Paramagnetic molecule induced strong antiferromagnetic exchange coupling on a magnetic tunnel junction based molecular spintronics device

Pawan Tyagi$^{1,3}$, Collin Baker$^1$ and Christopher D’Angelo$^2$

$^1$University of the District of Columbia, Department of Mechanical Engineering, 4200 Connecticut Avenue NW Washington DC-20008, USA
$^2$University of the District of Columbia, Department of Mathematics and Statistics, 4200 Connecticut Avenue NW Washington DC-20008, USA
$^3$University of Kentucky, Chemical and Materials Engineering Department, 177 F Paul Anderson Hall, Lexington, KY-40506, USA

E-mail: ptyagi@udc.edu

Received 24 April 2015, revised 10 June 2015
Accepted for publication 12 June 2015
Published 10 July 2015

Abstract

This paper reports our Monte Carlo (MC) studies aiming to explain the experimentally observed paramagnetic molecule induced antiferromagnetic coupling between ferromagnetic (FM) electrodes. Recently developed magnetic tunnel junction based molecular spintronics devices (MTJMSDs) were prepared by chemically bonding the paramagnetic molecules between the FM electrodes along the tunnel junction’s perimeter. These MTJMSDs exhibited molecule-induced strong antiferromagnetic coupling. We simulated the 3D atomic model analogous to the MTJMSD and studied the effect of molecule’s magnetic couplings with the two FM electrodes. Simulations show that when a molecule established ferromagnetic coupling with one electrode and antiferromagnetic coupling with the other electrode, then theoretical results effectively explained the experimental findings. Our studies suggest that in order to align MTJMSDs’ electrodes antiparallel to each other, the exchange coupling strength between a molecule and FM electrodes should be $\sim 50\%$ of the interatomic exchange coupling for the FM electrodes.

Keywords: Molecular spintronics devices, paramagnetic molecules, magnetic tunnel junctions, Monte Carlo simulations

(Some figures may appear in colour only in the online journal)
molecular magnets, and C_{60}-like [4] big molecules can dramatically alter the magnetic coupling between the FM electrodes to produce novel MSDs. However, there are negligible scientific studies focusing on the impact of strong molecule mediated inter-FM electrodes coupling on the magnetic properties of an MSD. To date, experimental research [4, 5] has mainly focused on the spin transport. Whereas, theoretical research [6–10] has been centered on studying the interaction between paramagnetic molecules and a single FM electrode. Density functional theory (DFT)-based theoretical research is limited to calculating the density of states and attributes of magnetic coupling between a single FM electrode and a molecule [6–10]. Due to several limitations, DFT studies are inadequate to simulate magnetic properties of an MSD. Recently, DFT has been combined with classical Monte Carlo (MC) simulations [10] to study the impact of the nature of the magnetic interaction between a single FM electrode and a specific molecule. However, difficulties in doing DFT studies on large MSDs, involving big organometallic molecules and two FM electrodes, may be prohibitive in combining DFT with MC simulations. We hypothesized that representing magnetic interactions between paramagnetic molecules and FM electrodes as two variables will provide a practical approach to study a complete MSD with MC simulations only. The accuracy of such studies can be checked by comparing MC results with the experimental data. This paper reports MC simulation explaining the experimental magnetic data obtained on MTJ-based MSDs (MTJMSDs) [11, 12]. MTJMSD fabrication necessitates the chemical bonding of molecular channels on the two FM electrodes to transform a prefabricated exposed edge MTJ (figure 1(a)) into an MTJMSD (figure 1(b)). For the first time, the MTJMSD approach exhibited the impact of strong molecular coupling on the magnetic properties of an MTJ at room temperature. To explain the experimental observations, we conducted MC simulations on a 3D model analogous to an MTJMSD. We investigated the impact of parameterized molecular exchange couplings with the FM electrodes, thermal energy (kT), and MTJMSDs sizes on equilibrium magnetic properties.

2. Experimental details and simulation methodology

For experimental magnetic studies, an array of several thousand MTJs (figure 1(a)) was treated with organometallic molecular clusters (OMCs) to yield MTJMSDs (figure 1(b)). These MTJs possess Ta (5 nm)/Co (3–5 nm)/NiFe (5–7 nm)/AlOx (2 nm)/NiFe (10 nm) and were used for all experimental magnetic studies, unless stated differently in the context of a specific experiment. After fabrication, MTJMSDs were characterized structurally (figure 1(c)) and magnetically with techniques like magnetic force microscopy (MFM) (figure 1(d)). Li et al [13] published an OMC synthesis method. MTJMSDs were magnetically characterized by a SQUID magnetometer, ferromagnetic resonance (FMR), and MFM. Additional information about MTJMSD fabrication and characterization are discussed in the SI section of the supplementary material. To understand the mechanism behind OMC-induced strong coupling, we conducted continuous MC simulations [14] on a 3D analog of MTJMSD (figure 1(e)). Our previous attempt to explain MTJMSD’s magnetic properties with non-vector spins and simplified 2D Ising model representation was unable to capture the underlying physics effectively [15].

The three dimensions of an MTJMSD model are governed by the indices representing height (H), width (W), and length (L). The MTJMSD’s dimension is represented by H × W × L (figure 1(e)). To represent the molecules on the edges (figure 1(e)), a plane containing atoms along the perimeter and with the empty interior was introduced between the two FM electrodes of equal volume. The molecular plane is inserted along the H dimension of an MTJMSD (figure 1(e)). The inter-FM electrode magnetic coupling is only occurring via the molecules (figure 1(f)). However, inter-FM electrode coupling via the empty region is set to zero. We performed MC simulations by varying molecular coupling strength with the top FM (J_{mt}) and bottom FM (J_{mb}) electrodes, kT, and MTJMSD dimensions (figure 1(f)). To achieve the equilibrium spin vector configurations of molecules and FM electrodes we ran ~1–50 million iterations in an MC simulation. For every new configuration, MTJMSD energy was calculated using equation (1) to select or reject a new state according to the Metropolis algorithm [14]. In equation (1), S represents the spin vector of individual atoms of FM electrodes and molecules. In equation (1), J_{T}, J_{F}, and J_{B}, are the Heisenberg exchange coupling strengths for the top and bottom FM electrodes, respectively (figure 1(f)). Additional details about MC simulations are presented in section S2 of the Supplementary Material.

\[
E = -J_T \sum_{i \in T} \sum_{i \in+} S_i S_{i+1} - J_B \sum_{i \in B} \sum_{i \in+} S_i S_{i+1} - J_{mt} \sum_{i \in T, i+1 \in mol} \tilde{S}_i \tilde{S}_{i+1} - J_{mb} \sum_{i \in+ \in mol, j \in B} \tilde{S}_{i+1} \tilde{S}_j \tag{1}
\]

After achieving equilibrium configurations, we ran additional iterations to record observables.

3. Results and discussion

The following sections discuss the experimental results on molecule-induced strong antiferromagnetic coupling and corresponding MC simulations to provide mechanistic insights.

3.1. Experimental study of MTJMSD

A Ta/Co/NiFe/AlOx/NiFe MTJ demonstrated dramatic changes in its magnetic properties after interacting with OMCs. An OMC aggregate possessed S = 6 spin state around 1 K [13]. However, we were unable to estimate the actual spin state of OMCs chemically bonded to two FM electrodes in an MTJMSD (figure 1(b)). To avoid difficulties in estimating the
effective spin state of an OMC in MTJMSD, we only considered an \( S = 1 \) spin in our MC studies. Each OMC, with four alkane tethers ending with thiol functional group, bonded with FM electrodes via metal-thiol bonding. Alkane tethers possess low spin-orbit and hyperfine splitting to ensure high spin coherence length and time [5]. In an MTJMSD, \( \sim 10^4 \) OMCs served as highly efficient spin channels between two FM electrodes and lead to strong exchange coupling at RT.

Experimental magnetic studies provided interesting results on MTJMSDs. The SQUID magnetometer studies, performed with Quantum Design MPMS®, showed a typical hysteresis loop for an array of bare MTJs (figure 2(a)). After interacting with OMCs, MTJs exhibited a linear magnetization versus a magnetic field curve (figure 2(a)). The linear magnetization data was hypothesized to be due to OMC-induced antiferromagnetic coupling between two FM electrodes [16]. The inverse of magnetic susceptibility (\( \chi^{-1} \)) versus temperature (\( T \)) showed that an MTJMSD exhibited a prominent transition around 350 K (inset, figure 2(a)). A linear fit to the encircled section suggests that for \( \chi^{-1} = 0 \), the corresponding \( T \) was \( -473 \) K. Another MTJMSD, produced in a different batch, showed corresponding \( T = -404 \) K for \( \chi^{-1} = 0 \). For \( \chi^{-1} = 0 \), the negative sign of \( T \) indicate the presence of Neel temperature (\( T_N \)), which is an attribute of antiferromagnetic ordering [17]. The existence of \( T_N \) indicates that OMCs induced a net antiferromagnetic coupling between the two FM electrodes of the MTJ. We compared the OMC-induced \( T_N \) with the Curie temperature (\( T_C \)) of the NiFe FM electrode; it is noteworthy that only NiFe is directly bonded with OMCs and possesses \( T_c \sim 800 \) K [18]. The \( T_N/T_C \) ratio was in the 0.5–0.54 range. However, according to the literature [14] and our simulations (section S3, supplementary material) \( T_c \approx J_A/k_B \approx J_B/k_B \). Replacing \( T_C \) with \( J_A \) or \( J_B/k_B \) suggesting the \( kT_N \) or OMC-induced antiferromagnetic coupling was of the order of 0.5 times of the NiFe’s interatomic ferromagnetic exchange coupling strength (i.e., \( J_A \) or \( J_B \)).

To investigate the nature of OMC’s magnetic interaction with a NiFe (top) and Co/NiFe (bottom) electrode of an MTJMSD, two additional tunnel junction testbeds were prepared. Both tunnel junctions contained palladium (Pd) as the common electrode, but another electrode was the top or bottom FM electrode of the MTJMSD (figures 2(b) and (c)). Interestingly, OMCs decreased the magnetic moment of Pd (10 nm)/AlOx (2 nm)/NiFe(10 nm) tunnel junction (figure 2(b)). On the other hand, OMCs increased the magnetic moment of Co(5 nm)/NiFe (5 nm)/AlOx (2 nm)/Pd (10 nm) tunnel junctions (figure 2(c)). Assuming that OMCs interaction with Pd was identical, the results in figures 2(b) and (c) suggest that OMCs made antiferromagnetic coupling with the NiFe electrode and ferromagnetic coupling with the

![Figure 1](image-url)
Co/NiFe electrode. If our interpretation of these experimental studies is correct, then MC simulations must exhibit a low magnetization state for the opposite signs of $J_mT$ and $J_mB$ in the MC simulations. We also performed FMR studies before and after transforming an MTJ (figure 1(a)) into an MTJMSD (figure 1(b)). It was observed that intensities of typical optical (low intensity) and acoustic resonance (high intensity) modes from the bare MTJs decreased dramatically after attaching OMCs (figure 2(d)). However, MTJs with the 4 nm thick AlOx spacer disabled OMCs (~3 nm long) to bridge between FM electrodes. As expected, no statistical difference was observed in the FMR spectra when OMCs failed to produce MTJMSD (figure 2(e)). This study proved that only successfully established OMC channels across the tunnel barrier.

Figure 2. (a) Magnetization versus magnetic field study of a Co/NiFe/AlOx/NiFe MTJ before and after hosting OMCs to become MTJMSD; inset graph shows plot of $\chi^{-1}$ versus $T$. Tunnel junctions with (b) Pd/AlOx/NiFe and (c) Co/NiFe/AlOx/Pd NiFe FM showing opposite response from OMCs. FMR study of Co/NiFe/AlOx/NiFe MTJ with (d) 2 nm and (e) 4 nm AlOx before and after OMCs interaction. (f) Topography and (g) MFM image of Co/NiFe/AlOx/NiFe MTJ based MTJMSD array.
produced strong antiferromagnetic coupling. A prior theoretical study provides an explanation for the disappearance of FMR modes on an MTJMSD (figure 2(d)) and strongly suggest that OMC produced strong antiferromagnetic coupling between two FM electrodes [19]. According to Layadi et al [19], if antiferromagnetic coupling strength between the two FM electrodes of similar thickness and material increases beyond a critical limit, then magnetization of the two FM electrodes aligns antiparallel to each other. In such a case, two usual FMR resonance modes disappear, and only a single mode appears at a higher magnetic field. To compliment SQUID (figure 2(a)) and FMR (figure 2(d)) studies, the MFM experiments were conducted. Digital Instruments Veeco Multimode AFM and a Co-coated magnetic cantilever (Nanoscience®) were employed. We observed that most of the MTJMSD’s scans produced unambiguous topographical images (figure 2(f)), but very faint or negligible magnetic contrast (figure 2(g)). This study evidenced that MTJMSDs are physically intact. Interestingly, in some MFM scans, MTJMSDs with high and low MFM contrast coexisted. We believed that high contrast MFM was due to those MTJs, whereas MTJMSDs with high and low MFM contrast coexisted. We also investigated the effect of MTJMSDs’ sizes and kT on the M versus JmT and Jmb plots. For this study, M was plotted for various MTJMSD sizes as a function of equal and opposite values of kT and JmB, i.e., JmT=−JmB (figures 3(b) and (c)). We varied the height of an MTJMSD with Hx10x10 dimension (figure 1(e)) to vary the number of atoms of the FM electrode without changing the number of molecules. For kT=0.05, increasing an MTJMSD’s size required a higher magnitude of M to settle in low state. At kT=0.25 most of the MTJMSDs settled in M=0 state. This result evidenced that FM electrodes for 3×10×10 and 7×10×10 size MTJMSDs settled in low state (figure 3(b)). For instance, 3×10×10 and 7×10×10 size MTJMSDs settled in low state when JmT=JmB were ~0.1 and ~0.5, respectively. It is noteworthy that FM electrodes for 3×10×10 and 7×10×10 are in 2D, whereas for H>3, FM electrodes are in 3D. For low kT oppositely aligned M and M_B cancel each other to yield M=M_m. Further increase in device size made it difficult for JmT and JmB to bring M close to zero. Interestingly, increasing kT assisted MTJMSDs to settle in low M state. At kT=0.25 most of the MTJMSD sizes settled in M=0 state. This result evidenced that availability of medium range kT can magnify the impact of JmT and JmB. We noticed that for MTJMSDs with 3D FM electrodes when JmT and JmB approached ~0.5 only then M

3.2. MC study on MTJMSDs

A molecule’s magnetic couplings with the top (JmT) and bottom (JmB) FM electrodes, respectively, are crucial in governing the magnetic properties of an MTJMSD (figure 1(e)). We first varied JmT and JmB at fixed kT to investigate the sign and magnitude necessary to attain strong antiferromagnetic couplings leading to the experimental observations on MTJMSDs (figure 2). As a key observable, overall magnetization M, where M=M_m (molecule magnetization) + M_T (top electrode magnetization) + M_B (bottom electrode magnetization), was recorded. In all our studies, the magnitude of M_T and M_B is equal. A 3D graph of M versus JmT and JmB at fixed kT was plotted (figure 3(a)). The 3D plot for 11×10×10 MTJMSD at kT=0.1 suggests that M approached M_m when M_T and M_B aligned in the opposite direction. Oppositely aligned M_T and M_B annihilated each other under the influence of opposite signs of JmT and JmB (figure 3(a)). For 11×10×10 size in a fully ordered state M_m is 3.6% of M_T+B. For higher kT molecules’ magnetic ordering become random due to thermal fluctuations and M=M_m approached zero. This MC result (figure 3(a)) confirms our interpretation of the experimental magnetization data (figures 2(b) and (c)) that OMC developed ferromagnetic (+) coupling with the Co/NiFe electrode and antiferromagnetic (−) coupling with the NiFe electrode. Hence, to observe the near zero MTJMSD’s magnetization at zero magnetic fields (figure 2(a), JmT and JmB must be of the opposite signs (figure 3(a)).

Figure 3. (a) Effect of J_mT and J_mB on magnetization (M) of the MTJMSD at kT=0.1. Effect of equal magnitude and opposite nature of J_mT and J_mB on M for the different size MTJMSDs at (b) kT=0.05 and (c) kT=0.25.
approached zero (figure 3(c)). This MC simulation supports the experimental estimation of OMC-induced coupling strength w.r.t. Curie temperature of the NiFe FM electrode. Since \( kT_c \) of FM electrodes in the MC study is of the order of \( J_F = J_B = 1 \) (S3, supplementary material), for observing oppositely aligned \( M_A \) and \( M_B \), the ratio of \( J_{nt}/kT_c \) or \( J_{anb}/kT_c \) will be of the order of 0.5. Interestingly, the ratio of molecule-induced antiferromagnetic coupling strength, represented by \( T_S \) and \( T_B \), was in the 0.5–0.54 range (figure 2(a)). Our MC simulation correctly estimated the order of molecule-induced coupling strength.

We also attempted to gain insight about the MFM studies, which showed negligible magnetic contrast at the sites of MTJMSDs (figure 2(g)). MFM images resulted from magnetic force \( (F) \) on the magnetic tip’s magnetization \( (m) \) by the stray field \( (H) \) originating from the magnetic sample in the ambience of magnetic permittivity \( (\mu) \) (figure 4(a)). \( F \) is given by \( \vec{F} = \mu(\vec{m} \cdot \vec{V} \times \vec{H}) \). We hypothesized that the oppositely aligned top and bottom FM electrodes produce stray magnetic fields of equal strength, but in the opposite direction. Two equal and opposite stray fields will produce counterbalancing forces on the MFM tip, leading to an overall negligible force and magnetic contrast from an MTJMSD site (figure 4(b)). However, as a condition to achieve negligible MF contrast magnetic moments of the top and bottom FM electrode, atoms should be oppositely aligned on all the topological sites of a MTJMSD. To check this hypothesis, we simulated the atomic and molecule site-specific spin vector profile. An atomic scale 3D vector plot of 3 × 5 × 5 MTJMSD for \( J_{nt} = -J_{anb} = 0.5 \) and \( kT = 0.1 \) is presented in figure 4(c). The small device size was chosen for uncluttered viewing: MTJMSDs with \( H > 3 \) also produced similar spin configurations. This 3D image (figure 4(c)) confirmed that our MC studies are simulating the correct MTJMSD analog model (figure 1(e)). We also calculated an average spatial spin magnitude for the MTJMSD \( (S_{MTJMSD}) \), the top \( (S_{FM-Bottom}) \), and the bottom \( (S_{FM-Bottom}) \) FM electrodes for \( 11 \times 10 \times 10 \) (figures 4(d) and (e)). To calculate \( S_{MTJMSD} \), we summed the spin vector of atoms of FM electrodes and molecules at each topological site along the H dimension for each coordinate on the X-Y plane (figure 2(e)). However, for \( S_{FM-Top} \) and \( S_{FM-Top} \) only atomic spin vectors were summed at each X-Y site for the top and bottom FM electrodes, respectively. The average spins of the top \( (S_{FM-Top}) \) and bottom \( (S_{FM-Top}) \) FM electrodes are of equal magnitude and opposite signs. Hence, cumulative \( S_{MTJMSD} \) spin for each X-Y site was nearly zero (figure 4(e)). However, at the edges \( S_{MTJMSD} \) represented molecule’s spin.

In actual microscopic MTJMSDs this \( S_{MTJMSD} \) is too small to detect experimentally. Such a small spatial magnetic moment \( S_{MTJMSD} \) at each spatial site will produce negligible stray field. This negligible stray field will yield nearly zero magnetic force contrast as observed in the experimental MFM image on the MTJMSD (figure 2(g)). Also \( J_{nt} \) and \( J_{anb} \) the variation of \( kT \) produced a pronounced effect on the MTJMSD magnetic state. Transition from high to low \( M \) for \( J_{nt} = -J_{anb} > 0.5 \) happened before \( kT = 0.1 \) for the \( 11 \times 10 \times 10 \) MTJMSD. As \( kT \) increased to \( kT_c = J_F = J_B = 1 \), thermal fluctuations destroyed the FM electrodes’ magnetic ordering suggesting that \( J_F \) and \( J_B \) are the order of \( kT_c \). This study confirmed our assumptions that \( J_F = J_B = kT_c \) (Figure S3a, supplementary material). Interestingly, the magnetization of the two FM electrodes, \( M_T \) and \( M_B \), decreased gradually and followed the trend \( T^{-}T_h^{\alpha} \). The magnitude of exponent \( \alpha \) for our \( M \) versus \( kT \) graph for FM electrodes was in the 0.4–0.5 range; this magnitude of \( \alpha \) is in the close agreement with the prior literature [17]. Section S3 of the Supplementary Material provides further discussion about the (a) effect of \( kT \) on the X, Y, and Z components of \( M_T \) and \( M_B \), (b) \( M \) versus \( kT \) graphs for different magnitude of \( J_{nt} \) and \( J_{anb} \) and MTJMSD dimensions, and (c) \( \chi^{-1} \) versus \( kT \) for the MTJMSD and two FM electrodes.

Insights from our MC simulations on MTJMSDs can be enhanced by existing and futuristic DFT studies. For instance, our assumption that \( J_{nt} \) and \( J_{anb} \) can be either ferromagnetic or antiferromagnetic is supported by DFT studies on magnetic interactions between a paramagnetic molecule and single FM electrode [5, 8, 9]. However, since previous DFT studies focus on specific molecules and a single FM electrode, we are unable to obtain directly relatable insights about the simultaneous determination of \( J_{nt} \) and \( J_{anb} \) for OMCs in an MTJMSD. To circumvent the need to determine molecular exchange coupling parameters for MC studies, we kept \( J_{nt} \) and \( J_{anb} \) as two variables. We investigated the suitable estimates of \( J_{nt} \) and \( J_{anb} \) by correlating MC simulations with corresponding experimental magnetic studies. We have studied different natures and magnitudes for \( J_{nt} \) and \( J_{anb} \) variables. Different permutations of \( J_{nt} \) and \( J_{anb} \) can be correlated with a variety of paramagnetic molecules to be integrated with the futuristic MTJMSDs. Undoubtedly, the concept of utilizing DFT studies for the simultaneous estimation of \( J_{nt} \) and \( J_{anb} \) is very useful. However, such undertakings may require overcoming the (1) difficulty in simulating a big paramagnetic molecule with the two 3D FM electrodes without sacrificing DFT’s strength and (2) difficulty in capturing all forms of magnetic interactions, including spin fluctuations [4], between two FM electrode exchange coupled by the paramagnetic molecule.

DFT studies were not shown to be effective in calculating cumulative magnetic properties as discussed in this paper. Recently, DFT studies have been combined with the classical MC simulation to calculate the overall magnetic properties like Curie temperature and the magnetic field effect [10, 20]. One pragmatic approach to simulate an MTJMSD with the combined strength of DFT and MC simulation may be to represent a complex paramagnetic molecule with the simpler entity like an atomic impurity [21] or quantum dot [4, 22]. The theoretical research by Martinek et al [22] on a quantum dot coupled to two FM electrodes was key in explaining the experimental observations of Kondo resonance peak splitting on \( C_{60} \) molecules coupled to two Ni electrodes [4]. Additionally, prior work on atomic impurity enhanced magnetic coupling on an MTJ can also be helpful in simulating the magnitude of molecule-enhanced coupling. Zhuralev et al [21] theoretically demonstrated that atomic defects within a tunnel barrier could enhance the magnetic coupling between
two FM electrodes of an MTJ by several orders. In the MTJMSD case, OMCs also enhanced the magnetic coupling between two FM electrodes of an MTJ. Due to the similarity in the effects produced by OMCs and atomic defects, we surmised an OMC to be equivalent to an atomic scale entity in our MC simulations, discussed in this paper. Our assumption for considering OMC or big molecule analogous to simpler entities is also based on the success of theoretical calculations on quantum dots [22] for explaining the complex phenomenon with C_{60} molecule based MSD [4]. Selzer et al [23] discussed the similarities in the device physics for the molecules and quantum dots.

4. Conclusions

Our MC simulations studied the effect of paramagnetic molecule-induced exchange coupling on the magnetic properties of the MTJMSD. We considered various permutations of the nature of magnetic interactions of a paramagnetic molecule with the two FM electrodes of a MTJMSD to understand the experimental results. Experimentally observed molecule-induced strong antiferromagnetic coupling was only possible when a paramagnetic molecule, or a molecule with a net spin state, established ferromagnetic coupling with a top (or bottom) FM electrode and antiferromagnetic coupling.
with the bottom (or top) FM electrode of an MTJ. Our MC simulations effectively explained the origin of the experimental data obtained from the SQUID magnetometer and MFM studies on MTJMSD. The experimentally estimated molecular coupling strength was in agreement with those estimated from our MC simulations. Increasing MTJMSD size was found to weaken the molecular coupling effect. However, it is quite possible that we underestimated the impact of molecular coupling on the MTJMSD size. In this study, we mainly focused on the Heisenberg-type magnetic interaction among nearest neighbors. In reality, molecules are expected to have other modes of couplings such as biquadratic coupling and dipolar coupling. Most importantly, paramagnetic molecules are also capable of invoking spin fluctuation assisted coupling between the two FM electrodes and need to be considered in future studies focusing on investigating MSD’s magnetic properties [4].

Acknowledgments

Our MCS study was in part supported by the National Science Foundation-Research Initiation Award (Contract #HRD-1238802), the Department of Energy/National Nuclear Security Agency (Subaward No. 0007701-100043016), and the Air Force Office of Sponsored Research (Award #FA9550-13-1-0152). Pawan Tyagi thanks Bruce Hinds and the Department of Chemical and Materials Engineering at the University of Kentucky for facilitating experimental work on an MTJMSD during his PhD. Stephen Holmes’s group produced OMC. V Durairaj, G Cao, A F Miller, and X Song assisted experimental magnetic studies. Any conclusions and remarks in this paper are those of the authors.

References

[1] Bogani L and Wernsdorfer W 2008 Molecular spintronics using single-molecule magnets Nat. Mater. 7 179–86
[2] Coronado E and Epstein A J 2009 Molecular spintronics and quantum computing J. Mater. Chem. 19 1670–1
[3] Miao G X, Munzenberg M and Moodera J S 2011 Tunneling path toward spintronics Rep. Prog. Phys. 74 036501
[4] Pasupathy A N, Bialczak R C, Martinek J, Grose J E, Donev L A K, McEuen P L and Ralph D C 2004 The Kondo effect in the presence of ferromagnetism Science 306 86–9
[5] Yoshida K, Hamada I, Sakata S, Umeno A, Tsukada M and Hirakawa K 2013 Gate-tunable large negative tunnel magnetoresistance in Ni–C60–Ni single molecule transistors Nano Lett. 13 481–5
[6] Atodiresei N, Brede J, Lazic P, Caciuc V, Hoffmann G, Wiesendanger R and Blugel S 2010 Design of the local spin polarization at the organic-ferromagnetic interface Phys. Rev. Lett. 105 066601
[7] Kawahara S L, Lagoute J, Repain V, Chacon C, Girard Y, Rousset S, Smogunov A and Barreteau C 2012 Large magnetoresistance through a single molecule due to a spin-split hybridized orbital Nano Lett. 12 4558–63
[8] Weber A P, Caruso A N, Vescovo E, Ali M E, Tarafder K, Janjua S Z, Sadowski J T and Oppeneer P M 2013 Magnetic coupling of Fe-porphyrin molecules adsorbed on clean and c (2 x 2) oxygen-reconstructed Co(100) investigated by spin-polarized photoemission spectroscopy Phys. Rev. B 87 184411
[9] Chylarecka D et al 2011 Indirect magnetic coupling of manganese porphyrin to a ferromagnetic cobalt substrate J. Phys. Chem. C 115 1295–301
[10] Friedrich R, Caciuc V, Kiselev N S, Atodiresei N and Blugel S 2015 Chemically functionalized magnetic exchange interactions of hybrid organic-ferromagnetic metal interfaces Phys. Rev. B 91 115432
[11] Tyagi P, Friebie E and Baker C 2015 Advantages of prefabricated tunnel junction based molecular spintronics devices Nano. 10 1550002
[12] Tyagi P 2011 Multilayer edge molecular electronics devices: a review J. Mater. Chem. 21 4733–42
[13] Li D F, Ruschman C, Clerc R and Holmes S M 2006 Ancillary ligand functionalization of cyanide-bridged S = 6 FeII4NiI4 complexes for molecule-based electronics Inorg. Chem. 45 7569
[14] Newman M E and Barkema G T 1999 Monte Carlo Methods in Statistical Physics (Oxford: Clarendon)
[15] Tyagi P, D’Angelo C and Baker C 2015 Monte Carlo and auxiliary ligand functionalization of cyanide-bridged S = 6 FeII4NiI4 complexes for molecule-based electronics Inorg. Chem. 45 7569
[14] Newman M E and Barkema G T 1999 Monte Carlo Methods in Statistical Physics (Oxford: Clarendon)
[15] Tyagi P, D’Angelo C and Baker C 2015 Monte Carlo and experimental magnetic studies of molecular spintronics devices Nano. 10 1550056
[16] Demokritov S O 1998 Biquadratic interlayer coupling in layered magnetic systems J. Phys. D: Appl. Phys. 31 925–41
[17] Coey J M 2010 Magnetism and Magnetic Materials (Cambridge: Cambridge University Press)
[18] Johnson M 2004 Magnetoelectronics (New York: Academic)
[19] Layadi A 1998 Ferromagnetic resonance modes in coupled layers with cubic magnetocrystalline anisotropy J. App. Phys. 83 3738–43
[20] Jakobsson A, Šašnová E, Mavropoulos P, Ležaić M, Sanyal B, Bihlmayer G and Blügel S 2013 Tuning the Curie temperature of FeCo compounds by tetragonal distortion App. Phys. Lett. 103 102404
[21] Zhuravlev M Y, Tsybubl E Y and Vedyayev A V 2005 Impurity-assisted interlayer exchange coupling across a tunnel barrier Phys. Rev. Lett. 94 026806
[22] Martinek J, Sindel M, Borda L, Barnas J, Konig J, Schon G and von Delft J 2003 Kondo effect in the presence of itinerant-electron ferromagnetism studied with the numerical renormalization group method Phys. Rev. Lett. 91 247202
[23] Selzer Y and Allara D L 2006 Single-molecule electrical junctions Ann. Rev. Phys. Chem. 57 593–623