Photo-switching of magnetization in iron nanoparticles

Nabil Al-Aqtash* and Renat Sabirianov

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Particularly, core of magnetization in iron nanoparticles can be strongly modified by the properties of surface atoms. Because of this, atomic local magnetic moments, and, more importantly, magnetic exchange interactions, occur between surface atoms. Because of this, surface termination, roughness, and symmetry. Furthermore, termination at the surface reduces the number of neighbors with which the surface (coordination) atoms interact. Because of this, atomic local magnetic moments, and, more importantly, magnetic exchange interactions of surface atoms can strongly be modified. Such sensitivity of nanoparticle properties to surface modification can be used to tune its magnetic properties by external stimuli such as an electric field or a pulse of light.

Photo-switching of magnetization in iron nanoparticles

Nabil Al-Aqtash* and Renat Sabirianov

We report the theoretical study of the light-induced switching of magnetization in core–shell nanoparticles. The core of the nanoparticle is made of iron (Fe) coated with the shell of azobenzene. Azobenzene is a photochromic material with reversible trans–cis photoisomerization upon irradiation by UV and visible light. The magnetization of nanoparticles can be reversibly switched using specific wavelengths of light. Using an ab initio parameterization of magnetic interactions we performed Monte Carlo simulations of the magnetization of the core–shell nanoparticle as a function of temperature. The results show that Fe nanoparticle magnetization can be switched by at least 50% because of the photoisomerization of azobenzene at room temperature. Ab initio calculations show that the exchange interaction in Fe dimer is ferromagnetic (FM), and shows a strong modification of exchange interaction parameters by 40% because of the trans–cis photoisomerization of azobenzene. An infinite planar Fe monolayer mimicking the surface of nanoparticle shows a strong modification of exchange interaction parameters (up to 50%) in the monolayer due to trans–cis photoisomerization. The local magnetic moments of Fe sheet increase by only 0.5% due to photoisomerization.

1. Introduction

In recent years, interest in nanoparticle magnetism has led to several advances in magnetic memory, biomedicine, and spintronics, among other fields. The size and temperature dependence of magnetization as well as magnetization reversal were studied both experimentally and theoretically in a variety of systems. The obtained results are system-dependent, suggesting the strong effects of surface morphology on the magnetic properties of nanoparticles, which may differ drastically from the properties of bulk materials. Because of their extreme size, nanoparticles are sensitive to the properties of their surfaces, i.e., surface termination, roughness, and symmetry. Furthermore, termination at the surface reduces the number of neighbors with which the surface (coordination) atoms interact. Because of this, atomic local magnetic moments, and, more importantly, magnetic exchange interactions of surface atoms can be strongly modified. Such sensitivity of nanoparticle properties to surface modification can be used to tune its magnetic properties by external stimuli such as an electric field or a pulse of light. Particularly, core–shell nanoparticles where the shell is sensitive to external stimuli can serve this purpose.

It has been recently observed that the magnetic properties of core–shell nanoparticles can be modified by specific wavelengths of light. The shell of these particles can be manufactured from photo-sensitive molecules, such as azobenzene, or other photochromic materials. Molecules such as azobenzene display photoisomerization or structural change in response to irradiation. This process is reversible using light of a different wavelength. Azobenzene chromophores can be switched between two geometric (trans and cis) isomers using ultraviolet and visible light pulses. This photoisomerization is rapid, reversible, and of high quantum yield. The wavelengths affecting the transformation can be tuned synthetically with substituent groups to the chromophores. Upon isomerization, there can be significant changes to the optical, geometric, mechanical, and chemical properties of azobenzene molecules, and these photoswitchable properties can often be transferred to large host systems into which azobenzene is incorporated.

In the cis, or “excited,” state, azobenzene exhibits an overall dipole moment of 3.0 D, whereas in the trans, or “ground,” state, the molecule has zero dipole moment. Reversible photoswitchable nanoparticles were achieved experimentally. Suda et al. designed reversible photoswitchable ferromagnetic (FM) FePt nanoparticles coated with azobenzene-derivatized ligands. They controlled the magnetic properties of the FM composite nanoparticles by alternating photoillumination at room temperature. In addition, a reversible photoswitching of the magnetization of iron oxide nanoparticles was achieved at room temperature by Mikami et al. However, possible mechanisms for controlling the magnetization in nanoparticle systems are yet to be clarified. The photoisomerization of azobenzene and other molecules with similar properties may provide a mechanism for varying exchange...
interaction on the surfaces of nanoparticles, and these exchange interactions affect magnetization.

In this study, we performed Monte Carlo simulations of the magnetization of the core–shell nanoparticle as a function of temperature to show that the magnetization of Fe nanoparticles can change because of the photoisomerization of azobenzene in the selected range of temperatures. We examine from first principles methods the effects of trans–cis photoisomerization of azobenzene on changing the surface local magnetic moments and the surface exchange interactions of Fe dimer and planar iron surface modeled by monolayer.

2. Model and computational methods

Interatomic exchange interaction parameters of the Heisenberg model are calculated from the energy difference of FM and antiferromagnetic (AFM) configurations. This approach to the finite temperature magnetic properties of base-(bcc) and face-(fcc) centered cubic structures of Fe have shown that the Heisenberg model based on electronic structure calculations predicts Curie temperature in good agreement with experimental results. We employ the Monte Carlo (MC) method with the Heisenberg Hamiltonian

$$H = - \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j,$$

where $J_{ij}$ is the pair exchange parameter, and summation is performed over the nearest neighbors. $J_{ij}$ is derived from the ab initio electronic structure calculations. If $J_{ij} > 0$, the exchange interaction is FM, and $J_{ij} < 0$ results in AFM interaction. We use Statistical MC method and Metropolis algorithm to simulate magnetization as a function of temperature in the nanoparticle. Effective exchange parameter $J_0 = - \sum J_{ij}$ determines the correspondence to Curie temperature in bulk systems. Here, we consider a core–shell nanoparticle in the shape of a truncated octahedron terminated by (1 1 1) and (0 0 1) facets, mimicking experimentally synthesized nanoparticles. The nanoparticle consists of 1297 atoms in face-centered cubic fcc structure.

Self-consistent, spin-polarized density functional theory (DFT) calculations are performed using SIESTA package, which uses numerical atomic orbitals as basis sets and Troullier-Martin type norm-conserving pseudopotentials. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) form is used for the exchange–correlation functional. Self-consistent calculations are performed with a 400 Ry mesh cutoff. A linear combination of numerical atomic orbitals with double-$\zeta$ polarization (DZP) basis set is used. The conjugate gradient method is used to relax all the atoms until the maximum absolute force is less than 0.01 eV Å$^{-1}$. We performed the spin-polarized calculations of Fe sheet for two configurations: (1) FM states (all spin up), and (2) AFM alignment of one atomic spin (down) maintaining the rest of the lattice in the initial state to determine the effective exchange interaction for Fe systems in all the cases.

The core of the nanoparticle is composed of Fe coated with the shell of azobenzene compound. The azobenzene molecule needs to be modified to attach to the surface. Here, e consider a molecule N(CH$_3$)$_2$C$_6$H$_4$–N–N–C$_4$H$_8$O–(CH$_2$)$_5$–COOH. It has been shown that this termination allows the molecule to attach to Fe sites on the surface. This molecule can form a self-assembled monolayer on the surfaces of metals and metal oxide.

3. Results and discussion

To elucidate the effect of surface exchange coupling on the magnetization of nanoparticle we performed the MC simulations of the magnetization of the model nanoparticle as a function of temperature. The effect of the trans–cis transition upon UV/visible light irradiation is modeled by altering the surface exchange parameters as derived from the ab initio calculations. We considered nearest exchange interactions between sites in the bulk ($J_{\text{ab}}$), between surface sites ($J_{\text{os}}$), and between surface and bulk sites ($J_{\text{os}}$) in the 1297 atom particle of fcc structure truncated in the shape of a cube–octahedron. Exchange interactions in the nanoparticle were altered from $R = J_{\text{ab}}/J_{\os}$ to 0.5, accounting for a 50% drop in surface exchange coupling upon photo-isomerization derived from the ab initio calculations. Using the parameterization of exchange interactions on the surface of Fe nanoparticle, we obtained magnetization as a function of temperature for Fe nanoparticle, which is shown in Fig. 1(a). The red curve (with circle points) shows the resulting magnetization with respect to temperature, $M(T)$, in the case of smaller surface exchange parameter, and the blue curve (with square points) shows $M(T)$ in the case of larger surface exchange, corresponding to cis and trans azobenzene isomers, respectively. Fig. 1(b) shows that Fe nanoparticle magnetization at selected temperatures ($T = 300$ K for our exchange parameters) can be switched by at least $R = 2 \cdot \frac{M_{\text{trans}} - M_{\text{cis}}}{M_{\text{trans}} + M_{\text{cis}}} = 50\%$ because of the trans–cis photo-isomerization of azobenzene. These results clearly show that magnetization switching is possible by the modification of surface exchange coupling alone. This effect can also be clearly seen in the enhancement of magnetic susceptibility near this range of temperatures, as shown in Fig. 1(b). Fig. 1(c) illustrates schematically photo-induced changes in the core–shell nanoparticles because of photoisomerization and potential change in Fe core magnetization. The trans–cis photoisomerization of azobenzene attached to the surface of magnetic nanoparticle may prove to be a way of optical stimulation of magnetization switching. This mechanism should not be confused with the all-optical magnetization reversal by circularly polarized light proposed for magnetic structures or similar approaches.

To quantify the effect of the photoisomerization of azobenzene on exchange interactions in nanoparticles, we performed the first-principles calculations of the magnetic properties of Fe systems modified by absorbed azobenzene. We started from the simplest system from which exchange interactions can be derived, i.e., Fe dimer attached to an azobenzene molecule through COOH termination. The molecule forms coordination bonds with the dimer. The relaxed structures of Fe–Fe pair attached to azobenzene in the case of trans and cis
isomers, as shown in Fig. 2, indicate bond formation between one of the Fe atoms and two oxygen atoms of azobenzene with a bond length of 2.1 Å, which is in good agreement with the experimental value of Fe–O bond length of 2.03 Å in FeO molecule.

Pair exchange parameter ($J_0$) is calculated as the difference in the energy of a dimer with co-aligned, $E(P)$, oppositely aligned, $E(AP)$, and local magnetic moments on Fe sites: $J_0 = E(AP) - E(P)$. The calculations show that the exchange interaction is FM, and the exchange parameter ($J_0$) in Fe dimer increases from 0.15 to 0.24 eV due to the trans–cis photoisomerization of azobenzene. Photoisomerization changes the energy states of azobenzene, and noticeably shifts the energy states of Fe-dimer that are hybridized with the states of azobenzene molecule. Fig. 3 shows the energy level diagram of molecular orbitals in Fe–azobenzene compound (Fe$_2$–N(CH$_3$)$_2$C$_6$H$_4$–N–N–C$_6$H$_2$O–(CH$_2$)$_7$–COOH) in AFM alignment of Fe local moments. Interestingly, there are small changes in Fe states near Fermi energy upon trans–cis transformation in co-aligned spin case. However, in anti-aligned spin configuration there is a noticeable difference between trans and cis isomers cases, as can be seen in Fig. 3. There is a minor variation in the energy of the minority (down) orbitals of Fe$_2$ states. However, there is noticeable shift in the energy of Fe$_2$ states of majority (up) orbitals near Fermi level. In addition to the energies of Fe state, cis–trans isomerization induces a shift and splitting of the O state to about 1.8 eV below HOMO, as shown in Fig. 3. This is an indication of change in interactions between oxygen electrons with Fe electrons, as well as Fe–Fe hybridization. As a result, the exchange coupling between Fe sites changes. One electron energy
The considered Fe planar sheet was taken to be 3.593 Å in the scope of force theorem approach is related to the exchange coupling parameter of the Heisenberg model.\textsuperscript{35} With “one-electron” eigenvalues, $\varepsilon_i$, shifting by 0.1–0.2 eV trans–cis isomerization clearly affects the energies on the scale of exchange interaction magnitudes.

To investigate the effects of the trans–cis photoisomerization of the azobenzene on exchange interactions at the surface of Fe nanoparticle, we attached trans azobenzene isomer to a planar Fe sheet containing 16 Fe atoms, and cis azobenzene isomer to a planar Fe sheet containing 24 Fe atoms, as shown in Fig. 4. Although the planar sheet of Fe may have exchange interactions that are somewhat different from the surface of Fe nanoparticle, the effect of photoisomerization on exchange coupling in a planar sheet can be estimated quantitatively using DFT calculations. The percentile of the change in exchange interaction in the planar sheet, mimicking the surface layer of nanoparticle, upon isomerization can be calculated. The lattice constant of the considered Fe planar sheet was taken to be 3.593 Å, corresponding to the calculated bulk fcc Fe. Calculations show the formation of Fe–O bonds at the interface of the molecule and Fe sheet. We find that after ionic relaxation, the Fe–O bonds are formed with bond lengths of around 2.25 Å, as shown in Fig. 4. These bond lengths are longer by 0.15 Å than that in Fe dimer with azobenzene. This is probably because of the additional bonding within the infinite Fe sheet (compared to Fe dimer), which reduces the number of electrons participating in Fe–O bonding. The change in atom positions at the contact points and the formation of chemical bonds may play a role in changing the local magnetic moments and induce magnetization on the surface of nanoparticle. This correlates well with substantial atomic displacements in the interfacial TiO$_2$ and PbO planes in ferroelectric/piezomagnetic heterostructures that also exhibit switchable magnetic state in the interfaces.\textsuperscript{36}

Our calculations show that the Fe sheet displays only a small change in the local magnetic moments due to the trans–cis photoisomerization of azobenzene. The local magnetic moments of Fe sheet increase by only 0.5% (from 3.580 $\mu_B$ with trans to 3.595 $\mu_B$ with cis isomer attached) due to photoisomerization. Upon the reversal of local magnetic moment of Fe in positions nearest to adsorption sites, $P_n$, shown in Fig. 4, the local magnetic moment on the reversed site is about 4.2 $\mu_B$. There is a small change in the magnitude of the local magnetic moment of reversed Fe by less than 2% upon trans–cis isomerization. Thus, we expect only a marginal effect on magnetization because of the changes induced in local magnetic moments.

Table 1. Calculated $J$ (eV) exchange coupling constant for Fe monolayer

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<th>Pure-Fe sheet</th>
<th>trans</th>
<th>cis</th>
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<tr>
<td>$P_1$</td>
<td>-0.1915745</td>
<td>-0.0824860</td>
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</tr>
<tr>
<td>$P_2$</td>
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<td>$P_3$</td>
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photoisomerization depends on the local surface atomic environment. Furthermore, the exchange interaction in Fe sheet is more AFM in the case of trans isomer than it is in the cis azobenzene isomer. If we introduce a photo-switching coefficient as a difference of exchange interaction parameter over its average value in two isomer configurations

\[ R_{\text{exch}} = 2 \cdot \frac{J_{\text{trans}} - J_{\text{cis}}}{J_{\text{trans}} + J_{\text{cis}}} \]

we find that \( R_{\text{exch}} \) is about 25-50%. Because the effective exchange parameter is linearly proportional to Curie temperature in bulk ferromagnet (\( T_C = \frac{2J_0}{3K_B} \)) or Neel temperature of antiferromagnet, the change in the exchange parameter will affect magnetization variation as a function of temperature in nanostructures.

The calculated switching in exchange parameters comes from the changes in electron density distribution at the interface between molecule and Fe sheet when trans-cis transformation occurs. This redistribution arises from both the formation of dipole moment in the molecule and also the change in Fe-O bond strength at the interface. We should point out that both azobenzene and COOH groups have large dipole moments, which are altered by the trans-cis transformation. Table 2 summarizes the values of electric dipole moments for trans and cis azobenzene isomers with terminating molecules before and after attachment to the Fe sheet. The electric dipole moments of trans and cis azobenzene isomers were changed due to the interaction with Fe sheet. This change may be a possible case of switching magnetization on the surface of Fe nanoparticle due to the trans-cis photoisomerization of azobenzene. The electric dipole moment of Fe-monolayer-azobenzene system is changed from 4.2 to −4.8 D due to trans-cis photoisomerization. This suggests that photo-induced changes in the electronic polarization of the electrons on the surface Fe atoms affect the magnetic properties of the Fe nanoparticle. Recently, it was found that changing the direction of electric polarization in the ferroelectric phase controlled the induced magnetization in the systems. This also agrees with the \( ab \) initio calculations that show the reversal of polarization results with change in the net magnetization of the ferroelectric/piezomagnetic heterostructure system by more than 50%.

The switching in magnetization is induced because of the modification of exchange interactions on the surfaces of Fe nanoparticle coupled to the switching in dipole moments of attached functionalized azobenzene molecule. Note that the interaction of Fe with O across the interface between molecule and nanoparticle is critical for large observed switching. Unattached azobenzene molecules would change their dipole and switch the electric fields near the surface of the nanoparticle.

However, this field would only marginally affect the exchange parameters between Fe spins and does not result in noticeable magnetization switching.

4. Conclusions

We investigate the mechanism of magnetization switching in core–shell nanoparticles (Fe-core) due to the photoisomerization of the shell (azobenzene). The results of Monte Carlo simulations show that Fe nanoparticle magnetization at a select temperature range can be switched reversibly by at least 50% because of the photoisomerization of azobenzene caused by a light pulse. \( ab \) initio calculations show that the exchange interaction in Fe dimer is FM, and shows a strong modification of exchange interaction parameters by 40% due to the trans–cis photoisomerization of azobenzene. Moreover, the calculations show that an infinite planar Fe monolayer displays a small change on surface local magnetic moments and a strong change on exchange interactions of surface atoms as a result of trans–cis azobenzene photoisomerization. The exchange interaction in Fe sheet is more AFM in the case of trans isomer than it is in the cis azobenzene isomer. Our calculations show up to 50% change in the exchange interaction parameters between trans and cis azobenzene isomers.

We believe that the magnetic photoswitching mechanism in nanoparticles due to photoisomerization described in this work should be helpful in practical research of nanoparticle materials with enhanced photomagnetic switching ratio. Therefore, we hope that our results will stimulate experimental work on the reversible photoswitching of the magnetization of nanoparticles and nanostructures.

Acknowledgements

This work was supported by NSF-MRSEC (Grant no. DMR-0820521) and NSF (Grant no. DMR-1310542). The University of Nebraska Holland Computing Center provided computation resources.

References


32. $J_{\text{eff}}$ is taken as 31.4 meV in our calculation, and Curie temperature is around 400 K, i.e. above room temperature.


