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The Role of Binary and Many-centre Molecular Interactions in Spin Crossover in the Solid State. Part II. Non-ideality Parameters Defined *via* Binary Molecular Potentials

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Summary. Parameters of the formalism [1–6] describing spin crossover in the solid state have been defined *via* molecular potentials in model systems of neutral and ionic complexes. In the first instance *Lennard-Jones* and electric dipole–dipole potentials have been used whereas in ionic systems *Lennard-Jones* and electric point-charge potentials have been used. Electric dipole–dipole interaction of neutral complexes brings about a positive excess energy controlled by the difference of electric dipole moments of HS and LS molecules. Differences of the order of $\Delta\mu = 1\text{–}2\,\mathrm{D}$ cause an abrupt spin crossover in systems with $T_{1/2} = 100\text{–}150\,\mathrm{K}$. Magnetic coupling contributes both to the excess energy and excess entropy, however the overall effect is equivalent to a modest positive excess energy. Ionic systems in the absence of specific interactions are characterised by very small excess energies corresponding to practically linear *van't Hoff* plots. Detectable positive and negative excess energies in these systems may arise from interactions of ligands belonging to neighbouring complexes. The HOMO–LUMO overlap in HS–LS pairs can bring about a nontrivial variation of the shape of transition curves. Examples of regression analysis of experimental transition curves in terms of molecular potentials are given.

Keywords. Molecular magnets; Molecular potentials; Solid state; Spin crossover; Thermodynamics.

Introduction

In our previous communications [1–6] we have developed a formalism that allows one to adequately parameterise quite complicated transition curves of spin

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crossover observed in the solid state. Parameters of this formalism arise from the changes of the partition function (or free energy $F = NkT\ln Z$) of a given molecule due to LS$\rightarrow$HS transition (i) of the molecule itself and (ii) of molecules in the nearest surroundings of the considered one. In the first instance these parameters are standard free energies of spin crossover in the state of pure compound $\Delta F^0 = F_{\mathrm{BBB}} - F_{\mathrm{AAA}}$ the index BBB denoting HS-molecule B in a homo-molecular environment (similar meaning has the index AAA with respect to LS-molecule A). Parameters of the second type are the excess free energy $\Delta F_{\mathrm{E}} = F_{\mathrm{ABA}} - F_{\mathrm{BBB}} + F_{\mathrm{BAB}} - F_{\mathrm{AAA}}$ (in which the indices ABA and BAB denote molecules B and A in hetero-molecular environments respectively) and the asymmetries of splittings $\Delta_i^{\mathrm{A}} = 2F_{\mathrm{AAB}} - F_{\mathrm{AAA}} - F_{\mathrm{BAB}}$, $\Delta_i^{\mathrm{B}} = 2F_{\mathrm{BBA}} - F_{\mathrm{BBB}} - F_{\mathrm{ABA}}$ characterising many-body interactions in the mixture of HS and LS isomers. Parameters of the first type can be independently determined from calorimetric measurements whereas those of the second type can only be estimated by regression of experimental transition curves or computed according to some theoretical model of molecular interactions. A short review of contemporary theoretical models of spin crossover equilibrium is given in the introduction to Part I of these communications [6]; more detailed information can be found in Refs. [7, 8].

A theoretically based molecular design of promising spin crossover compounds requires a method of an easy evaluation (for model structures) of the sharpness of spin crossover transition operating with simple molecular parameters such as interatomic distances, bond angles, electric dipole moments, *etc*. Molecular potentials such as the *Lennard-Jones* potential and those of coulombic dipole and point-charge interactions can be advantageously used for this purpose. Parameters of the formalism developed in Refs. [1–6] can be represented *via* energies derived from these potentials. Assuming entropic effects of molecular interactions (changes of electronic degeneracy, molecular volume, and vibrational frequencies due to spin transitions in the nearest surroundings) to be negligibly small, the non-ideality parameters of the model of triple interactions [1–5] can be written as shown by Eqs. (1)–(5) in which φ are binary and ψ are three-center potentials and the multiplier 3 appears as a result of summing energy over three coordinates assumed to be equivalent.

$$\begin{aligned}\Delta^{\mathrm{A}} &= (E_{\mathrm{AAB}} - E_{\mathrm{BAB}}) + (E_{\mathrm{AAB}} - E_{\mathrm{AAA}})\\ &= 3\times\{[\varphi_{\mathrm{AA}} - \varphi_{\mathrm{AB}}] + [\varphi_{\mathrm{AB}} - \varphi_{\mathrm{AA}}] + 2\psi_{\mathrm{AAB}} - \psi_{\mathrm{BAB}} - \psi_{\mathrm{AAA}}\}\\ &= 3\times(2\psi_{\mathrm{AAB}} - \psi_{\mathrm{BAB}} - \psi_{\mathrm{AAA}}) \qquad (1)\end{aligned}$$

$$\begin{aligned}\Delta^{\mathrm{B}} &= (E_{\mathrm{ABB}} - E_{\mathrm{ABA}}) + (E_{\mathrm{ABB}} - E_{\mathrm{BBB}})\\ &= 3\times\{[\varphi_{\mathrm{BB}} - \varphi_{\mathrm{AB}}] + [\varphi_{\mathrm{AB}} - \varphi_{\mathrm{BB}}] + 2\psi_{\mathrm{ABB}} - \psi_{\mathrm{ABA}} - \psi_{\mathrm{BBB}}\}\\ &= 3\times(2\psi_{\mathrm{ABB}} - \psi_{\mathrm{ABA}} - \psi_{\mathrm{BBB}}) \qquad (2)\end{aligned}$$

$$D_{\mathrm{A}} = E_{\mathrm{BAB}} - E_{\mathrm{AAA}} = 3\times(2\varphi_{\mathrm{AB}} - 2\varphi_{\mathrm{AA}} + \psi_{\mathrm{BAB}} - \psi_{\mathrm{AAA}}) \qquad (3)$$

$$D_{\mathrm{B}} = E_{\mathrm{ABA}} - E_{\mathrm{BBB}} = 3\times(2\varphi_{\mathrm{AB}} - 2\varphi_{\mathrm{BB}} + \psi_{\mathrm{ABA}} - \psi_{\mathrm{BBB}}) \qquad (4)$$

$$\begin{aligned}\Delta E^{\mathrm{E}} &= D_{\mathrm{A}} + D_{\mathrm{B}}\\ &= 3\times(4\varphi_{\mathrm{AB}} - 2\varphi_{\mathrm{AA}} - 2\varphi_{\mathrm{BB}} + \psi_{\mathrm{ABA}} - \psi_{\mathrm{BBB}} + \psi_{\mathrm{BAB}} - \psi_{\mathrm{AAA}}) \qquad (5)\end{aligned}$$

It must be emphasised that the energies E_{AAA}, E_{AAB}, *etc*. in Eqs. (1)–(5) are *the energy levels of the central molecule* and not the energies of these configurations. Therefore we do not take into account the energy of interaction of outer molecules (*e.g.* φ_{BB} in BAB).

In this paper we consider the effects of several binary molecular potentials on non-ideality parameters. Binary potentials in square brackets in Eqs. (1) and (2) compensate each other therefore the asymmetries must be controlled by ternary (and implicitly by higher order) interactions alone. According to Ref. [9] ternary interactions constitute up to several percents of the total lattice energy in alkali halide crystals, *i.e.* at least several kJ/mol. However, if some binary interactions act selectively in one or several configurations then one may expect certain contribution from such binary interactions towards $\Delta^{\mathrm{A(B)}}$ (see below, HOMO–LUMO Overlap in HS–LS Pairs). Macroscopically long-range elastic interactions [10] are implicitly taken into account in our model in a zero approximation as contributing towards the standard energy of spin crossover.

Results and Discussions

Systems of Neutral Molecules

Spin crossover compounds can be separated into two families, namely those of neutral (*e.g.* Fe(*phen*)$_2$(NCS)$_2$]) and ionic (*e.g.* [Fe(*ptz*)$_6$](BF$_4$)$_2$) compounds. In the latter case anions do not enter the first coordination sphere of Fe^{2+} surrounded by six nitrogen atoms belonging to neutral ligands. Major intermolecular forces in the first type of spin crossover compounds can be represented by *Lennard-Jones* and electric dipole–dipole potentials. Molecular interactions in complexes belonging to the second family are more correctly described by the combination of *Lennard-Jones* and electric point-charge potentials. In both cases these major interactions are accompanied by several specific interactions.

In order to calculate non-ideality parameters according to Eqs. (1)–(5) the knowledge of intermolecular distances corresponding to the minimum of the total potential is required. The distances in pure HS and LS states can be taken from experimental data on a 'prototype' compound. Parameters a_{ij} of the *Lennard-Jones* potential (*van der Waals* diameters) are usually unknown for spin crossover complexes, however they can be optimised in such a way that the minimum of the total potential occurs at the experimental distance (see Methods).

As the prototype compound for neutral complexes we have chosen *cis*-bis-(thiocyanato)bis[*N*-(2′-pyridylmethylene)-4-aminobiphenyl)]Fe(II), described in Ref. [11] (Fe(*PM-Bia*)$_2$(NCS)$_2$). Schematic arrangement of these molecules in the chain AAB is shown in Fig. 1. According to Ref. [11] an LS→HS transition in [Fe(*PM-Bia*)$_2$(NCS)$_2$] is accompanied with a change in Fe–Fe (average) distances from 10.739 Å (LS) to 10.948 Å (HS) yielding $\Delta r = 0.209$ Å. At the same time the average length of Fe–N bond is increased by 0.189 Å. Semi-empirical quantum chemical calculations (HyperChem 5$^{\mathrm{TM}}$, ZINDO/1) on [Fe(*PM-Bia*)$_2$(NCS)$_2$] show that these molecules possess large electric dipole moments: 22.426 D in HS and 22.812 D in LS states.

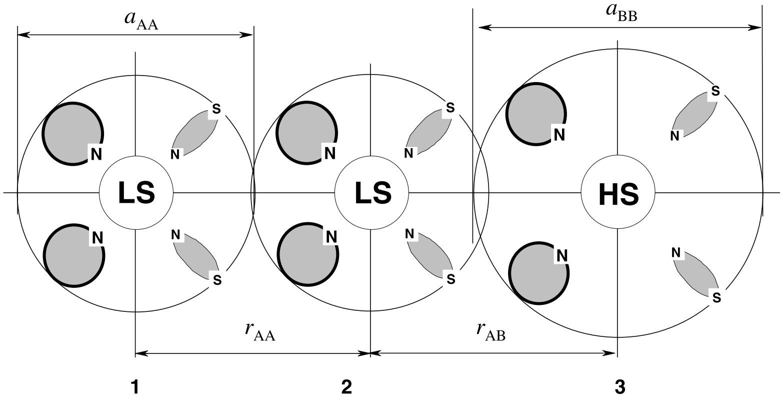

Fig. 1. Model chain of neutral complexes and their *van der Waals* diameters (configuration AAB)

A rough estimate of the depth of the potential well in the *Lennard-Jones* potential was derived from the evaporation heat of $Fe(CO)_5$ and assumed to be $\varepsilon_{AA} = 12\,kJ\,mol^{-1}$; a slightly larger value was assumed for the HS–HS pairs: $\varepsilon_{BB} = 14\,kJ\,mol^{-1}$, taking into account higher polarisability of the HS state.

The depth of the potential well in hetero-molecular pairs was calculated according to the modified *Berthelot*'s rule (Eq. (6)) in which α_ε reflects deviations due to interactions not explicitly included into the model.

$$\varepsilon_{AB} = (I + \alpha_\varepsilon)(\varepsilon_{AA}\varepsilon_{BB})^{1/2} \tag{6}$$

The effect of compression was explored by varying r_{AA}; other distances were assumed to change inversely proportional to the corresponding force constants. The latter were estimated by approximating the potential curves in a narrow region around the minimum by quadratic parabolas. Transition curves have been computed for a model system characterised by $\Delta E^0 = 14\,kJ\,mol^{-1}$ and $\Delta S^0 = 90\,J\,mol^{-1}\,K^{-1}$ ($T_{1/2} = 155.5\,K$); ΔE^0 and ΔS^0 have been considered as unaffected by compression. The critical value of the excess energy for the abrupt spin crossover in such systems ($\Delta E^E = 2RT_{1/2}$) equals $+2.58\,kJ/mol$ whereas the negative excess energy of a similar magnitude (at zero Δ^A and Δ^B) brings about a two-step spin crossover.

Lennard-Jones and Electric Dipole–Dipole Potentials (Basic Model)

The potential energy of a pair of polar molecules can be written as shown by Eq. (7) [12] in which $f(\theta)$ is the geometrical factor equal 2 for the "head-to-tail" arrangement of dipole moments μ_i, μ_j (according to XRD data [11]).

$$\varphi_{ij} = \varepsilon_{ij}\left[\left(\frac{a_{ij}}{r_{ij}}\right)^{12} - 2\left(\frac{a_{ij}}{r_{ij}}\right)^{6}\right] - \frac{\mu_i\mu_j}{r_{ij}^3}f(\theta) \tag{7}$$

The condition of mechanical equilibrium $d\varphi_{ij}/dr_{ij} = 0$ for this potential yields a cubic equation with respect to $(a_{ij}/r_{ij})^3$ (Eq. (8)).

$$\frac{d\varphi_{ij}}{dr_{ij}} = \frac{12\varepsilon_{ij}}{r_{ij}}\left[-\left(\frac{a_{ij}}{r_{ij}}\right)^{12} + \left(\frac{a_{ij}}{r_{ij}}\right)^{6}\right] + \frac{6\mu_i\mu_j}{r_{ij}^4} = 0 \tag{8}$$

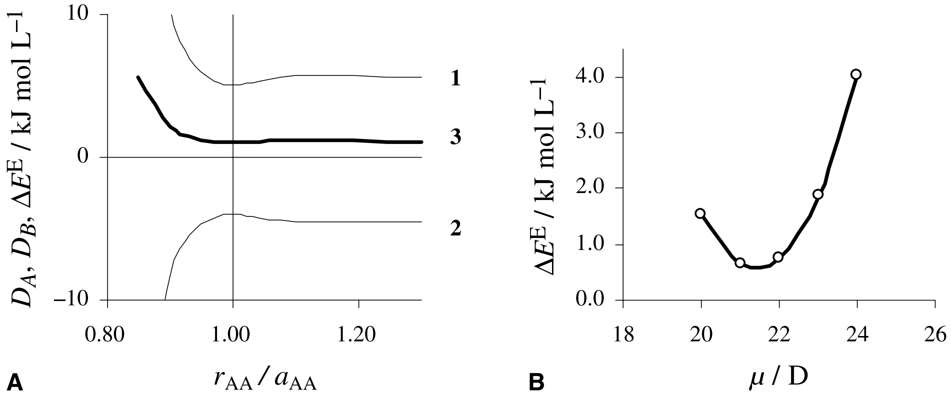

Fig. 2. Variations of D_A (1), D_B (2), and ΔE^E (3) with compression (**A**); graph **B** shows the dependence of ΔE^E on the electric dipole moments of A-species at constant $\mu_B = 22$ D

This equation can easily be solved numerically yielding equilibrium distances required for the calculation of energies. According to these calculations the considered basic system is characterised by a modest positive excess energy (*ca.* 1 kJ/mol), only slightly dependent on reasonable compressions ($r/r_{opt} = 0.98$–1.02, Fig. 2A). The pattern of energy levels corresponds to $E_{BAB} > E_{AAA}$ and $E_{ABA} < E_{BBB}$, *i.e.* $D_A > 0$, $D_B < 0$. This pattern is reversed at $\mu_B > \mu_A$ but the excess energy remains positive for both $\mu_B > \mu_A$ and $\mu_B < \mu_A$. It passes through a minimum (Fig. 2B) at $\mu_A \approx \mu_B$. Assuming the geometrical factor $f(\theta)$ to be unaffected by spin crossover the electrostatic component of ΔE^E can be written as given by Eq. (9) in which r is the mean intermolecular distance.

$$\Delta E^E = -6\frac{\mu_A\mu_B}{r^3}\left[2\left(\frac{r}{r_{AB}}\right)^3 - \frac{\mu_B}{\mu_A}\left(\frac{r}{r_{BB}}\right)^3 - \frac{\mu_A}{\mu_B}\left(\frac{r}{r_{AA}}\right)^3\right] \tag{9}$$

It changes at HS→LS transitions by less than 2%, therefore one can assume $r/r_{ij} \approx 1$, leading to Eq. (10).

$$\Delta E^E \approx \frac{6(\mu_A - \mu_B)^2}{r^3} \tag{10}$$

This quadratic dependence explains why ΔE^E remains positive when the sign of μ_A–μ_B is changed. The difference in electric dipole moments of HS and LS states required for the observation of the abrupt spin crossover (at $\alpha_\varepsilon = 0$) is *ca.* 1.35 D.

Table 1. Effects of deviations of ε_{AB} from *Berthelot*'s rule in the basic model system of neutral complexes

r_{AA}/r_{opt}	$\alpha_\varepsilon = +0.04$			$\alpha_\varepsilon = -0.02$		
	D_A / kJ/mol	D_B / kJ/mol	ΔE^E / kJ/mol	D_A / kJ/mol	D_B / kJ/mol	ΔE^E / kJ/mol
0.980	3.104	−6.220	−3.117	6.2358	−3.0884	3.1474
1.000	3.048	−6.116	−3.068	6.1326	−3.0318	3.1008
1.020	3.087	−6.182	−3.095	6.1980	−3.0702	3.1278

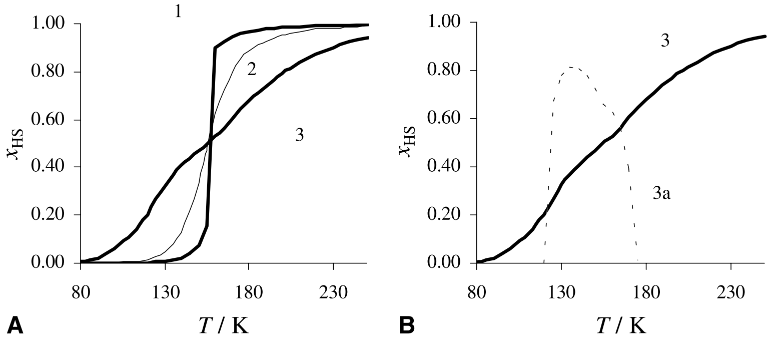

Fig. 3. Transition curves (at $r_{AA}/r_{opt} = 1.0$) showing effects of non-additive ε_{AB} (**A**); curves 1, 2, 3 correspond to $\alpha_\varepsilon = -0.02$, 0, and $+0.04$ respectively; graph **B** shows curve 3 along with the corresponding temperature dependence of the degree of order (the dashed line 3a)

Deviations of ε_{AB} from *Berthelot*'s rule (due to unaccounted interactions) bring about considerable excess energies: negative for $\alpha_\varepsilon > 0$ and positive for $\alpha_\varepsilon < 0$ (Table 1). Positive deviations above $\alpha_\varepsilon = +0.04$ may cause a two-step spin crossover (Fig. 3, curves 3, 3a); negative deviations with $|\alpha_\varepsilon| > 0.02$ cause an abrupt spin crossover (Fig. 3A, curve 1).

Overlap of HOMO and LUMO of Neighbouring Complexes in HS–LS Pairs

Among specific interactions in spin crossover compounds the overlap of HOMO (HS) and LUMO (LS) in HS–LS pairs can play an important role. If a semi-filled e_g orbital of an HS Fe(II) complex overlaps with an empty e_g orbital of a neighbouring LS complex then unpaired electrons of HS species can be transferred into a bonding 'intermolecular' orbital (Fig. 4) that causes a stabilisation of HS–LS pairs.

The effect of stabilisation of HS–LS pairs can be simulated by positive deviations from *Berthelot*'s rule. Splittings Δ_{st} (Fig. 4) of the order 100 cm^{-1} correspond to $\alpha_\varepsilon \approx 0.05$, sufficient to bring about a two-step spin crossover.

This HOMO–LUMO overlap can also cause a redistribution of electronic charge densities in the interacting species. This effect can be accounted for by selective variations of the energy of dipole–dipole interaction in HS–LS pairs (Eq. (11)) in which α_μ reflects the deviation of electric dipole moments due to overlap.

$$\varepsilon_{dd}(AB) = -(1 + a_\mu)\frac{2\mu_A\mu_B}{r_{AB}^3} \qquad (11)$$

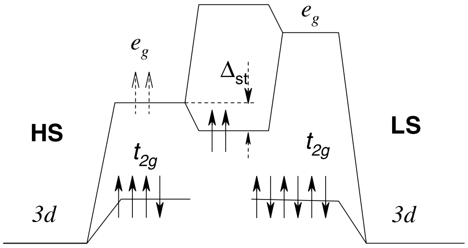

Fig. 4. Energy level diagram illustrating the overlap of e_g orbitals in a HS–LS molecular pair

Table 2. Effects of selectively varied energy of electric dipole–dipole interaction in LS–HS pairs: $\varepsilon_{\mathrm{dd}} = \mu_{\mathrm{A}}\mu_{\mathrm{B}}(1+\alpha_\mu)/r_{\mathrm{AB}}{}^3$; *Lennard-Jones* potentials are characterised by additive $\varepsilon_{\mathrm{AB}}$ ($\alpha_\varepsilon = 0$, $r_{\mathrm{AA}}/r_{\mathrm{opt}} = 1$)

α_μ	$\frac{D_{\mathrm{A}}}{\mathrm{kJ/mol}}$	$\frac{D_{\mathrm{B}}}{\mathrm{kJ/mol}}$	$\frac{\Delta E^{\mathrm{E}}}{\mathrm{kJ/mol}}$	α_μ	$\frac{D_{\mathrm{A}}}{\mathrm{kJ/mol}}$	$\frac{D_{\mathrm{B}}}{\mathrm{kJ/mol}}$	$\frac{\Delta E^{\mathrm{E}}}{\mathrm{kJ/mol}}$
0.0000	5.122	−4.042	1.080				
−0.002	5.702	−3.463	2.239	+0.002	4.543	−4.622	−0.079
−0.008	7.439	−1.725	5.714	+0.008	2.803	−6.362	−3.559

The energy of dipole–dipole interaction of neutral spin-crossover complexes is large therefore very small relative deviations α_μ strongly affect the excess energy (see Table 2).

The depression of dipolar energy by −0.004 brings about large positive $\Delta E^{\mathrm{E}} = +3.39\,\mathrm{kJ/mol}$, *i.e.* above the critical value for the abrupt spin crossover; negative excess energy of a similar magnitude ($\Delta E^{\mathrm{E}} = -3.56\,\mathrm{kJ/mol}$ corresponding to $\alpha_\mu = +0.008$) causes a conversion of a smooth transition curve into a two-step transition. The variation of non-ideality parameters arising from these effects with compression is insignificant.

Magnetic Scalar Coupling

The energy of magnetic scalar (exchange) interaction in transition metal complexes can be quite significant [13, 14] and therefore contributes towards the non-ideality parameters of spin crossover equilibrium. In complexes of 3*d* elements the exchange coupling constants vary from zero to several hundreds of cm^{-1}; the magnitude and sign of the coupling constant depends on the angle metal-bridge-metal but is apparently independent of the metal-to-metal distance [14]. To a first approximation this type of interaction can be assumed to be independent of intermolecular distances and compression. Experimentally it was found that magnetic exchange interaction occurs in polynuclear spin crossover compounds [15–17]; no such data exist on mononuclear compounds.

Magnetic scalar coupling occurs between HS species, *i.e.* in BBB and BBA configurations alone. The energy of magnetic exchange interaction in a pair can be calculated as shown by Eq. (12) [13] in which S is the spin of individual HS species and S' is the total spin of a pair.

$$E(S') = -J[S'(S'+1) - 2S(S+1)] \tag{12}$$

Computing the energy of molecular interactions *via* this mechanism implies averaging it over pairs with $S' = 0$, 1, 2, 3 and 4; this results in Eq. (13).

$$E = \frac{\sum E(S')(2S'+1)e^{-\frac{E(S')}{kT}}}{\sum (2S'+1)e^{-\frac{E(S')}{kT}}} = 6J\,\frac{-12e^{+\frac{8J}{kT}} + 5\left(e^{-\frac{6J}{kT}} + e^{-\frac{10J}{kT}}\right) + 2e^{-\frac{12J}{kT}}}{7 + 9e^{+\frac{8J}{kT}} + 5e^{-\frac{6J}{kT}} + 3e^{-\frac{10J}{kT}} + e^{-\frac{12J}{kT}}} \tag{13}$$

The energy of this interaction is negative for both ferro- ($J > 0$) and antiferromagnetic ($J < 0$) interactions and temperature dependent (Fig. 5). This interaction contributes therefore towards both the excess energy and excess entropy. Being approximated by straight lines the dependencies shown in Fig. 5A yield

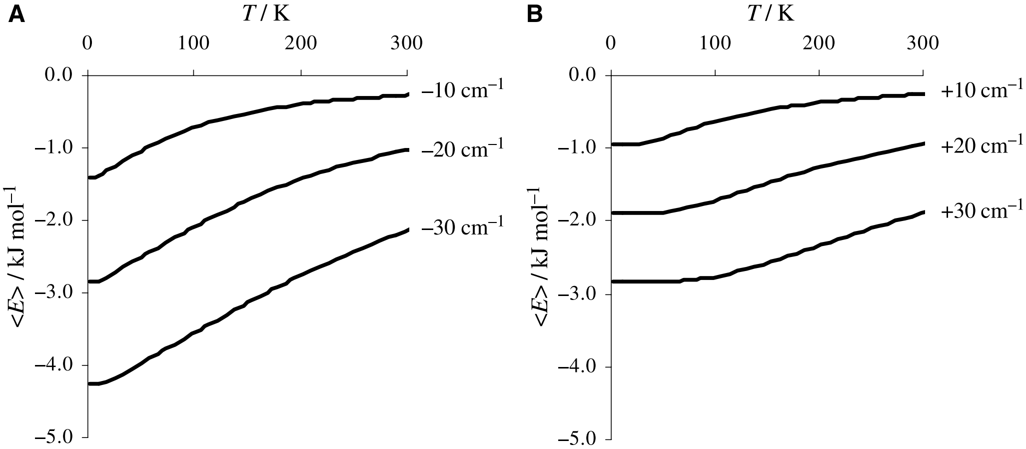

Fig. 5. Temperature dependencies of the energy of magnetic scalar coupling in pairs HS complexes of Fe(II) with antiferromagnetic ($J<0$, **A**) and ferromagnetic ($J>0$, **B**) interactions

Table 3. Contribution of magnetic scalar coupling towards excess energy and excess entropy

$\frac{J}{\mathrm{cm}^{-1}}$	$\frac{\Delta S^{\mathrm{E}}}{\mathrm{J\,mol^{-1}\,K^{-1}}}$	$\frac{\Delta E^{\mathrm{E}}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{J}{\mathrm{cm}^{-1}}$	$\frac{\Delta S^{\mathrm{E}}}{\mathrm{J\,mol^{-1}\,K^{-1}}}$	$\frac{\Delta E^{\mathrm{E}}}{\mathrm{kJ\,mol^{-1}}}$
−10	20.4	7.014	+10	14.4	5.478
−20	37.2	16.536	+20	22.2	12.144
−30	44.4	25.836	+30	21.6	18.222

considerable excess energies and entropies (Table 3). However these contributions compensate each other to a considerable extent.

Equation (13) being directly inserted into the simulation program yields small variations of the shape of transition curves due to magnetic scalar coupling typical for positive excess energies. Only the exceptionally strong interaction ($J<-40\,\mathrm{cm}^{-1}$ or $J>+50\,\mathrm{cm}^{-1}$) could bring about an abrupt spin crossover. Experiments only indicate a weak antiferromagnetic coupling in binuclear spin crossover compounds of Fe(II) [18] and Co(II) [19] with $J\approx-4\,\mathrm{cm}^{-1}$ and $J=-14\,\mathrm{cm}^{-1}$ respectively. Therefore one may only expect an insignificant increase of the slope of transition curve as a result of magnetic scalar coupling.

Magnetic scalar coupling not only contributes towards non-ideality parameters but also affects the effective magnetic moment of HS species, hence the results of calculations of the composition of spin crossover equilibrium mixture from magnetochemical data. This means that if such an interaction is suspected the estimation of non-ideality parameters should be done employing non-magnetic data (*Mössbauer* or optical spectroscopic data) or magnetochemical data normalised to *Mössbauer* measurements in several points. Purely magnetochemical data (most abundant in literature) on such systems can be parameterised in coordinates $\chi T-T$ the value of scalar coupling constant being one of the parameters of regression equation. However, these problems are beyond the scope of the present paper. We also do not consider magnetically ordered states arising from strong exchange interactions.

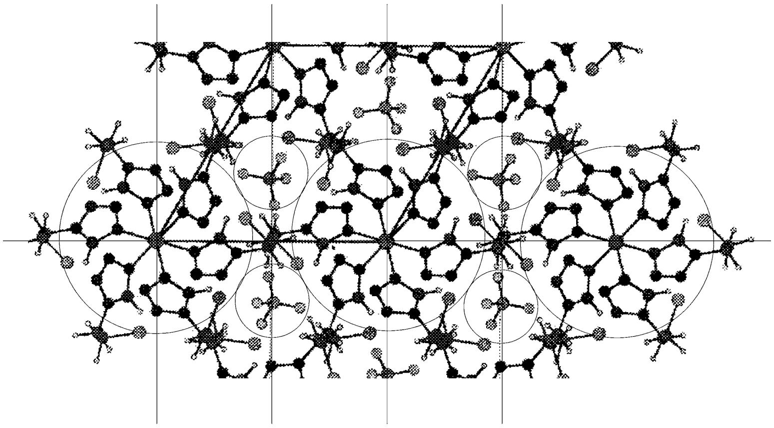

Fig. 6. Crystal structure of [Fe(*tee*Cl)$_6$](BF$_4$)$_2$ [21] with highlighted contacts between cations [Fe(*tee*Cl)$_6$]$^{2+}$ (larger circles) and anions (smaller circles)

Ionic Systems

As a prototype compound for ionic systems we have chosen [Fe(*tee*Cl)$_6$](BF$_4$)$_2$ (*tee*Cl = 1-(2-chloroethyl)tetrazole). According to Refs. [20, 21] this compound forms neutral sheets (Fig. 6); an LS → HS transition is accompanied by the change of Fe–Fe distance from 10.196 Å (LS) to 10.422 Å (HS), $\Delta r = 0.226$ Å; the average bond length Fe–N is increased by 0.352 Å ($r_{\text{Fe–N}} = 2.209$ Å (HS) and 1.856 Å (LS)). The distances Fe–BF$_4^-$ in HS and LS states are also known: 5.94 Å (HS) and 5.838 Å (LS). According to quantum chemical calculations (ZINDO/1 HyperChem 5$^{\text{TM}}$), the cation [FeL_6]$^{2+}$ in the prototype compound has a negligibly small electric dipole moment. Therefore the electric dipole–dipole interaction between [FeL_6]$^{2+}$ species is not included into the basic model.

In order to take into account the effects of the long-range coulombic forces the model system of ionic complexes includes a chain of 5 [FeL_6]$^{2+}$ units separated by 4 pairs of mono-charged anions. Two outer cations are supposed to be always in the LS state (Fig. 7). The model employed involves 78 binary point-charge interactions

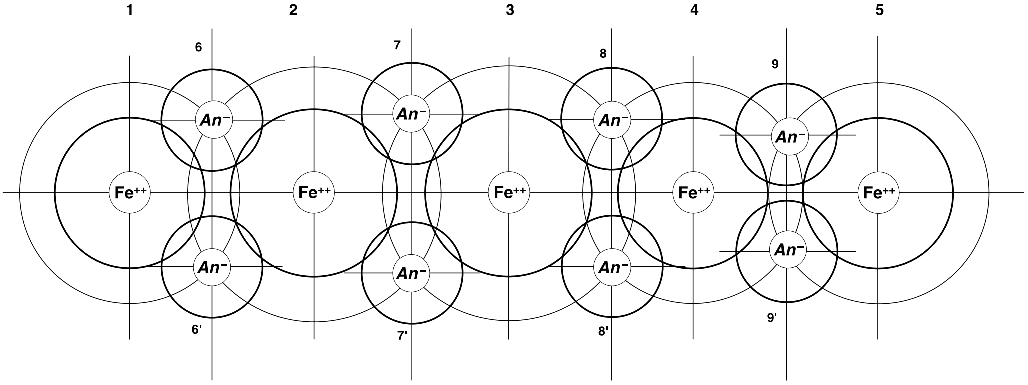

Fig. 7. Model system of ionic complexes involving 5 [FeL_6]$^{2+}$ cations separated by 4 pairs of (BF$_4$)$^-$ anions (spin state A**AAB**A)

between 13 ions. The *Lennard-Jones* contacts between $[FeL_6]^{2+}$ and BF_4^- (yielding the major contribution), as well as the contacts between $[Fe(teeX)_6]^{2+}$ species and BF_4^-–BF_4^- contacts have been taken into consideration (Fig. 7).

Basic distances in this model are: $r_{Fe(A)-Fe(A)}$, $r_{Fe(A)-An}$, $r_{Fe(B)-Fe(B)}$ and $r_{Fe(B)-An}$; the distances between Fe(II) ions in hetero-molecular pairs ($r_{Fe(A)-Fe(B)}$) were calculated according to the additivity rule. The distances r_{An-An} in Fe(A)–$(An)_2$–Fe(A), Fe(B)–$(An)_2$–Fe(B), and Fe(A)–$(An)_2$–Fe(B), were computed from geometry considerations. The depth of the *Lennard-Jones* potential has been assumed to be $\varepsilon_{Fe(A)-Fe(A)} = 12\,\mathrm{kJ/mol}$ and $\varepsilon_{Fe(B)-Fe(B)} = 14\,\mathrm{kJ/mol}$. The depth of the potential well in BF_4^-–BF_4^- pair was estimated from the evaporation heat of isoelectronic CF_4, ($\lambda = 13.0\,\mathrm{kJ/mol}$) yielding $\varepsilon_{An-An} = 2\lambda/c \approx 4\,\mathrm{kJ/mol}$. Employing *Berthelot*'s rule $\varepsilon_{Fe(A)-An} \approx 8\,\mathrm{kJ/mol}$ and $\varepsilon_{Fe(B)-An} \approx 9\,\mathrm{kJ/mol}$ have been obtained. The depth of the potential well in hetero-molecular pairs Fe(A)–Fe(B) has been calculated according to the modified *Berthelot*'s rule (Eq. (6)). The energy was minimised as described in the Methods.

Ionic systems have been explored at zero compression alone ($r/r_{opt} = 1$); transition curves were simulated for a system with $\Delta E^0 = 10\,\mathrm{kJ\,mol^{-1}}$ and $T_{1/2} = 155\,\mathrm{K}$ ($\Delta S^0 = 64.5\,\mathrm{J\,mol^{-1}\,K^{-1}}$), and non-ideality parameters computed for actual potentials. Effects of magnetic scalar coupling in ionic systems are similar to those in systems of neutral complexes and will not be considered.

Lennard-Jones and Coulombic Point-Charge Potentials

Equilibrium distances obtained for this system are shown in Table 4. Homogeneous distances vary from configuration to configuration, however these variations do not exceed 10^{-4} Å. The pattern of energy levels ($D_A > 0$, $D_B < 0$) implies that LS neighbours lower down the energy of a central molecule whereas HS neighbours increase it.

This model yields a very small negative excess energy $\Delta E^E = -0.353\,\mathrm{kJ/mol}$ and negligible negative asymmetries of splittings $|\Delta^{A(B)}| < 0.001\,\mathrm{kJ/mol}$. Such a system not merely follows the model of binary interactions: a pseudo-ideal law of mass action would describe it with a good accuracy. Experimental examples of such behaviour are known (*e.g.*, $[Fe(2\text{-}pic)_3]Cl_2MeOH$, [22]).

Larger excess energies can be obtained when ε_{AB} deviates from *Berthelot*'s rule. Deviations of the order $\alpha_\varepsilon = \pm 0.03$ bring about considerable excess energies causing critical phenomena: abrupt spin crossover at $\alpha_\varepsilon < 0$ and two-step spin

Table 4. Equilibrium distances computed for the basic model system of ionic complexes

	AAA	BBB	AAB	BAB	BBA	ABA
$r_{Fe(A)-An}$/ Å	5.838	–	5.838	5.838	5.838	5.838
			$-3.9\ 10^{-6}$	$+7.2\ 10^{-6}$	$+1.6\ 10^{-5}$	$+2.7\ 10^{-5}$
$r_{Fe(B)-An}$/ Å	–	5.940	5.940	5.940	5.940	5.940
			$-3.9\ 10^{-6}$	$+7.3\ 10^{-6}$	$+1.6\ 10^{-5}$	$+2.7\ 10^{-5}$
$r_{Fe(A)-Fe(A)}$/ Å	10.196	–	10.196	10.196	10.196	10.196
			$-6.8\ 10^{-6}$	$+1.3\ 10^{-5}$	$+2.7\ 10^{-5}$	$+4.7\ 10^{-5}$
$r_{Fe(B)-Fe(B)}$/ Å	–	10.422	10.422	10.422	10.422	10.422
			$-6.9\ 10^{-6}$	$-1.3\ 10^{-5}$	$+2.8\ 10^{-5}$	$+4.8\ 10^{-5}$

crossover at $\alpha_\varepsilon > 0$). These deviations do not affect the asymmetries Δ^{A} and Δ^{B} that remain negligibly small.

Electric Dipole–Dipole Interaction of Ligands

If the periphery parts of ligands contain polar groups then the ligands belonging to neighbouring complexes can interact *via* dipole–dipole mechanism as it has been shown for the prototype compound [Fe(*tee*Cl)$_6$](BF$_4$)$_2$ [3]. The contribution of this interaction towards non-ideality parameters can be estimated using a simplified model shown in Fig. 8: an LS→HS transition changes the distance between dipoles thus producing variations of the energy of dipole–dipole interaction. This interaction is characterised by two parameters: electric dipole moment (μ) and the effective length of the ligand (d_0, Fig. 8).

Ligand–ligand attraction brings about positive excess energy whereas the repulsion of ligands negatively contributes towards ΔE^{E}. Detectable changes can be expected when two dipoles $\mu = 2\,\mathrm{D}$ are at the distance of *ca.* 4 Å. Smaller

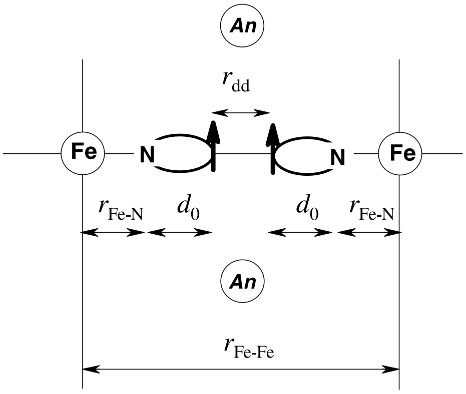

Fig. 8. A simplified model for the calculation of the contribution of dipole–dipole interaction of ligand towards non-ideality parameters

Table 5. Non-ideality parameters ΔE^{E} and $\Delta^{\mathrm{A(B)}}$ in systems with attractive and repulsive dipole–dipole interactions of ligands

	$\frac{\mu}{\mathrm{D}}$	$\frac{d_0}{\text{Å}}$	$\frac{\Delta E^{\mathrm{E}}}{\mathrm{kJ/mol}}$	$\frac{\Delta^{\mathrm{A}}}{\mathrm{kJ/mol}}$	$\frac{\Delta^{\mathrm{B}}}{\mathrm{kJ/mol}}$	$\frac{\mu}{\mathrm{D}}$	$\frac{d_0}{\text{Å}}$	$\frac{\Delta E^{\mathrm{E}}}{\mathrm{kJ/mol}}$	$\frac{\Delta^{\mathrm{A}}}{\mathrm{kJ/mol}}$	$\frac{\Delta^{\mathrm{B}}}{\mathrm{kJ/mol}}$
attr	2.0	2.2	+50.02	−0.955*	0.869*					
	2.0	1.6	+3.46	−0.005	0.004	4.0	1.5	10.87	−0.031	0.021
	2.0	1	+0.37	0.000	0.000	2.0	1.5	2.42	−0.003	0.002
	0.0		−0.35	0.000	0.000	0.0		−0.35	0.000	0.000
rep	2.0	1	−1.07	0.000	0.000	2.0	1.5	−3.10	−0.001	0.001
	2.0	1.6	−4.11	−0.002	0.002	4.0	1.5	−11.15	−0.027	0.018
	2.0	2.2	−41.91	−1.108*	0.877*					

* Nonzero asymmetries $\Delta^{\mathrm{A(B)}}$ at $d_0 > 2$ Å are most probably the result of an approximate character of the minimisation of energy employing numerical differentiation

distances and/or larger moments make this contribution quite considerable. The dependence of thus calculated excess energy on d_0 (Table 5) can be approximated by Eq. (14) in which $\Delta E^{0,\mathrm{E}} = -0.353\,\mathrm{kJ/mol}$ is the excess energy of the basic system in the absence of ligand–ligand interaction, a–$d_0 = r_{\mathrm{dd}}$ is the distance between dipoles, and b is a normalising coefficient.

$$\Delta E^{\mathrm{E}} = \frac{b}{(a - d_0)^3} + \Delta E^{0,\mathrm{E}} \tag{14}$$

The dependence of the excess energy on the magnitude of the dipole moment can be approximated by Eq. (15).

$$\Delta E^{\mathrm{E}} = \Delta E^{0,\mathrm{E}} + c\mu^2 \tag{15}$$

Such a linear relationship has been observed between estimates of the excess energy and the square of the electric dipole moment of the side chain of tetrazole ligand in a series of homologues of the prototype compounds $[\mathrm{Fe}(teeX)_6](\mathrm{BF}_4)_2$ (X = F, Cl, Br, and I [3]). Furthermore, the variations of ΔE^{E} in this series quantitatively corresponded to the electrostatic contribution computed using experimental interatomic distances [3].

At a first glance the dipole–dipole interaction of ligands should not bring about anything unusual into the behaviour of a spin crossover system. The increasing (due to variations of either μ or d_0) strength of interaction in pairs with repulsive arrangements of dipoles may bring about a conversion from the gradual to the two-step spin crossover (Fig. 9, curves 4 and 5). Attractive interaction, according to this model, must bring about an abrupt spin crossover (Fig. 9, curves 1 and 2).

One must however consider a specific feature of ionic systems in which (according to experimental data) Fe^{2+}–Fe^{2+} distances are only slightly affected by spin transitions compared to Fe^{2+}–N bond lengths. Under these conditions a ligand–ligand attraction causes a correlation of Fe^{2+}–N bond-lengths in neighbouring complexes: a contraction of this bond in one complex causes the corresponding bond elongation in its neighbours. Such a correlation stabilises HS–LS pairs, *i.e.* brings about negative excess energy leading to the two-step spin crossover. This mechanism ('ligand relocation mechanism' [4]) explains the dominating two-step character of spin crossover in polynuclear compounds – an extreme case of ligand–ligand

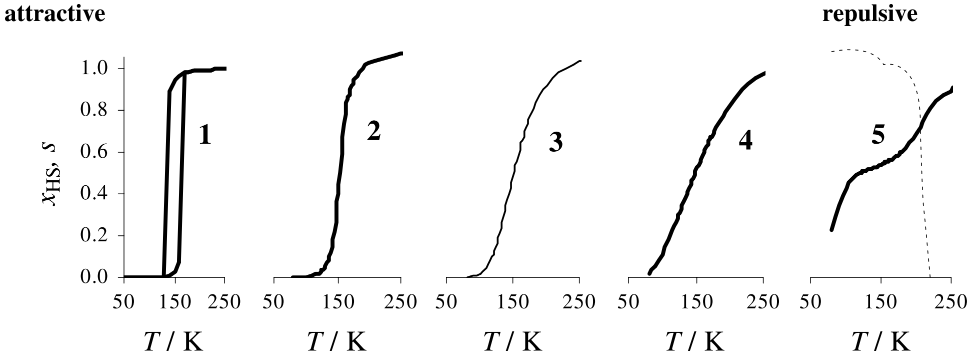

Fig. 9. Effects of the variation of electric dipole moment (μ) at constant $d_0 = 1.8\,\text{Å}$; attractive interaction: $\mu = 1.5\,\mathrm{D}$ (1), 1.0 D (2), 0.0 D (3); repulsive interaction: $\mu = 1.0\,\mathrm{D}$ (4), 1.5 D (5); the dashed line represents the degree of order

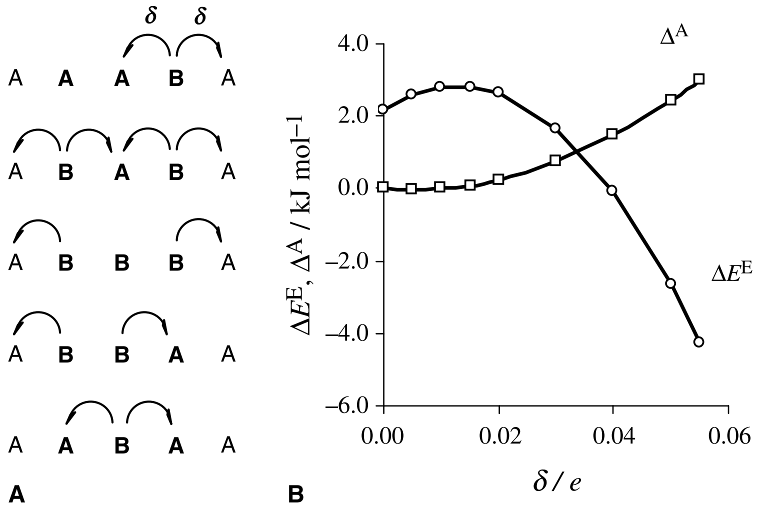

Fig. 10. Partial electron transfer due to the overlap of e_g orbitals in model ionic systems (**A**) and dependencies of non-ideality parameters on the transferred charge (**B**); model system includes attractive dipole–dipole interaction of ligands ($\mu = 1.9\,\mathrm{D}$, $d_0 = 1.5\,\text{Å}$)

attraction. The energy of stabilisation is apparently proportional to r^{-6} and can be accounted for by positive deviations from *Berthelot*'s rule.

HOMO–LUMO Overlap in HS–LS Pairs

In ionic systems this interaction can be described as a partial electron transfer from HS complexes to neighbouring LS complexes. In the configuration A**AAB**A this transfer increases the positive charge on the B (HS) cation by 2δ and decreases positive charge on two neighbouring A (LS) cations by δ. Similar schemes can be drawn for other configurations (Fig. 10A). Charge transfer according to this model affects the excess energy and unexpectedly brings about positive asymmetries of splittings ($\Delta^A \cong \Delta^B$). The dependence of $\Delta^{A(B)}$ on transferred charge is quadratic (Fig. 10B; Eq. (16)).

$$\Delta^{A(B)} = \Delta^B = 1201\delta^2 - 11.47\delta - 0.003 \tag{16}$$

The coefficients in Eq. (16) are practically independent of the strength of other interactions such as ligand–ligand attraction/repulsion. The excess energy is a quadratic function of δ passing through a maximum (Fig. 10B; Eq. (17)) in which $\Delta E^{0,E}$ is controlled by background interactions; other coefficients are constant and for the considered system $a = 104.1\,\mathrm{kJ\,mol^{-1}\,\bar{e}^{-1}}$ and $b = 4008\,\mathrm{kJ\,mol^{-1}\,\bar{e}^{-2}}$.

$$\Delta E^E = \Delta E^{0,E} + a\delta - b\delta^2 \tag{17}$$

The nature of critical phenomena expected from such charge transfer depends on the interplay of ΔE^E and asymmetries of splittings $\Delta^{A(B)}$. When the background excess energy is positive (*e.g.* due to ligand–ligand attraction) increasing charge transfer may cause quite non-trivial transformations of the shape of transition curve (Fig. 11).

At small δ, both ΔE^E and $\Delta^{A(B)}$ are small and spin crossover is gradual (Fig. 11, curve 1). Increasing δ increases positive excess energy that reaches its maximum

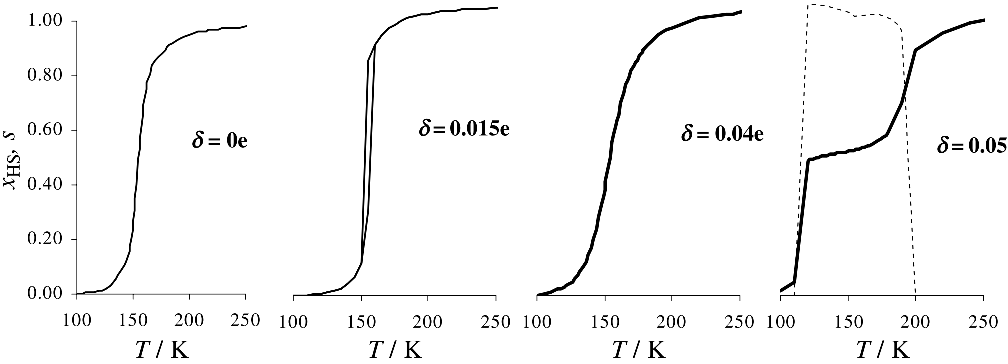

Fig. 11. Effects of HS→LS charge transfer due to the overlap of e_g orbitals of neighbouring complexes in a model ionic system with ligand–ligand attraction ($\mu = 1.9\,\mathrm{D}$, $d_0 = 1.5\,\mathrm{\AA}$); dashed line represents the degree of order

at $\delta \approx 0.015\,\bar{e}$. Assisted by small positive $\Delta^{A(B)}$ at this point it may cause an abrupt spin crossover with hysteresis (Fig. 11, curve 3). Further increasing δ causes ΔE^E to decrease and at a certain point it becomes negative. In combination with increasing positive asymmetries it may bring about ordering and the two-step spin crossover (Fig. 11, curve 4).

Regression of Experimental Data

Minimisation of energy in chains of three molecules of *neutral spin crossover complexes* can easily be inserted into the regression program allowing one to parameterise transition curves in terms of molecular potentials. There are several such potentials involved (see above) all of them defining one non-ideality parameter – the excess energy. The model is therefore overparameterised unless all potentials but one are fixed according to the available experimental and theoretical evidence. Let us consider possible scenarios on an example of parameterisation of spin crossover in Fe(*bipy*)[$H_2B(pz)_2$]$_2$ ($H_2B(pz)_2$ = dihydrobis(1-pyrazolyl)borate)

Table 6. Parameters of binary molecular interactions approximating the experimental transition curve of spin crossover in Fe(*bipy*)[$H_2B(pz)_2$]$_2$ [23]; standard energy of spin crossover has been fixed at $\Delta E^0 = 8.0\,\mathrm{kJ/mol}$ according to calorimetric data [23]

Potential	σ_{yx}	$\frac{T_{1/2}}{\mathrm{K}}$	$\frac{\varepsilon_{AA}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\varepsilon_{BB}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\mu_A}{\mathrm{D}}$	$\frac{\mu_B}{\mathrm{D}}$	α_μ
Lennard-Jones	0.022	162.1 ± 0.4	11.684 ± 0.114	15.931 ± 0.093	0	0	
Lennard-Jones + dipole–dipole	0.022	162.1 ± 0.4	12.000	16.056 ± 0.045	12.424	11.865	
Lennard-Jones + dipole–dipole	0.022	162.1 ± 0.4	16.050 ± 0.044	12.000	12.424	11.865	
Dipole–dipole ($\varepsilon_{AA} = \varepsilon_{BB}$)	0.022	162.1 ± 0.4	12.000	12.000	14.374	11.865	
Dipole–dipole ($\varepsilon_{AA} = \varepsilon_{BB}$)	0.022	162.1 ± 0.3	12.000	12.000	12.424	11.865	−0.023

[23]. For this compound lattice constants in HS and LS states are known [24] and may serve as rough estimates of intermolecular distances: $r_{AA} = 13.918\,\text{Å}$ and $r_{BB} = 14.135\,\text{Å}$. Semi-empirical calculations (HyperChem5^{TM}, ZINDO/1) on isolated molecules yield $\mu_A = 12.424\,\text{D}$ and $\mu_B = 11.865\,\text{D}$.

For purely *Lennard-Jones* binary interactions ($\mu_A = \mu_B = 0$, first row in Table 6) one can obtain a satisfactory description with $\varepsilon_{BB}-\varepsilon_{AA} = 4.25\,\text{kJ/mol}$. The introduction of electric dipole–dipole interactions with fixed electric dipole moments $\mu_A = 12.424\,\text{D}$ and $\mu_B = 11.865\,\text{D}$ slightly decreases this difference $\varepsilon_{BB}-\varepsilon_{AA} = 4.05\,\text{kJ/mol}$ (second row in Table 6). The excess energy is controlled by the *magnitude* of the difference of the depths of potential wells in HS–HS and LS–LS pairs, therefore the same description can be obtained at $\varepsilon_{AA} > \varepsilon_{BB}$ (third row in Table 6).

One can exclude the contribution of the *Lennard-Jones* potential towards the excess energy by setting $\varepsilon_{AA} = \varepsilon_{BB}$. Transition curves can then be parameterised by optimising electric dipole moments (*e.g.* having some reasons to doubt the results of quantum chemical calculations). The required difference of electric dipole moments proves to be *ca.* 2.5 D (fourth row in Table 6).

If there is some evidence that an HOMO–LUMO overlap occurs then one can fix the electric dipole moments and adjust the coefficient α_μ; in the actual case of spin crossover in $Fe(bipy)[H_2B(pz)_2]_2$ one has to suppose that HOMO–LUMO overlap brings about the depression of the energy of dipole interactions in HS–LS pairs by 2.3% (last row in Table 6).

We see that several reasonable scenarios of optimisation can be suggested for the parameterisation of transition curves in terms of molecular potentials. The actual choice depends on the available experimental and theoretical data on dielectric and other properties of investigated spin crossover compounds.

The procedure of minimization of energy in model systems of *ionic spin crossover compounds* is too complicated to be inserted into a regression program. Transition curves can be parameterised in terms of formal non-ideality parameters (ΔE^E, Δ^A, Δ^B). The latter can be further discussed from the point of view of model potentials as it has been done [3] for the homologues of the prototype compound mentioned above.

Another approach is to insert into the regression program simple relationships derived above. For example the effect of HOMO–LUMO overlap can be represented as the dependence of ΔE^E, Δ^A, and Δ^B on the transferred charge δ (Eqs. (16) and (17)). Using these equations one can parameterise transition curves in terms of ΔE^0, $T_{1/2}$, background excess energy $\Delta E^{0,E}$, and transferred charge δ. Let us apply this method to the description of the two-step spin crossover in $[Fe(2-pic)_3]Cl_2EtOH$ (data from Ref. [25]).

Under the condition $\Delta^A = \Delta^B$ the regression yields a satisfactory (although not completely adequate description (Fig. 12A) with parameters indicating the transfer of 0.045 electron from HS to LS species (first row in Table 7). As might be expected this description is similar to that obtained in terms of formal non-ideality ΔE^E and $\Delta^A = \Delta^B$ (see Ref. [6]). However the charge transfer mechanism implies a strong correlation between ΔE^E and $\Delta^{A(B)}$. Therefore the background excess energy in the latter case is a large positive value (+2.9 kJ/mol, Table 7), whereas when ΔE^E and $\Delta^{A(B)}$ were considered as independent parameters it was a small

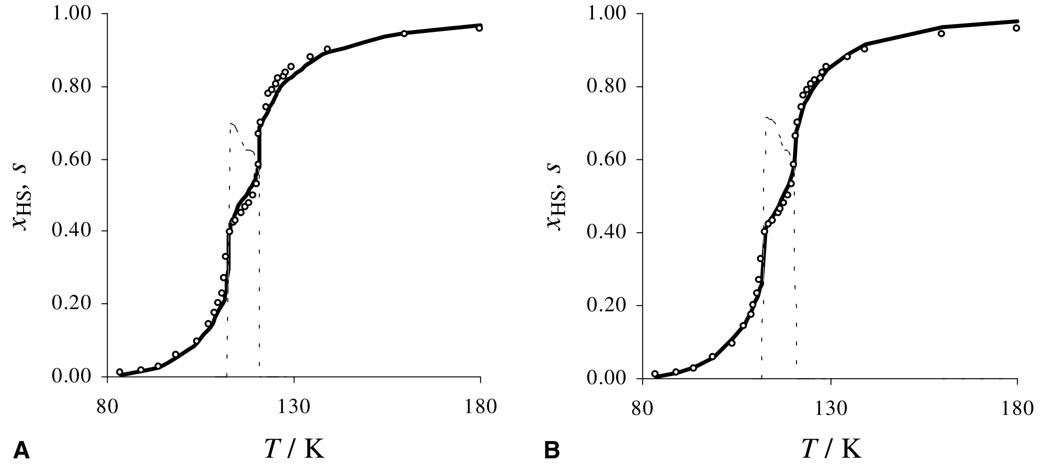

Fig. 12. Spin crossover in $[Fe(2\text{-}pic)_3]Cl_2EtOH$ [25] approximated by the model of HS→LS charge transfer under the condition $\Delta^A = \Delta^B$ (**A**) and with adjustable Δ^A/Δ^B (**B**); estimates of parameters are given in Table 7

Table 7. Estimates of parameters of the model of HS→LS charge transfer approximating spin crossover in $[Fe(2\text{-}pic)_3]Cl_2EtOH$ (data from Ref. [25]); temperature was used as the independent variable

σ_{yx}	$\frac{\Delta E^0}{\text{kJ mol}^{-1}}$	$\frac{T_{1/2}}{\text{K}}$	$\frac{\Delta E^{0,E}}{\text{kJ mol}^{-1}}$	$\frac{\delta}{\text{e}}$	Δ^A/Δ^B
0.029	6.773 ± 0.758	117.1 ± 0.2	2.931 ± 0.018	0.0446 ± 0.0001	1
0.021	7.996 ± 0.725	116.4 ± 0.2	2.953 ± 0.020	0.0450 ± 0.0001	0.882 ± 0.007

negative (−0.54 kJ/mol, see Ref. [6]). Therefore the interpretation of these results might be completely different; additional data are required in order to make a correct decision, *e.g.* some evidence of the HS–LS electron transfer.

As has been mentioned in Ref. [6] the condition $\Delta^A = \Delta^B$ represents a special case of pseudo-binary interactions in which parameters arising from ternary interactions affect the shape of transition curve within the range of the existence of ordered structures alone. More general case implies the unequal asymmetries of splittings $\Delta^A \neq \Delta^B$; ternary interactions then affect the shape of transition curve in the whole range of compositions. In the model of charge transfer this inequality can be introduced by additionally adjusting the ratio between Δ^A and Δ^B simulating thus the effect of ternary interactions. The regression according to this method yields a better description (second row in Table 7, Fig. 12B) however still not reaching the level of the model of completely independent ΔE^E, Δ^A, and Δ^B ($\sigma_{yx} = 0.019$, Ref. [6]). This is due to the strong correlation between the adjustable parameters defined by Eqs. (16) and (17). Therefore for practical purposes of obtaining the best fit it is more convenient to parameterise a transition curve in terms of formal parameters with subsequent analysis of their estimates according to some model of molecular interactions.

In the present paper we have defined the parameters of formalism developed earlier [1–6] in terms of molecular potentials. The combination of the *Lennard*-

Jones and electric dipole–dipole potentials, chosen as the basic model for neutral complexes, yields positive excess energies controlled by the difference of the depths of the *Lennard-Jones* potentials in HS–HS and LS–LS pairs as well as by the difference of electric dipole moments of HS and LS states. At $\Delta\varepsilon = 2\,\mathrm{kJ/mol}$ and $\Delta\mu = 0.4\,\mathrm{D}$ (prototype compound) one obtains a modest positive excess energy of *ca.* 1 kJ/mol that could cause an abrupt spin crossover in systems with $T_{1/2} < 70\,\mathrm{K}$. For systems with transition temperature above 150 K the abrupt spin crossover can be expected at $\Delta\varepsilon > 4\,\mathrm{kJ/mol}$ or at $\Delta\mu > 1.4\,\mathrm{D}$. These values are within a reasonable range, however choosing a proper scenario of regression requires additional information on dipolar and other properties of spin crossover compounds. The HOMO – LUMO overlap in HS–LS pairs can yield both positive and negative ΔE^{E} depending on the relative magnitude of two contributions: (i) stabilisation of HS–LS pairs (negative ΔE^{E}) and (ii) depression of the energy of dipole–dipole interactions in HS–LS pairs (positive ΔE^{E}). Magnetic scalar coupling yields a positive temperature-dependent ΔE^{E}, *i.e.* it contributes towards both ΔE^{E} and ΔS^{E}. The overall effect of this interaction is not large: one can expect a small increase of the slope of transition curve due to magnetic scalar coupling, both ferro- and antiferromagnetic. An abrupt spin crossover (in systems with $T_{1/2} = 150\,\mathrm{K}$) can only be expected at unrealistically large coupling constants $|J| > 40\,\mathrm{cm}^{-1}$.

The combination of *Lennard-Jones* and coulombic point-charge potentials (basic model for ionic complexes) yields very small ΔE^{E}; such systems can be approximated by linear *van't Hoff* plots with a good accuracy. Detectable excess energies in such systems may arise from interactions of the periphery parts of ligands belonging to neighbouring complexes. Ligand–ligand attraction, on the one hand, yields a positive ΔE^{E} but, on the other hand, it can stabilise HS–LS pairs *via* the "ligand-relocation mechanism" [3] equivalent to a negative excess energy. The HOMO–LUMO overlap in ionic systems considered as a partial electron transfer from HS complexes to neighbouring LS complexes produces correlated changes in both ΔE^{E} and asymmetries of splittings ($\Delta^{\mathrm{A}} \approx \Delta^{\mathrm{B}}$). In some cases this might bring about a non-trivial variation of the shape of transition curve: increasing charge transfer yields at first an abrupt spin crossover and then a two-step transition.

The description of experimental data given by the model of binary potentials is satisfactory but not exactly adequate. It can be improved by introducing ternary interactions, for example, represented by the *Axilrod-Teller* potential [26]. This subject is however beyond the scope of the present paper.

Methods

The minimisation of energy has been performed in Microsoft Excel™ worksheets using the Excel Solver tool. For systems of neutral complexes an analytical expression for the conditions of the minimum of energy has been derived. This allowed one to directly optimise parameters a_{AA} and a_{BB} of the *Lennard-Jones* potential for the minima of energy in AAA and BBB configurations at experimental distances (r_{AA} and r_{BB} known for the prototype compound). The parameter a_{AB} for hetero-molecular pairs has been calculated according to the additivity rule: $a_{\mathrm{AB}} = 1/2(a_{\mathrm{AA}} + a_{\mathrm{BB}})$. Then the *distance* in hetero-molecular pairs has been optimised for the minimum of energy in the BAB configuration. Thus obtained values have been used in calculations of energies in all other configurations yielding E_{AAA}, E_{AAB}, E_{BAB}, *etc.* and further D_{A}, D_{B}, Δ^{A}, and Δ^{B}.

A similar procedure has been employed in the minimisation of energy in model system of ionic complexes. The minimum of energy was found employing numerical differentiation in finite differences. At first the parameters $a_{\mathrm{Fe(A)}-An}$ and $a_{\mathrm{Fe(B)}-An}$ were optimised to the minima of energies in configurations AAA and BBB respectively at the fixed distances provided by XRD data on the prototype compound. Other parameters a_{ij} were computed according to the additivity rules.

At the second stage the distances $r_{\mathrm{Fe(A)-Fe(A)}}$, $r_{\mathrm{Fe(A)}-An}$, $r_{\mathrm{Fe(B)-Fe(B)}}$, and $r_{\mathrm{Fe(B)}-An}$ were optimised to the minimum of energy in configurations BAB, ABA, AAB, and BBA. There are four basic distances to be optimised each configuration that makes the model overparameterised. As a regularisation we have assumed that the ratios $r_{\mathrm{Fe(A)}-An}/r_{\mathrm{Fe(A)-Fe(A)}}$, $r_{\mathrm{Fe(B)-Fe(B)}}/r_{\mathrm{Fe(A)-Fe(A)}}$, $r_{\mathrm{Fe(B)}-An}/r_{\mathrm{Fe(A)-Fe(A)}}$, $r_{\mathrm{Fe(A)-N}}/r_{\mathrm{Fe(A)-Fe(A)}}$, and $r_{\mathrm{Fe(B)-N}}/r_{\mathrm{Fe(A)-Fe(A)}}$, are identical in all configurations. These ratios have been calculated from XRD data allowing us to optimise a single distance $r_{\mathrm{Fe(A)-Fe(A)}}$ each configuration.

Simulation of transition curves and parameterisation of experimental data have been achieved according to the described above equations employing a multipurpose non-linear regression program OPTIMI supplied with the monograph [27]. Methods of solving equations of the law of mass action with temperature as the independent variable have been described in Ref. [3].

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