AF–AP) (figure 1(*d*)) is nearly 0.2 eV more stable than the parallel coupling of FM dimers (FM–P) (figure 1(*a*)). At such a short distance, the magnetic coupling energy ΔE is dominated by the direct electronic hybridizations between the Mn atoms, very much like the exchange energy E_x within Mn_2. Therefore, a tendency to AP coupling is not surprising. The AF dimers with AP alignment show the largest number of antiparallel NN moments, and are thus energetically favoured. Moreover, one observes some hybridization-induced changes in the local magnetic moments μ_i of the Mn atoms. In the AF–AP configuration $\mu_i = 4.0\ \mu_B$ and $-3.6\ \mu_B$, while in the FM–P case we find $\mu_i = 3.9\ \mu_B$ and $3.7\ \mu_B$. In both cases the largest moments correspond to the less coordinated atoms.

For dimers at the second NNs distance (figure 4(*b*)) the relative alignment between the dimers is in general parallel ($\Delta E < 0$). Here, the energy differences between the configurations considered in figure 1 are dominated by two NN and two second-NN interactions. For the most negative considered value of $q/e = -0.075$, the overall ground-state configuration corresponds to a pair of FM dimers. This result is in agreement with the FM ground-state found for the isolated dimer. However, this is not the case for $q/e = -0.05$. For larger r only, the FM state of Mn_2 is recovered as the ground-state for both $q/e = -0.05$ and 0.075 (figures 4(*c*)–(*d*)). A similar

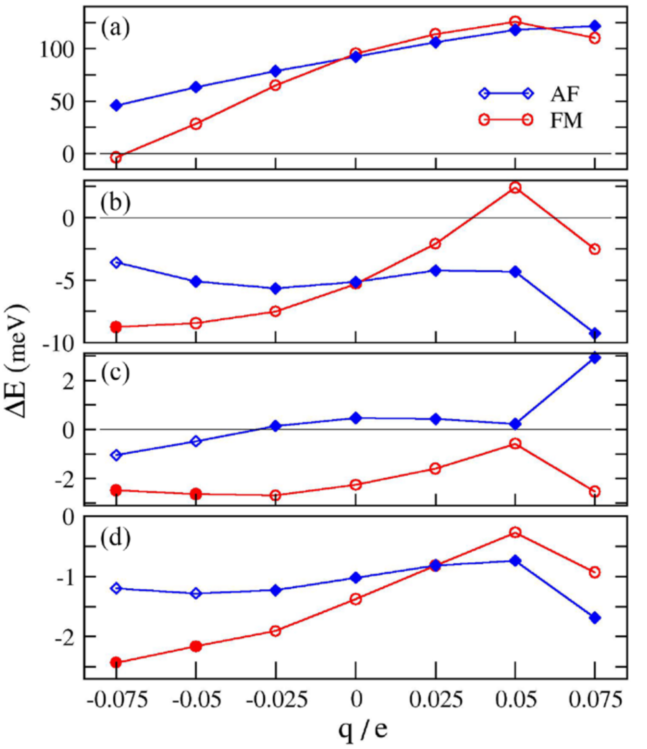

Figure 4. Exchange coupling energy ΔE between two FM (circles) and two AF (diamonds) Mn dimers as a function of q. Full symbols indicate the ground-state magnetic order within Mn$_2$. Results are shown for dimers at the (*a*) first-, (*b*) second-, (*c*) third- and (*d*) fourth-NNs distance along the [$1\bar{1}0$] direction of the Cu(1 1 1) surface.

behaviour is observed for a pair of dimers along the [$\bar{1}\bar{1}2$] direction. However, in this case the FM order within Mn$_2$ is only recovered for r beyond second-NNs interdimer distances, even for $q/e = -0.075$. These differences are related to the orientation of the dimers on the surface, as already observed in the context of figure 3. The separation distance between second-NN dimers is shorter along the [$\bar{1}\bar{1}2$] direction than in the case of [$1\bar{1}0$]. Thus, a stronger difference is expected in ΔE for FM and AF dimers along the [$\bar{1}\bar{1}2$] direction. The results reveal a competition between dimer interactions and EF effects. At very short distances the dimer interactions dominate over the energy changes induced by the EF, which affects the magnetic order of each dimer. At distances beyond second-NNs, the importance of the dimer–dimer interactions decreases. The FM state, which is the ground-state of the isolated Mn$_2$, is also found in the two-dimer of the ensemble.

3.3. Substrate-mediated long-range magnetic interactions

At relatively large distances ($r \gtrsim 7$ Å), the magnetic ground-state of the dimers is the same as for a single deposited Mn$_2$ (AF for $q > -0.05$ and FM for $q \leqslant -0.05$). The interaction mediated by the surface electrons is too weak to affect the magnetic order within the clusters. Figure 5 shows $\Delta E = E_P - E_{AP}$ for dimers deposited along the [$1\bar{1}0$] direction of Cu(1 1 1) as a function of the interdimer distance r. Positive and negative values of ΔE indicate antiparallel and parallel coupling, respectively, between the magnetic moments of the two dimers. In the absence of an external field and for inward EFs (e.g. $q/e = 0.05$), the dimers are AF. In these cases ΔE shows RKKY-like oscillations as a function of r. These differ from the typical substrate-mediated interaction between single adatoms, due to the specific dimer geometry and orientation [29, 34]. Under outwards-applied EF ($q = -0.05$), remarkable changes in the values and sign of ΔE are observed. This is a consequence of the change in the ground-state magnetic order within Mn$_2$, from AF for $q = 0.0$ to FM for $q = -0.05$, which directly affects the scattering of the spin-polarized electrons at the Cu surface and the resulting magnetic component of the RKKY interaction.

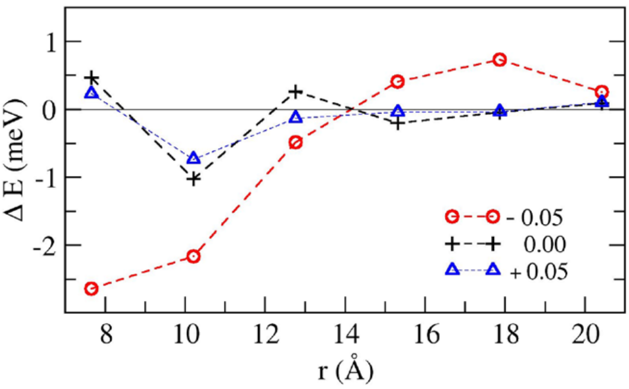

Figure 5. Exchange coupling energy $\Delta E = E_P - E_{AP}$ between two Mn dimers on Cu(1 1 1) as a function of the interdimer distance r. Results are shown for dimers located along the [$1\bar{1}0$] direction of the surface having their ground-state internal magnetic order. The values of the EF source charge q/e are indicated in the inset.

In addition, we find that the EF effects are in general stronger for FM dimers than for AF dimers. For FM Mn$_2$, outward EFs shift ΔE towards negative values ($r < 14$ Å), thus further stabilizing the parallel alignment between them. In contrast, inward EFs increase ΔE towards the antiparallel configuration. At large distances ($r > 14$ Å) the couplings are predominantly antiferromagnetic, and the strength of ΔE is enhanced and decreased, respectively, for outward and inward fields. The results obtained for other values of q follow similar trends. One concludes that applying EFs is a practical means of tuning the long-range exchange interactions between magnetic clusters on metal surfaces.

Further insight on the microscopic origin of the exchange couplings is obtained by analyzing the electronic structure from a local perspective. Figure 6 shows the spin-polarized local electronic density of states $\rho(\varepsilon_F)$ at the Fermi energy ε_F. Results are given for points located at a height $z = 2.1$ Å above the surface as a function of the distance r to a single Mn dimer. The FM and AF Mn$_2$ display qualitatively similar oscillations with a period $\lambda_F/2 \simeq 15$ Å, which are caused by the quantum interference of scattered surface electrons [30]. However, the quantitative differences are significant. One observes that the standing waves arising from the AF dimer are shifted, for majority-spin and minority-spin electrons,

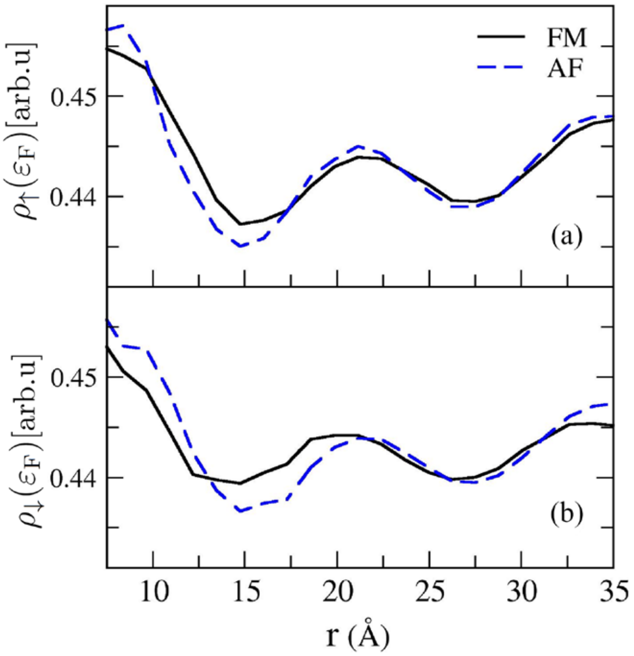

Figure 6. Spin-polarized local density of states $\rho_\sigma(\varepsilon_F)$ at the Fermi energy ε_F in the vicinity of a FM Mn_2 (solid curves) and an AF Mn_2 (dashed curves) on Cu(1 1 1). Results are given for points located at about 2.1 Å above the surface as a function of the distance r to the Mn dimer. Subfigure (*a*) corresponds to majority-spin states, and (*b*) to minority-spin states.

respectively, towards smaller and larger distances as compared to the FM case. These shifts are probably at the origin of the dependence of ΔE on the magnetic state of the interacting dimers.

4. Conclusions

The effects of applied external electrical fields on the magnetic order within and between Mn dimers deposited on Cu(1 1 1) have been investigated by performing first-principles calculations. We have shown that the magnetic ground-state of a single Mn_2 on Cu(1 1 1) can be switched from AF to FM by applying an EF in the outward direction to the surface. Inward EFs enhance the relative stability of the AF state. In addition, the magnetic coupling between pairs of dimers deposited along the $[1\bar{1}0]$ and $[\bar{1}\bar{1}2]$ directions has been investigated as a function of interdimer separation $r \leqslant 20$ Å. The exchange interaction energy ΔE shows RKKY-like oscillations as a function of r that differ from the single-adatom behaviour. Moreover, the dependence of the substrate-mediated interactions on the position and orientation of the dimers on the surface has been revealed.

The magnetic coupling between the dimers is also found to depend on the magnetic order within each Mn_2. This is due to the different scattering of the majority-spin and minority-spin surface electrons, which mediate the effective exchange interaction between the clusters. EFs have in general a stronger effect on FM dimers than on AF dimers. If the EF points outside the surface, the spill-off of electronic density is reduced and a parallel alignment of the magnetic moments of the two Mn_2 is favoured. In contrast, inward EFs favour an antiparallel alignment. An interesting interplay is observed between the magnetic interactions within and between the dimers on one side, and the changes in the charge distribution and electronic structure induced by the EF on the other side. The FM order within Mn_2 is stabilized by outgoing EFs only if the interdimer distance r is not too short, since at small r the strength of the dimer–dimer interaction overcomes the internal magnetic exchange couplings within Mn_2. For first and second NN dimer separations, an AF order is observed. This is important, since the substrate-mediated magnetic exchange interaction between small clusters are most sensitive to the magnetic order within the clusters. In conclusion, external EFs appear to be remarkable tools for tuning the magnetic interactions within and between clusters on metal surfaces.

The results reported in this study open a number of interesting future research directions. The strong sensitivity of the intercluster interactions to an applied EF suggests that similar, probably stronger field effects should be expected for extended ensembles of interacting clusters on surfaces. External EFs might affect the global magnetic order of such nanostructures and the associated dynamical magnetization processes. Larger clusters are also of considerable interest, not only from the point of view of applications, but also in order to elucidate the effect of interference between the scatterings at different atoms of the cluster. Besides noble metal substrates, one should also investigate the effects of EFs for magnetic clusters on highly polarizable substrates, such as Pd or Pt, since the nature of the magnetic interactions is here very different.

Acknowledgments

This work has been supported by the Deutsche Forschungsgemeinschaft and by the COST Action MP0903. LJR is a fellow of Deutscher Akademischer Austauschdienst.

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