High-spin–low-spin transitions in Fe(II) complexes by effective Hamiltonian method

Andrei L. Tchougréeff [a], Alexander V. Soudackov [b], Igor A. Misurkin [b],
Hélène Bolvin [a], Olivier Kahn [a]

[a] *Laboratoire de Chimie Inorganique, URA CNRS no. 420, Université de Paris-Sud, 91405 Orsay, France*
[b] *L.Y. Karpov Institute of Physical Chemistry, Vorontsovo pole, 10, 103064 Moscow, Russian Federation*

Abstract

The high-spin–low-spin (HS–LS) transition in iron(II) complexes was studied by the recently developed quantum chemical effective Hamiltonian method. This method uses a trial wave function which is an antisymmetrized product of the fully correlated function of d-electrons and of the Slater determinant of the ligand MOs instead of the conventional Hartree–Fock single determinant trial wave function built of the molecular orbitals spread over an entire complex. This approach allowed us to explicitly take into account the d-electron correlations, the weak covalence of the metal–ligand bonds, and the electronic structure of the ligands. The cooperativity effects in the HS–LS transition occurring in the crystals are briefly discussed and the contribution from the Coulomb forces to the intermolecular interaction responsible for the cooperativity is estimated.

1. Introduction

The transition between a low-spin (LS) low-temperature state and a high-spin (HS) high-temperature state observed in a series of the transition metal compounds (spin-active compounds) both in the crystal phase and in solution has attracted the attention of the researchers during the last two decades (for recent reviews see Refs. [1,2]). The most studied spin-active compounds are those containing the iron(II) ion. In quite a few compounds of that type the transition is cooperative (see below) in the crystal phase. Despite the extensive studies on spin transition, there were no attempts to apply quantum chemical approaches to study these molecules until recently [3]. The reasons are quite obvious: first, the molecules under consideration are usually very large, which makes any application of the standard quantum chemical techniques difficult. Second, but not less important, transition

metal complexes are known to present certain challenges [4] for quantum chemistry. The main reason why quantum chemistry faces problems when addressing transition metal complexes (TMC) is that the fundamental quantum chemical approximation, the self-consistent field approximation (SCF, Hartree–Fock, or single determinant approximations) fails when applied to TMC. The main problems the SCF approximation encounters are the following (for more detailed discussion see Ref. [5] and references therein):

(i) Koopmans' theorem is not valid for the states with large contributions from the atomic d-states;

(ii) The *Aufbauprinzip* is frequently violated for the orbitals with significant contributions from the atomic d-states;

(iii) The iteration procedures implied by the SCF approximation converge very slowly or oscillate.

The violation of Koopmans' theorem is the most

Table 1
d–d excitation energies for the test complexes

Transition	E^{calc} (cm^{-1})	E^{obs} (cm^{-1})
[Fe(py)$_6$]$^{2+}$, ground state $^5T_{2g}$		
$^5T_{2g} \rightarrow {}^5E_g$	5700	
$\rightarrow {}^3T_{1g}$	9400	
$\rightarrow {}^1A_{1g}$	11200	
$\rightarrow {}^3T_{2g}$	11700	
$\rightarrow {}^3T_{1g}$	14100	
[Fe(bipy)$_3$]$^{2+}$, ground state $^1A_{1g}$		
$^1A_{1g} \rightarrow {}^3T_{1g}$	11500	11500
$\rightarrow {}^5T_{2g}$	14800	
$\rightarrow {}^3T_{2g}$	15400	
$\rightarrow {}^1T_{1g}$	17400	

spectacular among the problems listed above. The theorem appears as a consequence of the SCF approximation where each electron is treated as if it moved in a mean field induced by nuclei and other electrons. The ionization potentials are then equal to negative energies of electrons in such a potential (negative orbital energies). This picture is an approximation since the mean field itself changes when an electron is removed from the system or added to it. The difference between the negative orbital energy which must be the ionization potential according to Koopmans' theorem and the real ionization potential is called the orbital relaxation energy. Usually for organic molecules the relaxation energies are small and the whole picture remains consistent. In the case of TMC the relaxation energies can reach values from 10 to 20 eV when the levels with some significant contribution from d-orbitals are involved [6]. This suggests that the real behavior of d-electrons in TMC does not fit the picture where independent electrons move in some external mean field induced by the nuclei and other electrons but by contrast they trace any motion of one other very carefully. In other words d-electrons are strongly correlated. At the same time namely d-electrons are known to be responsible for the ground state total spin and for the low energy excitations (d–d excitations) of TMC whereas the description of electrons in the ligands seems to be less problematic.

For the reasons cited the correct description of the ground state spin multiplicity as a function of some tiny coordinate displacements which are known [1,2] to cause the spin transition should be a difficult problem for quantum chemistry. In the present paper we apply a new method [5] recently designed to take into account the specific features of the electronic structure of transition metal complexes for the description of compounds exhibiting spin-transitions. Another problem we briefly consider here is the cooperativity of the spin-transitions in the crystal phase.

2. Account of the effective Hamiltonian method

Specific properties of transition metal complexes (TMC) are known to be determined by the d-electrons of the transition metal ion. Their low energy excitations are responsible for the absorption bands in the optical spectra and for the magnetic properties. The ground state spin depends on the balance between the electron repulsion of d-electrons and their interaction with the ligands which provide some external field. The excitations of the ligands have much larger energies than those in the d-shell and incidentally they have a closed electronic shell so that the ligands cannot directly affect the spin multiplicity of the complex. Practically this distinction between the ligands and the d-shell of TMC led to an idea to describe d-electrons and electrons in the ligand orbitals employing different levels of inclusion of the electron correlation effects. The following features must be included in the method simultaneously: (1) the multiplet structure of d-electrons in the central ion (to do so the correlation effects in the d-shell must be included); (2) the electronic structure of the ligands must be treated realistically, but the single determinant approximation is sufficient for them; and (3) the weak covalency resulting from the metal–ligand interactions must be included as well.

All the conditions and ideas formulated above apparently correspond to the situations covered by the crystal field theory (CFT) where all the interesting events take place in the d-shell of the transition metal ions whose ligand environment remains inert [7]. The picture provided by CFT is correct to a large extent; we remind that the majority of magnetic and optical experiments on TMC can be interpreted in the framework of the CFT operating with the multiplets of some fixed number of d-electrons in the external field of appropriate symmetry (see for example Ref. [8]). The reason why the CFT is that successful is the correct form of the electronic wave function which is implicitly used in it.

It obviously takes the wave function of the complex as an antisymmetrized product of the multiplet (full CI) state for some fixed number of d-electrons and of some closed shell state of the remaining electrons. However, the wave function of this remainder has never been considered explicitly and that is the reason why the splitting parameters of the CFT cannot be satisfactorily calculated within itself.

In the effective Hamiltonian method [5] all the concepts mentioned were put to work. Two most important features of the electronic structure of TMC, namely, the presence of an isolated group of strongly correlated d-electrons on the metal atom and the existence of the closed shell ligands are taken into account explicitly. The formal derivation proceeds as follows [5]. We separate the whole set of the valence atomic orbitals (AO) of the TMC (it includes the 4s, 4p and 3d AOs of the metal and the valence AOs of the ligand atoms) into two parts. The first part contains only 3d orbitals of the transition metal atom (d subsystem). The second part contains 4s and 4p AOs of the transition metal and the valence orbitals of the ligand atoms (ligand subsystem or ℓ subsystem). Then the total Hamiltonian for the TMC can be written as follows:

$$H = H_d + H_\ell + H_c + H_r ,$$ (1)

where H_d is the Hamiltonian for the d-electrons in the field of the atomic cores of TMC, H_ℓ is the Hamiltonian for the electrons of the ℓ subsystem in the field of the atomic core of the transition metal ion, H_c and H_r are respectively the Coulomb and the resonance interaction operators between the two subsystems.

For most of TMC with closed-shell ligands the excitations in the ligand subsystem are of very high energy as compared to the energies of the d–d excitations, and thus their contribution to the ground state is negligible. Thus the ground state of the ligand subsystem can be described by a single Slater determinant $\Phi_\ell(^1A_1)$ with zero total spin. To ensure the complete description of the correlations in the d shell the wave function Φ_n of a TMC is taken in the following form:

$$\Phi_n = \left(\sum_k C_k^n \, |n_dk\rangle \right) \wedge \Phi_L = \Phi_d^n \wedge \Phi_\ell ,$$ (2)

where $|n_dk\rangle$ are the spin and symmetry adapted n_d-electron wave functions constructed on the metal d orbitals; C_k^n are variation parameters. Both the spin

multiplicity and the point symmetry of the functions of this type coincide with the multiplicity and the symmetry of the functions Φ_d^n of the d-subsystem.

The wave functions of the type Eq. (2) correspond to the fixed integer number (n_d) of electrons in the d shell of the metal ion. It is not that bad from the point of view of description of electron distribution itself since for most of the complexes the total charge transfer between the d shell and the ligands usually does not exceed a few per cent of the total number of d electrons in the relevant valence state of the metal ion in TMC. A more serious problem is that all the matrix elements of the resonance operator H_r calculated with the functions of that type are vanishing. That prevents any correct description of the interaction between the ligands and the d-shell in the above class of the trial wave functions with the Hamiltonian Eq. (1). In order to include the effects of the resonance interaction between the subsystems we consider the *effective* Hamiltonian H^{eff} [5] which operates in the subspace spanned by the functions of Eq. (2). Its eigenvalues coincide with those of the exact Hamiltonian (1):

$$H^{eff} = PH_0P + H_{RR} ,$$

$$H_0 = H_d + H_\ell + H_c ,$$

$$H_{RR} = PH_rQ(EQ - QH_0Q)^{-1}QH_rP .$$ (3)

Here P is the projection operator on the subspace of functions with fixed number of d electrons; $Q = 1 - P$.

The approximate eigenfunction Φ_n (2) of the effective Hamiltonian H^{eff} can be found from the pair of interconnected equations for the functions Φ_d^n and Φ_ℓ (see Refs. [5,9]):

$$H_d^{eff} \Phi_d^n = E_d^n \Phi_d^n ,$$

$$H_\ell^{eff} \Phi_\ell = E_\ell \Phi_\ell ,$$ (4)

with the effective Hamiltonians for the subsystems given by

$$H_d^{eff} = H_d + \langle \Phi_\ell | H_c + H_{RR} | \Phi_\ell \rangle ,$$

$$H_\ell^{eff} = H_\ell + \langle \Phi_d^n | H_c + H_{RR} | \Phi_d^n \rangle .$$ (5)

Since the ℓ subsystem is described by a single Slater determinant Φ_ℓ the latter must be found from the self-consistent field procedure applied to the Fockian F_ℓ^{eff} which is derived from the Hamiltonian H_ℓ^{eff} by the standard way [9,10]. Proceeding semiempirically we apply the standard CNDO parameterization scheme

[10] for all ligand atoms and insert into Eq. (5) an initial density matrix ρ of the d subsystem of the form

$$\rho_{\mu\nu} = \delta_{\mu\nu} n_d / 5 ,$$

which describes a uniform distribution of electrons in the d orbitals of the metal atom. This gives the effective Fockian F_ℓ^{eff} which coincides with that of the CNDO approximation for all the ligand atoms and has the core attraction parameters W_{ss} and W_{pp} of the metal 4s and 4p orbitals and the metal core charge Z_M renormalized according to

$$W_{ss} \rightarrow W_{ss} + n_d g_{sd} ,$$

$$W_{pp} \rightarrow W_{pp} + n_d \bar{g}_{pd} ,$$

$$Z_M \rightarrow Z_M - n_d . \qquad (6)$$

Here $g_{sd} = (ss|dd) - (sd|ds)/2$; $\bar{g}_{pd}$ is the mean value of the integrals $g_{i\mu}$, where $i = 4p_x$, $4p_y$, $4p_z$ and $\mu = 3d_{z^2}, 3d_{xz}, 3d_{yz}, 3d_{x^2-y^2}, 3d_{xy}$.

The solution of the Hartree–Fock problem for the ℓ-subsystem with the above CNDO approximate Fockian gives the one electron density matrix P_{kl}, the energies of the molecular orbitals (MO) ϵ_i, and MO LCAO coefficients c_{ik}. These quantities completely describe the electronic structure of the ℓ subsystem within the accepted approximation. They are used to construct the effective Hamiltonian H_d^{eff} Eq. (5) in the following way. The operators H_c and H_{RR} are averaged over the ground state Φ_ℓ of the ℓ subsystem which leads to the effective Hamiltonian H_d^{eff} of the form [5]

$$H_d^{eff} = \sum_{\mu\sigma} \epsilon_\mu^{eff} d_{\mu\sigma}^+ d_{\mu\sigma}$$

$$+ \tfrac{1}{2} \sum_{\mu\nu\rho\eta} \sum_{\sigma\tau} (\mu\nu|\rho\eta) d_{\mu\sigma}^+ d_{\nu\sigma} d_{\rho\tau}^+ d_{\eta\tau} , \qquad (7)$$

where the Coulomb interaction between d electrons is taken as in the free ion and the effective core attraction parameters for metal d electrons ϵ_μ^{eff} contain the corrections originating both from the Coulomb and resonance interaction of d electrons with the ℓ subsystem:

$$\epsilon_\mu^{eff} = W_{dd} + W_\mu^{ion} + W_\mu^{cov} , \qquad (8)$$

where

$$W_\mu^{ion} = \sum_{i \in \{s,p\}} g_{\mu i} P_{ii} + \sum_L (P_{LL} - Z_L) V_{\mu\mu}^L$$

is an ionic term having the standard CFT form and

$$W_\mu^{cov} = - \sum_i \beta_{\mu i}^2 \left(\frac{(1-n_i/2)^2}{\Delta E_{\mu i}} - \frac{(n_i/2)^2}{\Delta E_{i\mu}} \right)$$

is a covalence term. Here P_{ii} is the diagonal matrix element of the one-electron density matrix of the ligand subsystem; $P_{LL} = \sum_{\ell \in L} P_{\ell\ell}$ is the electronic population on the ligand atom L; Z_L is the core charge of the ligand atom L; $V_{\mu\mu}^L$ is the matrix element of the potential energy operator describing the interaction between a d electron and an electron placed on the ligand atom L; n_i is the occupation number of the ith ligand MO ($n_i = 0$ or 2); $\Delta E_{\mu i}$ ($\Delta E_{i\mu}$) are the eigenvalues of the operator H_0 which correspond to the states with one electron transferred from the μth d orbital (from the ith MO) to the ith MO (to the μth d orbital); $\beta_{\mu i}$ is the resonance integral between the μth d orbital and the ith ligand MO which is expressed through the resonance integrals $\beta_{\mu k}$ between the μth d orbital and the kth ligand AO:

$$\beta_{\mu k} = - (I_d + I_k) S_{\mu k} \beta^{ML} ,$$

where I_d and I_k are the valence state ionization potentials, $S_{\mu k}$ is the overlap integral between the μth d AO and the kth ligand AO, and β^{ML} is the only fitting parameter specific for each ML pair where M stands for a transition metal atom and L stands for a donor atom in the ligand (like nitrogen, oxygen, etc.).

The covalence term dominating the d-level splitting is apparently analogous by its origin to the ligand field parameters of the angular overlap model (AOM) [11]. The important difference between them is that in the AOM all the ligand field parameters are fit to the experimental spectra for each ligand and are not transferable from one ligand to another even if the donor atom is the same. In our approach the electronic structure of the ligands is taken into account explicitly by the CNDO calculation. That allows to parameterize only β^{ML}, i.e., the magnitude of the hopping between the orbitals of the donor atom L and d orbitals of the transition metal M. The same value can be used for all the ligands containing a given donor atom [5]. That in turn makes it possible to reproduce the effects of the variations of the ligand electronic structure (due to chemical substitution, for example) on the crystal field they induce and thus on the d–d spectrum (see below).

After the effective Hamiltonian for d electrons is constructed the states of n_d electrons in the d shell are calculated by diagonalizing the full matrix associated with H_d^{eff} on the basis of n_d-electron wave functions.

Table 2
d–d excitation energies for [Fe(bipy)$_2$(NCS)$_2$]

[Fe(bipy)$_2$(NCS)$_2$], ground
state ^{1}"A$_{1g}$"

^{1}"A$_{1g}$" → ^{5}"T$_{2g}$"	$\left\{\begin{array}{c} 9000 \\ 9100 \\ 9800 \end{array}\right\}$	–
→ ^{3}"T$_{1g}$"	$\left\{\begin{array}{c} 9300 \\ 10200 \\ 10300 \end{array}\right\}$	104000
→ ^{1}"T$_{1g}$"	$\left\{\begin{array}{c} 17000 \\ 18000 \\ 18800 \end{array}\right\}$	185000

[Fe(bipy)$_2$(NCS)$_2$], ground
state ^{5}"T$_{2g}$"

^{5}"T$_{2g}$" → ^{5}"E$_g$"	$\left\{\begin{array}{c} 8600 \\ 10900 \end{array}\right\}$	11900
→ ^{3}"T$_{1g}$"	$\left\{\begin{array}{c} 9900 \\ 11000 \\ 11100 \end{array}\right\}$	–
→ ^{1}"A$_{1g}$"	10900	–

Table 3
Ionic (Δ^{ion}) and covalency (Δ^{cov}) contributions to the d-level splitting Δ(cm^{-1})

	[Fe(py)$_6$]$^{2+}$	[Fe(bipy)$_3$]$^{2+}$
Δ^{ion}	167	385
Δ^{cov}	5520	18782
Δ^{total}	5687	19167
Δ^{expt}		18000

The ground state of the whole complex is then obtained by taking the external product of the ligand Slater determinant and that of the n_d-electron wave function obtained by the diagonalization of H_d^{eff} which has the lowest eigenvalue. The d–d excited states are the low lying excitations of the whole complex. They are

obtained by multiplying other n_d-electron functions by the same Slater determinant. The d–d excitation energies can then be estimated as the differences between the eigenvalues of the corresponding eigenstates of the effective Hamiltonian H_d^{eff}.

3. Parameter fit and spin-transition calculations

The previous calculations [5,12] using the effective Hamiltonian method have shown that this method is appropriate to describe the spin multiplicity of the ground state and the low-lying d–d excitations of a great deal of TMC ranging from the hexafluoroanions MF$_6^{4-}$ to metallocenes. In order to extend this method to the iron(II) spin-active complexes we have first chosen the [Fe(py)$_6$]$^{2+}$ and (Fe(bipy)$_3$)$^{2+}$ complexes (here py stands for pyridine and bipy for bipyridyl), for which structural [13–15], magnetic and/or spectroscopic [16,17] data are available from the literature, to find the β^{Fe-N} parameter for further use. One of the complexes has the low-spin and another the high-spin ground state.

The experimental data and the calculation results are summarized in Tables 1–5. Our results concerning the ground and the low-lying excited d–d states (which are of interest for the interpretation of the spectroscopic and magnetic properties) of the fitting compounds are in good agreement with the available experimental data. For the nearly octahedral low-spin [Fe(bipy)$_3$]$^{2+}$ ion the only observed d–d transition is that to the ^{3}T$_{1g}$ state [16]. Both its energy and assignment are in fair agreement with our calculation (Table 1) provided the resonance parameter for the iron–nitrogen bond β^{Fe-N} was taken to be 1.505. The Racah parameters B and C for the iron(II) ion were taken to be 610 and 2450 cm^{-1}, respectively. These are the

Table 4
The energies ΔE_{if} (eV) of the zero order charge transfer states contributing to the Δ^{cov}, corresponding resonance integrals β_{if} (eV) and second order corrections $\beta^2/\Delta E$ (cm^{-1})

Complex	Charge transfer ($i \rightarrow f$)	ΔE_{if}	$|\beta_{if}|$	$\beta^2/\Delta E$
Fe(py)$_6^{2+}$	$(\sigma_{py}) \rightarrow d(e_g)$	13.4	1.75	1850
	$(\sigma_{py}) \rightarrow d(e_g)$	8.6	1.02	980
	$(\sigma_{py}) \rightarrow d(e_g)$	8.43	0.78	580
	HOMO$(\sigma_{py}) \rightarrow d(e_g)$	8.40	0.90	780
Fe(bipy)$_3^{2+}$	$(\sigma_{py}) \rightarrow d(e_g)$	13.9	3.47	7010
	$(\sigma_{py}) \rightarrow d(e_g)$	8.7	2.62	6380

Table 5
Electronic structure of the ligand subsystems

	$[Fe(py)_6]^{2+}$	$[Fe(bipy)_3]^{2+}$	$[Fe(bipy)_2(NCS)_2]$
energy gaps $\epsilon(LUMO) - \epsilon(HOMO)$ (eV):			
$\Delta\epsilon$	15.80	13.16	7.99
metal orbital populations:			
4s	0.40	0.40	0.42
4p	0.24	0.23	0.25
atomic charges:			
Fe	0.89	0.91	0.83
N_{py}	−0.23	−0.26	−0.22
S	–	–	−0.54
N_{NCS}	–	–	−0.43

averages of the values for the HS and LS complexes of iron(II) with nitrogen containing ligands taken from Ref. [18]. In contrast with the apparently very close $[Fe(bipy)_3]^{2+}$ ion the $[Fe(py)_6]^{2+}$ cation has the high-spin $^5T_{2g}$ ground state, in perfect agreement with the experiment [17]. We were not able to compare the calculated d–d transition energies of the $[Fe(py)_6]^{2+}$ cation with experimental results since its absorption spectrum seems to have never been measured.

After the resonance parameter β^{Fe-N} was found we applied the effective Hamiltonian method to the spin active cis-$[Fe(bipy)_2(NCS)_2]$ complex. It undergoes an abrupt transition from the high-spin to the low-spin form at $T_c = 176$ K. For the two spin isomers of this compound the molecular geometries are known from single-crystal X-ray diffraction [13]. It is known from experiment [18] (and it is one of the methods to observe the spin transition) that the optical absorption spectra significantly differ for the two spin isomers. Our method can fairly describe this picture. First, the ground state geometries of the two spin isomers of cis-$[Fe(bipy)_2(NCS)_2]$ are different only by the Fe–N bond lengths; they are about 0.2 Å longer in the HS isomer. The interatomic distances within the ligands remain the same in both spin isomers. The calculation by the effective Hamiltonian method for the LS geometry gives the singlet (low-spin) ground state and that with HS geometry gives the quintet ground state. For the HS ground state we found several spin-allowed transitions with the energies close to the observed ones. For the LS ground state the allowed singlet–singlet d–d transition has much higher energy. The excited singlet states originate from an octahedral T_{1g} term. It can be

easily seen that our calculation gives a triple of singlet excited states having an energy close to the energy of the observed d–d transition (Table 1).

4. Coulomb contribution to the intermolecular interaction

The cooperativity observed in some spin-transition compounds presents another problem not attacked by quantum chemical methods until now. The theories existing in this area are largely phenomenological and do not attempt to calculate the parameters describing the cooperative behavior (like the abruptness of the transition or the thermal hysteresis width) [1,2].

It has been pointed out recently [19] that the Coulomb interaction might be a possible source of interaction, leading to the observed cooperativity effects. Unfortunately, the approach adopted in Ref. [19] in order to calculate the effect of the spin transition on the Coulomb part of the intermolecular interaction did not allow one to estimate the value of the interaction parameter. In this section we consider the effect of the charge redistribution taking place upon the HS to LS transition on the intermolecular interaction.

In a pair of molecules capable of undergoing a spin transition either both molecules are in the LS state (and their interaction energy is then E_{LL}) or one of them is in the LS and another in the HS state (and the interaction energy is then E_{HL}) or both are in the HS state (and the interaction energy is E_{HH}). According to Ref. [19] the cooperativity effects are described by the interaction parameter W which has the form:

$$W = E_{HL} - (E_{LL} + E_{HH})/2 . \tag{9}$$

In Eq. (9) W simply shows what is energetically preferable for an assembly of molecules in different spin states assuming that the interaction only occurs between nearest neighbors: either to arrange themselves in such a way that the molecules of different spins are the nearest neighbors ($W < 0$) or to adopt a configuration where the molecules of the same spin are the nearest neighbors ($W > 0$). The Coulomb contribution to the interaction energy W can be estimated as follows. Let us denote the charges on the ith atom in the LS state as q_i^{LS} and that in the HS state as q_i^{HS}. The Coulomb parts of the interaction energy for the three possible pairs of molecules are

$$E_{HL}^{Coul} = \sum_{i,j} q_i^{HS} q_j^{LS} \, | r_{iA} - r_{jB} |^{-1} ,$$

$$E_{LL}^{Coul} = \sum_{i,j} q_i^{LS} q_j^{LS} \, | r_{iA} - r_{jB} |^{-1} ,$$

$$E_{HH}^{Coul} = \sum_{i,j} q_i^{HS} q_j^{HS} \, | r_{iA} - r_{jB} |^{-1} , \qquad (10)$$

where the radius vectors r_{iA} and r_{iB} correspond to the ith atom in the two interacting molecules. Substituting $q_i^{HS} = q_i^{LS} + \delta q_i$ in the above formulae easily results in:

$$W^{Coul} = -\tfrac{1}{2} \sum_{i,j} \delta q_i \, \delta q_j \, | r_{iA} - r_{jB} |^{-1} , \qquad (11)$$

which gives precisely the Coulomb contribution to the interaction parameter W.

We used the results of our calculation on the ligand subsystem of the LS and HS forms of cis-[Fe(bipy)$_2$(NCS)$_2$] in order to estimate the Coulomb contribution W^{Coul} for different structural arrangements of the two molecules occurring in the crystals. Though within the method [5] there is no direct coupling between the spin and charge degrees of freedom, so that the variation of the spin of the central ion does not affect per se the charge distribution in the ligands, the small variation of the geometry under the transition leads to the corresponding redistribution of the electron density. The absolute values of the charge variations δq_i do not exceed $0.02e$ for all atoms of the complex. They are the most pronounced for the nitrogen atoms immediately attached to the iron atom, which is in a line with the fact that only the iron–nitrogen distances change significantly under the HS–LS transition.

It is not surprising that the absolute variations of the atomic charges δq_i are small. Nevertheless, the overall effect is noticeable. For example for the pair of cis-[Fe(bipy)$_2$(NCS)$_2$] molecules with the Fe...Fe separation of 8.314 Å singled out from the crystal (the mutual orientation of the molecules in the pair is retained as it was determined in Ref. [13] for the Fe...Fe$_{ii}$ interacting pair) the value of W^{Coul} equals to 2.2 K in temperature units. On the other hand for the pair of the Fe...Fe$_i$ type with the Fe...Fe separation of 11.083 Å the value of W^{Coul} is -1.47 K.

We see that even the sign of the interaction may be different for the different mutual orientations of the interacting molecules in the real crystal, and that the

Coulomb contribution to the interaction W is about several kelvin. Since the spin transition in the crystalline cis-[Fe(bipy)$_2$(NCS)$_2$] is abrupt [1,21] the interaction parameter $\Gamma = zW$ (z is the number of neighbors of a given molecule in the crystal) must be about $2T_c$, i.e. 360 K. We see that the Coulomb energy calculated with δq_i found by the method [5] contributes at best to 10% of the total intermolecular interaction responsible for the cooperative character of the spin transition.

5. Discussion and conclusion

In the above treatment two problems concerning the spin transitions phenomena in TMC have been addressed. The first was the problem of the description of the spin transition in an isolated molecule. It turned out that by applying the method [5] the effects of the relatively small geometry variations on the crystal field are adequately reproduced. That allowed us to reproduce as well the ground state symmetries and multiplicities of the two spin isomers of the studied spin active compound and the energies and the symmetries of the low-lying (d–d) excitations of the spin isomers. That allows us to conclude that the effective Hamiltonian method [5] may serve as a useful tool in the studies of the spin-transition phenomena in TMC.

It is instructive to compare the results obtained by our method with those recently obtained in Ref. [3] by a version of the INDO method. As a general comment we mention that the calculation method used in Ref. [3] stresses the role of the relativistic effects rather than of the correlation ones. In this approach d orbitals are included in the general mean-field scheme and the effects of that have been discussed in Section 1. Concerning the results of Ref. [3] two major points deserve discussion here. First of all we note that the iron ions bear a significant negative charge (about $-0.4e$ in the LS form) in the complexes considered in Ref. [3] and that the LS–HS transition is accompanied by an order of magnitude larger electron transfer from the iron ion to the ligand nitrogens than our method gives. The overestimation of the negative metal charges is a well known shortcoming of the semi-empirical methods using Clack's parameterization scheme (for more discussion of this point see Ref. [5]). The large charge redistribution in the two spin forms indicates that the orbitals involved in the description of the spin-transi-

tion contain significant contributions of the ligand orbitals and cannot be considered as d-states. Second, the difference of 0.1 Wiberg indices are reported for the Fe–N bonds in the LS and the HS forms, indicating that the bond lengths must be larger in the HS isomer. However, the results of the geometry optimization for *both* LS and HS forms are not reported in Ref. [3]. For that reason it remains unclear whether the method used in Ref. [3] is able to reproduce the correct spin multiplets at the experimental geometries.

Another problem addressed in this work was the cooperativity between spin-active molecules, which may occur in the solid state. We propose an estimate of the cooperativity parameter in a crystal formed by the spin-active molecules on the basis of the molecular and crystal data. Our findings suggest that the Coulomb interaction accounts for only a small fraction of the experimentally observed cooperativity parameter. These results, however, are to be taken cautiously since there is no solid proof for the validity of the naive use of atomic charges obtained by the method [5] for calculating intermolecular interactions. If, however, the charge variations δq_i obtained from our calculation are valid that would mean that the Coulomb forces at least do not dominate the interactions responsible for the cooperativity and the latter would then be due to some other interactions, for example, the spin–phonon interactions may play the crucial rôle as proposed in Ref. [20] (see also Ref. [21]).

Acknowledgements

References

[1] E. König, G. Ritter and S. Kulshreshtha, Chem. Rev. 85 (1985) 219.

[2] O. Kahn, J. Kröber and C. Jay, Advan. Mater. 4 (1992) 718.

[3] W. Linert, M. Konecny and F. Renz, J. Chem. Soc. Dalton Trans. (1994) 1523.

[4] A. Veillard, Quantum chemistry: the challenge of transition metals and coordination chemistry (Reidel, Dordrecht, 1986).

[5] A.V. Soudackov, A.L. Tchougréeff and I.A. Misurkin, Theoret. Chim. Acta 83 (1992) 389; in: Electronic effects in low-dimensional conductors and superconductors, Research Reports in Physics, eds. A.A. Ovchinnikov and I.I. Ukrainskii (Springer, Berlin, 1991).

[6] M.C. Böhm and R. Gleiter, Theoret. Chim. Acta 57 (1980) 315; 59 (1981) 127; 60 (1981) 233.

[7] C.J. Ballhausen, Introduction to the ligand field theory (McGraw-Hill, New York, 1962).

[8] A.B.P. Lever, Inorganic electronic spectroscopy (Elsevier, Amsterdam, 1984).

[9] R. McWeeny and B.T. Sutcliffe, Methods of molecular quantum mechanics (Academic Press, London, 1969).

[10] J.A. Pople and D.L. Beveridge, Approximate molecular orbital theory (McGraw-Hill, New York, 1970).

[11] M. Gerloch and R.G. Wooley, Progr. Inorg. Chem. 31 (1984) 371.

[12] A.V. Soudackov, A.L. Tchougréeff and I.A. Misurkin, Russ. J. Phys. Chem. 68 (1994) 1257, 1265.

[13] B. Gallois, J.-A. Real, C. Hauw and J. Zarembowitch, Inorg. Chem. 29 (1990) 1152.

[14] R.J. Doedens and L.F. Dahl, J. Am. Chem. Soc. 88 (1966) 4847.

[15] A. Zalkin, D.H. Templeton and T. Ueki, Inorg. Chem. 12 (1973) 1641.

[16] E. König and K. Madeja, Inorg. Chem. 6 (1967) 48; R.A. Palmer and T.S. Piper, Inorg. Chem. 5 (1966) 864.

[17] W. Hieber and R. Werner, Chem. Ber. 90 (1957) 286.

[18] P. Gütlich, Struct. Bonding 44 (1981) 83.

[19] H. Bolvin and O. Kahn, to be published.

[20] S. Ramasesha, T.V. Ramakrishnan and C.N.R. Rao, J. Phys. C 12 (1979) 1307.

[21] A.L. Tchougréeff, Chem. Phys. Letters 214 (1993) 627.