Computational design of magnetic metal-organic complexes and coordination polymers with spin-switchable functionalities

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Magnetic metal-organic complexes and coordination polymer frameworks can exhibit a transition between two different spin states of the integrated transition-metal ion, an attribute known as a spin-crossover (SCO) transition. This is a spectacular phenomenon that provides magnetic bi-stability and reversible spin-switchability to the material. Consequently, the magnetic state of the metal-organic center can be externally steered by temperature, pressure, or light irradiation. SCO molecules therefore are promising materials for various technological applications, such as spintronics devices, photo-switches, color displays, and information storage units. In spite of the importance of SCO materials in spintronics and other applications, the materials-specific understanding of the SCO phenomenon has remained a challenge. Here we survey recent developments in first-principles computational design of SCO metal-organic materials. A major outcome of recent state-of-the-art investigations is that an accurate quantitative description and even computational design of SCO materials can be provided by density functional theory-based electronic structure calculations combined with *ab initio* molecular dynamics simulations.

Introduction

Spin-crossover is an extraordinary feature of certain metal-organic complexes and frameworks—consisting of transition-metal ions connected by organic ligands—and is typified by a bi-stable magnetic state of the metal ion center. A unique feature of the transition-metal ions with the surrounding ligands is the capacity of attaining different spin states, with a different total spin quantum number S, while keeping the same valence state. Upon application of an external stimulus, such as pressure, temperature, light irradiation, or magnetic field, the transition metal ion can be reversibly switched between different spin states, for example, between a low-spin (LS) state with the smallest possible value of the spin S, and a high-spin (HS) magnetic state with the highest possible value of S (see References 1 and 2 for recent reviews). This bi-stability of the spin state has attracted considerable technological interest, as it offers the possibility of designing functional units that can be switched reversibly. Accordingly, spin-crossover (SCO) complexes are currently being considered as potential elementary units in information storage,[3] spintronics devices,[4,5]

photo-switches,[6,7] color displays,[8,9] and, in connection with open frameworks, as gas sensors.[10] In addition to their spin reversibility, SCO metal-organic systems are versatile and offer many possibilities for chemical functionalization, through which the desired transition property (e.g., color, transition temperature) can be efficiently tuned.

The SCO phenomenon was discovered[11] more than 80 years ago in iron(III) tris-dithiocarbamate compounds. The SCO transition on the Fe ion is between a LS ($S = 1/2$) state and a HS ($S = 5/2$) state. In 1961, the first spin-crossover in a Co(II)-based compound ($Co(L)_2X_2$, where L = bis-[2,6-pyridindialdihydrazone] and X is a transcoordinated anion) was discovered.[12] The SCO transition occurred from a LS ($S = 1/2$) to a HS ($S = 3/2$) state. This was followed by the discovery[13] of SCO in a Fe(II) compound, $(Fe(phen)_2(SCN)_2,$ where phen = 1,10-phenanthroline), which involves the transition from a LS ($S = 0$) to a HS ($S = 2$) state. Decurtins et al. discovered a light-induced SCO transition in a Fe(II) complex in 1984,[6] which showed that light could be used to switch a sample from LS to a metastable HS state, which persisted for

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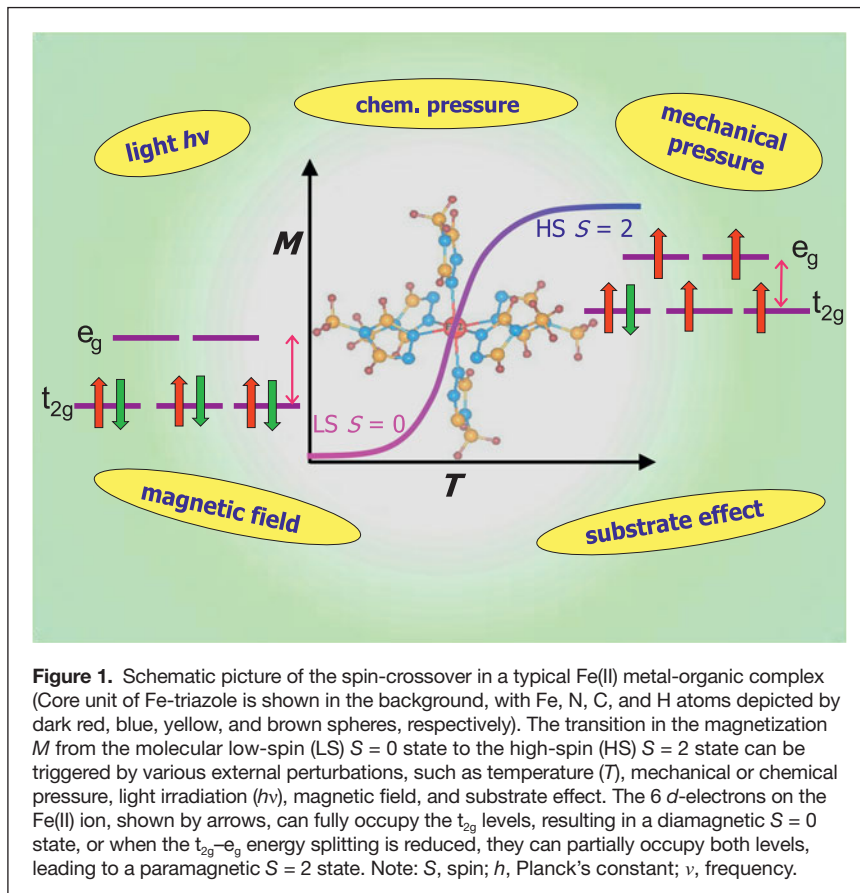
days to weeks. This observation of light-induced excited state spin-state trapping (LIESST) gave rise to invigorated interest in the SCO phenomenon.

Many different SCO complexes have since been synthesized, characterized, and studied in detail with available techniques, such as magnetic susceptibility, Mössbauer spectroscopy, x-ray crystallography, and extended x-ray absorption fine structure.[1,2] Although it was found that transition-metal ions having 4 to 7 d-electrons, such as Fe^{2+}, Fe^{3+}, Co^{2+}, or Co^{3+}, could exhibit SCO, most studies on SCO compounds today are carried out on Fe(II)-based compounds (having 6 d-electrons).[1,2,7,10] The reason for this is that SCO transitions in Fe(II) complexes are pronounced and abrupt, whereas they are more subtle in Co(II) complexes, for example.[14] Hence, this makes the SCO transition in Fe(II) complexes easier to follow and more suitable for applications, as these benefit from robust and prompt switching. A basic mechanism underlying the SCO transition was identified to be the change in the bond length of the metal ion to its ligand atoms (often nitrogen or carbon); for Fe(II) complexes, this bond length is typically ~0.2 Å shorter in the LS state than in the HS state.[15]

In spite of its technological importance, the SCO phenomenon is not yet well understood, especially on the atomistic level. In addition to the aforementioned change in bond length,[15] the SCO transition can be qualitatively understood, following ligand-field theory (i.e., the quantum theory that describes the energy levels of the spin-polarized d-electrons in a crystal field potential provided by the ligand atoms). Crystal-field theory explains the SCO transition as due to a competition between two possible occupations of the d-electrons of the transition-metal ion in a cubic crystal field. This is illustrated in **Figure 1** for the LS and HS configurations of a Fe(II) ion. The 6 d-electrons can fully occupy the three t_{2g} levels, giving a diamagnetic low-spin $S = 0$ state, or they can partially occupy the t_{2g} as well as e_g energy levels, leading to a paramagnetic high-spin $S = 2$ state. In the competition between these two states, the crystal field splitting of the t_{2g} and e_g energy levels plays a role, as does the magnetic exchange interaction that drives to maximize the magnetic moment by populating the levels as much as possible with electrons having parallel spin (so-called Hund's rule coupling). For large e_g–t_{2g} energy splitting, the 6 electrons will occupy the t_{2g} levels only, but if by some external stimuli this splitting is reduced, there is a gain due to the exchange interaction that favors a maximal spin state. Hence, the system displays bi-stability, as the energetics of the LS and HS states can be externally modified by one of the indicated stimuli. If there is, in addition, a structural deformation of the

metal ion's surrounding, the degenerate crystal field levels can split further.

Ligand-field theory offers a qualitative understanding of the involved LS and HS states, but it does not offer any predictive, materials-specific explanation of the phenomenon. It is a basic single-ion picture that does not take into account the building up of long-range order in a connected framework of SCO centers. To include long-range order and cooperativity, several modeling approaches have been developed. The theoretical studies can be broadly categorized as (1) those based on solutions of model Hamiltonians constructed from consideration of important interactions, and (2) those based on first-principles quantum-chemical calculations that have no adjustable parameters. In the model Hamiltonian approaches, elastic interactions are typically parameterized via an interaction term that defines local distortions around transition-metal centers that interact elastically to produce long-range effective interactions.[16–19] These approaches provide thermodynamic information (e.g., how generic phase diagrams would look for an interaction type). A disadvantage is understandably the lack of materials-specific information that could permit distinguishing between different SCO systems containing the same transition-metal ion. The second route, based on quantum-chemical calculations, aims to take into account the complex material structure and full chemical details to achieve atomistic understanding. This route is surveyed in the following.

Figure 1. Schematic picture of the spin-crossover in a typical Fe(II) metal-organic complex (Core unit of Fe-triazole is shown in the background, with Fe, N, C, and H atoms depicted by dark red, blue, yellow, and brown spheres, respectively). The transition in the magnetization M from the molecular low-spin (LS) $S = 0$ state to the high-spin (HS) $S = 2$ state can be triggered by various external perturbations, such as temperature (T), mechanical or chemical pressure, light irradiation ($h\nu$), magnetic field, and substrate effect. The 6 d-electrons on the Fe(II) ion, shown by arrows, can fully occupy the t_{2g} levels, resulting in a diamagnetic $S = 0$ state, or when the t_{2g}–e_g energy splitting is reduced, they can partially occupy both levels, leading to a paramagnetic $S = 2$ state. Note: S, spin; h, Planck's constant; ν, frequency.

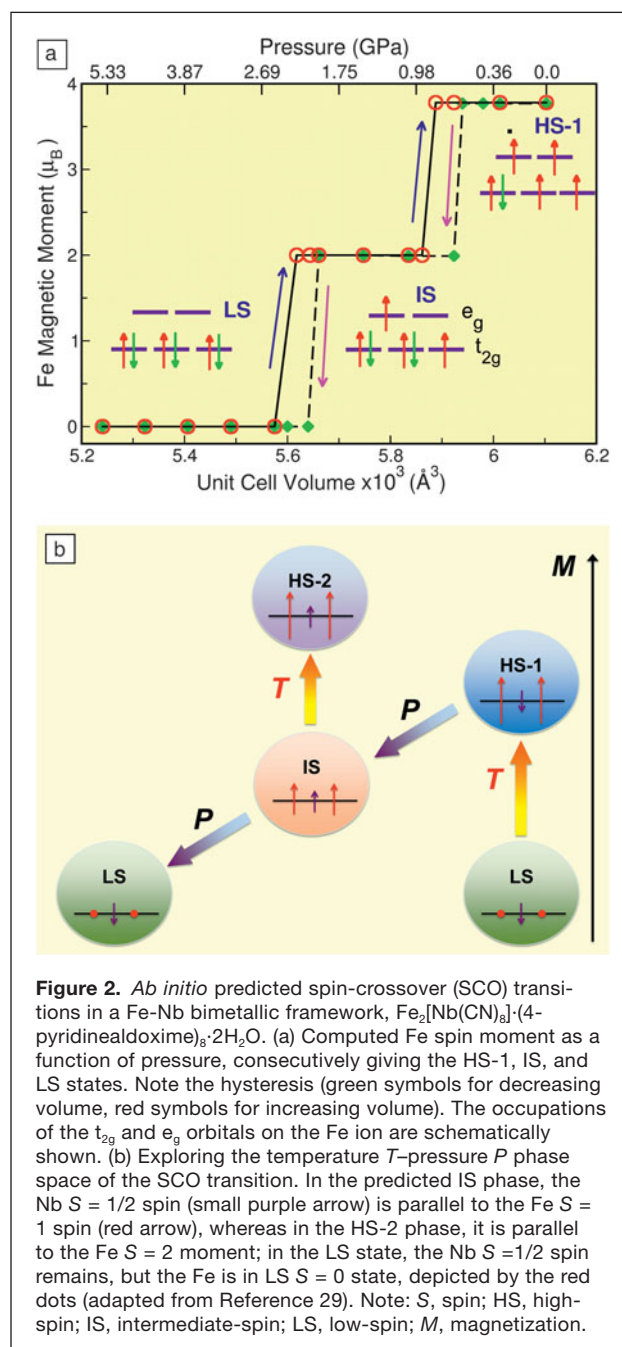## Quantum-chemical approaches to the spin-crossover transition

Quantum-chemical approaches aim to provide a full description of the chemical interaction of the metal ion with its ligands within metal-organic complexes. See Reference 20 for a recent overview of its application to SCO materials. This first-principles approach is very challenging, given the usually complex geometry of the SCO centers and their ligands in combination with the rather subtle modifications in geometry leading to the SCO. An adequate description of the SCO phenomenon requires the ability to handle such small changes in the crystal as well as electronic structure upon application of external stimuli. An additional complication that arises for transition-metal centers is that the d-electron interaction effects in the open d-shell are notoriously difficult to capture accurately in calculations.

Two different ways have been attempted to describe the essential electronic interactions within the open d-shell. The first one, wave-function-based complete active space (CAS) calculations, could provide an explanation for the LS and HS states of relatively small systems, for instance $[Fe(NCH)6]^{2+}$, which can be viewed as the core unit of the $Fe(phen)_2(NCS)_2$ SCO molecule.[21,22] An advantage of CAS calculations is that the many-electron state on the Fe center can be particularly well described. In addition, CAS calculations can provide insights into the charge reorganization that occurs at the LS-HS transition.[21] Concomitant with the aforementioned bond length change,[15] a redistribution of charges was found to take place between the Fe ion and its nitrogen ligands, leading to a ~0.4e higher electron occupancy on the Fe center in the HS state. Thus, the quantum-chemical calculations provided more detailed insight compared to the simpler crystal field picture shown in Figure 1. A disadvantage of this accurate method is the large computational effort that is required. Currently, this inhibits the application of CAS calculations to larger extended systems.

The second approach is based on density functional theory (DFT).[23] In this electron density-based approach, each electron is treated independently of the others, only experiencing an effective potential that is caused by all electrons. Although the DFT method is surprisingly accurate, it is known to have difficulties to describe electrons in open d- or f-shells. Fortunately, the treatment of open–shell systems within the DFT has greatly improved over the years (see Reference 24 for a recent review). In particular, the addition of an extra interaction term—in the form of a Hubbard U energy and exchange J term—to account for the missing strong on-site Coulomb U correlations has been shown to lead to good results. The resulting DFT+U approach[25] has demonstrated the capability of accurately describing open–shell transition-metal ions. An advantage of the DFT or DFT+U approach is that it can be readily employed to compute systems with a few hundred atoms in the simulation cell. Furthermore, recent DFT+U investigations have greatly improved confidence in the ability of DFT+U to accurately predict the subtle changes in the crystal structures of SCO frameworks.[26,27] A further recent and essential aspect in contemporary first-principles calculations is the possibility to include temperature effects through ab $initio$ molecular dynamics (AIMD) simulations.[28] This route has recently been initiated and has been shown to lead to a satisfactory, quantitative description of SCO frameworks under external perturbations such as pressure and temperature.[29,30] Note that light-induced SCO transitions have not yet been described by ab $initio$ simulations, which is the next goal to be reached.

In the following we review several recent achievements of DFT-based first-principles calculations to SCO materials.

Figure 2. *Ab initio* predicted spin-crossover (SCO) transitions in a Fe-Nb bimetallic framework, $Fe_2[Nb(CN)_8]\cdot(4$-pyridinealdoxime)$_8\cdot2H_2O$. (a) Computed Fe spin moment as a function of pressure, consecutively giving the HS-1, IS, and LS states. Note the hysteresis (green symbols for decreasing volume, red symbols for increasing volume). The occupations of the t_{2g} and e_g orbitals on the Fe ion are schematically shown. (b) Exploring the temperature T–pressure P phase space of the SCO transition. In the predicted IS phase, the Nb $S = 1/2$ spin (small purple arrow) is parallel to the Fe $S = 1$ spin (red arrow), whereas in the HS-2 phase, it is parallel to the Fe $S = 2$ moment; in the LS state, the Nb $S = 1/2$ spin remains, but the Fe is in LS $S = 0$ state, depicted by the red dots (adapted from Reference 29). Note: S, spin; HS, high-spin; IS, intermediate-spin; LS, low-spin; M, magnetization.

DFT-based simulations of spin-crossover materials

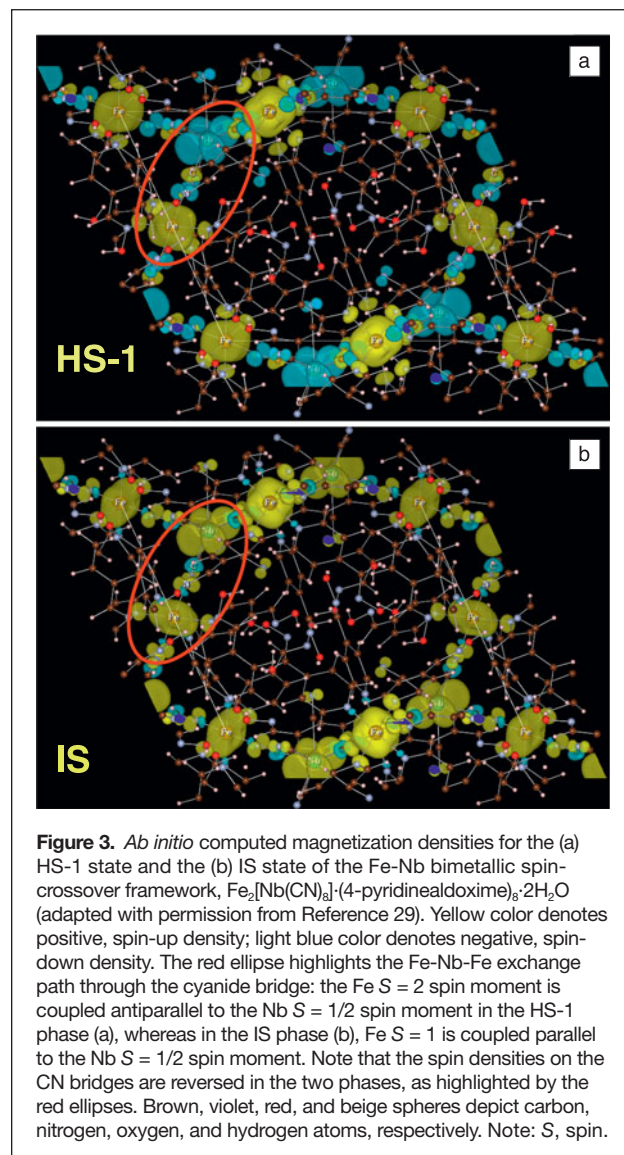### Static (T = 0K) or frozen-displacement calculations

First-principles calculations of SCO materials became feasible less than a decade ago. Some of the early DFT calculations focused on atomistic modeling of SCO compounds, taking their full lattice periodicity into account; the studied systems included Fe(btz)$_2$(NCS)$_2$ (btz = 2,2'-bi-4,5-dihydrothiazine)[31] and an Fe(II)-triazole coordination polymer.[32] To reduce the computational effort, an efficient way to prepare reliable model structures for the polymeric Fe-triazole compound was proposed. Using a subsequent *ab initio* DFT analysis and effective model considerations, it was shown that in polymeric Fe(II) SCO compounds, the magnetic exchange interaction between high-spin Fe centers is as important as elastic couplings for understanding the spin transition.[32]

First-principles studies of a series of Fe-porphyrins,[33] however, emphasized the shortcoming of the commonly used generalized-gradient approximation (GGA) exchange-correlation functional. Notably, the strong electron-electron interaction on the Fe site is underestimated, and, as a result, DFT-GGA fails to capture the experimental HS state, known for 5-coordinated Fe-porphyrins, for instance.[33] Such inability would severely reduce the prospects of performing any predictive calculations of SCO materials. It was shown that the correct HS state of 5- or 6-coordinated Fe-porphyrins could be obtained with DFT+U calculations,[34] with $U \approx 4$ eV and $J \approx 1$ eV. A first application of the DFT+U methodology to model periodic SCO compounds was undertaken by Lebègue et al.,[26] who computed Fe(phen)$_2$(NCS)$_2$ and Fe(btr)$_2$(NCS)$_2$H$_2$O (btr = bis-triazole). They found that for a U value of 2.5 eV, the adiabatic energy difference between static LS and HS states were comparable to experimental values and concluded that the additional Coulomb U term was needed. The calculations showed a correlation between the spin state and the structure, indicating the importance of magneto-elastic couplings.

Niel et al.[35] discovered an interesting SCO behavior for a series of cyanide-bridged bimetallic coordination polymers with the general formula [Fe(pmd)-(H$_2$O)M$_2$(CN)$_4$]·H$_2$O (with pmd = pyrimidine; M = Ag or Au). These coordination polymers form a 3D open network consisting of chains, Fe1–N–C–M–C–N–Fe2, that contain two different Fe(II) ions Fe1 and Fe2, a noble metal, Ag or Au, and, in addition, water molecules in the open structure. Through hydration/dehydration, the SCO temperature could be reversibly changed between 130 K and 230 K for the Ag-based coordination polymers; this transition was induced by the structural changes caused by water molecules in the networks. The hydration/dehydration behavior of the Au-based variety was notably different, with only a temperature-induced SCO transition occurring in the hydrated framework, but not in the dehydrated one.[35] Static DFT+U calculations could provide a complete explanation of these intricate SCO transitions.[27] The LS-HS transition was found to occur only on the sixfold nitrogen-coordinated Fe1 ion (Fe1N$_6$ octahedron), whereas the Fe2 ion, coordinated with four nitrogens and two

water molecule oxygens, remained in the HS $S = 2$ state. For the dehydrated compounds, the relativistic effects in Au caused differences in the degree of covalent bonding, which gave rise to a distinct behavior of the Au network as compared to the Ag one. The hydrated and dehydrated Ag networks were predicted to exhibit a LS-HS spin transition, whereas the dehydrated Au network was predicted to remain in a HS state.

The DFT+U investigations emphasized that the energy splitting of the various possible spin states was improved by the supplemented Coulomb interaction.[26,27,33] Another way of improving the DFT description of SCO molecules could be to use hybrid functionals, in which for the exchange-correlation part, a combination of the DFT exchange-correlation functional and the Hartree-Fock exchange is used. Test calculations on molecules such as [Fe(NH$_3$)$_6$]$^{2+}$ and [Fe(NCH)$_6$]$^{2+}$ showed that the hybrid functionals improve the energetics of the possible spin states[36] by improving the exchange energy. Also, hybrid functionals provided a good description of SCO

Figure 3. *Ab initio* computed magnetization densities for the (a) HS-1 state and the (b) IS state of the Fe-Nb bimetallic spin-crossover framework, Fe$_2$[Nb(CN)$_8$]·(4-pyridinealdoxime)$_8$·2H$_2$O (adapted with permission from Reference 29). Yellow color denotes positive, spin-up density; light blue color denotes negative, spin-down density. The red ellipse highlights the Fe-Nb-Fe exchange path through the cyanide bridge: the Fe $S = 2$ spin moment is coupled antiparallel to the Nb $S = 1/2$ spin moment in the HS-1 phase (a), whereas in the IS phase (b), Fe $S = 1$ is coupled parallel to the Nb $S = 1/2$ spin moment. Note that the spin densities on the CN bridges are reversed in the two phases, as highlighted by the red ellipses. Brown, violet, red, and beige spheres depict carbon, nitrogen, oxygen, and hydrogen atoms, respectively. Note: S, spin.

reactions in heme-related Fe porphyrins that are typically part of important hemoproteins, such as hemoglobin, and they were found to be equally competent as DFT+U.[37]
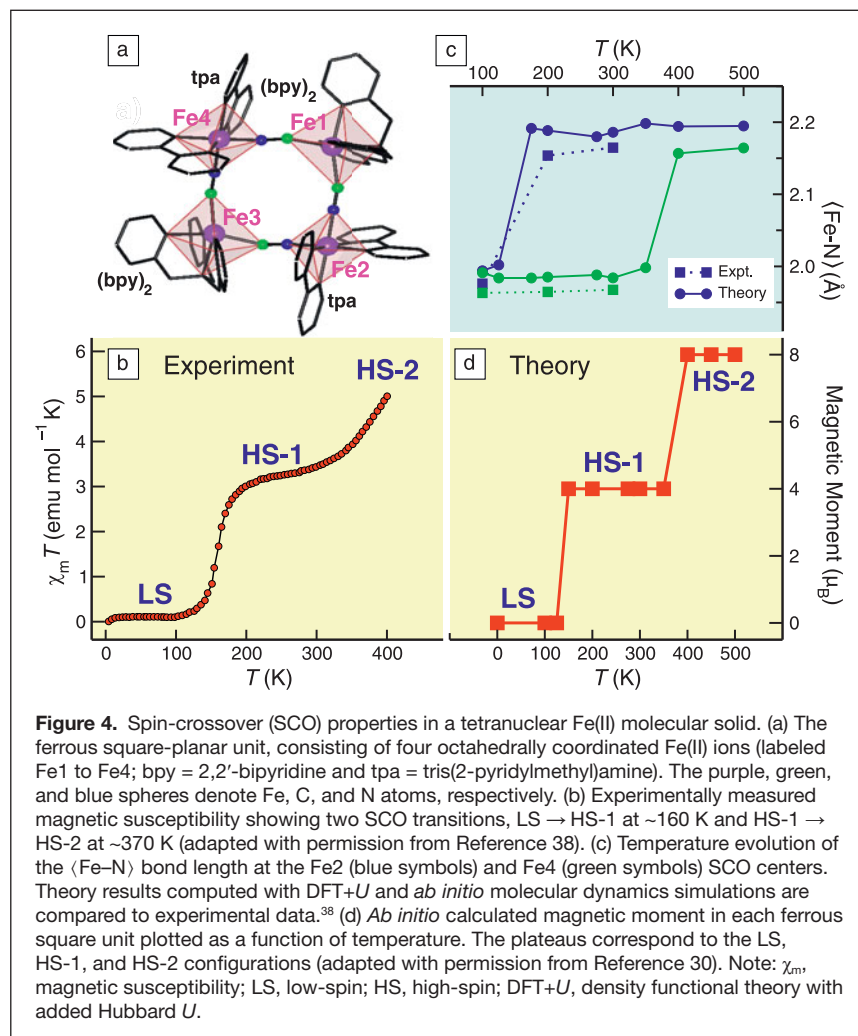
Finite-temperature calculations of SCO materials

Bucko et al.[28] were the first to include temperature in the first-principles simulations of SCO systems. They computed Fe(phen)$_2$(NCS)$_2$ as a single molecule and in a periodic crystal using the DFT+U approach. In addition to the static ($T = 0$ K) situation, they considered two different temperatures, 100 K and 500 K, employing AIMD simulations. In these, the finite-temperature ionic motion is given by Newton's equation, whereas the electronic motion is computed quantum mechanically, through the DFT+U approach, and electrostatic forces connect the two motions. Computing the average coordination number, a quantity that depends on the Fe–N distances, they found a temperature-related difference that reflected a change of the average Fe–N distances to larger values at 500 K.

Temperature-dependent AIMD simulations were subsequently performed on considerably larger systems.[29,30] One such system is a recently discovered Fe-Nb bimetallic framework, Fe$_2$[Nb(CN)$_8$]·(4-pyridinealdoxime)$_8$·2H$_2$O, which forms a 3D connected network of cyanide-bridged Fe-Nb atoms with 290 atoms in its unit cell.[7] This material was reported to display both a temperature- and light-induced SCO transition. In the LS state, the $S = 0$ Fe(II) centers are connected via a Nb(IV) ion in $S = 1/2$, whereas in the HS state above about 130 K, the $S = 2$ spins on Fe ions are coupled via an antiparallel $S = 1/2$ spin on the interconnecting Nb. Tarafder et al.[29] studied this Fe-based framework, employing a combination of DFT+U and AIMD simulations to sample stepwise the pressure-temperature phase space. They found that the experimentally observed temperature-driven SCO transition in the Fe variant could be accurately described. Moreover, novel spin-state transitions were predicted that could only be reached via specific pressure-temperature combinations, see **Figure 2**. One of these was a novel intermediate spin (IS) state $S = 1$ appearing on the Fe atoms at modest pressures before the LS state was reached at a higher pressure (Figure 2a). The sharp SCO transitions displayed a hysteresis depending on the increase or decrease in pressure, indicating the cooperative nature of the transitions. In this IS state, the Fe $S = 1$ and Nb $S = 1/2$ spins were aligned parallel, as illustrated by the computed magnetization densities in **Figure 3**. An exchange path along Fe–N–C–Nb–C–N–Fe (red ellipse) stabilizes long-range magnetism. Applying both pressure and temperature to this IS state, it was found that a further new HS state (HS-2)

could be reached. In this state, there is long-ranged order, as in HS-1, but with a parallel alignment of Fe $S = 2$ spins and Nb $S = 1/2$ spins. Increasing the pressure further turned the material to LS. One of the crucial parameters identified to trigger the SCO transitions with temperature or pressure was again the Fe–N bond length. The average Fe–N bond length along the cyanide bridges was reduced from 2.04 Å at the HS-1 state to 1.93 Å at the IS state and 1.91 Å at the LS state.

Metalorganic materials that contain several SCO centers can display more complex behavior. A two-step SCO transition was discovered in a tetranuclear Fe(II) molecular system, Fe(II)$_4$(μ-CN)$_4$(bpy)$_4$(tpa)$_2$](PF$_6$)$_4$ (where bpy = 2,2′-bipyridine and tpa = tris(2-pyridylmethyl)amine).[38] In the essential molecular unit, there are four inequivalent, octahedrally coordinated Fe centers in a planar square arrangement, see **Figure 4**a. The molecular units crystallize in a triclinic unit cell in which the ferrous squares are van der Waals bonded and separated by (PF$_6$)$_4^-$ counter ions. Upon heating, there is a first LS–HS-1 SCO transition observed at $T_1 \sim 160 \pm 20$ K, when one of the Fe atoms transforms to HS $S = 2$. Increasing the temperature further induces a second SCO transition at about $T_2 \sim 370 \pm 50$ K,

Figure 4. Spin-crossover (SCO) properties in a tetranuclear Fe(II) molecular solid. (a) The ferrous square-planar unit, consisting of four octahedrally coordinated Fe(II) ions (labeled Fe1 to Fe4; bpy = 2,2′-bipyridine and tpa = tris(2-pyridylmethyl)amine). The purple, green, and blue spheres denote Fe, C, and N atoms, respectively. (b) Experimentally measured magnetic susceptibility showing two SCO transitions, LS → HS-1 at ~160 K and HS-1 → HS-2 at ~370 K (adapted with permission from Reference 38). (c) Temperature evolution of the ⟨Fe–N⟩ bond length at the Fe2 (blue symbols) and Fe4 (green symbols) SCO centers. Theory results computed with DFT+U and ab initio molecular dynamics simulations are compared to experimental data.[38] (d) Ab initio calculated magnetic moment in each ferrous square unit plotted as a function of temperature. The plateaus correspond to the LS, HS-1, and HS-2 configurations (adapted with permission from Reference 30). Note: χ$_m$, magnetic susceptibility; LS, low-spin; HS, high-spin; DFT+U, density functional theory with added Hubbard U.

where a second Fe transforms to HS (Figure 4b), leading to HS-2. First-principles DFT+U calculations in combination with AIMD were applied[30] to simulate the temperature-dependent spin state of this large system, which contains 400 atoms in the unit cell. The temperature was varied stepwise between 0 K and 500 K. The *ab initio* calculated temperature-response showed a first SCO conversion at 138($\pm$10) K and a second one at 375($\pm$20) K, see Figure 4d, in excellent agreement with experiment. The Fe centers that were computed to undergo the LS-HS transition are those coordinated with six nitrogen atoms (Fe2 and Fe4 in Figure 4a), whereas those that remained in LS are coordinated by four nitrogen and two carbon atoms. This is in accordance with the chemically more rigid nature of the Fe–C bond. The calculated temperature evolution of the average $\langle$Fe–N$\rangle$ bond lengths at the Fe2 (blue curve) and Fe4 sites (green curve) are shown in Figure 4c and compared with experimentally reported $\langle$Fe–N$\rangle$ bond lengths.[38] There exists very good agreement between them. At the SCO transitions, bond length elongation from less than 2Å to ~2.18Å is predicted, consistent with the well-known relation between spin state and Fe–N bond length.[15]

The tetranuclear unit forms an open structure, which permits the incorporation of guest molecules such as CO_2, CS_2, and H_2O in the ferrous square. Exploring the possibility of chemo-induced switching, it was found that introduction of a guest molecule slightly increases the bond lengths and could thereby induce an LS–HS-1 transition at already low temperatures and a HS-1–HS-2 transition at medium temperatures (~250 K).[30] The option of chemo-induced switching would add a further dimensionality to this interesting material.

Outlook and summary

Spin-crossover (SCO) metalorganic materials hold bright prospects for many technological applications, as these molecules or coordination polymers can constitute the smallest elementary unit in switchable optical and spintronic devices. Many SCO materials have been synthesized in the recent decades,[1,2] and considerable progress has been made with chemical functionalization and tuning of SCO properties. The theoretical understanding has progressed most remarkably in recent years, from a basic understanding in terms of an occupation modification of the e_g and t_{2g} crystal field levels to the development of powerful first-principles modeling methods.[20] In particular, the combination of density functional theory (DFT) or Hubbard corrected DFT (DFT+U)-based electronic structure calculations and *ab initio* molecular dynamics simulations has provided detailed and accurate insights into the structural and electronic origins of the SCO transition. Strikingly, it was shown that even SCO transition temperatures can be accurately predicted. The recent results underline that the *ab initio* computational methodology offers a viable route to quantitatively describe the volume and temperature behavior of SCO coordination complexes. It can be anticipated that in the near future, this methodology can be employed to computationally design suitable SCO materials and functionalities.

Finally, for the near future, SCO devices in which the spin states are addressed electrically is one of the most appealing and challenging applications of SCO materials. Achieving this objective would prepare the way for fabrication of cost-effective assemblies in which the SCO complexes are integrated into electronic circuits and can act as the active switching units in the spintronic device. One of the hindrances in this development is the fabrication process. Fabrication of SCO thin films as well as patterning of SCO molecules are being attempted; yet, production of nanopatterned SCO materials requires further developments.

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