

Modeling spin-crossover compounds by periodic DFT+U approach

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The electronic properties of two spin-crossover compounds, namely, $\text{Fe}(\text{phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{btr})_2(\text{NCS})_2\text{H}_2\text{O}$, are studied with the GGA+U method taking explicitly into account the periodicity of the crystal. The magnetic state of the iron atom (low spin or high spin), which is strongly coupled to the lattice structure, depends on the chosen value for the parameter U and the total energies of various spin states varying linearly on the U parameter, each with a different slope. The adiabatic energy difference between the low and high spin states is in good agreement with the experiment for $U=2.5$ eV.

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I. INTRODUCTION

Among molecular magnets, some of them exhibit a transition between a low spin (LS) and a high spin (HS) state, under external perturbation such as change in temperature, application of pressure, or by light irradiation.^{1–5} This bistability appears to be promising for the building of molecular switches, for data storage, and in nonlinear optics.^{2,6} From a practical point of view, a number of devices^{2,6} such as displays, pressure captors, etc., are currently using this effect as the driving force of their mechanism. Spin-crossover (SCO) phenomena have also been shown to have a key role in the physics of the lower mantle of the earth.⁷ This transition is governed by the competition between the crystal-field strength that acts on the electrons and by the intra-atomic Hund exchange between them. This phenomenon is quite challenging theoretically since the characteristics of the transition (whether it actually happens or not, under which conditions, being smooth or abrupt, etc.) requires a high level of accuracy for the method employed. Even the correct ground state (LS or HS) is difficult to predict since these two states are often almost degenerate in energy. Numerous studies have been performed in the last ten years using quantum chemistry methods or density-functional theory. Wavefunction methods are numerically very costly and usually do not take into account the whole molecule.⁸ Density-functional calculations on spin-crossover compounds, which are more affordable, are not able to give a fully satisfactory answer since the results are strongly dependent on the exchange-correlation functional.^{9–11}

Moreover, such calculations usually neglect the periodicity of the system and therefore cannot be useful to understand cooperative effects, which are assisted by H bonds, by van der Waals forces, or simply by the packing of the molecules within the cell.⁶ On the opposite, in solid-state physics, the phenomenon of spin-crossover is widely studied in a periodic framework¹² but usually for systems with moderate size, which are not relevant for molecular magnetism. Also, recently, calculations concerning isolated or on a surface iron porphyrin complex were conducted^{13,14} using the DFT+U method. Even more recently, a work on a prototype SCO compound, the $\text{Fe}(\text{btz})_2(\text{NCS})_2$ was published—taking into account the periodicity of the crystal.¹⁵ These calculations

used the local-density approximation to the exchange-correlation potential within the framework of the atomic sphere approximation.¹⁵ However, contrary to the present study, the effect of strong correlation on the iron site was not taken into account.

In the following, we present an investigation of the electronic, magnetic, and energetic properties of two typical spin-crossover compounds: $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, where phen means phenanthroline with chemical formula $\text{C}_{12}\text{H}_8\text{N}_2$; and $[\text{Fe}(\text{btr})_2(\text{NCS})_2\text{H}_2\text{O}]$, where btr means bis-triazole with the chemical formula $\text{C}_4\text{N}_6\text{H}_4$. Unlike the overwhelming majority of electronic structure studies on SCO systems, the calculations are performed on the crystal by taking into account explicitly the periodicity within a PAW (projector augmented wave) framework. The well-known deficiencies of common functionals for transition-metal compounds are corrected by the GGA+U method. After providing some details about the computational method, we present our results concerning the influence of the U parameter on the total energies and in particular on the determination of the ground state. The electronic structure is characterized by the density of states (DOS) and by the electron deformation density of the Fe(II) ion in its low-temperature (LT) LS and high-temperature (HT) HS forms, and is compared with the one characterized experimentally by high-resolution x-ray diffraction. Finally, the last section concludes the main results of this work and indicates some future perspectives opened by the density functional theory (DFT) modeling of solid-state SCO systems.

II. COMPUTATIONAL DETAILS

The calculations have been performed by the PAW method¹⁶ as implemented in the Vienna Ab-initio Simulation Package (VASP).¹⁷ The PAW method takes advantage of the simplicity of pseudopotential methods but describes correctly the wave function in the augmentation regions, leading to a full potential and all-electron approach. In particular, the convergence with respect to the basis set is easily controlled, a point which has been shown to be crucial for a realistic description of spin-crossover systems.¹⁸ The PBE (Ref. 19) variant of the generalized gradient approximation (GGA) was used for the exchange-correlation functional.

In order to correct the failure of usual functionals in taking into account the strongly correlated character of the d electrons of iron, a Hubbard-like term is added to the Kohn-Sham Hamiltonian.^{20,21} The localized d electrons experienced an additional spin and orbital dependent potential, whereas the other electrons are continued to be described by GGA. The main effect of this additional potential is to correct the self-interaction error of GGA particularly strongly affecting these electrons that would lead—due to the strongly overestimated electron repulsion—to their artifactual delocalization, which is manifested, e.g., by strongly underestimated band gaps. The role of the Hubbard correction is to mimic an on-site Hartree-Fock treatment by a parametrized effective Hamiltonian. The basic physical effect is to introduce a penalty for the partial occupation of the localized d electrons and favoring either the fully occupied or completely empty d orbitals.²² This penalty is essentially tuned by the U parameter, which is usually determined empirically. In the present calculations, we used the rotationally invariant form of DFT+ U as implemented in VASP.²³ For all the calculations, J has been set to 0.95 eV; whereas the value of U was varied to study its influence on the electronic properties; U and J being the averaged on-site Coulomb and exchange integrals, respectively. Usually, J is known to have values between 0.9 and 1.0 eV for Fe. However, the value to be chosen for U is more delicate since U represents an effective interaction between d electrons but screened by s and p electrons.

To ensure the convergence of the relevant quantities, a cutoff of 450 eV was used for the plane-wave expansion of the wave function. For Brillouin zone integrations, a $2 \times 2 \times 2$ grid was used for $[\text{Fe}(\text{btr})_2(\text{NCS})_2\text{H}_2\text{O}]$; whereas a slightly larger grid of $2 \times 3 \times 2$ was necessary for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$.

For the two compounds investigated here and for the two possible magnetic states (HS or LS), the crystal structures were taken from the experiment.^{24–27} $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ crystallizes in the space group $Pbcn$ (orthorhombic, space-group 60) with four molecules per cell (204 atoms), whereas $[\text{Fe}(\text{btr})_2(\text{NCS})_2\text{H}_2\text{O}]$ crystallizes in the monoclinic space group $C2/c$ (space-group 15) with 152 atoms and also four molecular formula in the cell. As is well known, molecular solids undergo large thermal contraction effects as the temperature is decreased to cryogenic conditions. For the present HS vs LS comparison to be relevant, the crystal structure of the metastable HS state has been used for the calculations rather than the room temperature HS one. As a matter of fact, the LS and the metastable HS structures for both compounds were determined experimentally at exactly the same temperature ($T=15$ K), thus ruling out any bias due to thermal contraction. Notice that the crystal structure and the magnetic state are quite dependent from each other since, for example, in the case of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, the average bond length between the Fe atoms and its first neighbors is 1.970 Å in the low spin state; whereas it is 2.167 Å in the high spin state. This is also reflected in the volume of the cell, which changes from 2186.2(3) Å³ in the LS state to 2247.5(3) Å³ in the HS state. Then, starting from these experimental data, the position of hydrogen atoms were optimized. This step is necessary since the H-atom positions are

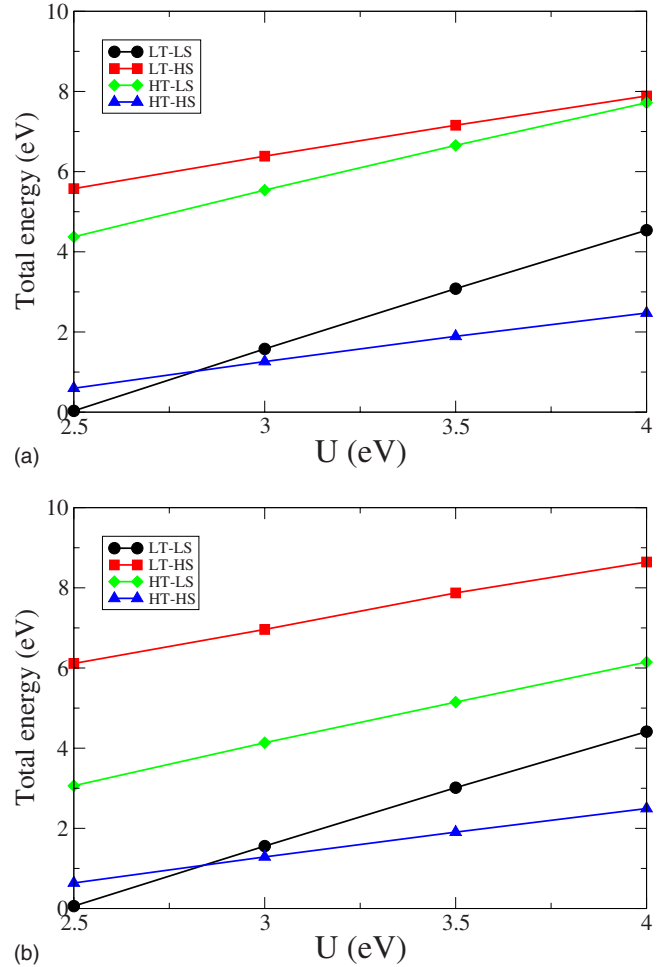


FIG. 1. (Color online) Upper plot: total energies of $\text{Fe}(\text{phen})_2(\text{NCS})_2$ computed with the GGA+ U method for several values of U (in electron volt) and for four different configurations: HT-HS, LT-LS, LT-HS, and HT-LS. The first part of the acronym refers to the crystal structure used to perform the calculation, while the second part refers to the magnetic state. The zero of energy is put arbitrarily at the obtained value for LT-LS with $U=2.5$ eV. Lower plot: analogous figure for the $\text{Fe}(\text{btr})_2(\text{NCS})_2$ compound.

usually not given accurately by x-ray diffraction experiments. Also, to study how magnetism and crystal structure are related, we performed for each compounds LT-LS, LT-HS, HT-LS, and HT-HS calculations—the first part of the acronym referring to the crystal structure (at either low temperature or high temperature) and the second one to the magnetic state. While the LT-LS and HT-HS are, respectively, the true minima for the LT and HT crystal structures, LT-HS and HT-LS states are electronic states that can be obtained by defining an appropriate initial guess in the self-consistent procedure and by controlling the convergence toward these local minima.

III. RESULTS

A. Total energies and magneto-elastic coupling

In Fig. 1, the computed total energies are presented for

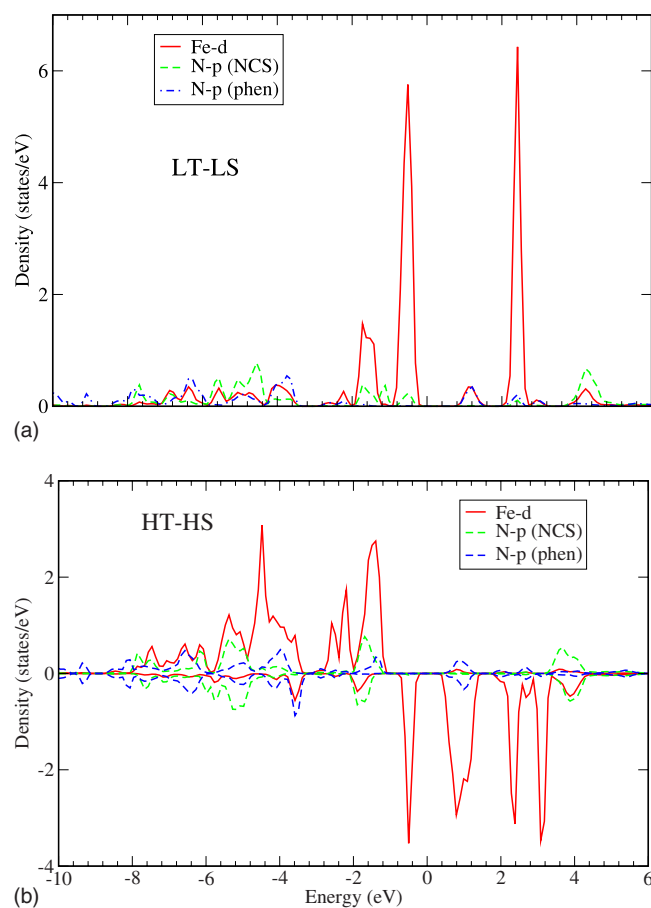


FIG. 2. (Color online) Partial density of states of $\text{Fe}(\text{Phen})_2(\text{NCS})_2$ for the LT-LS (upper plot) and HT-HS (lower plot) states. The top of the valence band is at zero electron volt.

different values of the parameter U for the compounds $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{btr})_2(\text{NCS})_2\text{H}_2\text{O}]$ for the four possible states mentioned above.

The dependence between the structure and the magnetic state is well reproduced by our calculations since the total energies for the LT-LS state (low spin crystal structure with $S=0$) and the HT-HS state (high spin crystal structure with $S=2$) are much lower than the energies of the LT-HS and HT-LS states. Furthermore, the computed pressures are much higher for the LT-HS and HT-LS states than for LT-LS and HT-HS states, indicating that we are far from being in equilibrium in the former cases.

While the above observation is true for a wide range of the U parameter, it is not obvious to find the ground state in agreement with experiment. At the value of $U=3.5$ eV the high spin HT-HS state is the lowest in energy, and only for relatively low values of the parameter U becomes the low spin state (in the corresponding crystal state) the ground state. The crossing point occurs for a value of $U \approx 2.8$ eV. This can be easily understood by considering the fact that for small values of U the crystal-field splitting overcomes the exchange coupling, thus favoring the LS state. On the opposite, for higher values of U , the exchange interaction takes over the crystal-field strength and the HS state is favored. This behavior is analogous to what has been found in the

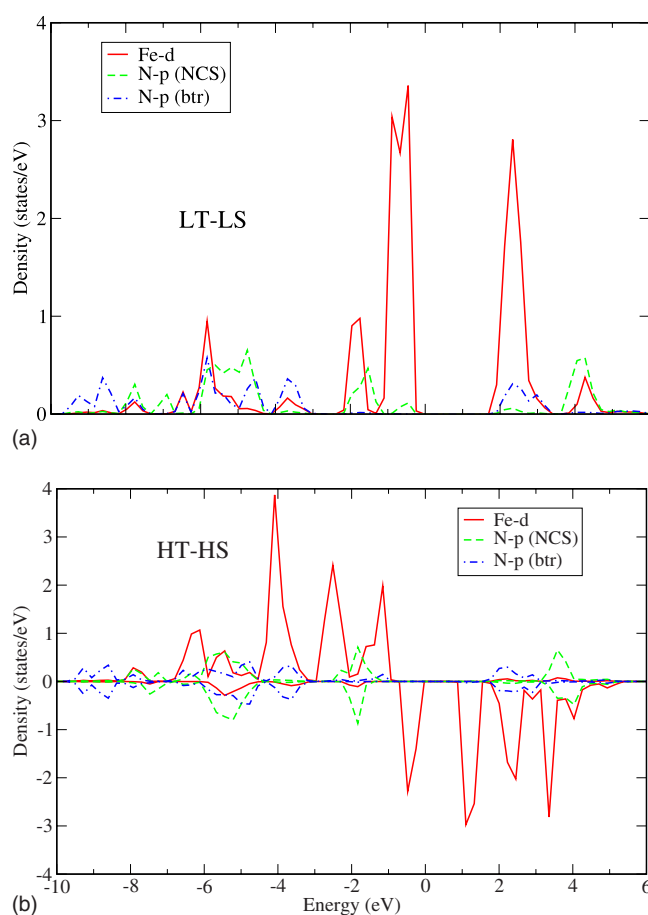


FIG. 3. (Color online) Partial density of states of $\text{Fe}(\text{btr})_2(\text{NCS})_2\text{H}_2\text{O}$ for the LT-LS (upper plot) and HT-HS (lower plot) states. The top of the valence band is at zero electron volt.

case of isolated molecules. According to the studies of Reiher *et al.*,¹⁸ the total energies of the various spin states vary linearly as a function of the Hartree-Fock exchange admixture parameter of the hybrid B3LYP functional and one has to reduce this parameter in order to obtain the right magnetic ground state. The U parameter plays an analogous role as the weight of the exact exchange in hybrid functionals. In fact, in the case of the GGA+ U method, high values of U lower the energy of the HS state by favoring more and more either the fully occupied or fully unoccupied states when increasing U . Similarly, the Hartree-Fock method favors high multiplicities by maximizing the number of electrons with the same spin.

In the case of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ the adiabatic energy difference, $\Delta E_{\text{HL}} = E_{\text{HS}}(r_{\text{HT}}) - E_{\text{LS}}(r_{\text{LT}})$ is experimentally known⁹ to be about 12.1 kJ/mol, the LS state being the ground state. This ΔE_{HL} can be quite well reproduced by choosing $U=2.5$ eV ($\Delta E_{\text{HL}}=13.6$ kJ/mol in this case). The same value of U leads to $\Delta E_{\text{HL}}=16.5$ kJ/mol for the $[\text{Fe}(\text{btr})_2(\text{NCS})_2]$ compound, which seems to be reasonable, even if there are no experimental estimates for this compound.

B. Density of states

In Figs. 2 and 3, the partial density of states (PDOS) are

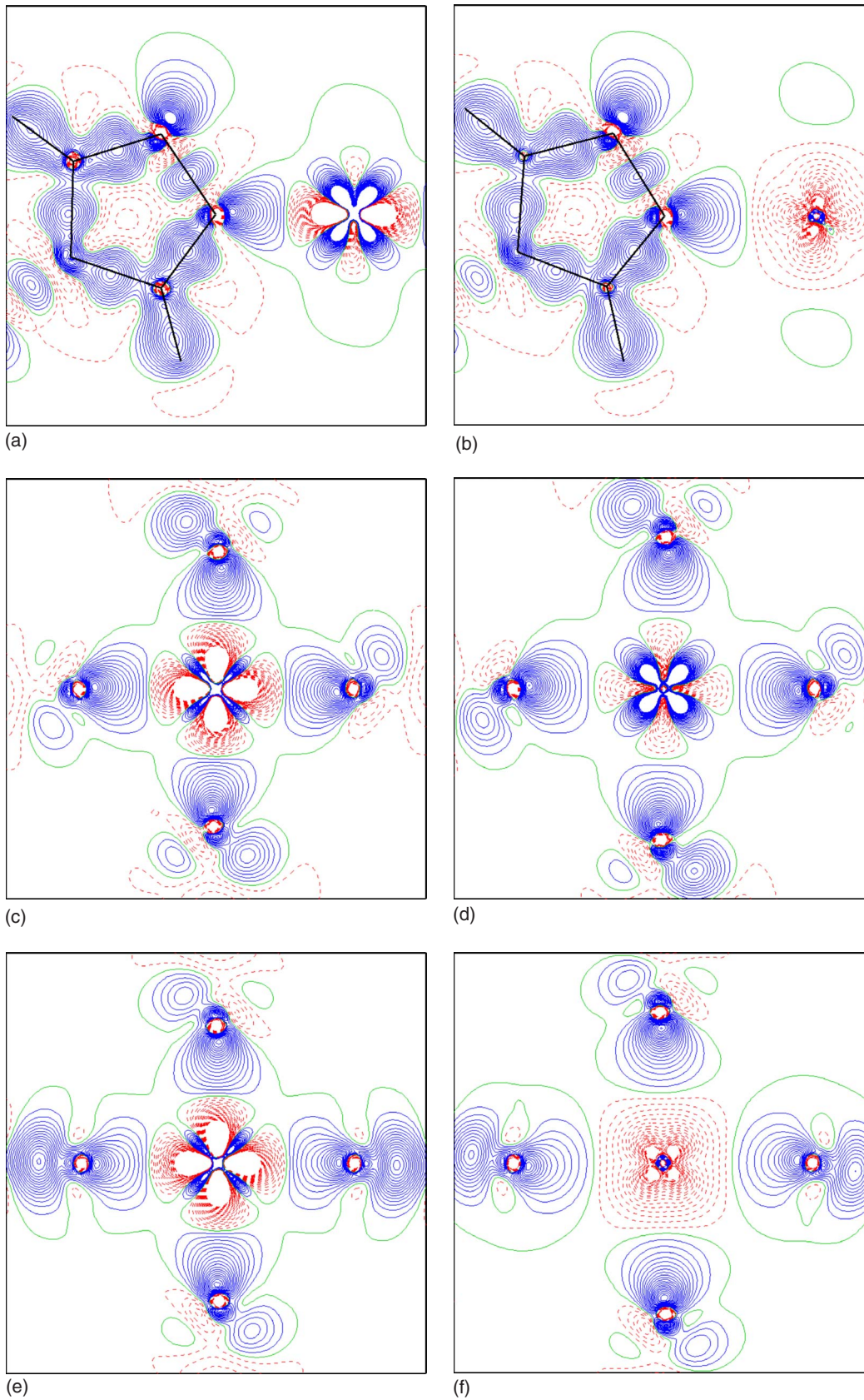


FIG. 4. (Color online) Deformation densities of the low (left column) and high (right column) temperature forms of the btr complex calculated for $U=2.5$ eV. Upper: in the plane of the triazole ring comprising the Fe(II) ion; middle: in the plane of the four triazole N ligands; lower: in the perpendicular plane containing the two axial NCS ligands. The contours are $0.05 e/\text{\AA}^3$ between $\pm 1.05 e/\text{\AA}^3$. Positive contours are solid (blue) lines and negative contours are dashed (red) lines.

displayed for $\text{Fe}(\text{phen})_2(\text{NCS})_2$ and $\text{Fe}(\text{btr})_2(\text{NCS})_2\text{H}_2\text{O}$, respectively, for $U=2.5$ eV. The Fe d states are plotted, as well as the states that can possibly hybridize with d electrons (namely, the p electrons of the nitrogen atoms neighboring the Fe atoms): from the NCS and phen groups for $\text{Fe}(\text{phen})_2(\text{NCS})_2$ and from the NCS and btr groups for $\text{Fe}(\text{btr})_2(\text{NCS})_2\text{H}_2\text{O}$. Both compounds show an insulating behavior in both magnetic states. This is a well-known feature of the DFT+U method, which repairs partly the problem of the band-gap inherent to DFT. From the PDOS plots of Fe- d , it appears that the splitting between the d states on each side of the band gap is more important in the case of a LT-LS state than for the HT-HS state because of stronger crystal field acting on the d electrons. As expected, the six electrons of iron fill the t_{2g} derived orbitals in the LS spin state; whereas all the spin-up orbitals are filled (of both t_{2g} and e_g derived character) together with one spin down t_{2g} derived orbital in the case of the HS state. Also, an important Fe-N hybridization is observed from the Fe- d and N- p PDOS. These remarks hold for the two compounds studied here; however differences can be seen in their respective densities of state. These small differences in the ligand iron interactions are known to be the driving force of the various behaviors occurring in SCO compounds. However, it seems to be difficult to establish a correlation between the obtained results and the characteristic features of the transition.

Also, we have found that the ordering of magnetic moments on Fe atoms (with a calculated value of $3.6 \mu_B$) is of the antiferromagnetic (AFM) kind for both compounds although the difference of energy between the ferromagnetic and the antiferromagnetic orders is small, of the order of a few millielectron volt [for example, in the case of the $\text{Fe}(\text{phen})_2(\text{NCS})_2$ compound; for $U=2.5$ eV in the LT-HS state, the difference in energy is 1.4 meV]. This reflects that the magnetic coupling between sites is weak and therefore cooperative effects in spin-crossover systems can only be understood via magneto-elastic coupling (as demonstrated also by Fig. 1, showing the correlation between the spin state and the structure). Moreover, small magnetic moments ($0.03 \mu_B$) are induced on the N atoms neighboring the Fe atom, which is reflected by the weak spin dependence of the N- p PDOS for both compounds.

C. Electron densities

The electron-density reorganization due to bonding effects in the $\text{Fe}(\text{btr})_2(\text{NCS})_2$ has recently been studied experimentally,²⁶ using high-resolution x-ray diffraction technique. The present theoretical densities (see Fig. 4) can be used to generate analogous deformation density maps; $\Delta\rho(r)$ is defined as the difference of the calculated (or observed) total static electron density and that of the spherically averaged isolated atoms.

For the LS state, the d_{xy} , d_{xz} , and d_{yz} orbitals are filled (positive deformation density around the Fe atom in Fig. 4) while the $d_{x^2-y^2}$ and d_{z^2} , pointing toward the neighboring nitrogen atoms, are empty (negative deformation density). Also, it is observed that the deformation densities of the nitrogen atoms point toward the Fe atom, indicating the existence of covalent bonds; a feature that is apparent also in the PDOS (see previous paragraph). For the HS state, the $d_{x^2-y^2}$ and d_{z^2} orbitals are partly filled, roughly with one electron each. However, since the spherically averaged density of the corresponding atom is subtracted from the density, only the orbital filled with two electrons appears positive on the deformation density map. This feature can therefore be assigned to the d_{xy} orbital (right-middle plot of Fig. 4). This is explained by the fact that the degeneracy is lifted between the plane of triazole ligands and the axis of NCS ligands. These observations are in reasonable agreement with the ones obtained experimentally (see Fig. 4 of Ref. 26) although the agreement seems to be better for the low spin compound.

IV. CONCLUSION

In summary, we have investigated the properties of two typical spin-crossover systems, taking into account the crystal lattice periodicity and the effect of strong correlation on the electronic structure of the Fe(II) ion. We have found that the LT-LS and HT-HS configurations are favored in energy; however the ground state is dependent on the value of U , which makes the predictive power of the method somewhat limited. Therefore, it appears to be necessary to go beyond the simple one-particle approximation and treat the iron centers with the first shell of ligands by a full many-body method. Alternatively, the development of new methodologies to correct the failure of conventional functionals for transition-metal systems appears to be necessary. Range separated hybrid functionals^{28,29} constitute such an alternative approach, which should be tested for SCO systems.

Also, by taking into account the periodicity in spin-crossover systems, our work opens the path for the study of cooperativity, which originates from magneto-elastic coupling effects. In particular, the calculation of the vibration frequencies for the crystal can be used to have a more precise description of the entropy. Another direction that we are currently exploring is the study of Co and Mn based spin-crossover compounds, as well as for other Fe based molecular magnets. Also, studies concerning molecules with several transition-metal centers are currently underway.

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