Ground State of Magnetic Dimers on Metal Surfaces

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We present model studies of the ground state for magnetic dimers on metal surfaces. We find it can be neither ferromagnetic nor antiferromagnetic, but is often canted for nearest neighbors. Thus, the system cannot be described using bilinear exchange. We give a criterion which can be used quite generally to interrogate the local stability of ferromagnetically or antiferromagnetically aligned dimers, and which also may be used to infer the canting angle when canted states are stable.

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The nature of spin dependent interactions between nearby magnetic solids is a fundamental topic that has occupied both theorists and experimentalists for decades. It is assumed widely that the bilinear exchange interaction of Heisenberg form is dominant. Then the interaction between two magnetic ions 1 and 2 is $-J_{12}\hat{e}_1 \cdot \hat{e}_2$, where $\hat{e}_1$ and $\hat{e}_2$ are unit vectors parallel to their moments. If J_{12} is positive (negative), the ground state is ferromagnetic (antiferromagnetic), and the state of maximum energy is antiferromagnetic (ferromagnetic). The ground state is an absolute minimum of the energy, while the highest energy state is an absolute maximum. Studies presented here show that for a simple system this picture is invalid. Our results question the use of bilinear exchange to describe spin dependent interactions in transition metal magnets by setting forth an example where this fails badly.

Whether bilinear exchange is sufficient to describe interactions between nearby magnetic ions has been discussed for a very long time. A careful analysis by Herring [1] concludes that the simple bilinear exchange dominates only in the limit of large separation between the ions. Also we know experimentally that, in two classical magnetic insulators, biquadratic exchange [an interaction proportional to $(\hat{e}_1 \cdot \hat{e}_2)^2$] enters importantly [2,3]. Reference [3] argues, correctly in our view, that such higher order exchange couplings are overlooked in the literature because many experiments probe only small amplitude spin motions. Such data can always be parametrized by combinations of bilinear coupling terms. More recently, in magnetic multilayers, biquadratic exchange enters importantly [4]. One finds noncollinear orientations of magnetic moments in neighboring ferromagnetic films, driven by biquadratic exchange.

We have carried out model calculations studying the dependence of the energy of magnetic dimers on model metal surfaces, as a function of the angle θ between their magnetic moments. These are motivated by very lovely theoretical and experimental studies of $3d$ transition metal dimers on the NiAl(100) surface [5]. We find, over wide parameter ranges, dramatic deviations from the simple $\cos\theta$ form provided by the simple Heisenberg model for the effective exchange between nearest neighbor adsorbates. Our results are described by an empirical Hamiltonian with bilinear and biquadratic exchange. Thus, for nearest neighbor adsorbate pairs on metal surfaces, we expect a qualitative breakdown of the simple bilinear exchange picture. We find that the ground state of the moment pair is often neither ferromagnetic nor antiferromagnetic, but rather canted with angle controlled by the ratio of the bilinear to biquadratic exchange. This is found for only nearest neighbor pairs. We find that adsorbates on next nearest neighbor sites or those with a larger separation display magnetic interactions that are compatible with bilinear exchange, as Herring's arguments require [1].

These results follow from a simple model description of magnetic dimers on a metal surface. Realistic studies would be desirable, for example, using density functional treatments of real systems. While the present computational schemes allow a comparison between energies of ferromagnetically and antiferromagnetically aligned moments [5], it is a challenge to carry out full calculations for canted dimers on real surfaces. At the moment, we rely on analyses of simpler models. Since we find canted ground states for a wide range of model parameters, we argue that such a behavior can be expected in real systems. Below we also discuss how current density functional studies of dimers can be used to inquire whether a canted state is more stable than either of the collinear states.

We explore a semi-infinite simple cubic lattice, with a (100) surface. There is a single orbital on each site, with nearest neighbor hopping integrals of strength t. We assume two magnetic ions, on nearby top sites, with a hopping integral t_d between them, and t' between each ion and the atom below. Magnetic moments are driven by intra-atomic Coulomb interactions of strength U, treated in mean field theory. A local spin quantization axis is erected on each magnetic ion site, and we treat the effective spin dependent potential as in empirical tight binding calculations of exchange energies in bulk systems [6]. We explore how the energy of the system changes as one moment is canted relative to the second by an angle θ, with self-consistency maintained as θ is scanned.

There are issues which must be addressed in such an analysis. If we change θ and minimize the energy, the total number of electrons in the system changes. This comes about since our substrate is semi-infinite, and electrons transfer from the surface complex into the bulk conduction band as the moments rotate; in effect, they wander off to infinity. This is encountered commonly in tight binding analyses of surface phenomena [7] and has its origin in the absence of the long ranged tail in the Coulomb interaction. The tail forces the substrate to remain electrically neutral, and electron charge transfer occurs only between the dimer and nearby surface atoms. We impose a Friedel sum rule at each step of our calculation, which fixes the total electron number. Then electron transfer occurs only locally. To satisfy the Friedel sum rule at each step, we shift the energy of the orbitals on the magnetic ions, as others have done [7].

The calculation of the total energy for each θ is problematic. One cannot simply sum the single particle energies, since the interaction energy is double counted. One can subtract half of the interaction energy, but it is not clear how to treat the energy shift of the orbitals on the magnetic ions when this is done. Formally, this is a self-energy correction associated with electron transfer, but this is not represented by an explicit term in the model Hamiltonian. However, the *derivative* of the energy with respect to θ can be computed from the single particle energies alone. If $\epsilon_i(\theta)$ is the energy associated with the single particle state i and $n_i(\theta)$ is its occupation number, then if $E_0(\theta)$ is the ground state energy when the canting angle is θ and we change θ by $\Delta\theta$, the change in ground state energy is $\Delta E_0(\theta) = \sum_i \epsilon_i(\theta)\Delta n_i(\theta)$. This may be calculated from the single particle Green's function. We calculate the energy as a function of θ from $\partial E_0(\theta)/\partial\theta$, which allows us to project the ground state energy forward in θ.

We choose model parameters with real materials in mind. We can crudely represent various substrates by positioning the Fermi level E_F within the bulk d band. We have in mind nonmagnetic substrates from the $4d$ transition metal series, and we mimic a given substrate by choosing E_F so that the number of electrons in our substrate band corresponds to the average number of electrons per d orbital in the real material. Thus, Mo is simulated by choosing E_F to give an orbital occupancy of 1.08 electrons (the zero of energy is the midpoint of our substrate energy band, and $t = 1$). We simulate particular adsorbates through the electron number in the d orbitals of the isolated adatom. For example, Mn is simulated through the choice 1.0, Cr by 0.8, and so on. We refer to the various complexes by elemental name to orient the reader regarding the qualitative nature of the system being considered.

We start by calculating the dimer ferromagnetic state ($\theta = 0$) self-consistently. In doing so, we shift the atomic-orbital energy of the magnetic ions (keeping E_F fixed) to obtain the required number of electrons n_d in the adsorbed ion sites. As an illustration, we begin by considering a Cr dimer adsorbed on Mo. We take $U = 8$, which leads to a local magnetic moment $m \approx 0.77$ on each ion for $t_d = t' = 1$. In Fig. 1 we show results for the change in the ground state energy calculated with respect to the ferromagnetic state $[\Delta E_0(\theta) = E_0(\theta) - E_0(0)]$ for different interion separations. The most striking curve is that for the nearest neighbor pair. Their ground state is canted, and both the ferromagnetic and antiferromagnetic states are in fact unstable. This feature has not been probed in density functional calculations such as those reported in Ref. [5], because the quantization axis is held rigidly fixed and is parallel (collinear) for both ions. When the ion pair is separated beyond the nearest neighbor distance, the ground state is either antiferromagnetic or ferromagnetic. In this case, the energy as a function of θ is accounted for nicely by the simple $\cos\theta$ from bilinear exchange. We see in Fig. 1 that, as we move the ion pair apart, the sign of the interaction energy alternates. In our calculations, we find canted ground states only for nearest neighbor pairs. We emphasize that the results displayed in Fig. 1 are not

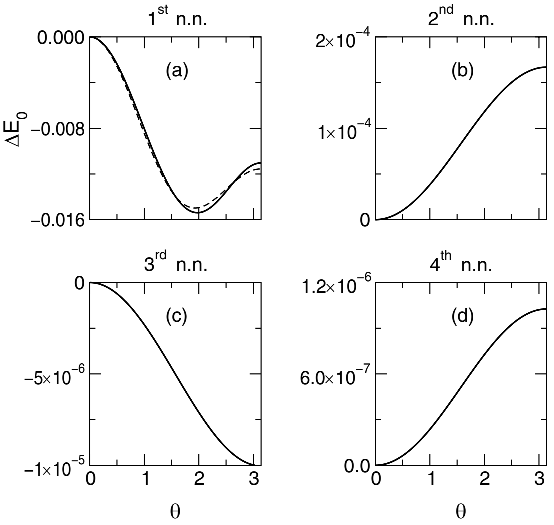

FIG. 1. For our simulation of a pair of Cr atoms on the Mo surface, we show the dependence of the interaction energy with the angle θ between the magnetic moments. In (a) we have the ions on nearest neighbor sites, and the ground state is canted. In (b)–(d) we show results for the case where the ions are on second, third, and fourth neighbor sites. Here the effective exchange coupling is well approximated by the simple bilinear exchange whose sign alternates with distance. The solid curves are our full calculations, and the dashed curve in (a) is a fit to the form $-J_1(\cos\theta - 1) - J_2(\cos^2\theta - 1)$. In the calculations, the occupation numbers are as described in the text; we have taken $t' = 1$, and we have direct hopping between the adsorbates of strength $t_d = 1$, but only for nearest neighbors.

obtained only for a narrow parameter range, but we find this behavior as we imitate various substrate-adsorbate combinations.

For nearest neighbor pairs, we can fit nicely the energy as a function of θ by assuming we have present bilinear and biquadratic exchange, so $\Delta E(\theta) = -J_1(\cos\theta - 1) - J_2(\cos^2\theta - 1)$. A fit to this form is the dashed curve in Fig. 1(a). One finds a canted ground state whenever $J_2 < -|J_1|/2$, a condition we commonly find for nearest neighbors. Most interesting would be a case where $J_2 > |J_1|/2$. Then both the antiferromagnetic and the ferromagnetic state are locally stable, with one being the true ground state. A barrier of substantial height would be present between the higher energy metastable state and the ground state. Such a situation would be of great interest, since one would realize a long lived metastable excited state. However, we have not encountered a model system which displays this behavior, though we see in principle no reason why this cannot occur.

In Fig. 2 we illustrate other substrate-adsorbate combinations where canted ground states are realized. Here E_F is 3.7, which gives a substrate band with 1.88 electrons per bulk site, simulating Pt. In Fig. 2(a) we show calculations for $n_d = 0.9$, whereas in Fig. 2(b) we have $n_d = 1.2$. The latter is a means of modeling a Co dimer on Pt. The solid curves are for $t' = t_d = 1$, the dashed curves are for $t' = 1.2$ and $t_d = 1$, and the dot-dashed curves are for $t' = 1$ and $t_d = 1.2$. The last two parameter sets model the contraction of bond lengths from lattice relaxation. The conclusion that the ground state is canted seems robust also with respect to this feature.

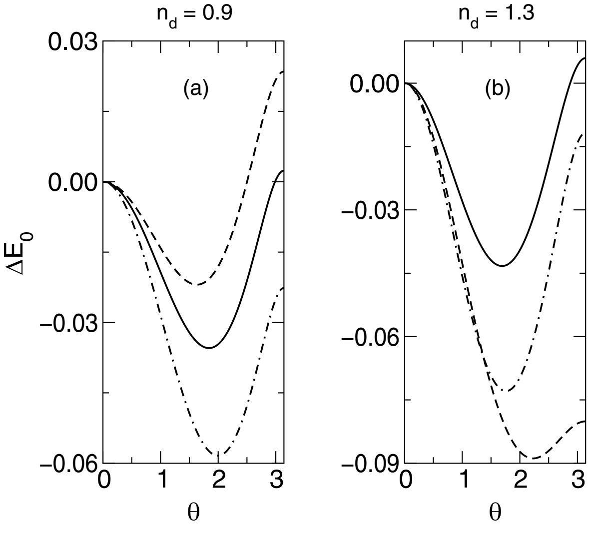

FIG. 2. The energy as a function of the canting angle of a dimer pair on a substrate with 1.88 electrons per orbital. In (a) the ions in the dimer have $n_d = 0.9$ electrons in each d shell, and in (b) the ions have $n_d = 1.3$ electrons. The solid curves are calculated for the case $t' = t_d = 1$, the dashed curves for $t' = 1.2$ and $t_d = 1$, and the dot-dashed curves for $t' = 1$ and $t_d = 1.2$.

In full density functional calculations such as those in Ref. [5], the energy of the optimized ferromagnetic state of the dimer is compared with the energy of the optimized antiferromagnetic state. That theory was not set up to explore whether a canted state exists whose energy is lower than that of these two special configurations. However, from such restricted calculations, one can explore the stability of both the ferromagnetic and antiferromagnetic states. One can generate an expression for the change in energy associated with very small cantings of the spins. This is done, for instance, when effective exchange couplings are calculated between nearby spins [8]. We may write the change in energy of the system as $D(\delta\theta)^2$, where $\delta\theta$ is the angular deviation from either the ferromagnetic or the antiferromagnetic configuration. If the ferromagnetic ground state is an absolute minimum, then D_{FM} is positive while D_{AFM} is negative. The converse is true if the antiferromagnetic ground state is an absolute minimum. If a canted state exists, both will be negative. One cannot tell from this criterion what the mean field canting angle will be, but the canting angle can be inferred if one assumes that only bilinear and biquadratic exchange is present, since J_1 and J_2 may be deduced by fits to the small angle behavior of the energy surface. Similarly, if D_{FM} and D_{AFM} are both positive, then we have the situation (not found by us) where the excited state is metastable. One may derive expressions for the two stiffnesses just described:

$$D_{\mathrm{FM}} = \frac{1}{4\pi}\int_{-\infty}^{E_F} d\epsilon\, \mathrm{Im}\,\mathrm{tr}\{\Delta_2 g_{21}^{\mathrm{FM}\uparrow}(\epsilon)\Delta_1 g_{12}^{\mathrm{FM}\downarrow}(\epsilon)\}, \tag{1a}$$

$$D_{\mathrm{AFM}} = -\frac{1}{4\pi}\int_{-\infty}^{E_F} d\epsilon\, \mathrm{Im}\,\mathrm{tr}\{\Delta_2 g_{21}^{\mathrm{AFM}\downarrow}(\epsilon)\Delta_1 g_{12}^{\mathrm{AFM}\uparrow}(\epsilon)\}. \tag{1b}$$

A derivation of Eq. (1a) is in Ref. [8(b)], and Eq. (1b) is obtained with a similar procedure. Here, g_{ij}^{σ} is the single particle Green's function for spin σ in real space, and the subscripts i and j refer to dimer sites. The quantity Δ_i is the intra-atomic exchange operator on site i. For our model, all quantities are scalars, and the trace may be removed. In a full calculation, one may express these quantities in a representation with additional subscripts in a local orbital representation, and then the trace is over orbital indices. We have calculated these two stiffnesses for various cases to test the method which works well. It would be of great interest to see calculations of these exchange stiffnesses for full density functional analyses. In the literature, one may find examples of such calculations for situations where the ferromagnetic ground state is stable [8], but we know of no examples where this has been done for antiferromagnetically coupled spins.

The frequency spectrum of small amplitude spin excitations of the dimer is of interest. We have carried out calculations by extending our earlier discussion [9] of isolated magnetic ions on metallic surfaces to dimers. Now the local frequency dependent transverse susceptibil-

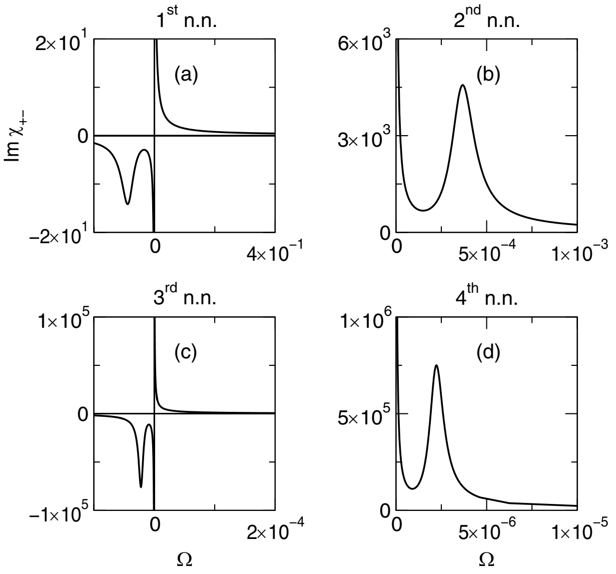

FIG. 3. The frequency spectrum of small amplitude spin fluctuations out of the ferromagnetic state for one of the ions in the dimer pair considered in Fig. 1. We illustrate the frequency spectrum through the calculation of $\mathrm{Im}\{\chi^{11}_{+,-}(\Omega)\}$, as discussed in the text. In (a) we have the spectrum of the nearest neighbor pair, in (b) that of next nearest neighbors, and in (c) and (d) that of third and fourth neighbors, respectively.

ity has indices (i, j) which refer to the adsorbate sites; i.e., we have now quantities we refer to as $\chi^{ij}_{+,-}(\Omega)$. In Fig. 3, for the dimer pair considered in Fig. 1, we display $\mathrm{Im}\{\chi^{11}_{+,-}(\Omega)\}$, which gives the frequency spectrum of spin fluctuations of one member of the dimer, when they are in the ferromagnetic state. In all four cases, we see the response function has a pole at zero frequency, which leads to the rapid rise in the frequency spectrum as the zero frequency is approached from above (in the calculations a small imaginary part is added to the frequency). This is the zero frequency Goldstone mode of the pair, a result of the invariance of the Hamiltonian under rigid spin rotations. When ferromagnetism is stable [(b) and (d)], we see a positive frequency optical mode, whereas the optical mode has a negative frequency when it is unstable [(a) and (c)].

The principal result of our study for nearest neighbor magnetic ions adsorbed on our model metal surface is that the simple picture of bilinear exchange coupling appears to break down qualitatively, to the point that the ground state can be neither ferromagnetic nor antiferromagnetic as commonly assumed, but rather is often canted. While our conclusions are based on a simple model, we are convinced that this possibility should be realized for real substrate-adsorbate combinations. We propose that future density functional studies of such systems examine the stability of the ferromagnetic and antiferromagnetic configurations through calculations of the exchange stiffness defined above in Eqs. (1). It should be noted that canted ground states driven by biquadratic exchange have been encountered in past studies. Its presence is well established in magnetic multilayers [10], and it has been suggested as well to explain spin canting in the compound Gd Mn [11].

Our final remark concerns the *ab initio* calculation of exchange couplings in magnetic metals, such as those described in Ref. [8]. What the authors actually calculate is the energy change associated with small amplitude twists in the spin system, very much as we discussed above in the paragraph which precedes our Eqs. (1). They then deduce bilinear exchange couplings between adjacent magnetic ions by *assuming* that only bilinear exchange is operative. The calculations reported here raise serious questions regarding the validity of such assumptions for nearest neighbor pairs. This may be one of the most important considerations when such microscopically derived effective exchange couplings are used to describe structures such as thin domain walls, where the angle between adjacent magnetic moments is not particularly small.

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