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# Oscillatory exchange coupling in magnetic molecules

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## Abstract

Recently, first-principles calculations based on the spin-dependent density functional theory (DFT) have revealed that the magnetic ground state of a finite linear carbon chain capped by two transition metal (TM) atoms alternates between ferromagnetic and antiferromagnetic configurations depending on the number of carbon atoms. The character of indirect exchange coupling in this nanoscale, quasi-zero-dimensional system is different from those analogous extended structures consisting of magnetic layers separated by a non-magnetic spacer (or magnetic impurities in a non-magnetic host material) and a formulation based on an atomic picture is needed. We present a tight-binding model which provides a theoretical framework to the underlying mechanism of the exchange coupling in molecular structures. The model calculations are capable of reproducing the essential features of the DFT results for the indirect exchange coupling and the atomic magnetic moments in the TM–C<sub>n</sub>–TM structures as functions of the number of carbon atoms. In nanostructures consisting of a few atoms the concepts of extended wavefunctions and the band theory lose their validity, and hence the oscillatory exchange coupling turns out to be a consequence of quantum interference effects due to the spin-dependent onsite and hopping energies.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Oscillatory interlayer exchange coupling can be defined as the exchange interaction between two ferromagnetic layers separated by a non-magnetic metallic spacer. The coupling oscillates in sign as the thickness of the spacer is varied and is mediated by the itinerant electrons of the spacer layer. It has been shown that the oscillatory coupling occurs for almost any metallic spacer [1].

Oscillatory exchange coupling (OEC) has been a field of intense research both theoretically and experimentally because of its relevance to the giant magnetoresistance (GMR) effect. A sequence of experiments [2–4] gave rise to a great interest not only in the possible applications

of interlayer exchange coupling [5, 6] but also in providing physical explanations of its oscillatory behaviour.

With the rapid developments in the miniaturization of conventional microelectronic devices, the efforts in achieving their functionality at the molecular scale are growing. In this respect, the spin-dependent effects are expected to be more prominent in molecular electronics [7–12], where carbon-based and organic molecules are the most promising materials. Molecules containing linear atomic chains of carbon with functional end groups (known as polyynes) are routinely synthesized [13, 14]. Monatomic carbon chains have impressive properties [15], and they could be used in realizing molecular-scale GMR-like spintronic effects when incorporated with magnetic entities.

In a recent letter [16]<sup>1</sup> we reported that isolated linear molecules composed of carbon atomic chains capped with single transition metal (TM) atoms (i.e. TM–C<sub>n</sub>–TM) have alternating ferromagnetic (F) and antiferromagnetic (AF) ground states as a function of the number of C atoms,  $n$ . Increasing or decreasing the value of  $n$  by one modifies the magnetic ground state from AF to F, or vice versa. The ground state magnetic order (F or AF) for a particular  $n$  depends on the type of the TM atom. These results have been obtained by performing first-principles calculations within density functional theory (DFT) using ultra-soft pseudo-potentials. For example, it is found that for CrC<sub>n</sub>Cr molecules the ground states are AF for even  $n$ , where the first excited state is F with a total magnetic moment  $\mu = 10 \mu_B$  ( $\mu_B$  is the Bohr magneton) [16]. However for odd  $n$  the ground state is F with  $\mu = 8 \mu_B$ . The difference in the total energies of the AF and F configurations,  $\Delta E_{F \rightarrow AF} = E_T(AF) - E_T(F)$ , is the energy required to invert the magnetic moment of one of the TM atoms in the lowest energy F state. It is a measure of the indirect exchange interaction between the TM atoms, and oscillates in sign as  $n$  is varied.

Calculations for the CoC<sub>n</sub>Co molecules show a similar but inverted behaviour. The ground state is AF for odd  $n$  and the energy difference  $\Delta E_{F \rightarrow AF}$  again oscillates in sign with the variation of  $n$  but the signs are inverted. In both cases the strength of the interaction decays with increasing  $n$ , as expected. In the present paper we investigate the origin and mechanism of this exchange interaction in these molecular size, quasi-zero-dimensional systems where existing theories cannot be applied owing to the discrete and local nature of the electronic states, and also strong coupling in short C chains.

The objective of the present work is not to provide more accurate results than those of the state-of-the-art *ab initio* methods, but to develop a framework to explain the underlying physics of the oscillatory coupling in small molecular systems. The well known theories of indirect exchange coupling in extended systems do not readily cover the molecular structures that we consider. In the present paper, we develop a theoretical framework based on the tight-binding method with an extension to the Hubbard model to explain the oscillatory exchange coupling. As spintronics of nanoscale devices, in other words nanospintronics, is rapidly progressing, the present study is expected to provide some insight into the indirect exchange coupling in magnetic molecules.

The organization of the paper is as follows. First we review the theoretical works on oscillatory exchange coupling in extended systems in section 2. In section 3.1 a simple Hückel-type model is presented for the oscillatory coupling in molecular structures. Then we consider the inclusion of a Hubbard term in section 3.2 and investigate its effect. In order to develop a more competent approach such that both the period of oscillations and the atomic

<sup>1</sup> First-principles plane-wave calculations are performed within DFT using ultra-soft pseudopotentials [28]. The exchange correlation potential is approximated by generalized gradient approximation [29]. The forces on the atoms are minimized, leaving the spin degree of freedom relaxed to reach the optimum atomic positions and magnetic moments. The results of plane-wave calculations are confirmed with methods employing local basis sets [27].

magnetic moments can be predicted, we propose an empirical tight-binding model with realistic parametrization in section 3.3. We discuss and compare the obtained results with those of the DFT calculations in section 4, and give our conclusions in section 5.

## 2. Theoretical background

A number of theoretical models have been proposed to explain the physical mechanism of oscillatory interlayer exchange coupling in magnetic multilayers (see reviews [17–20] and references therein). Interlayer exchange interaction is closely related to the RKKY [21] coupling between magnetic impurities in a non-magnetic metallic host, as both interactions are mediated by the electrons of the non-magnetic medium and both interactions are oscillatory. There is a consensus that interlayer exchange coupling is related to the sharp cut-offs in momentum space due to the Fermi surface of the spacer layer as in the case of RKKY coupling. Among various models, that of Bruno [22, 23] and Stiles [24] based on spin-dependent reflections at the interfaces provided a unified picture, which we will refer to as the interlayer exchange coupling (IEC) model.

The IEC model, as was put forward [22–24], explains the oscillations in terms of the change of the density of states due to quantum interferences generated by spin-dependent multiple reflections from the interfaces. For a three-dimensional layered system, the change in the integrated density of states of the spacer layer due to the reflections is given by

$$\Delta N(\epsilon) = -\frac{1}{2\pi^3} \text{Im} \int d\mathbf{k}_{\parallel} \ln(1 - r_L r_R e^{ik_{\perp}L}) \quad (1)$$

where  $r_L$  and  $r_R$  are the complex reflection amplitudes from the left and right interfaces,  $L$  is the thickness of the spacer layer and  $\mathbf{k}_{\parallel}$  and  $k_{\perp}$  are respectively the in-plane and perpendicular wavevectors. The change in energy per unit area due to the change in the density of states is defined as the interface energy and can be written as

$$\Delta E = \frac{1}{2\pi^3} \text{Im} \int d\mathbf{k}_{\parallel} \int_{-\infty}^{\infty} d\epsilon f(\epsilon) \ln(1 - r_L r_R e^{ik_{\perp}L}) \quad (2)$$

where  $f(\epsilon)$  is the Fermi–Dirac function. When the spacer is sandwiched between magnetic layers, the reflection amplitudes differ for different spins and the interlayer exchange coupling energy can be defined as the energy difference between antiferromagnetic and ferromagnetic configurations of the magnetic layers,

$$E_{\text{AF}} - E_{\text{F}} = \frac{1}{4\pi^3} \text{Im} \int d\mathbf{k}_{\parallel} \int_{-\infty}^{\infty} d\epsilon f(\epsilon) \ln \frac{(1 - r_L^{\uparrow} r_R^{\downarrow} e^{ik_{\perp}L})(1 - r_L^{\downarrow} r_R^{\uparrow} e^{ik_{\perp}L})}{(1 - r_L^{\uparrow} r_R^{\uparrow} e^{ik_{\perp}L})(1 - r_L^{\downarrow} r_R^{\downarrow} e^{ik_{\perp}L})} \quad (3)$$

where  $r_{L/R}^{\uparrow/\downarrow}$  is the reflection amplitude for a spin up/down electron from the left/right interface. For large values of the spacer thickness  $L$ , the exponential term in the integrand oscillates rapidly. In view of the fact that for large  $L$  most of the spacer layers gain bulk properties except for the effect of multiple reflections from the interfaces, the interlayer exchange coupling energy can be expressed in terms of the critical spanning vectors of the Fermi surface of the *extended* spacer material. For extended spacers the coupling becomes a Fermi surface property. On the other hand, in a molecular structure the effective dimensionality of the system is zero, that is the bulk properties of the spacer cannot characterize the system, hence the critical spanning vectors of the Fermi surface are not the relevant quantities for explaining the interaction. Therefore, the solution for the quasi-zero dimensional problem cannot be a natural extension of the IEC model and requires a different treatment at this molecular scale.

As a related problem, the theory of indirect exchange coupling of localized magnetic moments in a non-magnetic metallic host was earlier developed by Ruderman, Kittel, Kasuya,

and Yosida [21], and is known as the RKKY interaction. The RKKY coupling is defined via a perturbative Hamiltonian

$$H_{\text{RKKY}} = \sum_j A(\mathbf{x}_j - \mathbf{R}_0) \mathbf{S}_j \cdot \mathbf{I}_0 \quad (4)$$

where  $\mathbf{R}_0$  is the position and  $\mathbf{I}_0$  is the spin operator of a magnetic impurity, and  $\mathbf{S}_j$  is the spin operator of the  $j$ th conduction electron at position  $\mathbf{x}_j$ .  $A(\mathbf{x}_j - \mathbf{R}_0)$  is proportional to the delta function,  $A(\mathbf{x}) = J\delta(\mathbf{x})$ . For *extended hosts*, the conduction electrons can be expressed in terms of Bloch wavefunctions, and having written the Hamiltonian in second quantized form the indirect interaction between two magnetic moments located at  $\mathbf{R}_0$  and  $\mathbf{R}_1$  can be expressed with the second order term in the perturbation expansion as

$$H_{\text{RKKY}}^{(2)} = J^2 \vec{\beta}_0 \cdot \vec{\beta}_1 \phi(\mathbf{R}_1 - \mathbf{R}_0) \quad (5)$$

where  $\vec{\beta}_0$  and  $\vec{\beta}_1$  are the localized magnetic moments, and  $\phi$  is the range function of the interaction.  $\phi$  turns out to be an oscillatory function, the form of which depends on the dimensionality of the host material. The case of two magnetic impurities in a truly one-dimensional host was re-treated later by Yafet [25], and a correction to previous works was provided. Even though the TM-C<sub>n</sub>-TM molecular structures that we consider are finite in size, the RKKY prediction for the exchange interaction of two TM atoms in an *infinite* C chain could be instructive. In this case the range function for the one-dimensional extended host is given by [25]

$$\phi(x) = \frac{2m}{\pi \hbar^2} \left( \text{Si}(2k_F x) - \frac{\pi}{2} \right). \quad (6)$$

In the above expression  $k_F$  is the Fermi wavevector of the host and Si is the sine-integral function  $\text{Si}(x) = \int_0^x (\sin t)/t dt$ .

For a linear C chain of infinite length, the Fermi wavevector is  $\pi/(2a)$  ( $a$  being the interatomic distance); therefore, the indirect exchange energy within the RKKY treatment is

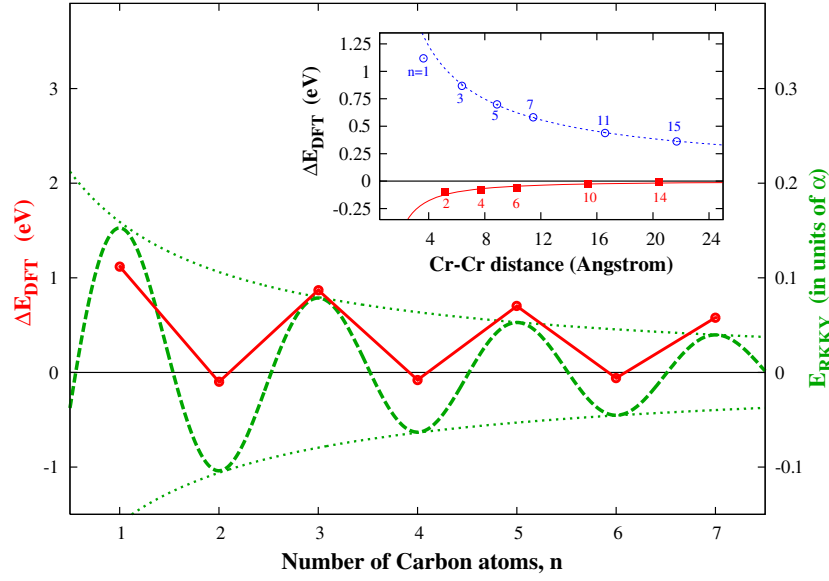
$$E_{\text{RKKY}} = \alpha \left( \text{Si}(\pi(n+1)) - \frac{\pi}{2} \right) \quad (7)$$

where  $n$  is the number of C atoms between the two TM atoms, and  $\alpha = (2mJ^2 \vec{\beta}_0 \cdot \vec{\beta}_1)/(\pi \hbar^2)$ .

In figure 1, the energy and decay rate of the exchange coupling calculated using the RKKY theory for the *infinite* C chain are plotted and compared with the DFT results [16] (see footnote 1) for the case of two TM atoms separated by a *finite* number of carbon atoms. Comparison of the results shows that RKKY theory predicts the period of oscillations correctly, but the decay rate of  $E_{\text{RKKY}}$  is not consistent with the DFT results. DFT calculations show that a single envelope cannot be fitted to the energies of both AF and F ground states. It is natural to expect that the RKKY approach (or generally speaking an approach which calculates indirect exchange energy by employing bulk properties of the spacer) loses its validity as the size of the spacer gets smaller and smaller. In our case, the size of the spacer is only a few atoms, that is too small to be considered as a periodic structure with negligible end effects, and too large for the TM atoms to interact directly, and it is our motivation to develop an understanding of the OEC using the language of atomic orbitals instead of the band theory.

### 3. Theoretical model

We propose a simple model in order to explain the dominant mechanism of the exchange interaction between the TM atoms through a quasi-zero-dimensional non-magnetic spacer,



**Figure 1.** Exchange coupling energy of a  $\text{Cr}_n\text{Cr}$  molecule calculated using DFT (solid line and left vertical axis) and that predicted by RKKY theory (dashed curve and right vertical axis). The inset shows the asymmetric decay rates of the coupling with the Cr–Cr separation for AF (square) and F (circle) states obtained from DFT results. The labels in the inset indicate the corresponding numbers of carbon atoms,  $n$ . The period of oscillations is the same in both calculations but RKKY predictions of decay rates (dotted curves) for AF and F configurations are the same, which is not verified by DFT results.  $\alpha$  is an exchange energy emerging in the RKKY formulation (see text).

i.e. the finite C chain. A preliminary version of this model has been discussed in [16] (see footnote 1). Here we include the the single level approximation in order to form a basis for an extended version of the model, and for the sake of completeness. The two main features of the interaction to be simulated within our model are (i) the oscillatory energy difference between the ferromagnetic and the antiferromagnetic ground states with respect to the number of carbon atoms of the spacer and (ii) the variation of the atomic magnetic moments through the molecule.

### 3.1. Single level approximation

Our starting approach will be to model the  $\text{TM}-\text{C}_n-\text{TM}$  structures using a Hückel-type Hamiltonian where each atom is represented with a two-level site, one for each spin type. We allow for only the nearest neighbour hoppings. The Hamiltonian is

$$H = \sum_{i=0;\sigma}^{n+1} \epsilon_{i,\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} - \sum_{i=0;\sigma}^n t_{i,i+1;\sigma} c_{i,\sigma}^\dagger c_{i+1,\sigma} + \text{h.c.} \quad (8)$$

where  $i$  is the site index. Zeroth and  $(n + 1)$  th sites are the TM sites; in between are the carbon sites.  $c_{i,\sigma}$  and  $c_{i,\sigma}^\dagger$  are the annihilation and creation operators for an electron with spin  $\sigma$  ( $\sigma = \uparrow, \downarrow$ ). The onsite energies  $\epsilon_{i,\sigma}$  and the hopping terms  $t_{i,i+1;\sigma}$  are both spin dependent. The non-magnetic carbon sites are represented by spin-degenerate parameters, and the effect of TM capping is simulated by assigning spin-dependent onsite and coupling parameters to the TM sites.

The relative strengths of the spin-dependent parameters of the TM sites can be inferred from the electronic structure of isolated TM atoms. The numbers of spin up and spin down electrons are different for a TM atom and the highest occupied (lowest unoccupied) spin up atomic level is different from that of the down spin. This enters our model as different onsite parameters for each spin. The effective coupling parameters of the two spin states to the neighbouring C sites will be different for the same reason.

We choose the magnetic moment of the left TM site as positive, and that of the right TM site is to be chosen with respect to the magnetic state of the molecule, that is, positive for ferromagnetic and negative for antiferromagnetic configurations.

An interpretation of this model is possible if one makes an analogy with a particle in a one dimensional potential well [24]. One needs to consider a different potential profile for the electrons of each spin type. The potential for the majority spin electrons at the left TM site is higher than the potential at the spacer, namely the well region. This leads to symmetric potential profiles for each spin type for the ferromagnetic configuration and antisymmetric ones for the antiferromagnetic case.

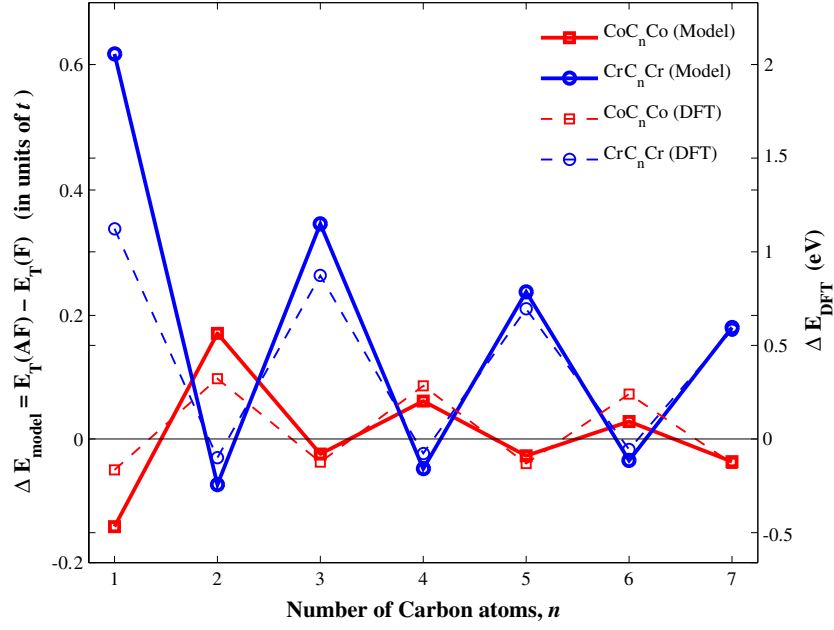
The Hamiltonian is then characterized in terms of parameters  $\{E_1, E_2, t_1, t_2\}$ , where  $E_1 = \epsilon_{0;\uparrow}$ ,  $E_2 = \epsilon_{0;\downarrow}$  are the onsite energies for the majority and minority spins of the left TM site, and  $t_1 = t_{0,1;\uparrow}$ ,  $t_2 = t_{0,1;\downarrow}$  are their coupling energies to the nearest carbon site. We set the onsite energy of the carbon sites to zero as reference, and the C–C hopping parameter to  $t$  for both spin types. As we consider the same species of TM atoms at both ends, the onsite and hopping parameters of the right TM site are chosen in accordance with the particular magnetic order of the molecule (F or AF). Having written each parameter in units of  $t$ , we diagonalize spin up and spin down Hamiltonians of the system separately, since we do not consider any spin-flip interactions. The energy spectrum for each spin type in both F and AF states of the molecule is calculated, and half filling is applied to the combined spectra to end up with the total energies of the F and AF configurations.

We consider Co and Cr as the cap TM atoms. Isolated Cr has five majority and zero minority spins in its d shell, where isolated Co has five majority and two minority spins. When the TM atom is chemically bound to the C chain from the left, the electrons of the leftmost C atom will experience different interaction potentials depending on their spins, and the coupling terms to the TM site will also be spin dependent.

The energy cost for a majority spin electron to hop from the C site to the TM site is expected to be comparable for both Co and Cr atoms in view of their isolated electronic configuration. On the other hand, the energy required for a minority spin electron to hop from the C site to the TM site should be larger for a Co atom than it is for a Cr atom. Similarly, the hopping terms are different for minority spin electrons hopping to Co or Cr atoms. Along these arguments, we find that the parameter sets  $\{1.0, 0.3, 1.5, 0.5\}$  and  $\{1.0, 0.0, 1.5, 1.0\}$  for Co and Cr, respectively, lead to results in fairly good qualitative agreement with the DFT calculations [26, 27]. The difference in the total energy of the molecules  $\Delta E = E_{AF} - E_F$  for varying number of C atoms is presented in figure 2. We should emphasize here that the relative values of the onsite energies in the parametrization lead to the inverted variations of the Cr and Co cases as found in the DFT calculations. Although the model does not include any self-consistent calculations for the electronic configuration it is capable of representing the basic physical mechanism underlying the magnetic state dependence of the TM-capped C chains on the number of atoms.

### 3.2. Hubbard term

The presented model does not include many body interactions. In order to simulate many body effects to some degree we incorporate Hubbard interaction within the single level treatment of



**Figure 2.** Energy difference of the AF and the lowest F states in the  $\text{CoC}_n\text{Co}$  and  $\text{CrC}_n\text{Cr}$  atomic chains within the single level per spin Hückel-type model. The dotted lines show the DFT results [16] (see footnote 1).

the model. To this end, we add onsite Coulomb repulsion terms to the Hückel Hamiltonian in equation (8) as

$$H_U = \sum_{i=0;\sigma}^{n+1} \epsilon_{i,\sigma} c_{i,\sigma}^+ c_{i,\sigma} - \sum_{i=0;\sigma}^n (t_{i,i+1;\sigma} c_{i,\sigma}^+ c_{i+1,\sigma} + \text{h.c.}) + \sum_{i=0}^{n+1} U_i n_{i,\uparrow} n_{i,\downarrow} \quad (9)$$

where  $n_{i,\sigma}$  is the number operator for electrons on site  $i$  with spin  $\sigma$  and  $U_i$  is the onsite Coulomb interaction between two electrons with opposite spins. We assume the repulsion energy to be site dependent, as it should be different for the TM and carbon atoms. Setting all  $U_i = 0$  reproduces the previous Hückel Hamiltonian.

Analysis of the effect of Hubbard interaction is performed within the Hartree–Fock approximation, by which the Hamiltonian can be rewritten in a simpler form as

$$H_U^{\text{HF}} = \sum_{i=0;\sigma}^{n+1} \tilde{\epsilon}_{i,\sigma} n_{i,\sigma} - \sum_{i=0;\sigma}^n (t_{i,i+1;\sigma} c_{i,\sigma}^+ c_{i+1,\sigma} + \text{h.c.}) \quad (10)$$

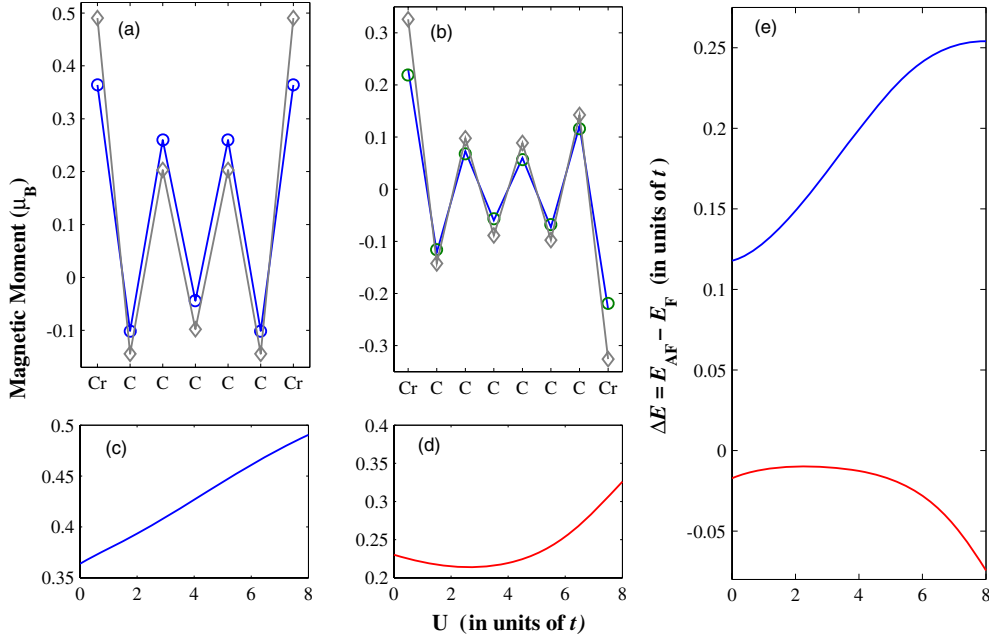
with

$$\tilde{\epsilon}_{i,\sigma} = \epsilon_{i,\sigma} + U_i \langle n_{i,\sigma'} \rangle \quad (11)$$

being the Hubbard-modified onsite energy where the mean occupations  $\langle n_{i,\sigma'} \rangle$  of the opposite spin level on the same site are to be calculated self-consistently.

DFT calculations show that the spin-dependent interactions in the molecule create distortions in the spin populations of the carbon atoms too, leading to induced magnetic moments of the order of  $\sim 0.1 \mu_B$  on them. The variation of the magnetic moments on the carbon atoms displays several distinct forms depending on the magnetic state of the molecule [16] (see footnote 1). We calculate the atomic magnetic moments throughout the





**Figure 3.** (a) Site magnetic moments for  $U = 0$  (dark) and  $U = 8t$  (light) in  $\text{Cr}_5\text{Cr}$ . (b) The same for  $\text{Cr}_6\text{Cr}$ . (c) Variation of magnitude of the magnetic moment of the Cr site as a function of  $U$  in  $\text{Cr}_5\text{Cr}$ . (d) The same for  $\text{Cr}_6\text{Cr}$ . (e) Variation of the exchange energy for  $\text{Cr}_5\text{Cr}$  ( $\Delta E > 0$ ) and  $\text{Cr}_6\text{Cr}$  ( $\Delta E < 0$ ). Inclusion of the Hubbard term does not change the type of the ground state.

molecule for different Hubbard terms and compare them with the  $U = 0$  case. The site magnetic moments are deduced from the occupation numbers and sample results are presented in figure 3. We set  $U_{\text{C}} = 0$ , and  $U_{\text{Cr}}$  is taken in units of the carbon–carbon hopping parameter  $t$ . We see that the inclusion of the Hubbard  $U$  term modifies the site magnetic moments. For  $\text{Cr}_5\text{Cr}$ , the magnetic moment of the Cr sites monotonically increases with  $U$ . For  $\text{Cr}_6\text{Cr}$ , however, the magnetic moments first slightly decrease before they start to increase as the value of  $U$  gets larger. Correspondingly, the difference between total energy of the molecules in their AF and F states varies with  $U$  as shown in figure 3(e). The overall content of figure 3 shows that the many body interactions included with the Hubbard term enhance the magnetic state of the molecules in general, but the type of the magnetic ground state is not altered with non-zero  $U$ . We should also note that the present single level approximation cannot predict the correct values of the atomic magnetic moments, but the qualitative form of how the atomic moments are distributed over the molecule is obtained.

### 3.3. Extension of single level approximation: LCAO-like parametrization

In section 3.1, it is shown that the model with a single level per spin on each atom in the half-filling regime is capable of representing the qualitative features of the OEC in quasi-zero dimensions; and in section 3.2 we have checked the influence of the Hubbard interaction on the arrangement of atomic magnetic moments. Having built a simple but promising model, we will now generalize it to include all atomic levels contributing to the indirect interaction. These levels and their contributions can be analysed with the use of total energy calculations implementing local basis sets, such as SIESTA [27]. In this work we have employed double- $\zeta$

**Table 1.** Valence orbitals of the TM and C atoms grouped with respect to their symmetry properties.

Group	Transition metal	Carbon
G <sub>1</sub>	4s, 3d <sub>z<sup>2</sup></sub> , 4Pp <sub>z</sub>	2s, 2p <sub>z</sub> , 2Pd <sub>z<sup>2</sup></sub>
G <sub>2</sub>	3d <sub>xz</sub> , 4Pp <sub>x</sub>	2p <sub>x</sub> , 2Pd <sub>xz</sub>
G <sub>3</sub>	3d <sub>yz</sub> , 4Pp <sub>y</sub>	2p <sub>y</sub> , 2Pd <sub>yz</sub>
G <sub>4</sub>	3d <sub>xy</sub>	2Pd <sub>xy</sub>
G <sub>5</sub>	3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	2Pd <sub>x<sup>2</sup>-y<sup>2</sup></sub>

plus polarization basis sets. The polarization orbitals are also included in the basis set in order to take into account the deformations caused by the bond formations. The polarization orbitals are generated using the atomic orbitals by applying a small electric field, and those with angular momentum  $l + 1$  are included in the basis [27]. In the case of Cr, the polarization orbitals are 4Pp<sub>x</sub>, 4Pp<sub>y</sub> and 4Pp<sub>z</sub> and for C they are 2Pd<sub>xy</sub>, 2Pd<sub>xz</sub>, 2Pd<sub>yz</sub>, 2Pd<sub>z<sup>2</sup></sub> and 2Pd<sub>x<sup>2</sup>-y<sup>2</sup></sub>.

We analyse the CrC<sub>n</sub>Cr molecules as a test case. The numbers of valence electrons for the Cr and C atoms are  $Q_{Cr} = 6$  and  $Q_C = 4$ , respectively. We calculate the molecular energy levels for each spin, and their projections on the localized orbitals. Filling the lowest lying  $m$  levels ( $m = 2 Q_{TM} + n Q_C$ ) one is able to resolve the atomic spin and charge distributions.

Before getting into the details of Mulliken analysis, we should remark that the atomic orbital basis used can be partitioned into distinct groups according to their symmetries as in table 1.

As the atomic orbitals belonging to different symmetry groups have zero overlap, the Hamiltonian can be written as

$$H = H_1 + H_2 + H_3 + H_4 + H_5 \quad (12)$$

where  $H_i$  is the Hamiltonian for the subgroup  $G_i$ .  $H_i$  are mutually non-interacting Hamiltonians with energy spectra  $\{\epsilon_j\}_i$  and the energy spectrum of the molecule is their combination  $\{\epsilon_j\} = \bigcup_{i=1}^5 \{\epsilon_j\}_i$ . The sizes of the Hamiltonian matrices  $H_i$  are  $\{3(n+2), 2(n+2), 2(n+2), (n+2), (n+2)\}$ , where  $n$  is the number of C atoms. Therefore,  $9(n+2)$  is the number of molecular levels to be obtained from the total Hamiltonian, where there are  $(4n+12)$  levels to be filled for the CrC<sub>n</sub>Cr molecule, i.e.  $(5n+6)$  levels will be unoccupied. It is easy to observe that  $H_2$  will be identical with  $H_3$ . In our LCAO-like treatment, we will not include all the orbitals but will try to simulate the effects of exchange interaction with a suitable parametrization of a reduced number of hybridized orbitals.

A major signature of the OEC is the asymmetry created in the numbers of electrons with different spins on the spacer atoms causing induced atomic magnetic moments through the spacer. Since the total energy of the molecule is the sum of the energies of the occupied molecular levels, the occupancies of the atomic orbitals are worth analysing. In order to determine the filled and empty atomic orbitals, we refer to the Mulliken analysis of the *ab initio* calculations [16] (see footnote 1).

We will make use of the information on the occupancies of the atomic orbitals in reducing the number of parameters in our LCAO-like treatment. The orbitals that are fully occupied or totally unoccupied in both F and AF configurations of the molecule do not contribute to the exchange energy. That is, unoccupied orbitals do not contribute to the total energy of the system. Fully occupied orbitals do contribute to the total energy, but in calculating the energy difference between the AF and F configurations their contribution is less important. The major contributions to both the atomic magnetic moments and the exchange energy come from the partially occupied atomic orbitals.

According to the Mulliken analysis, the polarization orbitals  $2Pd_{xy}$ ,  $2Pd_{yz}$ ,  $2Pd_{z^2}$ ,  $2Pd_{xz}$ , and  $2Pd_{x^2-y^2}$  on the C sites are high in energy compared to the remaining orbitals; accordingly, their partial occupancies in the molecule are negligible. For the TM atoms, the  $3d_{xy}$ ,  $3d_{x^2-y^2}$  orbitals are fully occupied by the majority spin electrons and totally unoccupied for the minority spin. Similarly, the  $3d_{xz}$  and  $3d_{yz}$  orbitals are almost fully occupied (unoccupied) by the majority (minority) spin electrons. The  $4Pp_z$  orbital has negligible occupancy for both spin directions.

We will consider the remaining orbitals with an appropriate parametrization such that the parameters will also reflect the minor contributions to exchange energy from fully occupied orbitals. For the TM atoms, we account for the  $4s$  and the  $3d_{z^2}$  orbitals in their hybridized form (only one of them lies below the HOMO level); similarly,  $4Pp_x$  and  $4Pp_y$  orbitals will be represented by a single level. For C, the  $2s$  and  $2p_z$  are considered in their hybridized form (again, only one of them lies below the HOMO level), and the  $2p_x$  and  $2p_y$  orbitals will be represented by one level. In the calculation of atomic magnetic moments, however, we take into account the occupied orbitals that are excluded in the calculation of  $\Delta E_{F \rightarrow AF}$ .

#### 4. Results and discussion

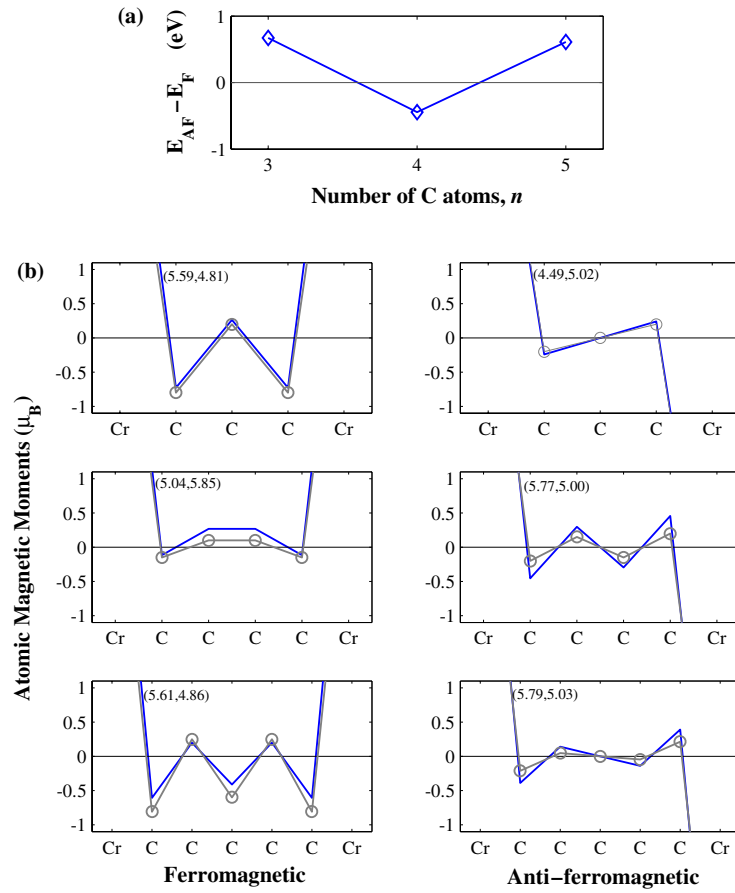
In this section we will present the results of the LCAO-like parametrization outlined in section 3.3. The energies of the F and AF ground states and the atomic magnetic moments of the  $Cr_nCr$  molecule will be calculated with the given scheme and will be compared with the results of the first-principles calculations.

Our convention is to choose the majority spin of the left Cr atom as spin up. Accordingly, the majority spin of the right Cr atom will be spin up in the F configuration and spin down in the AF configuration. There are five neglected levels on the Cr atoms, all of which belong to the majority spin electrons. We represent each atom by two levels per spin for both Cr and C. Each level is for the lower lying hybridization orbital of the two atomic orbitals; namely, for Cr the lower lying hybrids of  $4s$  with  $3d_{z^2}$  and  $4Pp_x$  with  $4Pp_y$ ; for C the lower lying hybrids of  $2s$  with  $2p_z$  and  $2p_x$  with  $2p_y$  are considered. From the symmetry group point of view, we consider one ‘orbital’ from Cr and one for C from  $G_1$ , and one ‘orbital’ from Cr and one for C from the linear combination of  $G_2$  and  $G_3$ . We call these new sets of atomic levels  $a$  for those coming from  $G_1$ , and  $b$  for those belonging to  $G_2 + G_3$ . Since levels of  $a$  and  $b$  emerge from different symmetry groups they can be treated separately. These representative atomic levels are not only intended to reflect the contributions from the atomic orbitals they are hybridized from but they are optimized in order to include the minor contributions from the totally filled/empty orbitals, and from the many body corrections as well.

The parameters for the two groups are  $P_a = \{E_{C,a}, t_{C,a}, E_{1,a}, E_{2,a}, t_{1,a}, t_{2,a}\}$  and  $P_b = \{E_{C,b}, t_{C,b}, E_{1,b}, E_{2,b}, t_{1,b}, t_{2,b}\}$  where  $E_{C,x}$  and  $t_{C,x}$  are the carbon onsite energy and the carbon–carbon coupling energy respectively.  $E_{1,x}$  and  $E_{2,x}$  are the onsite energies for the majority and minority spins of the Cr sites, and  $t_{1,x}$  and  $t_{2,x}$  are their coupling energies to the nearest carbon site.

The exchange coupling energy,  $\Delta E_{F \rightarrow AF} = E_T(AF) - E_T(F)$ , as calculated using the above procedure is plotted in figure 4(a) for  $n = 3, 4, 5$ . The projection of molecular levels onto the atomic orbital basis provides us with the information of spin-dependent occupancies on each atom and the difference  $n_\mu = n_\uparrow - n_\downarrow$  for a particular atom stands for the contribution to the atomic magnetic moment coming from the hybridized orbitals of groups  $a$  and  $b$ . The contributions of the fully occupied orbitals on magnetic moments are to be accounted for separately.

For the hybridized orbitals of groups  $a$  and  $b$ , we use the parameter sets  $P_a = \{0.00, 1.00, 3.14, -0.10, 1.72, 0.15\}$  and  $P_b = \{0.25, 1.00, 3.39, 0.15, 1.72, 0.15\}$  which are



**Figure 4.** (a) Exchange coupling energy for the ground state configuration of  $\text{CrC}_n\text{Cr}$  molecules for  $n = 3, 4$ , and 5 as calculated by using the LCAO-like parametrization. (b) Atomic magnetic moments of  $\text{CrC}_n\text{Cr}$  molecules for F (left column) and AF (right column) configurations for  $n = 3, 4$ , and 5. The grey lines in (b) are the DFT results [16] (see footnote 1). The pair of numbers denotes the values of the magnetic moments on the TM atoms as calculated using the present model and DFT [27], respectively.

written in units of the carbon–carbon coupling parameter. Using the same parameters, the magnetic moments of the atoms can be calculated more accurately (see figure 4(b)) than the previous simpler model. The values of the parameters have been obtained by fitting the coupling energy and the atomic magnetic moments simultaneously to their DFT-calculated values.

## 5. Conclusions

Oscillatory exchange coupling in quasi-zero dimensions for the case of TM-capped C-chain molecules is investigated and a theoretical model is presented to provide a framework to study the underlying mechanism of the coupling. A novel property of the TM– $\text{C}_n$ –TM molecules is that changing the value of  $n$  by one modifies the magnetic ground state from AF to F or vice versa. For Cr, molecules with odd  $n$  have F ground state whereas even  $n$  gives rise to AF ground state. For Co, odd numbers of carbons yield AF, even numbers of carbons yield F

ground states [16] (see footnote 1). That is, the interaction is altering in sign with the smallest possible period.

As the TM atoms are well separated by the C chain, the interaction is indirect and mediated by the C-chain spacer. Earlier, such mediated magnetic interactions were explained using the RKKY theory [21] and IEC model [22–24] for structures of large extent or higher dimensionality. RKKY theory explains the interaction between magnetic impurities in a non-magnetic host in terms of a perturbative treatment in momentum space around the sharp cut-off at the Fermi surface of the impurity-free bulk medium. The IEC model explains the interaction as a consequence of spin-dependent reflections at the magnetic–non-magnetic interfaces. In other words, interlayer exchange coupling is a quantum interference effect due to spin-dependent reflection amplitudes. As the thickness of the non-magnetic spacer can be up to hundreds of monolayers, the IEC model describes the coupling in terms of the bulk properties of the spacer. In the case of TM-capped C-chain molecules (quasi-zero-dimensional nanoscale system), we are not able to consider the bulk properties of the C-chain spacer, therefore another description of the underlying mechanism is required.

The single level version of our model can predict the oscillations in the exchange energy, and also the variations of the induced atomic magnetic moments, but it is not possible to obtain the moments on the TM sites, which can exceed  $5 \mu_B$ , within this approximation. We have also shown that the inclusion of many body interactions has no major effect on the atomic magnetic moment oscillations within the chosen parameters. The prediction of both the exchange energy and the atomic magnetic moments is possible by taking the contributions of all the valence electrons into account. We have developed a parametrization scheme and applied it to one of the cases which produces results in acceptable agreement with the density functional theory calculations of [16] (see footnote 1).

In summary, the spacer mediated exchange interactions in magnetic multilayers can generally be explained as a result of quantum interference phenomena. For a large spacer thickness, the interaction is characterized by the spin-dependent reflection–transmission amplitudes. In our case of a molecular spacer, however, the interaction can be explained as a quantum interference effect based on the spin-dependent hopping and onsite energies of the atomic sites of the structure.

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