

THE EFFECTIVE CRYSTAL FIELD METHODOLOGY AS USED TO INCORPORATE TRANSITION METALS INTO MOLECULAR MECHANICS

ANDREI L. TCHOUGRÉEFF

*Karpov Institute of Physical Chemistry,
Vorontsovo pole 10, Moscow 103064, Russia*

and

*Center for Computational Chemistry,
Keldysh Institute for Applied Mathematics,
Miusskaya pl. 4, Moscow 125047, Russia*

1. Introduction

Transition metal complexes (TMC) of biological significance are too large for a complete quantum chemical treatment. Thus incorporation of transition metal atoms (TMA) into the general molecular mechanics (MM) formalism [1] would be highly desirable [2, 3]. However, the problem of molecular modeling TMA must not be limited to obtaining appropriate MM potentials. The ability of the MM approach (when extended to TMA) to describe potential energy surfaces for different low energy electronic states of TMCs is of equal importance. Such states are accessible, for example, in experiments on spin transitions [4]. Multiple spin states are also involved in oxygen binding by the heme containing proteins [5]. The most important feature of such a combined method is the necessity to implement different levels of the description of electronic structure in the different parts of the system. These parts are (i) the isolated group of strongly correlated d -electrons on the metal atom and (ii) electrons in the closed shell of the ligands. The physical reason for a distinction between electrons in the ligands and those in the d -shell is that in an organic molecule one can never distinguish the multiplet terms of the component atoms. In contrast, the d -shell of a transition metal ion in a complex largely retains the system of electronic terms that it had in the free state. Due to specific properties of electrons in the d -shell, different levels of electron correlation must be achieved to describe electrons in the d -shell and those in the ligand orbitals

properly. This requirement has been successfully implemented in the effective crystal field (ECF) method [6]. In Sect. 2 of the present paper we discuss the underlying principles and give an account of the ECF method. Sect. 3 is a brief review of the current implementation of the ECF approach and of some recent results. In Sect. 4 new developments and extensions of the ECF methodology, including its combination with MM are reviewed.

2. Theoretical Background

Both semi-empirical and *ab-initio* methods based upon the self consistent field (SCF) approximation [7] have been used to calculate the ground and low energy excited states of TMCs [8]. Although *ab-initio* calculations involving large CI expansions or a special set of configurations in the MCSCF wave function can lead to a reasonable agreement of the calculated and observed characteristics of TMC, these calculations are restricted to relatively small systems and can hardly be used for screening large portions of the configurational space which is necessary for molecular dynamics modeling of metal containing enzymes.

Despite the reasonable agreement between the observed properties of TMCs and those calculated by SCF based semi-empirical methods some fundamental problems remain unsolved. These include (for more detailed discussion see [6, 9] and references therein):

- (i) the Koopmans Theorem is not valid for the states with large contributions from the atomic *d*-states;
- (ii) the *Aufbau*-principle frequently breaks down for orbitals with significant contributions from atomic *d*-states;
- (iii) the iteration procedures implied by the SCF scheme oscillate or converge very slowly.

The Koopmans Theorem relates the SCF orbital energies to ionization potentials. For organic molecules the difference between the minus orbital energy (*i.e.* the ionization potential according to Koopmans Theorem) and the experimental ionization potential is usually small. For TMCs the disagreement with experiment can amount to 10 ÷ 20 eV for levels with significant contribution from *d*-orbitals (see [9] and references therein). This suggests that the behavior of *d*-electrons in TMCs is not consistent with the SCF picture, where independent electrons move in the mean field induced by the nuclei and other electrons. In contrast, *d*-electrons are strongly correlated.

Another rarely recognized problem is the break down of the *Aufbau*-principle (*i.e.* the rule that the MO's are filled with pairs of electrons starting from the lowest energy orbital). This occurs frequently in the semi-empirical calculations of TMCs, where empty or singly occupied orbitals

are calculated to have lower orbital energies than some doubly occupied orbitals. This generally happens to orbitals derived from d -atomic orbitals. It can be checked [6] that the Slater determinants which break the *Aufbau*-principle do not represent minima of the SCF energy functionals but saddle points. Namely this causes the well known but rarely reported problems with the convergence of the SCF iterations. More distressing than the convergence problems is the fact that the success of SCF based semi-empirical methods is achieved by the loss of the confidence that the obtained Slater determinants represent the minima of the SCF energy functional. The parameterization of a semi-empirical Fock operator for TMAs, that uses a trial wave function which is not a stable solution of the SCF problem is a doubtful procedure.

It follows that there are some fundamental problems in the quantum chemical description of the electronic structure of TMCs. They are due to the important role of electron correlations in the d -shell. The description of electrons in the ligands with SCF methods seems to cause less problems.

The state of the quantum chemical description of TMCs described above is in sharp contrast to the situation with understanding of their electronic structure. The experimental data on d - d excitation spectra can be successfully interpreted with models equivalent to the crystal field theory (CFT) [10, 11]. This is because the specific properties of TMCs are controlled by the d -electrons. Their low energy excitations are responsible for the characteristic absorption bands in the optical spectra and for the magnetic properties. The ground state spin depends on the balance between Coulomb repulsion of d -electrons and their interaction with the ligands which induce an external field. These features apparently correspond to the situation described by the naïve CFT where all interesting events happen in the d -shell of TMA's whose ligand environment remains inert [10]. Thus the qualitative physical picture provided by the CFT is correct to a large extent. This is due to the correct form of the electronic wave function which is used implicitly. The wave function of a complex in the CFT is a product of the multiplet (full CI) state for a fixed number of d -electrons and of an unspecified closed shell state of the remaining electrons in the ligands. The ligand electrons are not considered explicitly, and that is why crystal fields can not be satisfactorily calculated within the CFT's own framework. This has been achieved in the ECF method [6].

The formal derivation of the Effective Crystal Field method proceeds as described in the literature [6]. The whole set of the valence atomic orbitals (AO) of a TMC (including the $4s$ -, $4p$ -, and $3d$ -AO's of the metal center and the valence AO's of all ligand atoms) is separated into two parts. The first contains only $3d$ -orbitals of the TMA (d -system). The second part contains $4s$ - and $4p$ -AO's of the TMA and the valence orbitals of the ligand atoms

(ligand system or l -system). The total Hamiltonian for a TMC can be written as the sum:

$$H = H_d + H_l + H_c + H_r \quad (1)$$

where H_d is the Hamiltonian for the d -electrons in the field of atomic cores of the TMC, H_l is the Hamiltonian for the electrons of the l -system, H_c and H_r are operators for the Coulomb and resonance interactions between the two systems.

The exact wave function $\Phi(N)$ for any N -electron state of a TMC can be presented in the form [12]:

$$\Phi(N) = \sum_{nkm} C_{km}(n; N-n) \Phi_d^k(n) \wedge \Phi_l^m(N-n) \quad (2)$$

where $\Phi_d^k(n)$ are the n -electron wave functions for the metal d -orbitals; $\Phi_l^m(N-n)$ are the $(N-n)$ -electron wave functions for the l -orbitals; $C_{km}(n; N-n)$ are variation parameters. For most of the Werner-type TMCs $\Phi_d^k(n)$ functions with a specific value n give a major contribution to eq. (2). This particular value of n depends on the oxidation state of the transition metal atom in the TMC. The terms in eq. (2) with other values of n provide some smaller corrections. The wave function Φ_n for the n 'th electronic state of a TMC is then assumed to take the form:

$$\Phi_n = \Phi_d^n(n_d) \wedge \Phi_l(N-n_d) \quad (3)$$

where $\Phi_d^n(n_d)$ is the spin and symmetry adapted n_d -electron wave function of the metal d -orbitals, and Φ_l is the $(N-n_d)$ -electron wave function of the l -orbitals. For TMCs with closed-shell ligands, the ground state of the l -system can also be described by a closed-shell Slater determinant $\Phi_l(^1A_1)$ with zero total spin. Thus, both the spin multiplicity and the point symmetry of the function eq. (3) coincide with those of the functions Φ_d^n of the d -system.

The two function multipliers in eq. (3) must be determined from the energy minimum condition. A serious problem arises due to the fact that wave functions of the type used in eq. (3) correspond to a fixed integer number of electrons in the d -shell. Therefore, all matrix elements of the resonance (electron hopping) operator H_r for the functions of that type vanish. In order to include the effects of the resonance interaction between the subsystems, we consider the *effective* Hamiltonian H^{eff} [6, 7] which operates in the subspace spanned by the functions of eq. (3). Its eigenvalues coincide with those of the exact Hamiltonian of eq. (1):

$$\begin{aligned}
H^{eff} &= PH_oP + H_{RR} \\
H_o &= H_d + H_l + H_c \\
H_{RR} &= PH_rQ(EQ - QH_oQ)^{-1}QH_rP
\end{aligned}
\tag{4}$$

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

The variational problem for the effective Hamiltonian H^{eff} of eq. (4) in the P -subspace transforms into a system of equations for the functions Φ_d^n and Φ_l (see *e.g.* [6, 7]):

$$\begin{aligned}
H_d^{eff} \Phi_d^n &= E_d^n \Phi_d^n \\
H_l^{eff} \Phi_l &= E_l \Phi_l \\
H_d^{eff} &= H_d + \langle \Phi_l | H_c + H_{RR} | \Phi_l \rangle \\
H_l^{eff} &= H_l + \langle \Phi_d^n | H_c + H_{RR} | \Phi_d^n \rangle
\end{aligned}
\tag{5}$$

Since the l -system is described by a single Slater determinant Φ_l , the latter must be found from the SCF procedure applied to the Fockian F_l^{eff} , derived from the Hamiltonian H_l^{eff} by the standard method [7, 13]. Proceeding semi-empirically we use the CNDO parameterization [13] for all the l -AO's. The solution of the SCF problem for the l -system with the approximate CNDO Fock operator 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 -system. They are used to construct the effective Hamiltonian H_d^{eff} of eq. (5) by averaging the operators H_c and H_{RR} over the ground state Φ_l of the l -system. This yields the effective Hamiltonian H_d^{eff} in the form [6]:

$$H_d^{eff} = \sum_{\mu\nu\sigma} U_{\mu\nu}^{eff} d_{\mu\sigma}^+ d_{\nu\sigma} + \frac{1}{2} \sum_{\mu\nu\rho\eta} \sum_{\sigma\tau} (\mu\nu | \rho\eta) d_{\mu\sigma}^+ d_{\nu\sigma} d_{\rho\tau}^+ d_{\eta\tau}
\tag{6}$$

where the d -electron Coulomb interaction term is that of the free ion and the effective core attraction parameters $U_{\mu\nu}^{eff}$ contain contributions from the Coulomb and the resonance interaction of the d - and l -systems:

$$U_{\mu\nu}^{eff} = \delta_{\mu\nu} U_{dd} + W_{\mu\nu}^{atom} + W_{\mu\nu}^{field} + W_{\mu\nu}^{cov}
\tag{7}$$

where

$$W_{\mu\nu}^{atom} = \delta_{\mu\nu} \left(\sum_{i \in s,p} g_{\mu i} P_{ii} \right)
\tag{8}$$

is the repulsion of electrons in the d -shell from those in the $4s$ - and $4p$ -AO's of the metal;

$$W_{\mu\nu}^{field} = \sum_L (P_{LL} - Z_L) V_{\mu\nu}^L \quad (9)$$

is the Coulomb interaction of d -electrons with the net charges on the ligand atoms, in the standard CFT form; and

$$W_{\mu\nu}^{cov} = - \sum_i \beta_{\mu i} \beta_{\nu i} \left(\frac{1 - n_i}{\Delta E_{di}} - \frac{n_i}{\Delta E_{id}} \right) \quad (10)$$

takes into account the resonance. In eqs. (8)-(10) P_{ii} is the diagonal matrix element of the one-electron density matrix of the l -system; $P_{LL} = \sum_{l \in L} P_{ll}$ is the electron population of the ligand atom L ; Z_L is the core charge of the ligand atom L ; $V_{\mu\nu}^L$ 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 i 'th l -MO ($n_i = 0$ or 1); ΔE_{di} (ΔE_{id}) is the energy necessary to transfer an electron from the d -shell (from the i 'th MO) to the i 'th MO (to the d -shell):

$$\begin{aligned} \Delta E_{di} &= I_i - A_d - g_{id} \\ \Delta E_{id} &= I_d - A_i - g_{id} \end{aligned} \quad (11)$$

$\beta_{\mu i}$ is the resonance integral between the μ 'th d -orbital and the i 'th l -MO, described by the resonance integrals $\beta_{\mu k}$ between the μ 'th d -AO and the k 'th l -AO:

$$\beta_{\mu k} = -(I_d + I_k) S_{\mu k} \beta^{ML} \quad (12)$$

where I_d and I_k are the valence state ionization potentials, $S_{\mu k}$ is the overlap integral between the μ 'th d -AO and the k 'th l -AO, and β^{ML} is the only adjustable parameter (see below), specific for each ML pair, where M stands for a transition metal atom and L stands for a ligand donor atom (nitrogen, oxygen *etc.*).

After establishing the form of the effective Hamiltonian for d -electrons, the states of n_d electrons in the d -shell are calculated by diagonalization of the matrix associated with H_d^{eff} in the n_d -electron wave function basis set. The ground state of the complex is given by the external product of the ligand Slater determinant and the n_d -electron wave function, obtained by diagonalization of H_d^{eff} , which leads to the lowest eigenvalue. The d - d excited states are products of other n_d -electron functions with the same Slater determinant. The excitation energies are equal to differences between the eigenvalues of H_d^{eff} .

3. Standard Implementation and Recent Results

The ECF method has been developed originally with a specific aim to calculate $d-d$ spectra of TMCs. The only interest in the electronic structure of the ligands was to estimate the ECF. Therefore, the simplest semi-empirical CNDO method [13] was used to calculate the characteristics of the l -system. From eqs. (7)-(12) it follows that all quantities that are involved in the determination of the ECF (*i.e.* ionization potentials, partial atomic charges) may be obtained with reasonable accuracy from CNDO calculations on organic molecules. Calculations for a series of octahedral ML_6^{2+} and ML_6^{4-} complexes, where $M = Ti, V, Cr, Mn, Fe, Co, Ni, Cu$; $L = H_2O, NH_3, F^-, Cl^-, CN^-$ were reported [6, 14, 15]. From these, the parameters β^{ML} were obtained by comparison to experimental values of $10Dq$ [16]. In all cases we observe excellent agreement between calculated and experimental spin state and symmetry of the ground state. $d-d$ Spectra of the excitations were reproduced with the accuracy of 2000 cm^{-1} . We also applied the ECF/CNDO method to ML_4Z_2 compounds with the same ligands L as above and $Z = H_2O, Py, NCS^-$ [17], and to metalloporphyrins [9]. The spin multiplicities and the spatial symmetry of the ground states of the mixed ligand complexes are correctly reproduced by the ECF/CNDO method. The same is true for the energies and symmetries of the lower excited states.

Based on the successful prediction of the ground state spin and symmetry for a variety of TMCs we studied the spin transition of *cis*-[Fe(bipy)₂-(NCS)₂] [18] which is well documented [4] and where the experimental molecular geometries are known for both spin isomers [19]. The ECF/CNDO calculations reproduce the change of the total spin of this quasi-octahedral d^6 complex from $S = 0$ (low-spin) to $S=2$ (high-spin) which accompanies the increase of the Fe-N distances by $\sim 0.15 - 0.20\text{ \AA}$. It was also possible to predict low-energy $d-d$ excited states for both spin forms in acceptable agreement with the experiment.

The successful description of the Fe(II) spin isomers motivated us to address the problem of the spin states of myoglobin (Mb) [20]. The interpretation of the kinetics of the binding of small molecules like CO, O₂ or NO to Mb is controversial [5, 21, 22]. It is known that the reaction rates are controlled by the electronic states of the reactants and products. The ground state of Mb is a quintet, CO and O₂ have singlet ($^1\Sigma^+$) and triplet ($^3\Sigma_g$) ground states, respectively, and MbCO as well as MbO₂ both have singlet ground states. According to the spin coupling rules [23], the binding of both CO and O₂ is a spin forbidden process for Mb in the $S=2$ ground state since a change of the total spin of either systems (Mb + CO or Mb + O₂) is required. It emerges that an interpretation of the low-energy electronic spectrum of Mb might be useful for the analysis of the binding

kinetics. We note that SCF *ab-initio* calculations of iron porphyrins (FeP) may give erroneous results with a bias towards high-spin ground states. A high-quality *ab-initio* study on FeP the ground state has erroneously been found to be a quintet [24]. Moreover, *ab-initio* approaches are too expensive to use for screening of large portions of the nuclear configuration space. We have studied the ground state spin and symmetry of the iron(II) porphyrine imidazole complex in dependence of the coordination sphere geometry [20]. Following earlier suggestions [5] we computed its electronic ground and several low-energy excited states for a two dimensional area in the coordinate space defined by two internal coordinates: namely, by that of the shift of the Fe atom perpendicular to the porphyrine plane (r_{Fe-Ctr}), and by the distance between the Fe atom and the imidazole nitrogen atom (r_{Fe-N_ϵ}). The results are depicted on Fig. 1. Three types of ground states are possible in a rectangle with $r_{Fe-Ctr} = 0.0 - 0.5 \text{ \AA}$ and $r_{Fe-N_\epsilon} = 2.0 - 2.3 \text{ \AA}$. The $^5B_{2g}$ state is the ground state in a small region with a large shift of Fe from the center of the porphyrin ring. The experimental geometry of Mb falls in this area, and Mb has a quintet ground state [21]. With a short Fe - N $_\epsilon$ distance ($r_{Fe-N_\epsilon} = 2.0 \text{ \AA}$) the ground state is a singlet ($^1A_{1g}$) provided the r_{Fe-Ctr} distance is smaller than 0.45 \AA . A relatively small elongation of the axial Fe-N $_\epsilon$ bond results in a triplet (3E_g) ground state. This is not surprising, since the ECF/CNDO calculation [9] of the four coordinated iron(II) porphyrine yields this ground state, in agreement with *ab-initio* calculations and experiment [25].

The analysis of the electronic states found in the the ECF/CNDO study [20] may have consequences for the interpretation of the binding mechanism. This follows from the accepted idea [5] that slow motions of the protein backbone are transferred to the iron center and can change its spin state and consequently its reactivity towards dioxygen binding. The motions of the axial imidazole ligand may bring the heme to areas in the coordinate space where it has either singlet or triplet electronic state. The binding of CO (singlet) or O $_2$ (triplet) are then spin allowed processes. The binding kinetics of these small molecules is therefore affected by the rate with which the heme enters the areas in the coordinate space where it has the ground state required for either reaction.

4. Further Developments

Up to this point we have described the ECF method and analyzed the results of its application to the calculation of the d -level splitting and d - d spectra in a series of TMCs. The ECF method allowed us to perform systematic calculations of the crystal field for various ligand environments. The results of these calculations are in fair agreement with the experimental

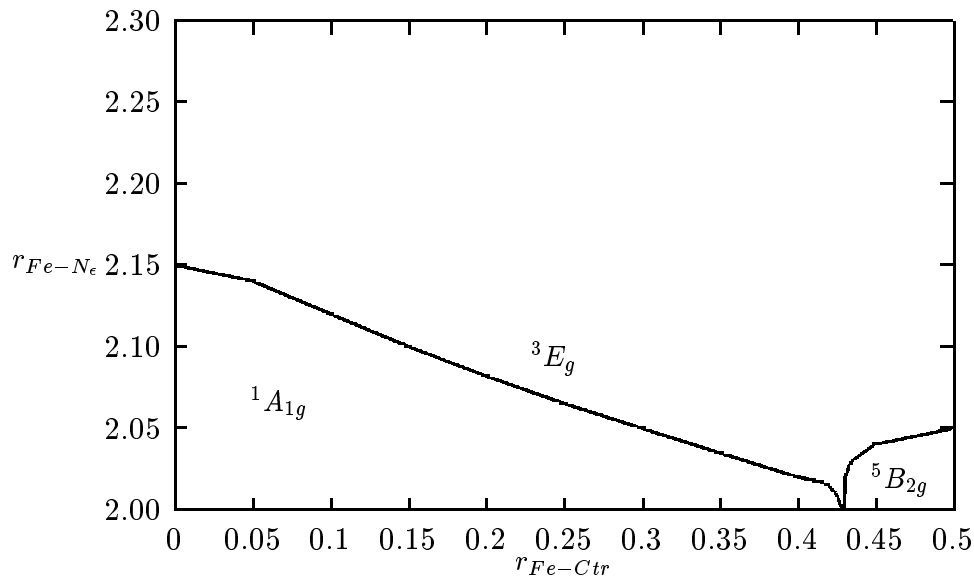


Figure 1. Map of the ground state spin of heme as a function of the Fe-N_e and Fe-Ctr distances.

data, particularly with respect to the spin multiplicity of the ground states of the complexes. Let us turn now to possible extensions of the method.

In the simple version of the ECF/CNDO method the electronic structure of the ligands is treated within the CNDO approximation. A more detailed description of the ligand electronic structure can be obtained with the INDO parameterization [13]. This has been done for a series of octahedral complexes, metalloporphyrins, and chlorocuprates [26]. In all cases the ground states and the excitation spectra of the compounds are in agreement with available experimental data.

A further application of the ECF methodology is to develop a method for the calculation of potential energy surfaces (PESs) of TMCs. This is possible with the representation of the total energy of the TMC in the form [7, 29]:

$$E_n = E_d^{eff}(n) + E_L \quad (13)$$

where $E_d^{eff}(n)$ is the energy of the n 'th state of the effective Hamiltonian of eq. (6) for d -electrons, E_L is the energy of the ligands. This expression is general [7] and represents the total electronic energy of the n 'th state of a TMC if it is described by the electronic wave function of the form of eq. (3). The CNDO or INDO parameterizations for the ligands are probably of high enough accuracy when we only need the charge distribution in the ligands and the orbital energies at fixed experimental geometries. However,

these methods are not accurate enough for geometry optimizations (or more generally for computations of PESs) of TMCs since an accurate core-core repulsion will be required. Therefore in a recent study [27] the SINDO/1 method [28] was used for the calculation of the electronic structure of the ligand sphere. So far the ECF/SINDO1 method has only been tested for a few molecules at their experimental geometries. These results are promising and they provide an accurate description of the ground state spins, symmetries and excitation energies. In cases where the SINDO/1 method can be used for the analysis of the geometry of the ligands the combined ECF/SINDO1 method must also lead to acceptable results in the analysis of complex geometries and PESs. In fact, any semi-empirical method that gives a reasonable description of the PES of organic molecules can be used in combination with the ECF methodology for the d -shell of TMAs. Currently, we are testing the possibility to combine the ECF approach with the MINDO/3 parameterization [30] for the ligands.

An alternative to the step by step improvement of semi-empirical descriptions of the ligand's electronic structure for the computation of the PES of TMCs is to use the MM approximation to calculate the ligand's energy E_L . Here the ECF/CNDO or ECF/INDO method is only retained for the d -shell electrons [29]. This simply replaces the ligand's energy E_L by E_{mm} , estimated by an MM calculation. The total energy of the n -th electronic state of the complex then has the form:

$$E_n = E_d^{eff}(n) + E_{mm} \quad (14)$$

The energies $E_d^{eff}(n)$ of the d -shells are calculated with the ECF/CNDO (or ECF/INDO) method. Two aspects are important here: First, the ECF/MM approach based on eq. (14) allows the use of a single MM potential for the ligands for all electronic states of the metal center. This is because the electronic energy of the d -shell is calculated explicitly. This approach does not require different parameters of the MM potentials for different spin states of the complex. The "different ionic radii" for the ions of the different spin states are obsolete (see below). Second, the MM potentials for TMAs extracted from structural data on TMCs cannot be used directly in eq. (14) since they include implicitly effects of the d -shells.

The ECF/MM approach has been used to calculate energy profiles of *cis*-[Fe(bipy)₂(NCS)₂] (see also Sect. 3) [29]. The ECF/CNDO method used before [18] must now be completed by the MM potential representing ligand's energy. We used the standard MM2 parameterization for all atoms except iron, for which no bending or torsional terms were used and the bond stretching potential was modeled by a Morse function:

$$E_b^{Fe-N} = D_{Fe-N} (1 - e^{-\alpha_{Fe-N}(r - r_{Fe-N}^0)})^2, \quad (15)$$

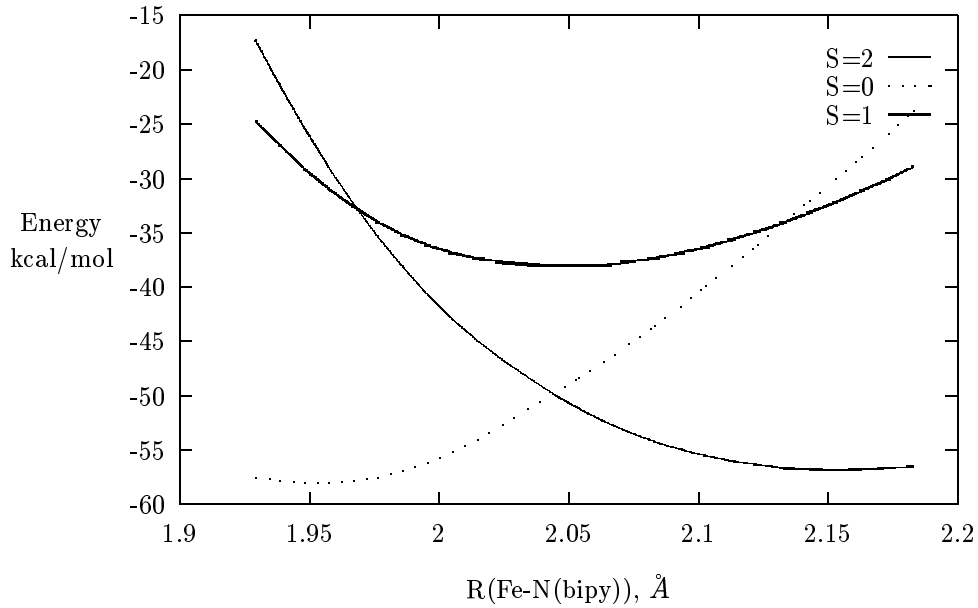


Figure 2. Calculated energy profiles for the spin states of *cis*-[Fe(bipy)₂(NCS)₂].

The following parameter values were used to reproduce the experimentally determined positions of the PES's minima along the Fe-N bond-length coordinates for the low-spin and high-spin states:

$$\begin{aligned} r_{Fe-N_{bipy}}^0 &= 2.035 \text{ \AA}, D_{Fe-N_{bipy}} = 70.0 \text{ kcal/mol}, \alpha_{Fe-N_{bipy}} = 2.0 \text{ \AA}^{-1}; \\ r_{Fe-N_{NCS}}^0 &= 1.975 \text{ \AA}, D_{Fe-N_{NCS}} = 40.0 \text{ kcal/mol}, \alpha_{Fe-N_{NCS}} = 3.0 \text{ \AA}^{-1}. \end{aligned} \quad (16)$$

Results of our calculation are shown in Fig. 2. It is indeed possible to reproduce the whole qualitative picture of the lowest electronic terms derived from experiment [4, 31] with a single MM potential for the ligands and the ECF/CNDO *d*-electron energy. Different Fe-N distances for the hs and ls forms of the complex result from the well balanced contributions of a single ligand potential for each donor (eq. (16)) and the geometry sensitive *d*-shell energy obtained by the ECF/CNDO procedure. The *d*-electron energy is specific for each spin state since it is obtained by diagonalization of the n_d -electron effective Hamiltonian of eq. (6) in each point along the path in the coordinate space. Thus energy profiles such as Fig. 2 may now be *calculated* [29] rather than drawn by hand [4, 31].

We can now return to the discussion of the Mb ground states. With eqs. (13), (14) the PES of Mb can be obtained with an appropriate MM potential. In the vicinity of the boundaries (solid lines in Fig.1) the energy differences between the states are comparable to the spin-orbit interaction.

Thus along these boundaries the ground states contain significant contributions from all states with total spins of 0, 1, and 2. The energy profile along the internal coordinate of a simultaneous shift of the iron atom and the imidazole ligand (with a constant $r_{Fe-N_e} = 2.0 \text{ \AA}$) is therefore likely to be adiabatic rather than nonadiabatic. That means that for the corresponding vibration anharmonic corrections may be significant. These must be taken into account, for example, in the analysis of protein dynamics by a combination of normal-mode and Mössbauer techniques [32].

5. General Discussion and Conclusions

In the present paper we have demonstrated how the ECF methodology can be applied to the calculation of the d -level splitting, d - d excitation spectra, and PES of TMCs. The ECF method allows the performance of systematic calculations of the crystal field for various ligand environments. The results of these calculations are in fair agreement with experimental data. The basis for this success is a physically justifiable form of the trial wave function of TMCs (eq.(3)).

We will now consider differences between the ECF methodology and other approaches that have been used together with MM of TMA. The angular overlap model (AOM) [33, 34] has to be mentioned here. The effective Hamiltonian for the d -shell (eq. (6)) has the form of the standard crystal field Hamiltonian. The covalence term of eq. (10) dominates the d -level splitting appears analogous and its form is similar to the AOM parameters e_σ and e_π . However, the differences between the two approaches are very important. The AOM is obtained by applying second order perturbation theory (PT) in H_r (eq. (1)) to obtain one-electron d -states of the TMC. This involves the matrix equation for the one-electron MO's of the whole complex and treats the part of the secular equation which corresponds to d - l mixing. Therefore the estimates for the complex MO's and for the orbital energies are of somewhat lower quality. This also applies to the formalism based on Green's function, reviewed in [35]. Thus the AOM approach is based on the SCF approximation but the MO's are replaced by estimates based on PT. The consequences of the SCF approximation with respect to the numerical procedures (see Sect. 2) are not known since corresponding calculations of the ligand field have not been reported [33, 35].

The ECF method applies second order PT in H_r to the many-electron states of the form of eq. (3). This formal difference leads to apparent differences in the final formulae for the crystal field matrices and to different numerical results. In the AOM, there is no difference between the influence of the occupied and empty l -MO's on the position of the d -levels and it does not distinguish between electron transfer from and to the d -shell. These dif-

ferences are rather important. The ECF approach considers the energetics of the localized and strongly interacting electrons in the d -shell explicitly. This allows the *calculation* of the crystal field as a function of the ligand environment, both in terms of the ligand geometry and the chemical nature. In the AOM the crystal field parameters e_σ and e_π are fitted to experimental spectra. They are specific for each ligand and not transferable, even for constant donor atoms. In the ECF approach the electronic structure of the ligands is taken into account explicitly. Only the magnitude of the resonance (eq. (12)) between orbitals of a given donor atom and d -orbitals of a given transition metal is parameterized. The same value is used for all the ligands containing a given donor atom, since the details of the ligand electronic structure are taken into account by the SCF calculation of the ligands.

A Cellular Ligand Field Stabilization Energy (CLFSE) term has been added to the MM energy of TMCs [36]. This term is by definition the sum of one-electron energies of the d -levels, obtained by diagonalization of the 5×5 crystal field matrix taken as a sum of cellular contributions from different ligands [33, 34]. The electronic states of the d -shell are then simulated by ascribing different occupation numbers to the one-electron d -levels obtained by the crystal field matrix diagonalization. This is an approximate procedure in contrast to the ECF approach, where the d -electron energy is obtained by exact diagonalization of the effective Hamiltonian H_d^{eff} of eq. (6) in the many-electron basis. However, to the extent to which the electronic structure of TMCs can be described by a single determinant with some definite d -level filling the CLSFE/MM method [36] is capable to reproduce characteristic features of the PES of TMCs. For example, the structures of Cu(II) complexes which are dominated by the Jahn-Teller distortion can be described within the CLFSE/MM approach, due to the fact that the d^9 complexes of Cu(II) can be exactly described on the single determinant level. Nevertheless, some problems may arise with complexes where electron correlations are more important. This is the case with complexes like *cis*-[Fe(bipy)₂(NCS)₂], where spin transitions are possible. In this example it has been shown that the electronic wave function of the low spin form is sufficiently multiconfigurational [37]. It is known that configuration mixing is an important contribution to the stabilization of the low spin configuration of the d -shell. The spin isomerism itself is a consequence of a balance between the crystal field strength, electron correlation and the exchange energy. The high spin states can be represented by a single determinant and thus, they are not stabilized by configuration mixing. The crystal field and the CI push into the same direction – they both stabilize the low spin states. For this reason, in any single determinant based approach the crystal field required to achieve the low spin state (when going from the high

spin free ion) is stronger than it is if the full CI description of the d -shell is used. This may lead to certain imbalances in the parameterization of one-electron schemes.

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