Influence of the Dipolar Interactions on the Relative Stability in Spin Crossover Systems

Salvador Cardona-Serra* and Stefano Sanvito

Molecules exhibiting a spin-crossover transition have been proposed for a number of applications such as molecular switches, spintronic tunable interfaces, and single molecule gates. Both the rational design of new spin-crossover systems and the improvement of the properties of the already existing ones require a theoretical understanding of the relative energy of the high (HS) and low spin state (LS) molecules in the solid-state. This has proved to be very challenging so far. Here, we shed some light on the importance of considering the symmetry and the geometry of the crystallographic cell to correctly evaluate the influence of the dipolar interactions on the relative energies of the molecular complex in both different spin states. Moreover, in the case of $Fe(SCN)_2(phen)_2$ dipolar interactions are found to play an important role for the stabilization of the LS complex. © 2016 Wiley Periodicals, Inc.

DOI: 10.1002/jcc.24676

Introduction

Spin-crossover (SCO) molecules are considered as one of the most promising molecular systems for magnetic information storage.[1] There are proposals that their spin state can be manipulated by an external electric field and coherent electronic transport has been calculated to be significantly different depending of the molecule magnetic configuration.[2] The unique possibilities offered by these molecular systems match the main ideas and concepts of inorganic spintronics making them very promising within the framework of molecular spintronics.[3,4] For instance, SCO molecules as environment-dependent bistable objects can be the active component in memories or in sensors,[5] with the advantage of being low-cost and processable from solution as well as by sublimation.[6] Compounds that exhibit a SCO behavior show specific advantages regarding the external manipulation, such as their ability to reversibly change from high to low spin (LS) state with different stimulus like temperature, pressure or light.[7]

However, mainstream every-day applications require a spin transition at room temperature. Toward that goal, a large number of theoretical approaches have been developed in the last decades.[8–10] Whereas ligand field theory[11] focuses in the single-molecule consideration and the Fe(II) 3d orbital splitting (10Dq) producing the useful Tanabe-Sugano[12] diagrams, this vision is restricted to the case of a single molecule. But understanding the large-scale behavior requires to go beyond the isolated complex and include molecule–molecule and molecule–lattice interactions. From the solid-state view, new models accounting for these macroscopic interactions are being developed. As an example, a contribution concerning molecule-phonon coupling has been recently published.[13] Here, we deal with the inclusion of the electric dipolar interaction between molecules in the real crystal environment, which to the best of our knowledge, has been never considered before in this context.

For at least one decade, the calculation of the total energy difference (ΔE_{tot}) between high and low configurations in molecular-based SCO materials has been a hard problem, difficult to address either by theoretical chemists or physicists.[14–16] The main issue with these systems is related with the high computational cost associated to calculating, at a high level of accuracy, such tiny quantity, related to materials containing a large number of atoms.

To overcome such problem one has to carry out calculations by accepting a number of assumptions. The first consists in the level of electronic structure theory considered. The most widely used approach is to perform total energy calculations with density functional theory (DFT).[17] Here, however, the choice of exchange and correlation functional becomes paramount.

In general, local and semi-local functionals, such as the local density approximation (LDA) or the generalized gradient approximation (GGA), tend to under-estimate energy difference between the expanded ($S = 2$) and contracted ($S = 0$) conformations. This is usually corrected by a specifically engineering a functional incorporating some fraction of Hartree–Fock (HF) exchange energy.[18] But the actual amount of HF exchange needed varies from molecule to molecule and a true predictive power is difficult to achieve. An additional problem is that usually these total energy calculations are performed in gas phase molecules (either in their experimental geometry, when available, or in that obtained by DFT relaxation). Neither of these situations is ideal, as they do not correspond to the actual samples, where the molecules are in a solid-state single crystal form together with counter-ions.

This leads us to consider a single molecule in its actual molecular environment, that is, as part of total crystal. In this

S. Cardona-Serra, S. Sanvito
School of Physics and CRANN, Trinity College Dublin, Dublin 2, Ireland
E-mail: salvador.cardona@uv.es

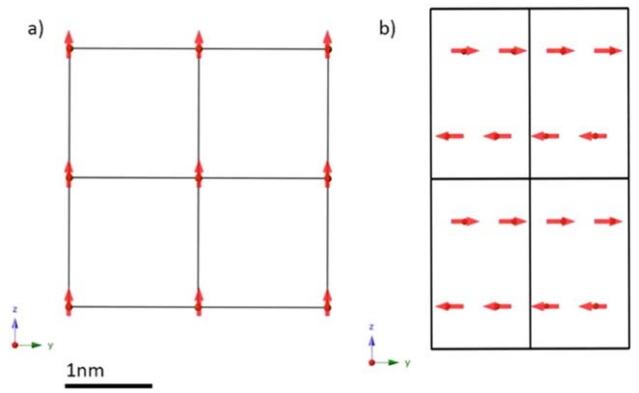

Figure 1. Schematic representation of the dipolar models. a) Previous elementary model to mimic the Madelung field. b) The proposed model presented in this work that keeps the dipolar orientation and the symmetry of the experimental crystal. [Color figure can be viewed at wileyonlinelibrary.com]

case, one can account for intermolecular dipolar interactions, which may be decisive for determining the relative stability of both conformations. In a recent publication, complete unit cell calculations have been used for first time to obtain effective parameters about the dynamic properties of the SCO transition.[19] Unfortunately, considering the complete unit cell (and its long-range interactions) using periodic boundary conditions has been proved to be extremely computational expensive to achieve. A possible way around this problem is that of introducing an effective Madelung field in the simulations to mimic the rest of the crystal.[20] Thus, an *effective* fictitious unit cell has sometimes been used to simulate such a field: the main complex has been simulated by positioning a lone Fe ion surrounded by six nitrogen in octahedral positions arranged collinearly in a pseudo-cubic cell. This model is clearly very far from being realistic, not only in terms of the ligand truncation (it partially eliminates the molecular dipoles) but also in terms of the orientation of the molecular entities.

In this article, we first perform point-charges embedded DFT (see *ab initio* calculations) and we go beyond such model and propose a different effective approach that considers the complete dipolar interactions present in a specific crystal symmetry. In particular, we explore whether such factor affects the total energy difference between the two states of the complex. The differences between the two models are shown in Figure 1.

Methods

Ab initio calculations

The Gaussian09[21] code has been selected as the tool to perform the molecular *ab initio* calculations. The theoretical level of description was set using the hybrid functional (20% HF) UB3LYP[22]/TZP which is known to give accurate results for many chemical problems. In contrast to the common practice, we have avoided to parameterize the functional to obtain the energy difference for the gas-phase molecule in both states. Instead we demonstrate that including long-range dipolar interactions, which account for the single-crystal symmetry, can approach the value to the experimentally measured. We have also tested a GGA functional UPBE[23]/TZP. The latter is known to overestabilize the LS complex because of a large self-interaction error, but it is included for completeness. Thus, the energy of a specific configuration and the dipolar moment of such state are obtained. It is important to note that, as the property is usually measured in a single crystal, the geometry of the molecule used in the calculations should reflect that fixed structure. Thus, the molecular coordinates, for both configurations extracted from crystal diffraction measurements, were used without further relaxation.

To complete our *ab initio* model with the intermolecular interactions present in the solid state, we have extended the DFT calculation with the inclusion of a neutral sphere of dipoles formed by point charges following the crystal geometry on each case. These dipoles should account for the dipole-dipole effect explicitly.

Dipolar model

Let us start describing the electric field in a single point (reference) created by a dipole:

$$E(\vec{r}) = \frac{1}{4\pi\epsilon_0}\left[3\frac{\vec{p}\cdot\left(\vec{r}-\vec{r}'\right)}{|\vec{r}-\vec{r}'|^5}\cdot\left(\vec{r}-\vec{r}'\right)-\frac{\vec{p}}{|\vec{r}-\vec{r}'|^3}\right] \quad (1)$$

where $\vec{r}$ and $\vec{r}'$ are the coordinates of two dipoles (reference and measured), $\vec{p}$ the vectorial coordinates of the measured dipole, and ε_0 the vacuum permittivity.

Thus, it is possible to calculate a sphere of dipoles located in their crystallographic positions and add their electric field applied over a central dipole using:

$$U_0 = \sum_i^{\text{sphere}} E(\vec{r}_i)\cdot\vec{p}_0 \quad (2)$$

with $\vec{p}_0$ the vectorial coordinates of the reference dipole.

Considering these formulas, it is immediate to realize that the vectorial nature of the dipoles makes it decisive to include their orientation and position. Each individual dipole is considered to be located at the position of the metal ion and to point in the direction established by the DFT calculation. As this orientation depends on how the molecule arrange in the crystal phase, and not all the molecules are necessarily in equivalent positions, their dipolar vectors may not be collinear.

These data have been introduced as input in a homemade FORTRAN code that accounts for such dipole summation. Thus, knowing the crystal structure of a SCO complex (measured at both geometric configurations) one can estimate the dipolar contributions to each state in a very time-inexpensive calculation. We considered spheres of increasing size, which include dipoles located on the metal crystalline positions, until achieving convergence. This calibration was tested in the LS state of B3LYP (the one that presents the highest dipolar moment). The radius of the sphere was increased in steps of

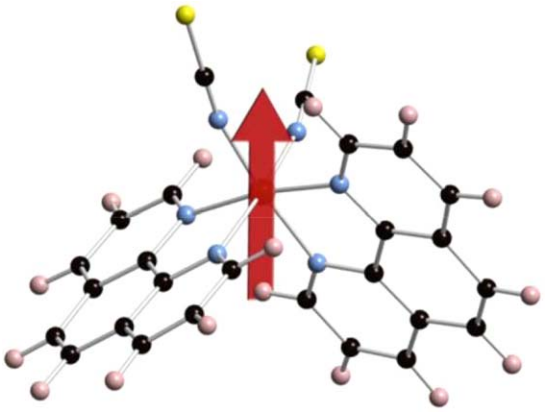

Figure 2. Molecular representation of the molecule $Fe(SCN)_2(Phen)_2$. A schematic arrow has been depicted to show the molecular electric dipole. [Color figure can be viewed at wileyonlinelibrary.com]

10 Å starting at 100 Å. The final convergence was achieved for a radius of 150 Å with an error < 0.01 eV (energy difference between that calculation and the previous in size), which means about 24,000 dipoles considered.

The contribution to the energy difference obtained from intramolecular interacctions will then be used to calculate the total gap as a correction to gas phase DFT calculations [see eq. (3)]. This equation proposes that the total stabilization energy for a complex configuration is the sum of its isolated energy plus a term concerning the intermolecular non-covalent interaction, as has been assumed elsewhere.[24]

$$\Delta E_{\mathrm{tot}_{HS-LS}} = \Delta E_{\mathrm{gas}_{HS-LS}} + \Delta E_{\mathrm{dip}_{HS-LS}} \quad (3)$$

Results and Discussion

As a test case study for our approach, we have selected the widely studied $[Fe(SCN)_2(phen)_2]$ molecule, as this SCO entity is simple and it crystallizes without counterions.[25]

Crystallographic data for this complex show two different structures determined at two different temperatures, namely at 293 K and 130 K. The SCO transition in $Fe(SCN)_2(phen)_2$ occurs at 176 K, meaning that those two geometric states can be assigned to the high spin (HS) and the low spin (LS) configuration respectively.

In both structures, the Fe(II) ion shows a coordination sphere formed by four nitrogen atoms from two phenantroline ligands and two nitrogen atoms from both thiocyanate anions. The presence of the two latter charged ligands coordinating the Fe^{2+} cation suggests the formation of an electric dipole pointing along the direction going from the Fe ion to a midpoint between the SCN^- ligands (see Fig. 2).

Using the methods described in the "theoretical model – *Ab initio* calculations" section, the relative energy differences and the dipolar vectors for both complex geometries have been obtained. Note that these are for the molecules in the gas phase, any intermolecular interaction has been considered yet. These results are consistent with those previously obtained by other authors.[18a, 26] Thus, we have obtained an energy difference ($\Delta E_{\mathrm{gas}_{HS-LS}}$) of -0.24 eV for B3LYP and $+0.59$ eV for PBE. A previous study showed that the PBE functional overstabilizes the $S = 0$ conformation, showing an unrealistic energy gap due to the self-interact error, whereas B3LYP may produce the configuration with $S = 2$ as ground state, which is in contradiction with the experimental results.[25]

Table 1. Dipolar moment (in Debyes) of a single $Fe(SCN)_2(phen)_2$ molecule for HS and LS at two different functional levels.

Dipolar moment	HS state (D)	LS state (D)	ΔD (D)	ΔE_{dip}(eV)
B3LYP	19.60	20.27	0.67	0.31
PBE	16.13	17.89	1.76	0.64

In addition, the use of the B3LYP functional results in higher absolute values of the electrical dipole although the relative energy difference between the two spin-states is lower than that obtained using PBE. In both cases, the LS geometry seems to present a higher dipolar moment. This behavior can be explained by comparing the distribution of the electronic density in both spin states. In the more expanded case, most of the positive charge is located on the iron atom. On the contrary, the more contracted case presents the positive charge slightly spread to the carbon atoms of the phenantroline ligands farther away from the negative charge that resides on the SCN^- anions. This effect is likely due to the lower distance between the ligands and the iron in the latter configuration, which promotes the charge transfer.

As a first estimation of the dipolar interaction contribution we considered an embedded DFT by adding point charges that were adapted to give the previously obtained dipoles. We performed this calculation using B3LYP/TZP to establish a lower bound in the dipolar stabilization energy.

The obtained results showed a partial stabilization of the LS complex compared to the HS with total gap value of -0.19eV. This would give a dipolar contribution of 0.05eV favoring the LS complex, but not strongly enough to obtain it as the ground state. This problem has been previously studied in the literature and many author have claimed DFT methods fail in the calculation of non-covalent intermolecular interactions.[27]

Finally, the second effective model permitted us to estimate the dipolar interaction energy using an inexpensive classical model implemented in a FORTRAN code (see theoretical model section). The differences in the dipolar stabilization energy are $\Delta E_{\mathrm{dip}_{HS-LS}} = 0.31$ eV for the B3LYP calculations and 0.64 eV for the PBE ones. This results in a favorable stabilization of the higher dipole configuration against the lower one, proportional to the difference in the dipolar moments calculated at the two different levels of theory, as seen in Table 1.

These results can be used to extend the single molecule gas phase calculations to the solid-state resulting in a total energy difference ΔE_{tot} as defined in eq. (3).

By adding such energy differences, we have found that the LS has now becomes stabilized enough to be the ground state with $\Delta E_{\mathrm{tot}} = 0.07$ eV using B3LYP. If we assume a typical entropy change of 50 J K/mol[25] and considering the transition temperature at 176K, we can estimate an experimental energy

gap of 0.088 eV, which is then very consistent with our estimate. While there exists some deviation, it is remarkable that the improvement of considering such effect is worth the inexpensive cost of the method.

Conclusions

This work tackles a crucial problem in SCO complexes, namely the calculation of the relative stability of the molecular complexes in both spin states. We show that, with both point-charges embedded DFT and with a classical effective model, the dipolar contribution to the energy of each state of remarkably important. Thus, we claim that the inclusion of such effect is a must when trying to extend the gas phase calculations to the solid state. As expected, DFT results showed a considerable smaller dipolar interaction than the effective model while evaluating the magnitude of this non-covalent interaction although it also predicts a major stabilization of the LS complex. The effective dipolar model contrary emerges as a simple and inexpensive method to approximately evaluate the magnitude of such interaction. This, applied to an example complex, the $Fe(SCN)_2(phen)_2$ molecule, and combined with the fact that larger electronic dipoles are found in the contracted state due to the distribution of the electronic density yields a better consideration of the molecular behavior in the solid state.

This model is applicable to all the SCO families in which an electric dipole can be defined. It remains uncertain whether additional corrections, such as including higher order terms, can be important for complexes without net electric dipole.

Acknowledgment

Salvador Cardona-Serra thanks the Generalitat Valenciana for a Val I + D postdoctoral grant. Stefano Sanvito acknowledges the Quest project funded by European Research Council. Both authors thank COST action CA15128 Molecular Spintronics (MOLSPIN) and the Trinity Centre for High Performance Computing (TCHPC) for providing the computational resources.

Keywords: spin crossover · dipolar interactions · molecular spintronics · molecular magnetism

How to cite this article: S. Cardona-Serra, S. Sanvito. *J. Comput. Chem.* **2017**, *38*, 224–227. DOI: 10.1002/jcc.24676

[1] P. Gütlich, Y. García, T. Woike, *Coord. Chem. Rev.* **2001**, *219–221*, 839.
[2] (a) D. Aravena, E. Ruiz, *J. Am. Chem. Soc.* **2011**, *134*, 777; (b) N. Baadji, S. Sanvito, *Phys. Rev. Lett.* **2012**, *108*, 217201.
[3] (a) S. Sanvito, Nat. Phys. **2010**, *6*, 562; (b) S. Sanvito, *J. Mater. Chem.* **2007**, *17*, 4455; (c) L. Bogani, W. Wernsdorfer, *Nat. Mater.* **2008**, *7*, 179; (d) S. Sanvito, *Chem. Soc. Rev.* **2011**, *40*, 3336.
[4] F. Prins, M. Monrabal-Capilla, E. A. Osorio, E. Coronado, H. Van Der Zant, *Adv. Mater.* **2011**, *23*, 1545.
[5] A. Galet, A. B. Gaspar, M. C. Muñoz, G. V. Bukin, G. Levchenko, J. A. Real, *Adv. Mater.* **2005**, *17*, 2949.
[6] S. Shi, G. Schmerber, J. Arabski, J. B. Beaufrand, D. J. Kim, S. Boukari, M. Bowen, N. T. Kemp, N. Viart, G. Rogez, E. Beaurepaire, H. Aubriet, J. Petersen, C. Becker, D. Ruch, *Appl. Phys. Lett.* **2009**, *95*, 043303-043.
[7] (a) A. Bousseksou, G. Molnár, L. Salmon, W. Nicolazzi, Chem. Soc. Rev. **2011**, *40*, 3313; (b) P. Gütlich, Y. Garcia, H. A. Goodwin, *Chem. Soc. Rev.* **2000**, *29*, 419.
[8] P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed.* **1994**, *33*, 2024.
[9] A. Hauser, In Spin Crossover in Transition Metal Compounds II, Vol. *234*; P. Gütlich, H. A. Goodwin, Eds.; *Top. Curr. Chem*., Springer-Verlag: Berlin, Heidelberg, **2004**; pp. 155–198.
[10] T. Kawamoto, S. Abe, *Chem. Commun.* **2005**, 3933.
[11] H. L. Schläfer, G. Gliemann, Einführung in die Ligandenfeldtheorie; Akademische Verlagsgesellschaft: Wiesbaden, Germany, **1980**.
[12] Y. Tanabe, S. Sugano, *J. Phys. Soc. Jap.* **1954**, *9*, 753. *Ibid*, 766-779. *Ibid*, 1956, *11* (8), 864-779.
[13] (a) A. Palii, S. Ostrovsky, O. Reu, B. Tsukerblat, S. Decurtins, S.-X. Liu, S. Klokishner, J. Chem. Phys. **2015**, *143*, 084502; (b) N. Sasaki, T. Kambara, *J. Chem. Phys.* **1981**, *74*, 3472.
[14] (a) S. Vela, M. Fumanal, J. Ribas-Arino, V. Robert, *Phys. Chem. Chem. Phys.* **2015**, *17*, 16306.
[15] (a) A. Droghetti, D. Alfè, S. Sanvito, J. Chem. Phys. **2012**, *137*, 124303; (b) A. Droghetti, D. Alfè, S. Sanvito, *Phys. Rev. B* **2013**, *87*, 205114.
[16] (a) S. Zein, S. A. Borshch, P. Fleurat-Lessard, J. Chem. Phys. **2007**, *126*, 014105; (b) M. Swart, A. Groenhof, A. W. Ehlers, K. Lammertsma, *J. Phys. Chem.* **2004**, *108*, 5479; (c) S. Mebs, B. Braun, R. Kositzki, C. Limberg, M. Haumann, *Inorg. Chem.* **2015**, *54*, 11606.
[17] (a) P. Hohenberg, W. Kohn, Phys. Rev. **1964**, *136*, B864; (b) W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140*, A1133.
[18] (a) M. Reiher, Inorg. Chem. **2002**, *41*, 6928; (b) M. Reiher, O. Salomon, B. A. Hess, *Theor. Chem. Acc.* **2001**, *107*, 48; (c) K. P. Kepp, *Inorg. Chem.* **2016**, *55*, 2717; (d) S. Ye, F. Neese, *Inorg. Chem.* **2010**, *49*, 772.
[19] H. Paulsen, *Magnetochemistry* **2016**, *2*, 14.
[20] (a) M. Kepenekian, B. Le Guennic, V. Robert, J. Am. Chem. Soc. **2009**, *131*, 11498; (b) M. Kepenekian, B. Le Guennic, V. Robert, *Phys. Rev. B* **2009**, *79*, 094428.
[21] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision **A.1**; Gaussian, Inc.: Wallingford, CT, **2009**
[22] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
[23] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
[24] (a) N. Kovačević, A. Kokalj, *J. Phys. Chem. C* **2011**, *115*, 24189; (b) E. J. Meijer, M. Sprik, *J. Chem. Phys.* **1996**, *105*, 8684.
[25] E. König, K. Madeja, *Chem. Commun.* **1966**, 61.
[26] H. Paulsen, A. X. Trautwein, *J. Phys. Chem. Solids* **2004**, *65*, 793.
[27] (a) G. A. DiLabio, A. Otero-de-la-Roza, Noncovalent Interactions in Density Functional Theory, in Reviews in Computational Chemistry, Volume *29*; A. L. Parrill, K. B. Lipkowitz, Eds.; John Wiley & Sons, Inc: Hoboken, NJ, **2016**. doi: 10.1002/9781119148739.ch1; (b) E. S. Kryachko, Struct. Bond. **2013**, *150*, 65. And references herein.

Received: 28 October 2016
Revised: 7 November 2016
Accepted: 8 November 2016
Published online on 24 November 2016