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Electronic structure and optical spectra of transition metal complexes by the effective Hamiltonian method

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Summary. A semiempirical effective Hamiltonian treatment is proposed for transition metal complexes, taking into account *d*-electron correlations, weak covalency of the metal-ligand bonds and the electronic structure of the ligand sphere. The technique uses the variation wave function which differs from the usual Hartree–Fock antisymmetrized product of molecular orbitals extended over the whole complex. The scheme is implemented and parameters describing the metal-ligand interactions are adjusted to reproduce *d*-*d*-excitation spectra of a number of octahedral MF_6^{4-} (M = Mn, Fe, Co, Ni) anions, $Mn(FH)_6^{2+}$ cation, $CoCl_6^{4-}$ anion, and a tetrahedral $CoCl_4^{2-}$ anion. The values of the parameters are reasonable, thus confirming the validity of the proposed scheme.

Key words: Electronic structure – Transition metal complexes – *d*-*d*-excitation spectra – Effective Hamiltonian

1. Introduction

The electronic structure of transition metal complexes (TMC) has some specific features accounted for by the *d*-electrons of the transition metal atom. These unusual characteristics become apparent in the optical absorption spectra, in the magnetic properties of the TMC, etc. It is common practice to fit the experimental electronic spectra of TMC and the results of magnetic measurements to the crystal field (CF) theory [1] (see also [2–6]) which implies that *nd*-electrons of the central ion of the complex (here *n* is the principal quantum number) form an isolated system placed in the electrostatic field of point charges (or point dipoles) modelling the ligand sphere. All other electrons placed either in the ligand or in the outer valence ($(n+1)s$ and $(n+1)p$) metal orbitals are not considered explicitly.

In contrast with the CF scheme, the calculation methods applied to TMC usually account for either all or at least the valence electrons both in the central ion and in the ligands. These methods are mainly based upon the Hartree–Fock–Roothan (HFR) approximation [7]. An exception is the Generalized Valence Bond (GVB) method [8] which has been recently applied to TMC [9–11]. The calculations in the HFR approximation are carried out both on the *ab-initio* and semiempirical level. For the *ab-initio* calculations with extended configuration interaction (CI) (see for example [12–16] and references therein) and the semiempirical ones with elaborated parameterization (see for example [17–22] and references therein) the calculated transition energies are in quite good agreement with those observed in experiment. Despite numerical agreement between the HFR calculations and the experimental excitation spectra, the entire body of experimental data and theoretical calculations concerning TMC is in certain disagreement with the Hartree–Fock picture of the electronic structure of TMC as a whole. The major contradictions are the following:

(i) The Koopmans' theorem is not valid for the ionization transitions involving one-electron states with a large contribution from atomic *d*-orbitals [23].

(ii) The *Aufbauprinzip* is frequently violated for the orbitals with large contributions from atomic *d*-orbitals [24–26].

(ii) The HFR self-consistency procedure in the calculations of TMC either converges very slowly or oscillates [27].

The nonvalidity of the Koopmans' theorem by itself raises questions about the HFR picture of the electronic structure of TMC. The Hartree–Fock many-electron wave function is an antisymmetrized product of one-electron states (molecular orbitals, MO) delocalized over the whole complex. Each electron is considered as if it moved in the mean (self-consistent) field induced by nuclei and all other electrons. However, it is meaningless to speak about the self-consistent field when it turns out to be completely different for different ionic forms of a complex or for its different spin states. Quantitatively that phenomenon is usually discussed in terms of orbital relaxation energies. Removal of an electron from the MO with large contribution from metal *d*-orbitals can be accompanied by relaxation of the orbital energy by about 10–20 eV (!) [27]. Indeed the statement that the SCF strongly changes when a TMC molecule is ionized or excited means that electrons do not experience any mean field but by contrast trace any motion of each other very carefully. Therefore electrons in that case cannot be treated as independent particles in some external (though self-consistent) field, but in contrast their motion is strongly correlated.

Violation of the *Aufbauprinzip* also indicates the particular importance of electron correlation effects. Clearly, the CI procedure can take into account all these effects, but it is known that the CI series taking the HFR orbitals as a one-electron basis set converge quite slowly [28] and a large number of configurations should be considered. Thus the qualitative picture which is possible only when one or two configurations give the main contribution to the expansion of the ground-state wave function turns out to be lost.

Even the most successful parameterization scheme developed for TMC (the INDO-parameterization by Zerner and coworkers [19–22, 27]) based on the HFR approximation is not free from the general contradictions outlined above, which are inherent to the HFR scheme. For example, the HFR ground states of both $CuCl_4^{2-}$ and $CoCl_4^{2-}$ obtained in [27] violate the *Aufbauprinzip* and thus they are not minima of the Hartree–Fock energy functional. The same situation occurs in the recent calculations on iron (II) porphyrins [21]. All the HFR states with nonzero spin violate the *Aufbauprinzip*, namely, all the singly occupied orbitals in the Slater determinants representing these states have lower orbital energies than some doubly occupied orbitals. It naturally leads to the instability of the Hartree–Fock solution. The self-consistent orbitals [21, 22] for the intermediate and high spin states of iron porphyrins are not those of correct symmetry, thus indicating serious problems in the HFR approximation itself.

Summarizing the above observations we can state that a partially filled *d*-shell causes considerable complications in the HFR treatment of the electronic structure of TMC. The agreement between HFR calculations and experiments is achieved either by elaborated adjustment of parameters or at a heavy cost of loss of any qualitative picture of the problem. For these reasons we tried to find a point of view of the electronic structure of TMC different from the commonly adopted HFR one. Our purpose is to describe the electronic structure of TMC conserving some qualitative view and to try to avoid the above-mentioned contradictions which are inherent to the HFR approximation.

The origin of all these contradictions lies in the strong Coulomb interaction between electrons in the *d*-orbitals of the central atom and relatively weak resonance interaction of these orbitals with other orbitals in the TMC molecule. In the NiF_6^{4-} anion the ratios of the one-center Coulomb repulsion parameters to the resonance integrals between Ni orbitals and F $2p$-orbitals are about 50 for $3d$-orbitals, about 1.5 for $4s$-orbitals, and about 1 for $4p$-orbitals of the Ni atom (parameters are taken from [29]). Similar values can be obtained for other complexes and other parameterizations. By comparison, this ratio for π-orbitals in benzene is about 4 (PPP parameters). Harrison notes the similar situation in magnetic insulators and crystals with paramagnetic impurities [30]. In this case, when intraatomic matrix elements of the Coulomb interaction turn out to be more significant than the interatomic matrix elements taken as a basis for band structure calculations (the Coulomb-to-resonance ratio $\gg 1$), electrons in the crystal are to be described with use of local states rather than Bloch states delocalized over whole crystal. The excitation spectrum of the crystal (for example MnO) coincides with the band spectrum of the simple ionic crystal CaO completed with the spectrum of *d*-shells splitted by the crystal field.

In the case of TMC the molecular orbitals take part of the delocalized Bloch states in crystals. As in the case of crystals with partially filled *d*-shells it seems to be inappropriate to consider in a unified approach the orbitals for which the Coulomb-to-resonance ratios differ by orders of magnitude. It is natural to unite the orbitals with modest (e.g. smaller than 10) Coulomb-to-resonance ratios in one group (called below the ligand subsystem) and consider them in the framework of the HFR approach as it is done with the states which are responsible for formation of the CaO-like band structure in the theory of transition metal monoxides [30]. This is indirectly supported by the observation that the above-mentioned contradictions (i)–(iii) usually do not arise for the orbitals formed mainly by the ligand atomic orbitals.

The orbitals for which the Coulomb-to-resonance ratios exceed 10 (*d*-orbitals) should be considered separately as the CF theory does. The general picture of the electronic structure of TMC which arises in the framework of the CF theory is very attractive. The CF theory implies that the spectra of TMC are completely determined by excitations in their *d*-shells. That attribution is correct with an obvious exception of charge-transfer excitations and, moreover, it is perfectly correct for low energy excitations which are responsible for the magnetic properties [5] and which are important for the catalytic activity of TMC [31]. The CF theory takes into account the correlation effects in the *d*-shell of the central ion by inclusion of full configurational manifold for the given number of *d*-electrons. However, the problem is that the CF parameters obtained by numerical fit of the observed energy level to the computations strongly differ from those obtained by direct calculations based upon the original CF model (with the ligands modelled as point charges). This discrepancy indicates that some other effects not included in the original electrostatic CF model (first of all the effects of metal-ligand covalency, i.e., the resonance interaction between *d*-orbitals and the ligand ones) are important and must be taken into account.

From our point of view, a physically adequate method for the description of the electronic structure of TMC should be constructed as follows:

(a) Electrons in the ligands together with those in the metal's outer valence (*s*- and *p*-) orbitals should be treated in the HFR approximation.

(b) Electrons in the *d*-orbitals of the metal should be considered in the framework of the CF approach.

(c) The resonance interaction of the *d*-subsystem with the ligand subsystem (effects of covalency) should be included into the scheme by perturbative (for example, Löwdin projection) technique giving an effective CF Hamiltonian for *d*-electrons.

The paper is organized as follows. In Sect. 2.1 we derive an effective Hamiltonian for TMC with isolated *d*-shell. In Sects. 2.2 and 2.3, respectively, the effective Hamiltonians for *d*- and ligand subsystems are derived. Introducing physical assumptions we parameterize our scheme in Sect. 3.1 and present results of calculations in Sect. 3.2. Some discussions and comments are given in Sect. 4. Derivations of complex formulae are presented in the Appendices A and B.

2. Theory

2.1. *Effective Hamiltonian for TMC*

Let us consider the one-electron basis functions of TMC. In the valence approximations 4*s*-, 4*p*- and 3*d*-orbitals of the metal atom and valence orbitals of the ligand atoms are the basis orbitals. The chosen basis of atomic orbitals (AO) can be divided into two parts with respect to their Coulomb-to-resonance ratios. The first part contains 3*d*-orbitals of the transition metal atom which have large Coulomb-to-resonance ratio (*d*-subsystem). The second part contains 4*s*-, 4*p*-orbitals of the transition metal atom and valence orbitals of the ligand atoms with relatively small Coulomb-to-resonance ratios (ligand subsystem). The exact valence Hamiltonian for TMC can be written without loss of generality in the form:

$$H = H_d + H_L + H_c + H_r \tag{1}$$

where H_d is the Hamiltonian for *d*-electrons in the field of the atomic cores of TMC, H_L is the Hamiltonian for electrons in the ligand subsystem, H_c and H_r are, respectively, operators of the Coulomb and the resonance interaction between the subsystems.

The exact wave function of the ground state of TMC can be presented as a superposition of functions which describe different distributions of N valence electrons among the subsystems:

$$\Psi = \sum_n \sum_i C_i(n, N-n)\Phi_i(n, N-n) \tag{2}$$

where n is the number of electrons in the d-subsystem. We however intend to describe the electronic structure of TMC using an approximate wave function with fixed number of d-electrons which coincides with the number of d-electrons in the relevant valence state of the metal ion of TMC. The configurations with other numbers of d-electrons will be taken into account with use of the Löwdin partition technique [32] (see also Ref. [33]).

Following the Löwdin partition technique, we introduce the projection operator on the subspace which is spanned by the functions with a fixed number of d-electrons n_d and with $n_L = N - n_d$ electrons in the ligand subsystem:

$$P = \sum_i |\Phi_i(n_d n_L)\rangle\langle\Phi_i(n_d n_L)| \tag{3}$$

and the complementary operator $Q = 1 - P$. Inserting the identity $\Psi = P\Psi + Q\Psi$ into the Schrödinger equation $H\Psi = E\Psi$ where H is the exact Hamiltonian Eq. (1), and multiplying the result in turn by P and Q from the left, one obtains the pair of equations:

$$PHPP\Psi + PHQQ\Psi = EP\Psi \tag{4}$$

$$QHPP\Psi + QHQQ\Psi = EQ\Psi \tag{5}$$

Solving formally Eq. (5) with respect to $Q\Psi$ and inserting the result into Eq. (4), one obtains the equation for the function $P\Psi$:

$$[PHP + PHQ(EQ - QHQ)^{-1}QHP]P\Psi = EP\Psi \tag{6}$$

The expression in square brackets is the effective Hamiltonian $H^{eff}(E)$. It operates in the subspace spanned by the functions with a fixed number of d-electrons (in the P-block), but its eigenvalues coincide with those of the exact Hamiltonian Eq. (1). For further simplification let us assume that the operator H_c does not change the number of electrons in the subsystems. This means that in the Coulomb interaction operator we neglect the terms which mix the functions with different numbers of d-electrons (terms with different n in Eq. (2)). Therefore only the one-electron operator H_r mixes functions with n's differing by 1 and thus gives a nonvanishing contribution to the resolvent term of the effective Hamiltonian Eq. (6). Thus $H^{eff}(E)$ can be rewritten in the form:

$$H^{eff} = PH_0P + H_{RR} \tag{7}$$

where

$$H_0 = H_d + H_L + H_c \tag{8}$$

$$H_{RR} = PH_rQ(EQ - QH_0Q)^{-1}QH_rP \tag{9}$$

The energies of the states of TMC are to be found from the equation:

$$\langle\Phi_n|H^{eff}(E_n)|\Phi_n\rangle = E_n \tag{10}$$

where variation wave functions Φ_n belong to the P-block and will be defined explicitly below.

In order to find the n-th eigenvalue of H, the latter equation has to be solved iteratively until convergence in E_n is achieved. However, it has been noted in Ref. [34] that the dependence of the effective Hamiltonian of the type Eq. (6) on energy is weak enough in the case when all resolvent poles are far enough from the energy eigenvalue to be found. Since the energy of the lowest charge transfer (between the subsystems) state is considerably higher than the energies of excitations in the d-subsystem, we neglect this dependence and consider the effective Hamiltonian $H^{eff}(E_0)$ where E_0 is the ground-state energy of the Hamiltonian H_0. The energy E_0 is assumed to be the zero energy. The effective operator $H^{eff}(E_0)$ corresponds to the second order of the operator perturbation theory with resonance operator H_r as a perturbation [35].

The symmetry- and spin-adapted external products of the group functions of the subsystems form the basis in the P-block. They are the functions of the definite total spin $\bar{S}$ and spin projection $\bar{\sigma}$ and belong to the definite row $\bar{\gamma}$ of the definite irreducible representation $\bar{\Gamma}$ of the point symmetry group. The total number of electrons N equals to $n_d + n_L$:

$$|n_d k; n_L k'\rangle = |n_d S\Gamma; n_L S'\Gamma'; N\bar{S}\bar{\sigma}\bar{\Gamma}\bar{\gamma}\rangle \tag{11}$$

Here n_d is the number of d-electrons in the ground state of the free transition metal ion, n_L is the number of electrons in the ligand subsystem.

The functions Φ_n from Eq. (10) can be presented as linear combinations of the basis states defined by Eq. (11):

$$\Phi_n = \sum_{k,k'} C^n_{kk'} |n_d k; n_L k'\rangle \tag{12}$$

In the present consideration we restrict ourselves to the case of the complexes where excitations in the ligand subsystem (and also ligand-to-metal and metal-to-ligand charge transfer ones) are of relatively high energy as compared to the excitations in the d-subsystem and thus their interference is negligible. The major group of TMC with the ligands having closed electronic shells (e.g., halogen anions, closed-shell donors like ammines, water, etc.) satisfies this condition. In such complexes the number of electrons in the ligand subsystem is even, therefore the ground state of the ligand subsystem can be described by a Slater determinant $\Phi_L(^1A_1)$ with zero total spin. The wave function Φ_n is transformed to the simple form:

$$\Phi_n = \left(\sum_k C^n_k |n_d k\rangle \right) \wedge \Phi_L = \Phi^n_d \wedge \Phi_L \tag{13}$$

According to the group theory rules, both the spin multiplicity and the point symmetry of the functions of the type Eq. (13) coincide with those of the functions Φ^n_d. Note that the wave function in the form of Eq. (13) satisfies our qualitative conditions (a) and (b) formulated in the Introduction. The function of the ligand subsystem Φ_L is a single Slater determinant formed by delocalized MOs and it is analogous to the wave function describing the CaO-like part of transition metal monoxides. The function Φ^n_d is the function of d-electrons only, and it can be selected from the full CI manifold of n_d electrons distributed in five d-orbitals.

The variation functions Φ^n_d and Φ_L can be found by the minimization of the following functional:

$$\Im[\Phi_n] \equiv \Im[\Phi^n_d, \Phi_L] = \langle \Phi_n | H^{eff}(E_0) | \Phi_n \rangle \tag{14}$$

with respect to the strong orthogonality condition [36], which we assume to be satisfied.

The minimization of the functional Eq. (14) gives a pair of interconnected equations for the functions Φ^n_d and Φ_L (see Ref. [33]):

$$H^{eff}_d \Phi^n_d = E^n_d \Phi^n_d \tag{15}$$

$$H^{eff}_L \Phi_L = E_L \Phi_L \tag{16}$$

The effective Hamiltonians for the subsystems are given by:

$$H_d^{eff} = H_d + \langle \Phi_L | H_c + H_{RR} | \Phi_L \rangle \tag{17}$$

$$H_L^{eff} = H_L + \langle \Phi_d^n | H_c + H_{RR} | \Phi_d^n \rangle \tag{18}$$

To derive the Hamiltonians of Eqs. (17) and (18) the explicit forms of the functions Φ_d^n and Φ_L are not needed. All the necessary information is condensed in the corresponding density matrices. According to Ref. [33] the system of Eqs. (15) and (16) has to be solved by iterations. We replace the iteration procedure by setting effective parameters into H_L^{eff} and H_d^{eff}. In effect we do not need to parameterize the Hamiltonian H_L^{eff}. Since the function Φ_L is to be found in the HFR approximation we need the effective Fock operator F_L^{eff} only. We start from an initial density matrix ϱ of the d-subsystem. Using this matrix we construct the effective Fock operator F_L^{eff} and then find the ground-state Slater determinant Φ_L and orbital energies ε_i. Thorough analysis of Eq. (9) reveals, however, that the energies of the charge-transfer states (the poles of the resolvent) are to be calculated for the Hamiltonian H_0 (Eq. (8)) where the resonance term is absent. Therefore the orbital energies of the ligand subsystem ε_i are also to be calculated without H_r. Hence we omit the term H_{RR} in Eq. (18). Inserting the result of the calculation on the ligand subsystem Φ_L and ε_i in Eq. (17) we get the effective Hamiltonian H_d^{eff}. The diagonalization of the latter gives the energies of the d-electron terms of TMC. In this model they are equivalent to the energies of low-lying excited states of the entire complex. The energies of the relevant charge transfer states correspond to the poles of the resolvent factor in the definition of the operator H_{RR}, Eq. (9).

2.2. Derivation of H_L^{eff} (Eq. 18) and F_L^{eff}

The definition of H_L^{eff} (Eq. (18)) can be rewritten in the form:

$$H_L^{eff} = H_L + \langle\!\langle H_c \rangle\!\rangle_d + \langle\!\langle H_{RR} \rangle\!\rangle_d$$

where $\langle\!\langle \cdots \rangle\!\rangle_d$ denotes the average over degrees of freedom of d-subsystem. According to the previous section, the term $\langle\!\langle H_{RR} \rangle\!\rangle_d$ is to be omitted.

The Hamiltonian H_L for electrons in the ligand subsystem can be written as:

$$\begin{aligned} H_L = {} & \sum_{i,\sigma} \left(U_{ii} - \sum_L V_{ML} \right) b_{i\sigma}^{+} b_{i\sigma} + \sum_L \sum_{\substack{l \in L \\ \sigma}} \left(U_{ll} - \sum_{L' \neq L} V_{LL'} - V_{LM} \right) b_{l\sigma}^{+} b_{l\sigma} \\ & + \sum_{\substack{i,l \\ \sigma}} \beta_{il} (b_{i\sigma}^{+} b_{l\sigma} + h.c.) + \sum_{\substack{ll' \\ \sigma}} \beta_{ll'} b_{l\sigma}^{+} b_{l'\sigma} + \tfrac{1}{2} \sum_{\substack{rstu \\ \sigma\tau}} (rs|tu) b_{r\sigma}^{+} b_{s\sigma} b_{t\tau}^{+} b_{u\tau} \end{aligned} \tag{19}$$

where $b_{i\sigma}^{+}$ ($b_{i\sigma}$) are the creation (annihilation) operators of an electron with the spin projection σ on the i-th valence AO of the ligand subsystem. The first term describes the interactions of electrons on the metal $4s$- and $4p$-orbitals ($i = 4s, 4p_x, 4p_y, 4p_z$) with the metal core (parameters $U_{ii} < 0$) and with the ligand atom cores (parameters $V_{ML} > 0$). The second term describes the interactions of electrons in the ligand AO's with their cores (parameters $U_{ll} < 0$), with the cores of the other ligand atoms (parameters $V_{LL'} > 0$) and with the metal core (parameter $V_{LM} > 0$). The third and the fourth terms describe the resonance interactions in the ligand subsystem (parameters $\beta_{il} < 0$ and $\beta_{ll'} < 0$). The last term describes the Coulomb interactions of electrons ($(rs\,|\,tu)$ are the corresponding Coulomb integrals).

The influence of d-electrons upon the ligand subsystem electrons is condensed in the term $\langle\!\langle H_c \rangle\!\rangle_d$. According to Ref. [33] the averages of the Coulomb interaction operator over some subsystem density matrix gives contributions only to the one-electron part of the effective Hamiltonian of another subsystem. Correspondingly, only the one-electron part of the subsystem Fock operator will be renormalized by the $\langle\!\langle H_c \rangle\!\rangle_d$ term. Let us take the initial density matrix of the d-subsystem (ϱ) in the form:

$$\begin{aligned} \varrho_{\mu\nu} &= \delta_{\mu\nu} n_d / 5 \\ \mathrm{Tr}[\varrho] &= n_d \end{aligned} \tag{20}$$

Such a matrix describes a uniform distribution of electrons in the d-orbitals of the metal atom. The operator H_c comprises two terms:

$$H_c = H_c^{(1)} + H_c^{(2)} \tag{21}$$

where $H_c^{(1)}$ is the operator for the *intra*atomic Coulomb interaction of d-electrons with $4s$- and $4p$-electrons on the metal and $H_c^{(2)}$ is the operator for the *inter*atomic Coulomb interaction of d-electrons with ligand electrons.

Averaging the operator $H_c^{(1)}$ over the one-electron density matrix ϱ one obtains [33]:

$$\langle\!\langle H_c^{(1)} \rangle\!\rangle_d = \sum_{i,j} \sum_{\sigma} \left(J_{ij} - \tfrac{1}{2} K_{ij} \right) b_{i\sigma}^{+} b_{j\sigma} \tag{22}$$

where

$$J_{ij} = \sum_{\mu,\nu} \varrho_{\mu\nu} (\mu\nu\,|\,ij)$$

$$K_{ij} = \sum_{\mu,\nu} \varrho_{\mu\nu} (\mu i\,|\,\nu j)$$

Taking into account the special form of $\varrho_{\mu\nu}$ (Eq. (20)) one obtains:

$$\langle\!\langle H_c^{(1)} \rangle\!\rangle_d = \sum_{i,j} \sum_{\sigma} \frac{n_d}{5} \left[\sum_{\mu} (\mu\mu\,|\,ij) - \tfrac{1}{2} (\mu i\,|\,\mu j) \right] b_{i\sigma}^{+} b_{j\sigma} \tag{23}$$

Due to spherical symmetry of atoms, the integrals $(\mu\mu\,|\,ij)$ and $(\mu i\,|\,\mu j)$ are nonvanishing if $i = j$ only (see [27]). Thus we have:

$$\langle\!\langle H_c^{(1)} \rangle\!\rangle_d = \sum_{i} \frac{n_d}{5} \sum_{\mu} g_{\mu i} \hat{n}_i \tag{24}$$

where $g_{\mu i} = (\mu\mu\,|\,ii) - \frac{1}{2}(\mu i\,|\,\mu i)$, and $\hat{n}_i = \sum_\sigma b_{i\sigma}^{+} b_{i\sigma}$ is the electron number operator for the i-th AO.

The operator $H_c^{(2)}$ can be written in the form:

$$\begin{aligned} H_c^{(2)} &= \sum_{\mu,\mu'} \sum_{l} \sum_{\sigma,\tau} (\mu\mu'\,|\,ll) d_{\mu\sigma}^{+} d_{\mu'\sigma} b_{l\tau}^{+} b_{l\tau} = \sum_{\mu,\mu'} \sum_{\sigma} \sum_{L} V_{\mu\mu'}^{L} d_{\mu\sigma}^{+} d_{\mu'\sigma} \sum_{l \in L} \hat{n}_l \\ &= \sum_{m,m'} \sum_{\sigma} \sum_{L} V_{mm'}^{L} d_{m\sigma}^{+} d_{m'\sigma} \sum_{l \in L} \hat{n}_l \end{aligned} \tag{25}$$

where $(\mu\mu'\,|\,ll)$ is the Coulomb integral which we assume to have the same value $V_{\mu\mu'}^{L}$ for all the AO's l centered on the ligand atom L. $d_{\mu\sigma}^{+}$, $d_{m\sigma}^{+}$ ($d_{\mu'\sigma}$, $d_{m'\sigma}$) stand for the operators of creation (annihilation) of an electron either on the μ-th (μ'-th) real d-AO (with the angular part taken as cubic harmonic) or on the complex d-AO (the angular part of the complex function is taken as a familiar spherical harmonic) with the angular momentum projection quantum number m (m'). The given form of the operator $H_c^{(2)}$ corresponds to the following approximation. The Coulomb interaction of d-electrons with an electron in the ligand AO l is considered as the interaction of the d-electron with point unit charge placed on the ligand atom L. All the Coulomb integrals $(\mu\mu'|ll)$ where AO l is centered on the ligand atom L are set equal to $V^L_{\mu\mu'}$ which is the matrix element of the operator for the potential energy of d-electron interacting with a unit charge placed on the ligand atom L. The matrix elements of the latter operator in the basis of the spherical harmonics have the form:

$$V^L_{mm'} = \langle m|\frac{e^2}{|r - R_L|}|m'\rangle = e^2 \sum_{k=0,2,4} F_k(R_L) Y_k^{m-m'}(\theta_L, \phi_L) A_k^{mm'} \tag{26}$$

Here e is the electron charge; (R_L, θ_L, ϕ_L) are the spherical coordinates of the ligand atom L (the coordinates of the metal atom are $(0, 0, 0)$);

$$F_k(R) = R^{-(k+1)} \int_0^R r^k R^2_{3d}(r) r^2 \,\mathrm{d}r + R^k \int_R^\infty r^{-(k+1)} R^2_{3d}(r) r^2 \,\mathrm{d}r \tag{27}$$

are the functions of the distance R_L between the metal atom and the ligand atom L ($R_{3d}(r)$ are the radial functions for d-orbitals); $Y_k^{m-m'}(\theta_L, \phi_L)$ are the spherical functions; $A_k^{mm'}$ are the coefficients which are related to the Wigner $3j$-symbols by the following formula:

$$A_k^{mm'} = (-1)^{m'} 5[4\pi/(2k+1)]^{1/2} \begin{pmatrix} 2 & k & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 2 & k & 2 \\ -m & m-m' & m' \end{pmatrix} \tag{28}$$

The matrix elements $V^L_{\mu\mu'}$ can be yielded from $V^L_{mm'}$ by an unitary transformation from the $|m\rangle$-basis to the $|\mu\rangle$-basis.

Averaging $H_c^{(2)}$ over the density matrix ϱ (Eq. (20)) one obtains:

$$\langle\langle H_c^{(2)} \rangle\rangle_d = \sum_L \lambda_L \sum_{l \in L} \hat{n}_l \tag{29}$$

where

$$\lambda_L = \frac{n_d}{5} \sum_\mu V^L_{\mu\mu}$$

The trace of the matrix V^L is invariant with respect to unitary transformations of the basis, thus:

$$\sum_m V^L_{mm} = \mathrm{Tr}[V^L] = \sum_\mu V^L_{\mu\mu}$$

Using Eq. (26) and the explicit form of the matrices A_k (Eq. (28)) one obtains:

$$\sum_\mu V^L_{\mu\mu} = 5e^2 F_0(R_L) \tag{30}$$

Finally we have:

$$\langle\langle H_c \rangle\rangle_d = \sum_i \left\{ \tfrac{1}{5} n_d \sum_\mu g_{\mu i} \right\} \hat{n}_i + \sum_L e^2 n_d F_0(R_L) \sum_{l \in L} \hat{n}_l \tag{31}$$

Comparing Eqs. (31) and (19) we can see that the term $\langle\!\langle H_c \rangle\!\rangle_d$ changes the metal core attraction parameters by the formulae:

$$U_{ii}^{eff} = U_{ii} + \tfrac{1}{5} n_d \sum_{\mu} g_{\mu i} \tag{32}$$

$$V_{LM}^{eff} = V_{LM} - e^2 n_d F_0(R_L) \tag{33}$$

According to Eq. (32), attraction of 4*s*- and 4*p*-electrons to the metal core is reduced by the Coulomb interaction with *d*-electrons of the same atom. The second term in Eq. (33) describes the screening of the metal core by *d*-electrons.

2.3. *Derivation of H_d^{eff} (Eq. 17)*

The operator H_d has the form:

$$H_d = U_{dd} \sum_{\mu\sigma} d^{+}_{\mu\sigma} d_{\mu\sigma} + \sum_{\mu\nu\sigma} V^{core}_{\mu\nu} d^{+}_{\mu\sigma} d_{\nu\sigma} + \tfrac{1}{2} \sum_{\mu\nu\rho\eta} \sum_{\sigma\tau} (\mu\nu|\rho\eta) d^{+}_{\mu\sigma} d_{\nu\sigma} d^{+}_{\varrho\tau} d_{\eta\tau} \tag{34}$$

where $d^{+}_{\mu\sigma}$ ($d_{\mu\sigma}$) are the operators of creation (annihilation) of an electron with the spin projection σ in the μ-th real *d*-orbital; U_{dd} is the attraction parameter of *d*-electrons to the metal core; $V^{core}_{\mu\nu} = \langle \mu | V^{core} | \nu \rangle$ is the matrix element of the total interaction of *d*-electrons with all the ligand atom cores; $(\mu\nu|\varrho\eta)$ is the two-electron Coulomb integral.

The matrix element of the operator V^{core} for a pair of *d*-functions having the angular momentum projections *m* and *m'* has the form:

$$V^{core}_{mm'} = \langle m| - \sum_{L} \frac{Z_L e^2}{|r - R_L|} |m'\rangle = - \sum_{L} Z_L V^{L}_{mm'} \tag{35}$$

Here Z_L is the core charge of the ligand atom *L*.

According to Eq. (17) we average the operators H_c and H_{RR} over the ground-state wave function Φ_L of the ligand subsystem.

For $H_c^{(1)}$ one obtains an expression similar to Eq. (22):

$$\langle\!\langle H_c^{(1)} \rangle\!\rangle_L = \sum_{\mu,\nu} \sum_{\sigma} (J_{\mu\nu} - \tfrac{1}{2} K_{\mu\nu}) d^{+}_{\mu\sigma} d_{\nu\sigma} \tag{36}$$

where

$$J_{\mu\nu} = \sum_{i,j} P_{ij} (ij|\mu\nu); \qquad K_{\mu\nu} = \sum_{i,j} P_{ij} (i\mu|j\nu)$$

Here P_{ij} is the matrix element of the one-electron density matrix of the ligand subsystem.

Applying the following condition to the one-center two-electron integrals on the metal atom:

$$(ij|\mu\nu) = \delta_{ij} \delta_{\mu\nu} (ii|\mu\mu)$$

$$(i\mu|j\nu) = \delta_{ij} \delta_{\mu\nu} (i\mu|i\mu)$$

we reduce Eq. (36) to the form:

$$\langle\!\langle H_c^{(1)} \rangle\!\rangle_L = \sum_{\mu} \sum_{i} g_{\mu i} P_{ii} \hat{n}_{\mu} \tag{37}$$

where $\hat{n}_\mu = \sum_\sigma d^{+}_{\mu\sigma} d_{\mu\sigma}$ is the electron number operator for the μ-th *d*-orbital.

For $H_c^{(2)}$ one has (see also Eq. (25)):

$$\langle\!\langle H_c^{(2)} \rangle\!\rangle_L = \sum_{\mu,\nu} \sum_{\sigma} \sum_{L} V^L_{\mu\nu} P_{LL} d^+_{\mu\sigma} d_{\nu\sigma} \qquad (38)$$

where $P_{LL} = \sum_{l \in L} P_{ll}$ is the electronic population on the ligand atom L.

Finally $\langle\!\langle H_c \rangle\!\rangle_L$ takes the form:

$$\langle\!\langle H_c \rangle\!\rangle_L = \langle\!\langle H_c^{(1)} \rangle\!\rangle_L + \langle\!\langle H_c^{(2)} \rangle\!\rangle_L = \sum_{\mu} \sum_{i} g_{\mu i} P_{ii} \hat{n}_\mu + \sum_{\mu,\nu} \sum_{\sigma} \sum_{L} V^L_{\mu\nu} P_{LL} d^+_{\mu\sigma} d_{\nu\sigma} \qquad (39)$$

The first term of this expression describes shifts of d-levels due to Coulomb interaction between d-electrons and electrons in the metal 4s- and 4p-orbitals. The second term is the contribution from the interaction with electrons in the valence AO's of the ligand atoms. The sum of the latter term and of the second term of Eq. (34) has the form of the operator of the crystal field induced by effective charges located on the ligand atoms:

$$V^{cf} = \sum_{m,m'} \sum_{\sigma} \sum_{L} (P_{LL} - Z_L) V^L_{mm'} d^+_{m\sigma} d_{m'\sigma} \qquad (40)$$

When the spatial symmetry of the ligand sphere is high enough, for example when there exists a C_n or S_n axis ($n > 3$), the operator V^{cf} becomes diagonal in the basis of the real d-orbitals (μ-basis):

$$V^{cf} = \sum_{\mu} \sum_{\sigma} \sum_{L} (P_{LL} - Z_L) V^L_{\mu\mu} d^+_{\mu\sigma} d_{\mu\sigma} \qquad (41)$$

The operator $\langle\!\langle H_{RR} \rangle\!\rangle_L$ also takes the most simple form in that basis (for derivation see Appendix A):

$$\langle\!\langle H_{RR} \rangle\!\rangle_L = \langle \Phi_L | H_{RR} | \Phi_L \rangle$$

$$= -\sum_{\sigma} \sum_{\mu j} \beta^2_{\mu j} \left\{ \frac{(1 - n_j/2)^2}{\Delta E_{\mu j}} - \frac{(n_j/2)^2}{\Delta E_{j\mu}} \right\} d^+_{\mu\sigma} d_{\mu\sigma} - \sum_{\sigma} \sum_{\mu j} \beta^2_{\mu j} \frac{(n_j/2)^2}{\Delta E_{j\mu}} \qquad (42)$$

where n_j is the number of electrons in the j-th ligand MO ($n_j = 0$ or 2); $\Delta E_{\mu j}$ ($\Delta E_{j\mu}$) is the energy necessary to transfer an electron from the μ-th d-orbital (from the j-th MO) to the j-th MO (to the μ-th d-orbital).

As a result, the Hamiltonian H_d^{eff} becomes:

$$H_d^{eff} = C + \sum_{\mu\sigma} U^{eff}_{\mu\mu} d^+_{\mu\sigma} d_{\mu\sigma} + \tfrac{1}{2} \sum_{\mu\nu\varrho\eta} \sum_{\sigma\tau} (\mu\nu | \rho\eta) d^+_{\mu\sigma} d_{\nu\sigma} d^+_{\varrho\tau} d_{\eta\tau}$$

where $C = \text{const}$ and the effective core attraction parameters for metal d-electrons $U^{eff}_{\mu\mu}$ contain the corrections originating both from the Coulomb and the resonance interaction with the ligand subsystem:

$$U^{eff}_{\mu\mu} = U_{dd} + W_\mu^{\text{ion}} + W_\mu^{\text{cov}} \qquad (43)$$

Here the ionic term is:

$$W_\mu^{\text{ion}} = \sum_{i \in s,p} g_{\mu i} P_{ii} + \sum_{L} (P_{LL} - Z_L) V^L_{\mu\mu} \qquad (44)$$

and the covalent term is:

$$W_\mu^{\text{cov}} = -\sum_{j}^{(MO)} \beta^2_{\mu j} \left\{ \frac{(1 - n_j/2)^2}{\Delta E_{\mu j}} - \frac{(n_j/2)^2}{\Delta E_{j\mu}} \right\} \qquad (45)$$

Thus we derive simple expressions for effective parameters of the Hamiltonian for isolated *d*-electrons. These formulae contain contributions from the Coulomb interactions between *d*-electrons and electrons in the ligands and account the resonance interactions between *d*- and ligand subsystems perturbatively according to the contribution (c) formulated above in the Introduction.

3. Implementation of the theory

In the previous section we derived general formulae for the effective Hamiltonians of the subsystems. To carry out particular calculations, some parameterization scheme for the effective Hamiltonians is to be chosen. In general the *ab-initio* level may be accepted for both the ligand and *d*-subsystem. However, *ab-initio* calculations are too cumbersome for complex molecules and some semiempirical level of approximation, for both the ligand subsystem and *d*-subsystem seems to be reasonable to be used.

In this section we describe a possible way to implement the above theory for TMC and discuss the calculated results for a number of TMC. Particular emphasis is put on the reproduction of the spin and symmetry properties of the ground state and *d*-*d*-spectra of TMC.

3.1. Parameterization

3.1.1. Parameterization of H_L^{eff}. As it is noted above, the electron correlation effects in the ligand subsystem of TMC are not as important as those in the *d*-subsystem. Thus for the ligand subsystem we have accepted the single configuration self-consistent-field approximation. As a base for parameterization of the effective Fock operator F_L^{eff} for the ligand subsystem we use the CNDO/2 scheme. For the ligand atoms (C, N, O, F, H etc.) the system of CNDO/2 parameters [37] is used. In effect only the parameters for metal 4*s*- and 4*p*-orbitals and for their interaction with ligand atoms are to be parameterized.

Let us express the core attraction parameters U_{ss}^{eff} and U_{pp}^{eff}, entering into both H_L^{eff} and F_L^{eff}, in terms of quantities used in the CNDO method. For transition metal atoms (Mn through Ni) we assume the valence state configuration s^2d^n. Then the parameters U_{ss} and U_{pp} are given by [29]:

$$U_{ss} = -\tfrac{1}{2}(I_s + A_s) - g_{sp}/2 - g_{ss} - n_d g_{sd} \tag{46}$$

$$U_{pp} = -\tfrac{1}{2}(I_p + A_p) - 3g_{sp}/2 - n_d \bar{g}_{pd} \tag{47}$$

Here $\frac{1}{2}(I_s - A_s)$ and $\frac{1}{2}(I_p + A_p)$ are the orbital electronegativities (OE) of the metal 4*s*- and 4*p*-orbitals, respectively; g_{ss}, g_{sp}, g_{pp}, and $\bar{g}_{pd} = \frac{1}{5}\sum_\mu g_{p\mu}$ are the Coulomb repulsion parameters which are related to the Slater–Condon factors F^k and G^k [38] by simple formulae [27]. These OE are used in the calculations provided that the ionization potentials and the electron affinities for *s* and *p* orbitals I_s, A_s, and I_p, A_p are defined by the following relations:

$$\begin{aligned} -I_s &= E(s^2d^n) - E(sd^n) \\ -A_s &= E(s^2pd^n) - E(spd^n) \\ -I_p &= E(spd^n) - E(sd^n) \\ -A_p &= E(s^2pd^n) - E(s^2d^n) \end{aligned} \tag{48}$$

where *E*'s are averaged energies of the configuration indicated in the brackets.

The choice of the valence state configurations in Eq. (48) is enforced by the structure of the proposed model. The model implies a fixed number of electrons in the d-shell of the transition metal atom. Therefore we retain only the valence-state configurations with the given number of d-electrons n.

Substituting the U_{ii} terms in Eq. (32) by the expressions for U_{ss} and U_{pp}, Eqs. (46), (47), we have:

$$U_{ss}^{eff} = -\tfrac{1}{2}(I_s + A_s) - g_{sp}/2 - g_{ss} \tag{49}$$

$$U_{pp}^{eff} = -\tfrac{1}{2}(I_p + A_p) - 3g_{sp}/2 \tag{50}$$

These coincide with the standard CNDO/INDO formulae for U_{ss} and U_{pp}, Eqs. (46), (47), where the terms, describing the Coulomb interaction of electrons in the $4s$-, $4p$-orbitals with d-electrons, discarded. Hence we can use the values of the OE for the $4s$- and $4p$-AO's of the metal atoms of the first transition row, which have been adjusted in Ref. [29] to reproduce the results of *ab-initio* HFR calculations of diatomics including transition metal atoms. For the Coulomb repulsion parameters g_{ij} we use the values which have been found by Oleari et al. [39] from atomic spectroscopy data.

According to the standard rules of the CNDO method, the expression for the metal-ligand interaction parameter V_{LM} will be:

$$V_{LM} = Z_M \gamma_{LM} \tag{51}$$

where Z_M is the core charge of the metal atom M, γ_{LM} is the two-center Coulomb integral. Hence:

$$V_{LM}^{eff} = Z_M \gamma_{LM} - e^2 n_d F_0(R_L) \tag{52}$$

We approximate the two-center integral γ_{LM} by the isotropic part of the crystal field potential:

$$\gamma_{LM} = e^2 F_0(R_L) Y_0^0(\theta_L, \phi_L) A_0^{mm} = e^2 F_0(R_L) \tag{53}$$

For the metal-ligand distances characteristic for TMC (2 Å) this approximation is valid [40]. As a result, the expression Eq. (33) takes the form:

$$V_{LM}^{eff} = Z_M^{eff} \gamma_{LM} \tag{54}$$

where $Z_M^{eff} = Z_M - n_d$ is the effective core charge of the metal atom. It means that electrons in the ligands experience only a part of the total metal core charge (namely Z_M^{eff}). The remaining part of the core charge is considered to be completely screened by the d-electrons.

The remaining parameters are chosen as follows. For the Slater $4s$- and $4p$-orbitals of transition metal atoms Burns' exponents ($\zeta_{4s} \neq \zeta_{4p}$) are used as it was done in Ref. [41]. For two-center resonance integrals the standard Pople's approximation [37]:

$$\beta_{ij} = -(\beta_i^0 + \beta_j^0) S_{ij}/2, \quad i \in A, j \in B$$

is used (S_{ij} is an overlap integral). The resonance parameters β_{4s}^0 and β_{4p}^0 for transition metal atoms are set equal to valence ionization potentials of the corresponding orbitals [41]. Our choice of $\beta_{4s}^0 \neq \beta_{4p}^0$ is done in a line with Labarre et al. [42, 43] to avoid overpopulation of the metal $4p$-orbitals which is inherent, for example, in calculations with use of Clack's resonance parameter set [44]. The one-center Coulomb interaction of electrons, occupying the metal $4s$- and $4p$-orbitals, is determined by the Slater–Condon parameters $F^0(ss)$,

$F^0(sp)$, and $F^0(pp)$ which are estimated from the corresponding Oleari parameters g_{ij} [39]:

$$\begin{aligned} &F^0(ss) = g_{ss}, \qquad F^0(pp) = (8g_{xy} + 7g_{pp})/15, \\ &F^0(sp) = [F^0(ss) + F^0(pp)]/2 \end{aligned} \tag{55}$$

3.1.2. Parameterization of H_d^{eff}. The parameters entering Eqs. (44) and (45) are chosen as follows. The one-center two-electron Coulomb integrals $g_{\mu i}$ are taken from Ref. [39]. The one-center core attraction parameters U_{dd} were estimated by a numerical fit of the ionization potentials (I_d^{exp}) of $3d$-electrons from the free doubly charged transition metal ions [45] to the calculations within the Oleari scheme [39]:

$$U_{dd} = -I_d^{\text{exp}} - (n_d - 1)g_{dd} \tag{56}$$

The two-center integrals $V_{\mu\mu}^L$ are calculated by the formula Eq. (29). When evaluating the radial integrals $F_k(R_L)$ the Slater $3d$-orbitals with the Burns' exponents [41] were taken.

The excitation energies entering the denominators of Eq. (42) are the energies of the electron transfer between the subsystems. In the mean field approximation they are estimated as follows:

$$\begin{aligned} \Delta E_{\mu j} &= I_\mu + \epsilon_j - G_{\mu j} \\ \Delta E_{j\mu} &= -\epsilon_j - A_\mu - G_{\mu j} \end{aligned} \tag{57}$$

Here ϵ_j is the orbital energy of the j-th MO in the ligand subsystem. The MO energies are obtained from the solution of the Hartree–Fock equations with the effective Fock operator F_L^{eff} derived from the effective Hamiltonian H_L^{eff} without the $\langle\!\langle H_{RR} \rangle\!\rangle_d$ term; $G_{\mu j}$ is the energy of the Coulomb interaction between an electron and a hole which are located on the μ-th d-orbital and the j-th ligand MO. The latter has the form:

$$G_{\mu j} = \sum_i c_{ji}^2 g_{\mu i} + \sum_L V_{\mu\mu}^L \sum_{l \in L} c_{jl}^2 \tag{58}$$

where c_{ji} are the LCAO coefficients, i runs over the metal $4s$- and $4p$-orbitals, l runs over the ligand atomic orbitals.

Quantities I_μ and A_μ are respectively the ionization potential and the electron affinity of the μ-th d-orbital, which we estimate in the mean field approximation provided the complex is described by the Hamiltonian H_0:

$$\begin{aligned} I_\mu &= -U_{dd} - W_\mu^{\text{ion}} - (n_d - 1)g_{dd} \\ A_\mu &= -U_{dd} - W_\mu^{\text{ion}} - n_d g_{dd} \end{aligned} \tag{59}$$

The resonance integrals between the μ-th d-orbital and the j-th MO of the ligand subsystem $\beta_{\mu j}$ are calculated by the formula:

$$\beta_{\mu j} = \sum_k c_{kj} \beta_{\mu k} \tag{60}$$

where c_{kj} are the LCAO coefficients for the j-th MO; $\beta_{\mu k}$ are the resonance integrals for the μ-th d-AO and the k-th AO in the ligand subsystem. For interatomic resonance integrals $\beta_{\mu k}$, the formula resembling that of the MINDO/3 method [46] is used:

$$\beta_{\mu k} = -(I_d + I_k) S_{\mu k} \beta^{M-L}, \quad \mu \in M, k \in L \tag{61}$$

Here I_d and I_k are the valence ionization potentials [41] of d-AO and of the k-th AO; $S_{\mu k}$ is their overlap integral. The values of the dimensionless pair resonance parameters β^{M-L} are fitted to approximate the energy of the first observable d-d transition in the optical spectra of considered complexes. They are given in Table 1.

The Coulomb interaction parameters $(\mu\nu|\varrho\eta)$ are expressed through the Racah parameters A, B, C. The parameters A are set equal to the Oleari parameter g_{dd}. The parameters B and C are set equal to those for free transition metal ions [2] except the cases of MnF_6^{4-}, $Mn(FH)_6^{2+}$, $CoCl_6^{4-}$, and $CoCl_4^{2-}$. For these complexes the values of the parameters are taken from the corresponding spectroscopic data and used in our calculations.

The parameter set for transition metal atoms used in our calculations is given in Table 2.

Table 1. Pair resonance parameters $\beta^{M\text{-}L}$

	Mn	Fe	Co	Ni
F	1.225	1.431	1.826	1.775
Cl			1.588	

Table 2. Transition metal parameters (eV)

Parameter	Mn	Fe	Co	Ni
$\zeta(4s)$	1.450	1.575	1.700	1.825
$\zeta(4p)$	0.900	0.975	1.050	1.125
$\zeta(3d)$	2.935	3.152	3.369	3.586
$I(4s)$	6.820	7.060	7.310	7.560
$I(4p)$	3.590	3.720	3.840	3.840
$I(3d)$	7.930	8.670	9.420	10.040
$\chi(4s)^a$	3.983	4.120	4.170	4.306
$\chi(4p)^a$	0.975	1.062	1.160	1.260
$-U_{ss}$	61.220	72.600	84.500	96.920
$-U_{pp}$	49.240	58.540	68.270	78.430
$-U_{dd}$	92.490	107.490	129.790	153.130
$F^0(ss)$	7.090	7.380	7.670	7.690
$F^0(sp)$	6.200	6.430	6.660	6.880
$F^0(pp)$	5.950	6.100	6.250	6.400
$F^2(pp)$	1.271	1.333	1.395	1.457
$G^1(sp)$	1.060	1.116	1.172	1.227
g_{sd}	9.130	9.410	9.690	9.970
g_{z,z^2}	7.820	8.060	8.300	8.540
g_{x,z^2}	7.590	7.820	8.050	8.280
$g_{z,xz}$	7.740	7.980	8.220	8.460
$g_{z,xy}$	7.510	7.740	7.970	8.200
g_{dd}	14.700	15.370	16.040	16.710
B (cm^{-1})^b	860	917	971	1030
C (cm^{-1})^b	3850	4040	4497	4850

[a] $\chi_i = (I_i + A_i)/2$

[b] These values correspond to free double charged ions [2]

3.2. Calculation results and discussion

In our method the ground-state wave function of a complex is an external product of the Slater determinant function of the ligand subsystem, which is found by a SCF calculation, and of the ground-state function of *d*-electrons which is determined by diagonalization of the effective Hamiltonian H_d^{eff} in the complete basis of n_d-electron functions. The wave functions of the lowest excited states are the external products of the ligand ground-state determinant function and of the corresponding eigenfunctions of the effective Hamiltonian H_d^{eff}. The transition energies are equal to the differences of the corresponding eigenvalues of H_d^{eff} which are obtained by the diagonalization of the latter.

In this paper we applied the proposed semiempirical scheme to simple divalent transition metal complexes in order to check the validity of the approximations accepted. The chosen complexes are octahedral hexafluoroanions MF_6^{4-} (M = Mn, Fe, Co, Ni), complex cation $Mn(FH)_6^{2+}$, octahedral anion $CoCl_6^{4-}$, and tetrahedral anion $CoCl_4^{2-}$. There are reliable experimental data on the optical absorption spectra of these complexes [6, 47–49]. Also the calculations on the electronic structure of these complexes have been carried out on both *ab-initio* [50, 51] and semiempirical [44, 52] levels.

Geometry of the complexes MF_6^{4-} used in the calculations has been taken from Ref. [52]. The following bond lengths are assumed: R(Mn–F) = 2.12 Å, R(Fe–F) = 2.08 Å, R(Co–F) = 2.05 Å, R(Ni–F) = 2.01 Å. For the chlorocomplexes of divalent cobalt we use the experimental bond lengths: for $CoCl_6^{4-}$ R(Co–Cl) = 2.340 Å (as in $CoCl_2$ crystal [53]), and for $CoCl_4^{2-}$ R(Co–Cl) = 2.252 Å [51].

The present version of the proposed method is aimed at a detailed description of the *d*-subsystem, and particularly at *d*-*d*-excitations. The calculation results obtained for the MF_6^{4-} and $CoCl_6^{4-}$ complexes are presented in Tables 3 and 4, respectively. They are compared with experimental data obtained on the MnF_2, FeF_2, $KCoF_3$, $KNiF_3$, and $CoCl_2$ crystals. Such comparisons of the calculations performed for the finite clusters involving only first coordination sphere with *d*-*d*-spectra of transition metal ions in the ionic crystals is common practice. Moreover, it has been shown [54] by *ab-initio* MCSCF–CI calculation on $CoCl_4^{2-}$ that the *d*-*d* transition energies for the finite clusters are farily independent of the Madelung potential from the surrounding crystal. A similar conclusion can be drawn from the results of *ab-initio* SCF-CI calculations on various cluster models of the K_2CuF_4 crystal [55].

The values of the pair resonance parameters ($\beta^{M-F}, \beta^{M-Cl}$) are fitted to reproduce *d*-*d*-excitation energies for these complexes. They range between 1.2 and 1.8 (see Table 1) for various metal atoms. These values seem to be reasonable. Calculations with these parameters reproduce the point symmetry and the spin multiplicity of the ground state for all the complexes used for the fit. We nevertheless consider this result to be nontrivial because predictions of the ground-state multiplicity of TMC in the framework of the SCF approximation requires special efforts [27]. The calculated excitation energies are also in fair agreement with experimental data (see Tables 3, 4).

In order to check the transferability of the resonance parameters β^{M-L}, we calculated *d*-*d*-excitation energies for the dication $Mn(FH)_6^{2+}$ and the tetrahedral chloroanion $CoCl_4^{2-}$.

There is no direct experimental data on the molecular structure of $Mn(FH)_6^{2+}$. This complex with hydrogen fluoride FH as a ligand has been

Table 3. *d-d* Excitation energies for the MF_6^{4-} complexes

Transition	$E^{\text{calc a}}$, cm^{-1}	$E^{\text{obs b}}$, cm^{-1}
	MnF_6^{4-}, ground state $^6A_{1g}$	
$^6A_{1g} \rightarrow {}^4T_{1g}$	19451	19440
$\rightarrow {}^4T_{2g}$	22869	23500
$\rightarrow {}^4A_{1g}; {}^4E_g$	25295	25300
$\rightarrow {}^4T_{2g}(D)$	28407	28120
$\rightarrow {}^4E_g(D)$	30223	30230
$\rightarrow {}^4T_{1g}(P)$	35144	33060
	Fe_6^{4-}, ground state $^5T_{2g}$	
$^5T_{2g} \rightarrow {}^5E_g$	6987	6990 (10600)
	Co_6^{4-}, ground state $^4T_{1g}$	
$^4T_{1g} \rightarrow {}^4T_{2g}$	7150	7150
$\rightarrow {}^4A_{2g}$	15407	15200
$\rightarrow {}^4T_{1g}$	20607	19200
	NiF_6^{4-}, ground state $^3A_{2g}$	
$^3A_{2g} \rightarrow {}^3T_{2g}$	7236	7250
$\rightarrow {}^3T_{1g}$	12316	12530
$\rightarrow {}^1E_g$	17158	15440
$\rightarrow {}^1T_{2g}$	23849	20920
$\rightarrow {}^3T_{1g}(P)$	24842	23810

[a] For MnF_6^{4-} the values of Racah parameters $B = 704\,cm^{-1}$ and $C = 3651\,cm^{-1}$ are obtained from two transition energies which are independent of $10\,Dq$: $E(^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g) = 10B + 5C$ and $E(^6A_{1g} \rightarrow {}^4E_g(D)) = 17B + 5C$

[b] From Ref. [6]

Table 4. *d-d* Excitation energies for the $CoCl_6^{4-}$ complex

Transition	$E^{\text{calc a}}$, cm^{-1}	$E^{\text{obs b}}$, cm^{-1}
	$CoCl_6^{4-}$, ground state $^4T_{1g}$	
$^4T_{1g} \rightarrow {}^4T_{2g}$	6600	6600
$\rightarrow {}^2E_g$	8447	—
$\rightarrow {}^4A_{2g}$	14167	13300
$\rightarrow {}^2T_{1g}$	14420	—
$\rightarrow {}^2T_{2g}$	14748	—
$\rightarrow {}^4T_{1g}$	17332	17150 (17350)

[a] The values of Racah parameters for $CoCl_6^{4-}$ ($B = 780\,cm^{-1}$ and $C = 3432\,cm^{-1}$) are taken from Ref. [48]

[b] From Ref. [48]

postulated [47] to explain the fact that the *d-d*-excitation spectrum of the Mn^{2+} in anhydrous hydrogen fluoride fairly fits to the CF picture for octahedrally coordinated d^5 ion (Mn^{2+}). The Raman spectra also give some evidence for HF coordination [47]. We set the bond lengths in octahedral $Mn(FH)_6^{2+}$ as follows: $R(Mn\text{–}F) = 2.15$ Å, $R(F\text{–}H) = 0.83$ Å. The results of our calculation on *d-d-*

Table 5. *d*-*d* Excitation energies for $\mathrm{Mn(FH)_6^{2+}}$ and $\mathrm{CoCl_4^{2-}}$

Transition	$E^{\mathrm{calc}\,a}$, $\mathrm{cm^{-1}}$	$E^{\mathrm{obs}\,b}$, $\mathrm{cm^{-1}}$
	$\mathrm{Mn(FH)_6^{2+}}$, ground state $^6A_{1g}$	
$^6A_{1g} \rightarrow {}^4T_{1g}$	23772	22700
$\rightarrow {}^4T_{2g}$	25219	24700
$\rightarrow {}^4A_{1g}, {}^4E_g$	25645	25800
$\rightarrow {}^4T_{2g}$	30123	30800
$\rightarrow {}^4E_g$	30776	29800
$\rightarrow {}^4T_{1g}$	32449	—
$\rightarrow {}^4A_{2g}$	41767	—
$\rightarrow {}^4T_{1g}$	41963	42200
	$\mathrm{CoCl_4^{2-}}$, ground state $^4A_2$	
$^4A_2 \rightarrow {}^4T_2$	4413	—
$\rightarrow {}^4T_1(F)$	7571	5220–5700
$\rightarrow {}^2E$	14375	14600–14800
$\rightarrow {}^2T_1$	14917	—
$\rightarrow {}^4T_1(P)$	16318	15750(16230)

[a] The values of the Racah parameters for $\mathrm{Mn(FH)_6^{2+}}$ ($B = 733\ \mathrm{cm^{-1}}$ and $C = 3663\ \mathrm{cm^{-1}}$) are taken from Ref. [47]; the values for $\mathrm{CoCl_4^{2-}}$ ($B = 710\ \mathrm{cm^{-1}}$ and $C = 3290\ \mathrm{cm^{-1}}$) are taken from Ref. [49]

[b] $\mathrm{Mn(FH)_6^{2+}}$: from Ref. [47]; $\mathrm{CoCl_4^{2-}}$: from Ref. [49]

spectrum of the $\mathrm{Mn(FH)_6^{2+}}$ moiety with the $\beta^{Mn\text{-}F}$ parameter adjusted for the $\mathrm{MnF_6^{4-}}$ anion are presented in Table 5. As it can be seen, the calculated *d*-*d*-spectrum coincides fairly with the observed one. This can be taken as additional evidence for HF coordination.

The predicted spatial symmetry and spin multiplicity of the ground state and calculated excitation energies of the $\mathrm{CoCl_4^{2-}}$ anion also coincide fairly well with those from the experiment [49] (see Table 5) though the $\beta^{Co\text{-}Cl}$ parameter was adjusted to reproduce *d*-*d*-excitation spectra of the $\mathrm{CoCl_6^{4-}}$ anion. The calculations on the mixed-ligand complexes, testing the transferability of the resonance parameters systematically, are still in progress.

In order to elucidate the nature of *d*-level splitting in the complexes considered, we compared the ionic and the covalent contributions to the calculated crystal field splitting parameter $10Dq$. It follows from Eq. (43) that the splitting parameter is related to the effective parameters of H_d^{eff} by the formula:

$$10Dq = (W_{e_g}^{\mathrm{ion}} - W_{t_{2g}}^{\mathrm{ion}}) + (W_{e_g}^{\mathrm{cov}} - W_{t_{2g}}^{\mathrm{cov}}) = 10Dq^{\mathrm{ion}} + 10Dq^{\mathrm{cov}} \qquad (62)$$

where t_{2g} and e_g are the symmetry indices for *d*-orbitals in the field of cubic symmetry. The results of the calculations are given in Table 6. The ionic contribution is quite small for all the considered complexes. Similar results were obtained by Hubbard et al. [34]. Their calculations of $\mathrm{NiF_6^{4-}}$ give the value of $1390\ \mathrm{cm^{-1}}$ for the ionic contribution to $10Dq$. This value comes to only 22 percent of the total. Our estimate of the ionic contribution for $\mathrm{NiF_6^{4-}}$ is about twice as low ($647\ \mathrm{cm^{-1}}$), because we use more localized atomic *d*-functions than those of Ref. [34]. These results confirm that the point ion model does not suffice even to describe such complexes as transition metal hexafluoroanions which can

Table 6. Ionic (Δ^{ion}) and covalency (Δ^{cov}) contributions to the *d*-level splitting Δ (cm^{-1})

	MnF_6^{4-}	FeF_6^{4-}	CoF_6^{4-}	NiF_6^{4-}	$Mn(FH)_6^{2+}$	$CoCl_6^{4-}$	$CoCl_4^{2-}$
Δ^{ion}	1246	1050	805	647	265	403	187
Δ^{cov}	7208	5937	7452	6568	3600	7154	4226
Δ^{total}	8454	6987	8257	7215	3865	7557	4413
Δ^{expt}	7750[a]	—	8050[a]	7250[a]	5128[b]	6900[a]	3130[c]

[a] From Ref. [6]
[b] From Ref. [47]
[c] From Ref. [49]

seem to be purely ionic at the first glance. The covalent contributions to 10*Dq* which are presented in Table 6 are about 90 percent of the total splitting for all the considered complexes. Thus the resonance interaction in our method plays a decisive role in the splitting of the *d*-levels in TMC. This conclusion is also confirmed by *ab-initio* calculations with use of many-body perturbation theory developed in Refs. [56, 57]. For MnF^+ diatomic it has been shown [58] that the leading contributions to the crystal field parameters of *d*-electrons arise from the second-order terms of perturbation series describing the corrections from the excitations transferring an electron from the ligand orbitals to the manganese 3*d*-orbitals (covalent contribution).

The covalent contributions to the *d*-level splitting arise from the interactions with charge transfer (CT) states of TMC (i.e., from the virtual charge transfer). The importance of these interactions has also been stressed by Janssen and Nieuwpoort [49]. They have demonstrated that the inclusion of the configuration interaction with the CT states in the *ab-initio* calculation scheme leads to substantial increase of the effective *d*-level splitting which is always underestimated at the Hartree–Fock level. In the framework of our method this interaction renormalizes the one-electron parameters of the Hamiltonian for isolated *d*-electrons or, in other words, changes the *d*-orbital energies. The virtual charge transfer from the metal *d*-orbitals to the ligand subsystem MO's lowers the *d*-orbital energy, whereas the virtual transfer in the opposite direction increases it. In Table 7 the most significant contributions from the CT states to the *d*-level splitting are presented.

In the case of the MF_6^{4-} anions, these states are generated by the electron transfer from the HOMO which is composed of the fluorine p_σ-orbitals to the metal *d*-orbitals of the e_g symmetry. In the case of the $Mn(FH)_6^{2+}$ cation, there are two "ligand-to-metal" CT states which contribute to $\langle\!\langle H_{RR} \rangle\!\rangle$. The first one is generated by the electron transfer from the occupied MO which is composed of the fluorine p_σ-orbitals to the metal *d*-orbitals of e_g symmetry. The second one is generated by the electron transfer from the occupied MO which is composed of the fluorine p_π-orbitals to the metal *d*-orbitals of t_{2g} symmetry and gives the small contribution because of the low value of the corresponding resonance integral (see Table 7). Thus, for both MF_6^{4-} anions and $Mn(FH)_6^{2+}$ cation the covalent contribution to the 10*Dq* is mainly determined by the virtual charge transfer from the fluorine p_σ-orbitals to the metal *d*-orbitals of the e_g symmetry. For the $CoCl_6^{4-}$ anion, a similar qualitative picture is obtained. However, as distinct from the fluorocomplexes, in the case of $CoCl_6^{4-}$, there are noticeable contributions to the splitting from the virtual charge transfer from metal

Table 7. The energies ΔE_{if} (eV) of the 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 ($i \to f$)	ΔE_{if}	$\lvert\beta_{if}\rvert$	$\beta^2/\Delta E$
MnF_6^{4-}	HOMO(p_σF) $\to d(e_g)$	7.27	2.22	5469
FeF_6^{4-}	HOMO(p_σF) $\to d(e_g)$	11.75	2.46	4194
CoF_6^{4-}	HOMO(p_σF) $\to d(e_g)$	9.80	2.61	5646
NiF_6^{4-}	HOMO(p_σF) $\to d(e_g)$	8.42	2.10	4194
$Mn(FH)_6^{2+}$	MO(p_πF) $\to d(t_{2g})$	12.12	0.58	225
	MO(p_σF) $\to d(e_g)$	14.58	2.21	2700
$CoCl_6^{4-}$	MO(p_πCl) $\to d(t_{2g})$	11.00	1.01	749
	HOMO(p_σCl) $\to d(e_g)$	9.30	2.86	7109
	$d(t_{2g}) \to$ Mo(dCl)	14.37	0.99	−550
	$d(e_g) \to$ MO(dCl)	15.60	1.72	−1536
$CoCl_4^{2-}$	MO(p_πCl) $\to d(e)$	8.49	1.03	1004
	MO(s_σCl) $\to d(t_2)$	23.22	1.81	1134
	HOMO(p_πCl) $\to d(t_2)$	7.64	2.21	5147
	$d(t_2) \to$ MO($\sigma^*\pi^*$)	11.97	1.05	−735
	$d(t_2) \to$ MO(dCl)	16.67	1.26	−772

d-orbitals to unoccupied d-orbitals of chlorine atoms. It indicates a weak bonding between metal d-orbitals and chlorine ones. In the case of the $CoCl_4^{2-}$ anion, the main contribution to the stabilization energy of metal d-orbitals of tetrahedral t_2 symmetry (d_{xz}, d_{yz}, d_{xy}) arises from virtual charge transfer to these orbitals from low-lying MO involving s-orbitals of chlorine atoms and from HOMO involving p_π-orbitals of chlorine atoms. Partial stabilization of metal t_2-orbitals arises from virtual charge transfer from these ones to unoccupied MO's of σ^* and π^* types, and also to MO's involving d-orbitals of chlorine atoms.

The results of the calculations on the ligand subsystem of the considered complexes also deserve some attention. They are given in Table 8 compared with the results of some semiempirical [27, 44, 52] and *ab-initio* [50, 51] calculations on TMC. In the framework of the proposed method, HFR calculations on the ligand subsystem give only intermediate results. Strictly speaking they are only internal quantities in our method. Nevertheless, we compare these data with those obtained in all-valence electron calculations for two reasons. First, these results seem to be reasonable and thus indicate internal consistency of the method. And second, such a comparison shows an extent of influence of the metal d-electrons on the charge distribution in the ligand subsystem.

Electronic populations on the metal atomic orbitals reflect the extent of the charge transfer from the ligands to the metal, which turns out to be neither very large nor very small. This is in accordance with the well-known Pauling electroneutrality principle which states that the absolute values of effective charges on the atoms in a molecule do not exceed unity. The trends of the effective atomic charges and orbital populations observed in the present work for the hexafluoro anions coincide with those known from previous calculations [44, 52]. However, there are sufficient differences between the orbital occupancies calculated by the different methods. The very large occupancies of the metal 4s- and 4p-orbitals and, respectively, too small effective positive charges on the

Table 8. Electronic structure of the ligand subsystem of a number of transition metal complexes

	MnF_6^{4-}	FeF_6^{4-}	CoF_6^{4-}	NiF_6^{4-}	$Mn(FH)_6^{2+}$	$CoCl_6^{4-}$	$CoCl_4^{2-}$
Energy gaps ϵ(LUMO) − ϵ(HOMO) (eV):							
$\Delta\epsilon$	16.85	18.32	19.43	20.45	25.53	16.91	16.22
Metal orbital populations:							
4*s*	0.36	0.38	0.39	0.40	0.21	0.481	0.537
	0.48^{a}	0.51^{a}	0.53^{a}	0.55^{a}			0.290^{d}
				0.07^{c}			0.444^{e}
4*p*	0.25	0.26	0.28	0.29	0.11	0.359	0.342
	0.41^{a}	0.47^{a}	0.44^{a}	0.49^{a}			0.170^{d}
				0.06^{c}			0.328^{e}
Atomic charges:							
M	0.89	0.83	0.78	0.72	1.44	0.442	0.437
	0.17^{a}	0.06^{a}	-0.03^{a}	-0.12^{a}			1.360^{d}
	-0.89^{b}	-0.53^{b}	-0.71^{b}	-0.76^{b}		-1.254^{b}	0.422^{e}
				1.82^{c}			
X	−0.82	−0.80	−0.80	−0.79	−0.25	−0.740	−0.609
	-0.52^{b}	-0.57^{b}	-0.55^{b}	-0.54^{b}		-0.456^{b}	-0.840^{d}
				-0.97^{c}			-0.606^{e}

[a] CNDO [52]
[b] INDO [44]
[c] *ab initio* [50]
[d] *ab initio* [51] (Mulliken population analysis)
[e] INDO/1 UHF [27]

metal atom (sometimes the negative ones) obtained by the semiempirical methods with use of Clack's parameter set [44, 52] seem to be unreliable. In contrast, the *ab-initio* calculations [50] yield very small occupancies of the metal 4*s*- and 4*p*-orbitals and effective charges on the metal atom close to +2 (free ion charge). From our point of view these calculations underestimate the charge transfer from the ligands to the metal 4*s*- and 4*p*-orbitals. Our calculations of the orbital occupancies in the ligand subsystem of $CoCl_4^{2-}$ (without *d*-electrons) are in good agreement with the results of all-valence INDO/1 calculations with thoroughly elaborated parameterization by Bacon and Zerner [27].

It is worthwhile to note that though the electron distribution (in the ligand subsystem) within our approach is close to that obtained in the HFR-based INDO/1 approximation [27], the total pictures of the electronic structure of TMC in the two approaches are completely different. The charge distribution in $CoCl_4^{2-}$ has been obtained in [27] with the HFR wave function which violates the *Aufbauprinzip* (see the Introduction). In the framework of our approach, the HFR wave function for the ligand system (Φ_L) obeys the *Aufbauprinzip*. For all the considered complexes, the energy gaps between the lowest unoccupied MO (LUMO) and the highest occupied MO (HOMO) of the ligand subsystem (see Table 8) are large as compared to the *d*-*d*-excitation energies. This confirms our assumption that the excited configurations of the ligand subsystem do not interfere significantly in ground and lower excited states of the complexes. The gaps in the energy spectrum of the ligand subsystem are also large as compared to any two-electron interaction matrix element between the Φ_L state and excited states of the ligand subsystem, thus providing a certain assurance for the stability of the HFR state of the ligand subsystem. At the same time, *d*-electrons which caused instabilities in the HFR-based methods are treated as a separate subsystem and the electron-electron repulsion in that subsystem is taken into account exactly (within the CI scheme).

4. Conclusions

In this paper a new treatment of the electronic structure of TMC, invoking the effective Hamiltonian method, is presented. Earlier a similar method was used by Hubbard et al. (Ref. [34]) to describe the electronic structure of the crystals of $KNiF_3$ and $KMnF_3$. The method of Ref. [34] takes into account both the effects of weak covalency and electron correlation with use of the configuration interaction method. The wave function of the system was assumed to have the form of a ground-state configuration $M^{2+}F_6^-$ in which the number of *d*-electrons in the metal atom is fixed with small admixture of the $M^+FF_5^-$ configurations in which one electron is transferred from the fluorine atoms to the *d*-shell of the metal atom. With use of the effective Hamiltonian technique the problem was reduced to the crystal field model with an effective potential taking into account the interactions with charge-transfer states. The numerical calculations were performed at *ab-initio* level and quite reasonable results for the splitting of one-electron *d*-levels of the transition metal ion were obtained [34]. Recently, these ideas were used in the *ab-initio* calculations [55, 59] of TMC with extended CI for selection of more important electronic configurations. It turns out that namely the excited configurations within the *d*-shell of the transition metal atom and the single excited ligand-to-metal CT configurations are to be included in the CI manifold to obtain consistent results for the transition energies.

The main difference between our model and that used in Ref. [34] is concerned with involvement of the metal outer valence *s*- and *p*-orbital into metal-ligand bonding. In Ref. [34] these orbitals are left out of consideration, whereas in our model they play an important role in the formation of the bonding MOs delocalized over the whole complex. The important role of the metal outer valence *s*-orbital has also been stressed by Ohanessian and Goddard [60]. They considered bonding in transition metal hybride diatomic cations MH^+. As it follows from the results of *ab-initio* GVB calculations reviewed in Ref. [60], the M–H bond in these molecules is formed by the spin-pairing of an unpaired electron in the metal outer valence *s*-orbital with an electron in the hydrogen 1*s*-orbital. The spin and symmetry of the ground state of the transition metal hydride cations are completely determined by the arrangement of electrons in the *d*-shell of transition metal ion, which in its turn minimizes the total Coulomb repulsion. It should be noted that, according to Ref. [60], the electronic configuration of the transition metal ion in its hydride cations is s^1d^{n-1}. That is not surprising from the viewpoint of the total energy for those metal ions which have this configuration in their ground states, but the singly charged metal ions having in their ground state d^n configuration are promoted to the lowest s^1d^{n-1} excited state when the MH^+ molecule is formed. Thus, in transition metal hydride cations the outer valence *s*- and *p*-orbitals of transition metal ion and valence orbitals of ligands are mainly involved in the bond formation. This is likely to be generally valid for other TMC with more complex ligands than the hydrogen atom.

In the framework of our present method the above picture of the electronic structure of MH^+ arises by construction. Indeed, the ligand and d-subystems in our method are separated. Moreover, the number of electrons in the metal d-shell coincides with that for the ground-state configuration of the free ion M^{2+} (it equals to the corresponding group number in the Periodic Table) and also with the number of d-electrons $(n-1)$ in the configuration s^1d^{n-1} of the ion M^+. The qualitative description of bonding in TMC in the framework of our model is also very similar to the GVB description. Specifically, in our method transition metal hydride cations could be considered as complexes of doubly charged ions M^{2+}, having as many d-electrons as in the ground-state configuration d^n of the free ion M^{2+}, with single hydride anion as a ligand. Two electrons originally occuping the $1s$-orbital of the hydride ion H^- will be delocalized over the molecule. The ligand wave function will be the closed-shell Slater determinant for two electrons on a σ-type bonding MO involving the $1s$-orbital of the hydrogen atom and outer valence s- (and p- in less extent) orbitals of transition metal atom. This MO being occupied describes the chemical bond between the transition metal atom and hydrogen atom. Electrons in the d-shell are by definition arranged to have a minimal Coulomb repulsion because their arrangement is obtained from diagonalization of the atomic-like CI Hamiltonian for d-electrons which also accounts for the splitting.

The proposed method might also be considered as a way to derive the widely used angular overlap model (AOM) [61–63], starting from the exact Hamiltonian for valence electrons Eq. (1). The proposed method gives formulas for the corrections to the d-orbital energies, which contain both the ionic and covalent terms. The latter have a form which closely resembles the perturbation expressions for the AOM parameters [62], though the terms obtained in our method are sums of contributions from MOs of the ligand subsystem rather than from separate ligands. Under certain conditions these MO contributions can be transformed to those from separate ligands as it should be in the AOM. The ligand contributions can be treated as estimates for the conventional AOM parameters $e_\lambda(L)$. We also luckily manage to avoid difficulties which arose in justifying the AOM approach from the first principles [64, 65]. Specifically, we manage to treat the density of d-electrons correctly. Our method takes into account both occupied ligand orbitals with corresponding destabilizing contributions to d-orbital energies and vacant ligand orbitals with corresponding stabilizing contributions. The common derivations of AOM involve only destabilizing contributions [65].

The present paper stresses the local character of d-shell in transition metal complexes. The proposed method can be implemented in different ways ranging from qualitative analysis of different contributions to the d-level splitting to *ab-initio* calculations with use of the proposed class of wave functions.

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Appendix A

The expression for the operator H_{RR} (Eq. (9)) at $E = E_0$ has the form of the second-order perturbation correction with H_r as perturbation:

$$H_{RR} = PH_rQR(E_0)QH_rP, \tag{A1}$$

where $R(E_0) \equiv (E_0Q - QH_0Q)^{-1}$ is the resolvent for the operator QH_0Q, E_0 is the ground-state energy of the Hamiltonian PH_0P. This becomes evident when the resolvent is rewritten in the following form [28]:

$$R(E_0) = \sum_i \frac{|i\rangle\langle i|}{E_0 - E_i} \tag{A2}$$

where $|i\rangle$ stands for the eigenfunctions of the operator QH_0Q with the eigenvalues E_i, $i = 1, \ldots, N_Q$ (N_Q is the dimension of the subspace defined by the projection operator Q or the dimension of the Q-block).

We define the basis functions of the Q-block as follows:

$$|i', \sigma', k, n_1\rangle = a^+_{i'\sigma'}|\Phi_L\rangle \wedge |\Phi_k(n_1)\rangle, \quad n_1 = n_d - 1 \tag{A3$'$}$$

$$|i', \sigma', l, n_2\rangle = a_{i'\sigma'}|\Phi_L\rangle \wedge |\Phi_l(n_2)\rangle, \quad n_2 = n_d + 1 \tag{A3$''$}$$

where $a^+_{i\sigma}$ ($a_{i\sigma}$) are operators of creation (annihilation) of an electron having the spin projection σ on the i-th MO; $|\Phi_L\rangle$ is the single determinant wave function of the ground state of the ligand subsystem, obtained from the SCF-type calculation; $|\Phi_k(n_1)\rangle$ and $|\Phi_l(n_2)\rangle$ are single determinant wave functions of n_1 and n_2 d-electrons, respectively:

$$|\Phi_k(n_1)\rangle = \prod_{\alpha=1}^{n_1} d^+_{\mu_\alpha\sigma_\alpha}|0\rangle, \quad k = k(\mu_1\sigma_1 \cdots \mu_{n_1}\sigma_{n_1})$$

$$|\Phi_1(n_2)\rangle = \prod_{\alpha=1}^{n_2} d^+_{\nu_\alpha\tau_\alpha}|0\rangle, \quad l = l(\nu_1\tau_1 \cdots \nu_{n_2}\tau_{n_2}),$$

$d^+_{\mu\sigma}$ are the operators of creation of an electron having the spin projection σ on the μ-th d-AO; $|0\rangle$ is the vacuum state for d-electrons. The basis functions of Eqs. (A3′) and (A3″), respectively, describe the states with one extra electron in the ligand subsystem or in the d-subsystem.

To simplify the subsequent evaluation let us neglect the configuration interaction between the functions of the Q-block. Henceforth, Eqs. (A3′) and (A3″) became the eigenfunctions of the operator QH_0Q. As we are not interested in the detailed description of the charge transfer states this assumption is acceptable.

The resonance operator H_r has the form:

$$H_r = \sum_{\sigma} \sum_{\mu,j} \beta_{\mu j}(d^+_{\mu\sigma} a_{j\sigma} + a^+_{j\sigma} d_{\mu\sigma})$$

where j runs through the ligand MO's, $\beta_{\mu j}$ is the resonance integral between the μ-th d-orbital and the j-th ligand MO. Then H_{RR} takes the form:

$$\begin{aligned} H_{RR} = \sum_{\sigma,\tau} \sum_{\mu,\nu} \sum_{i,j} \beta_{\mu i}\beta_{\nu j} \Bigg\{ & P d^+_{\mu\sigma} a_{i\sigma} Q \sum_{i'\sigma'} \sum_{k} \frac{a^+_{i'\sigma'}|\Phi_L\rangle \wedge |\Phi_k(n_1)\rangle\langle\Phi_k(n_1)| \wedge \langle\Phi_L|a_{i'\sigma'}}{E_0 - E(i', \sigma', k, n_1)} \\ & \times Q a^+_{j\tau} d_{\nu\tau} P + P d_{\mu\sigma} a^+_{i\sigma} Q \sum_{i'\sigma'} \sum_{l} \frac{a_{i'\sigma'}|\Phi_L\rangle \wedge |\Phi_l(n_2)\rangle\langle\Phi_l(n_2)| \wedge \langle\Phi_L|a^+_{i'\sigma'}}{E_0 - E(i', \sigma', l, n_2)} \\ & \times Q a_{j\tau} d^+_{\nu\tau} P \Bigg\} \end{aligned}$$

As the Q-block basis functions are orthonormal, the first term in the braces contains only the states of the type of Eq. (A3′) and the second term contains only the states of the type of Eq. (A3″).

Averaging Eq. (A4) over the ground state of the ligand subsystem $|\Phi_L\rangle$ one obtains:

$$\begin{aligned} \langle\!\langle H_{RR} \rangle\!\rangle_L = \sum_{\sigma,\tau} \sum_{\mu,\nu} \sum_{i,j} \beta_{\mu i}\beta_{\nu j} \Bigg\{ & d^+_{\mu\sigma} \sum_{i'\sigma'} \left(\sum_{k} \frac{\langle a_{i\sigma} a^+_{i'\sigma'}\rangle |\Phi_k(n_1)\rangle\langle\Phi_k(n_1)| \langle a_{i'\sigma'} a^+_{j\tau}\rangle}{E_0 - E(i', \sigma', k, n_1)} \right) d_{\nu\tau} \\ & + d_{\mu\sigma} \sum_{i'\sigma'} \left(\sum_{l} \frac{\langle a^+_{i\sigma} a_{i'\sigma'}\rangle |\Phi_l(n_2)\rangle\langle\Phi_l(n_2)| \langle a^+_{i'\sigma'} a_{j\tau}\rangle}{E_0 - E(i', \sigma', l, n_2)} \right) d^+_{\nu\tau} \Bigg\} \end{aligned} \tag{A5}$$

Introducing obvious relations:

$$\langle a_{i\sigma} a^+_{i'\sigma}\rangle \equiv \langle\Phi_L|a_{i\sigma} a^+_{i'\sigma'}|\Phi_L\rangle = \delta_{ii'}\delta_{\sigma\sigma'}(1 - n_{i\sigma})$$

$$\langle a_{i'\sigma'} a^+_{j\tau}\rangle \equiv \langle\Phi_L|a_{i'\sigma'} a^+_{j\tau}|\Phi_L\rangle = \delta_{i'j}\delta_{\sigma'\tau}(1 - n_{j\tau})$$

$$\langle a^+_{i\sigma} a_{i'\sigma'}\rangle \equiv \langle\Phi_L|a^+_{i\sigma} a_{i'\sigma'}|\Phi_L\rangle = \delta_{ii'}\delta_{\sigma\sigma'} n_{i\sigma}$$

$$\langle a^+_{i'\sigma'} a_{j\tau}\rangle \equiv \langle\Phi_L|a^+_{i'\sigma'} a_{j\tau}|\Phi_L\rangle = \delta_{i'j}\delta_{\sigma'\tau} n_{j\tau}$$

($n_{i\sigma}$ is the number of electrons on the i-th MO having a spin projection σ) and taking into account that in the case of high symmetry the product $\beta_{\mu i}\beta_{\nu i}$ is not vanishing only when $\mu = \nu$ (it is because that the different d-orbitals have different symmetry properties and therefore the different d-orbitals $|\mu\rangle$ and $|\nu\rangle$ can not overlap with the same ligand orbital $|i\rangle$) one reduces Eq. (A5) to the form:

$$\begin{aligned} \langle\!\langle H_R \rangle\!\rangle_L = \sum_{\sigma} \sum_{\mu} \sum_{i} \beta^2_{\mu i} \Bigg\{ & (1 - n_{i\sigma})^2 d^+_{\mu\sigma} \left(\sum_{k} \frac{|\Phi_k(n_1)\rangle\langle\Phi_k(n_1)|}{E_0 - E(i, \sigma, k, n_1)} \right) d_{\mu\sigma} \\ & + n^2_{i\sigma} d_{\mu\sigma} \left(\sum_{l} \frac{|\Phi_l(n_2)\rangle\langle\Phi_l(n_2)|}{E_0 - E(i, \sigma, l, n_2)} \right) d^+_{\mu\sigma} \Bigg\} \end{aligned} \tag{A6}$$

The energy denominators in Eq. (A6) are estimated with use of the mean field approximation which ascribes the same energy to all the terms of the given configuration. It means that the energy denominators should be substituted according to Eq. (A7):

$$\begin{aligned} E_0 - E(i, \sigma, k, n_1) &\to -\Delta E(\mu\sigma\ i\sigma) \quad \textit{for all } k : \mu \notin k \\ E_0 - E(i, \sigma, l, n_2) &\to -\Delta E(i\sigma\ \mu\sigma) \quad \textit{for all } l : \mu \in l \end{aligned} \tag{A7}$$

After this substitution it turns out that for the given i and μ all the denominators in the sums over k and l in Eq. (A6) can be factorized. Comparing the explicit forms of the functions Φ_k and Φ_l with those of the projection operators $\mathbb{O}(n, \mu\sigma)$ and $\mathbb{O}(n, \overline{\mu\sigma})$ (Appendix B) one can see that the sums over k and l are transformed into the projection operators $\mathbb{O}(n, \mu\sigma)$ and $\mathbb{O}(n, \overline{\mu\sigma})$ multiplied by an energy denominator. This leads to the following expression for $\langle\!\langle H_{RR} \rangle\!\rangle_L$:

$$\begin{aligned} \langle\!\langle H_{RR} \rangle\!\rangle_L = -\sum_\sigma \sum_\mu \sum_i \beta_{\mu i}^2 \Bigg\{ &\frac{(1-n_{i\sigma})^2}{\Delta E(\mu\sigma\ i\sigma)} d_{\mu\sigma}^+ \mathbb{O}(n_1, \overline{\mu\sigma}) d_{\mu\sigma} \\ &+ \frac{n_{i\sigma}^2}{\Delta E(i\sigma\ \mu\sigma)} d_{\mu\sigma} \mathbb{O}(n_2, \mu\sigma) d_{\mu\sigma}^+ \Bigg\} \end{aligned} \tag{A8}$$

Substituting the relation $\mathbb{O} = \mathbb{O}^2$ for projection operators and Eqs. (B1), (B2) into Eq. (A8), we obtain:

$$\begin{aligned} \langle\langle H_{RR} \rangle\rangle_L = -\sum_\sigma \sum_\mu \sum_i \beta_{\mu i}^2 \Bigg\{ &\frac{(1-n_{i\sigma})^2}{\Delta E(\mu\sigma\ i\sigma)} \mathbb{O}(n_d, \mu\sigma) d_{\mu\sigma}^+ d_{\mu\sigma} \mathbb{O}(n_d, \mu\sigma) \\ &+ \frac{n_{i\sigma}^2}{\Delta E(i\sigma\ \mu\sigma)} \mathbb{O}(n_d, \overline{\mu\sigma}) d_{\mu\sigma} d_{\mu\sigma}^+ \mathbb{O}(n_d, \overline{\mu\sigma}) \Bigg\} \end{aligned} \tag{A9}$$

Replacing the projection operators $\mathbb{O}(n_d, \mu\sigma)$ and $\mathbb{O}(n_d, \overline{\mu\sigma})$ (according to Eqs. (B3), (B4)) by $\mathbb{O}(n_d) d_{\mu\sigma}^+ d_{\mu\sigma}$ and $\mathbb{O}(n_d) d_{\mu\sigma} d_{\mu\sigma}^+$, respectively, and taking into account, that the occupation number operators $d_{\mu\sigma}^+ d_{\mu\sigma}$ are idempotent, one obtains the final expression for $\langle\!\langle H_{RR} \rangle\!\rangle_L$:

$$\begin{aligned} \langle\!\langle HH_{RR} \rangle\!\rangle_L = &-\sum_\sigma \sum_\mu \sum_i \beta_{\mu i}^2 \frac{n_{i\sigma}^2}{\Delta E(i\sigma\ \mu\sigma)} \mathbb{O}(n_d) \\ &-\sum_\sigma \sum_\mu \sum_i \beta_{\mu i}^2 \left\{ \frac{(1-n_{i\sigma})^2}{\Delta E(\mu\sigma\ i\sigma)} - \frac{n_{i\sigma}^2}{\Delta E(i\sigma\ \mu\sigma)} \right\} \mathbb{O}(n_d) d_{\mu\sigma}^+ d_{\mu\sigma} \mathbb{O}(n_d) \end{aligned} \tag{A10}$$

The projection operators $\mathbb{O}(n_d)$ in Eq. (A10) can be omitted because the operator $\langle\!\langle H_{RR} \rangle\!\rangle_L$ by definition operates in the subspace of n_d-electron functions. Thus, Eq. (A10) is transformed into Eq. (42) of Sect. 2.3.

Appendix B

Here we prove some useful relations for the projection and creation (annihilation) operators which are used in the text.

$$a_k^+ \mathbb{O}(n-1, \bar{k}) = \mathbb{O}(n, k) a_k^+ \tag{B1}$$

where a_k^+ is the operator of creation of an electron on the spin-orbital k; $\mathbb{O}(n, k)$ and $\mathbb{O}(n, \bar{k})$ are the operators which project a function of the Fock space to the subspaces spanned by the n-electron functions with the spin-orbital k either occupied or unoccupied, respectively. The explicit forms of the operators $\mathbb{O}(n, \bar{k})$ and $\mathbb{O}(n, k)$ are, respectively:

$$\mathbb{O}(n, \bar{k}) = \sum_{\substack{\{\mu_\alpha\}\\(\mu_\alpha \neq k)}} \prod_{\alpha=1}^{n} a_{\mu_\alpha}^+ |0\rangle\langle 0| \prod_{\alpha=1}^{n} a_{\mu_\alpha}$$

$$\mathbb{O}(n, k) = a_k^+ \left(\sum_{\substack{\{\mu_\alpha\}\\(\mu_\alpha \neq k)}} \prod_{\alpha=1}^{n-1} a_{\mu_\alpha}^+ |0\rangle\langle 0| \prod_{\alpha=1}^{n-1} a_{\mu_\alpha} \right) a_k$$

Comparing these two definitions one immediately obtains:

$$\mathbb{O}(n, k) = a_k^+ \, \mathbb{O}(n-1, \bar{k}) a_k$$

Multiplying the left-hand side of Eq. (B1) by:

$$a_k^+ a_k + a_k a_k^+ = 1$$

from the right, one obtains:

$$a_k^+ \, \mathbb{O}(n-1, \bar{k})(a_k^+ a_k + a_k a_k^+) = a_k^+ \, \mathbb{O}(n-1, \bar{k}) a_k^+ a_k + a_k^+ \, \mathbb{O}(n-1, \bar{k}) a_k a_k^+$$

The first term of the expression on the right-hand side always vanishes, but the second term is exactly the right-hand side of Eq. (B1).

$$\mathbb{O}(n-1, \bar{k}) a_k = a_k \, \mathbb{O}(n, k) \tag{B2}$$

Multiplying the left-hand side by $a_k^+ a_k + a_k a_k^+ = 1$ from the left and carrying out the same transformations as in the case of Eq. (B1) we yield the right-hand side of Eq. (B2).

$$\mathbb{O}(n, k) = \mathbb{O}(n) a_k^+ a_k \tag{B3}$$

This relation, where $\mathbb{O}(n)$ is the projector on the subspace spanned by the n-electron functions, can be proved by the following equality chain (the underlined terms are zero):

$$\begin{aligned} \mathbb{O}(n, k) &= [\mathbb{O}(n) - \mathbb{O}(n, \bar{k})](a_k^+ a_k + a_k a_k^+) \\ &= \mathbb{O}(n) a_k^+ a_k - \underline{\mathbb{O}(n, \bar{k}) a_k^+ a_k} + \mathbb{O}(n) a_k a_k^+ - \mathbb{O}(n, \bar{k}) a_k a_k^+ \\ &= \mathbb{O}(n) a_k^+ a_k + [\mathbb{O}(n) - \mathbb{O}(n, \bar{k})] a_k a_k^+ \\ &= \mathbb{O}(n) a_k^+ a_k + \underline{\mathbb{O}(n, k) a_k a_k^+} = \mathbb{O}(n) a_k^+ a_k \end{aligned}$$

The following relation:

$$\mathbb{O}(n, \bar{k}) = \mathbb{O}(n) a_k a_k^+ \tag{B4}$$

can be proven analogously.