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# Effective Crystal Field for Trivalent First Transition Row Ions

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**ABSTRACT:** In the present work the semiempirical effective crystal field (ECF) method previously designed for electronic structure calculations of transition metal complexes and utilizing non-Hartree–Fock trial wave function and parameterized for complexes of doubly charged Cr<sup>2+</sup>, V<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> cations is extended to complexes of triply charged cations of 3d-elements. With the parameters adjusted the ECF method is applied to calculations of ground states and low-energy spectra of the d-shells of fluoro-, chloro-, aqua-, amino-, and cyano-complexes of the triply charged cations. Obtained total spin and symmetry of the ground states match the experimentally observed ones. Satisfactory agreement between the calculated and experimental d-shell electronic transition energies is achieved as well. © 2002 Wiley Periodicals, Inc. *Int J Quantum Chem* 88: 370–379, 2002

**Key words:** effective crystal field method; transition metal complexes; trivalent ions

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## Introduction

Calculations on magnetic and optical properties of transition metal complexes (TMCs) are important problems of theoretical chemistry. Semiempirical [1–5] as well as *ab initio* methods [6–13] were applied for that, both substantially using the Hartree–Fock–Roothaan [or the self-consistent field (SCF) molecular orbital (MO)-LCAO] approximation. The *ab initio* calculations are highly

time consuming when applied to TMCs. The reason is a huge number of electronic states to be included in the configuration interaction (CI) procedure, due to poor convergence of the CI series when the canonical Hartree–Fock (MOs) are used for constructing the configurations. Thus, *ab initio* calculations can be performed only for relatively small systems, for which nevertheless a considerable agreement of calculated and experimental transition energies can be obtained [11, 12]. Semiempirical methods based on the SCF approximation are less demanding for computational resources, although results obtained strongly depend on parameterization of numerous molecular integrals.

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The application of semiempirical and *ab initio* methods based on Hartree–Fock approximation to the TMC electronic structure calculations is, however, complicated by violation of the SCF approximation itself. This is exhibited in some of its important consequences [14]. Namely, the *Aufbau* principle and Koopman’s theorem are not fulfilled for the MOs with considerable weight of the atomic *d*-orbitals; the relaxation energy for the latter (the difference between the ionization potential calculated by the Koopman’s theorem and its experimental value) can achieve 10 or even 20 eV for ionization from these MOs, and the MOs being higher in energy can turn out to be occupied while MOs of lower energy remain vacant or singly occupied. Also, the SCF iteration process often converges slowly or oscillates.

All these observations indicate that behavior of *d*-electrons in the TMC goes beyond the SCF approximation’s frames, which can be characterized as a motion of independent electrons in the SCF induced by nuclear cores and other electrons. In contrast, *d*-electrons in TMCs are strongly correlated (as compared to those in the ligand orbitals) and form a well-localized separate group. As ground-state spin and low-energy excitations of TMCs mainly depend on *d*-electrons’ state [15], accounting for correlations of the latter is of principal importance for the description of magnetic and optical properties of the TMCs.

For interpreting experimental data and explaining properties of TMCs the phenomenological crystal field theory (CFT) [15, 16] is widely used. The latter describes the TMCs in terms of excitations of their *d*-shells only. According to the CFT the one-electron states in the *d*-shells are split by an electrostatic field induced by effective charges residing in the ligands. The main defect of the CFT is lack of details of the ligand electronic structure that entails the limitation of the interaction between the *d*-shell of the central atom and the ligands to the purely electrostatic one. For that reason, the *d*-level splitting parameter  $10Dq$  is essentially underestimated and the one-electron splitting parameters cannot be calculated within the CFT itself, and remain independent parameters of the theory. The ligand field theory (LFT) [15, 16] partially takes into account the covalent character of interactions between the ligands and the central ion. However, the LFT calculations are in fact equivalent to the Hartree–Fock approximation and reduce to taking into account the MOs symmetry when making linear combinations with the *d*-orbitals. For this reason, splitting

characteristics calculated within the model are different from ones fitting in experimental data analysis.

For taking into account in the semiempirical realm qualitative features induced by both electron correlation and covalency effects and circumventing the problems of the original naive CFT and LFT, the effective crystal field (ECF) method was proposed [14], which is based on a combination of the effective Hamiltonian method and the group function technique [17, 18]. Basic features and formulae of this method are given below.

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### Effective Crystal Field Method

The trial wave function  $\Phi$  of electrons in TMC has the form of the antisymmetrized product of the full CI wave function for *d*-electrons  $\Psi_M$ , and the single determinant wave function  $\Psi_L$  for remaining electrons of the TMC:

$$\Phi = \Psi_M(n_d) \wedge \Psi_L(n_l). \quad (1)$$

Such a function is a special case of the group function [18] approximation where the groups are formed by electrons in the *d*-shell and those in other orbitals, respectively. This form of the wave function allows the use of the difference of the characteristic values of interaction parameters in the *d*-shell and in the ligands for taking into account electron correlations at different levels.

To arrive at the above form of the trial wave function, we note that the general form of the exact wave function can be presented as a linear combination of the functions having all possible electron distributions between the two subsystems singled out. However, in Ref. [14] it was shown that the wave function Eq. (1) with a fixed number  $n_d$  of electrons in the *d*-shell, which is equal to their number in the ground state of the corresponding free metal ion, must be obtained from the mentioned linear combination by projecting onto subspace spanned by the functions of the form Eq. (1).

Within the ECF theory the total Hamiltonian is rewritten in the form

$$H = H_d + H_l + H_c + H_r, \quad (2)$$

where  $H_d$  is the Hamiltonian for *d*-electrons in the field of the TMC atomic cores,  $H_l$  is the Hamiltonian for the ligand subsystem electrons, and  $H_c$  and  $H_r$

are, respectively, the operators of Coulomb and resonance interactions between two subsystems of the TMC.

For the charge transfer states, the Löwdin partition technique [17] as a version of effective Hamiltonian method was used in Ref. [14]. After projecting the exact Hamiltonian, Eq. (2) is replaced by the effective one acting in the subspace spanned by the functions with the fixed number  $n_d$  of  $d$ -electrons. Eigenvalues of the effective Hamiltonian coincide with exact Hamiltonian eigenvalues by construction. By simple algebra the explicit form of the effective Hamiltonian is obtained [14]:

$$\begin{aligned} H^{\text{eff}} &= PH_0P + H_{rr} \\ H_0 &= H_d + H_l + H_c \\ H_{rr} &= PH_rQ(EQ - QH_0Q)^{-1}QH_rP \end{aligned} \quad (3)$$

where  $P$  is the operator projecting to the subspace of the functions with the fixed number  $n_d$  of the  $d$ -shell electrons,  $n_l = N - n_d$  is that of the ligand subsystem electrons, and  $Q = 1 - P$ .

The TMC eigenstate energies must be obtained from the relation

$$E_n = \langle \Phi_n | H^{\text{eff}}(E_n) | \Phi_n \rangle. \quad (4)$$

Because the effective Hamiltonian depends on energy, the last equation must be solved iteratively until convergence in energy is achieved. However, because the charge transfer states (determining the poles of the above resolvent term) lay significantly higher in energy than the  $d$ -shell excitations this dependence turns out to be weak and can be neglected, so one can set

$$H^{\text{eff}}(E_n) \approx H^{\text{eff}}(E_0), \quad (5)$$

where  $E_0$  is the ground-state energy of the Hamiltonian  $H_0$ . Thus, the obtained effective Hamiltonian corresponds to the second order of the Raleigh–Schrödinger perturbation theory in  $H_r$ . Variation principle applied to the effective Hamiltonian with the trial function of the above form leads to the self-consistent system of equations:

$$\begin{aligned} H_d^{\text{eff}} \Phi_n^d &= E_n^d \Phi_n^d \\ H_l^{\text{eff}} \Phi^l &= E^l \Phi^l \\ H_d^{\text{eff}} &= H_d + \langle \Phi^l | H_c + H_{rr} | \Phi^l \rangle \end{aligned}$$

$$H_l^{\text{eff}} = H_l + \langle \Phi_n^d | H_c + H_{rr} | \Phi_n^d \rangle. \quad (6)$$

In the above system, the effective Hamiltonian  $H_d^{\text{eff}}$  for the  $d$ -electron subsystem depends on the wave function of the ligand subsystem  $\Phi^l$ , and in turn the effective Hamiltonian  $H_l^{\text{eff}}$  for the ligand subsystem depends on the  $d$ -electrons' wave functions  $\Phi_n^d$ . These equations must be solved self-consistently as well. In the ECF method [14], the Slater determinant  $\Phi^l$  is constructed of MOs of the ligand subsystem, obtained from the Hartree–Fock equations in the CNDO/2 approximation for the valence electrons of the ligands. In this case the transition from the bare Hamiltonian  $H_l^{\text{eff}}$  for the ligand subsystem to the corresponding effective (dressed) Hamiltonian reduces to renormalization of one-electron parameters related to the transition metal ion:

$$\begin{aligned} U_{ii}^{\text{eff}} &= U_{ii} + \frac{1}{5} n_d \sum_{\mu} g_{\mu i} \\ Z_M^{\text{eff}} &= Z_M - n_d, \end{aligned} \quad (7)$$

where  $U_{ii}$  is the parameter of the interaction of  $4s$ - and  $4p$ -electrons ( $i = 4s, 4p_x, 4p_y, 4p_z$ ) with the metal core,  $Z_M$  is metal core charge, and  $g_{\mu i}$  are the Oleari parameters of intraatomic Coulomb interactions. The  $\Phi^l$  function thus obtained is used further for constructing the effective Hamiltonian for the  $d$ -shell. Diagonalization of the latter gives both the wave functions of the  $d$ -shell and the  $d$ -electron state energies. The effective Hamiltonian for the  $d$ -shell after averaging Eq. (6) intersubsystem interaction operators  $H_c$  and  $H_{rr}$  over the ground state of the ligand system takes the form

$$H_d^{\text{eff}} = \sum_{\mu\nu\sigma} U_{\mu\nu}^{\text{eff}} d_{\mu\sigma}^+ d_{\nu\sigma} + \frac{1}{2} \sum_{\mu\nu\rho\eta} \sum_{\sigma\tau} (\mu\nu|\rho\eta) d_{\mu\sigma}^+ d_{\rho\tau}^+ d_{\eta\tau} d_{\nu\sigma}, \quad (8)$$

where  $d_{\mu\sigma}^+$  ( $d_{\nu\sigma}$ ) are operators of creation (annihilation) of electron with the spin projection  $\sigma$  on the  $\mu$ th  $d$ -atomic orbital (AO) and  $(\mu\nu|\rho\eta)$  are the two-electron integrals of the Coulomb interaction in the  $d$ -shell. Effective one-electron parameters  $U_{\mu\nu}^{\text{eff}}$  of the  $d$ -shell contain contributions from the Coulomb and from the projected [Eq. (5)] resonance interaction with the ligand subsystem:

$$U_{\mu\nu}^{\text{eff}} = \delta_{\mu\nu} U_{dd} + W_{\mu\nu}^{\text{atom}} + W_{\mu\nu}^{\text{ion}} + W_{\mu\nu}^{\text{cov}}, \quad (9)$$

where

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

$$W_{\mu\nu}^{\text{ion}} = \sum_l (P_{ll} - Z_l) V_{\mu\nu}^l \quad (10)$$

Here  $P_{ii}$  is the one-electron density matrix element for the ligand subsystem,  $P_{ll} = \sum_{i \in l} P_{ii}$ ,  $Z_l$  is the  $l$ th atom core charge, and  $V_{\mu\nu}^l$  is the matrix element of the  $d$ -electron potential energy in the electrostatic field of a unit point charge placed on the  $l$ th ligand atom. The covalence contribution to the ECF is given by

$$W_{\mu\nu}^{\text{cov}} = - \sum_i^{(\text{MO})} \beta_{\mu i} \beta_{\nu i} \left\{ \frac{(1 - n_i)^2}{\Delta E_{di}} - \frac{n_i^2}{\Delta E_{id}} \right\} \quad (11)$$

where  $\beta_{\mu i}$  is the resonance integral between the  $\mu$ th  $d$ -orbital and the  $i$ th ligand MO,  $n_j$  ( $=0, 1$ ) is the occupation number of the  $j$ th MO, and  $\Delta E_{di}$  ( $\Delta E_{id}$ ) are excitation energies required to transfer an electron from the  $d$ -shell ( $i$ th MO) to the  $i$ th MO ( $d$ -shell). The intersubsystem's resonance integrals are calculated by the equation

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

where  $I_d$  and  $I_k$  are valence ionization potentials of the  $d$ -shell and of the  $k$ th AO in the ligand subsystem, respectively,  $S_{\mu k}$  is the AO's overlap integral, and  $\beta^{M-L}$  is a dimensionless parameter scaling the resonance interaction between the  $d$ -shell and a ligand atom. Charge transfer energies  $\Delta E_{di}$  and  $\Delta E_{id}$  are estimated according to

$$\Delta E_{di} = I_d + \epsilon_i - G_{dir}$$

$$\Delta E_{id} = -A_d - \epsilon_i - G_{dir} \quad (13)$$

where  $\epsilon_i$  is the  $i$ th MO energy,  $G_{di}$  is the Coulomb interaction energy between an electron and a hole localized in the  $d$ -shell and on the  $i$ th MO, respectively, and  $I_d$  and  $A_d$  are, respectively, the ionization potential and electron affinity of the  $d$ -shell.

The effective Hamiltonian for the  $d$ -shell Eq. (8) formally coincides with the CFT Hamiltonian. The substantial difference is the covalence contribution Eq. (11) to the  $d$ -shell one-electron parameters Eq. (9), taking into account the effect of virtual charge

transfers between the metal  $d$ -shell and the ligands. Thereby, the ECF contains not only electrostatic but also covalence terms coming from the resonance interactions between the  $d$ -shell and the ligands.

According to calculations performed in Refs. [14] and [19–22] for the TMCs of divalent cations, the covalence contribution to the splitting parameter  $10Dq$  dominates and gives up to 90% of the total. This stresses the importance of the procedures described above aimed to include the covalence interaction in an economic and transparent fashion into the effective Hamiltonian parameters. The parameters of the ECF method for the complexes of divalent cations of the first transition range metals have been found, tested, and employed in Refs. [14] and [19–22]. They allowed the correct description of the symmetry of the ground states and optical  $d$ - $d$ -transition energies with precision up to  $1000 \text{ cm}^{-1}$  for about 100 of the TMCs of the first transition row divalent cations ranging from hexafluoroanions to porphyrine complexes. Therefore, the use of the ECF allows significant improvement of semiempirical description of TMC electronic structure.

## Results and Discussion

The purpose of the present work was to explore the possibility to extend the parameterization of Refs. [14] and [19–22] to the complexes of trivalent ions of the first transition row. Note that when talking about di- and trivalent cations we imply the Werner complexes for which the  $d$ -electron subsystem contains the same number of electrons as the  $3d$ -shell of the corresponding isolated cation, for example, the  $d$ -electron subsystem of the  $\text{Fe}^{3+}$  complexes has  $3d^5$  configuration with five  $d$ -electrons.

The whole set of the parameters of the ECF method consists of those of the CNDO/2 method for the ligand atoms, specific parameters  $U_{dd}$ ,  $\zeta_d$ ,  $B$ , and  $C$  (see below) for the  $d$ -shell, and Oleari parameters describing the intraatomic part of the Coulomb interaction between subsystems. In this article only the core attraction of  $d$ -electrons  $U_{dd}$  for each metal ion and the  $\beta^{M-L}$  resonance parameters for each pair metal ( $M$ )–donor atom ( $L$ ) have been fitted. The  $\beta^{M-L}$  parameters have been adjusted to fit the calculated excitation energies to the experimental ones for the complexes with organic amines, pyridine and its derivatives, and other nitrogen- and oxygen-containing, ligands, halogen, anions, and so forth.

**TABLE I**  
**Covalent and ionic contributions to the  $d$ -level crystal field splitting parameter  $10Dq$  in octahedral complexes of trivalent cations ( $\text{cm}^{-1}$ ).**

M	$10Dq^{\text{ion}}$	$10Dq^{\text{cov}}$	$10Dq^{\text{total}}$	$10Dq^{\text{expt}}$ [23, 24]
		[MF <sub>6</sub> ] <sup>3-</sup>		
V	2769	13304	16073	15900
Cr	2388	12941	15329	15200
Fe	1330	12580	13910	13900
Co	885	12229	13114	13100
		[MCl <sub>6</sub> ] <sup>3-</sup>		
Cr	646	12560	13206	13800
Mn	565	16987	17552	17540
Fe([FeCl <sub>4</sub> ] <sup>-</sup> )	263	4721	4984	5000
		[M(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>		
V	1088	16512	17600	18400
Cr	769	16638	17407	17390
Fe	1329	12621	13950	14200
Co	221	17936	18157	18160
		[M(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>		
Cr	554	20984	21538	21550
Co	343	22532	22875	22870
		[M(CN) <sub>6</sub> ] <sup>3-</sup>		
Cr	772	26061	26833	26770
Fe	603	34401	35004	35000
Co	518	32075	32593	32200

In this article the ECF calculations on octahedral complexes of trivalent cations of the first transition row have been performed. We considered only those complexes whose both geometry and transition energies and the corresponding symmetries of the excited states are known, namely, V<sup>3+</sup>, Cr<sup>3+</sup>, Mn<sup>3+</sup>, Fe<sup>3+</sup>, and Co<sup>3+</sup>. (The data on Ni<sup>3+</sup> and Cu<sup>3+</sup> complexes are not readily available because the latter are largely unstable.) The geometry structure parameters—the atomic coordinates, bond lengths, and valence angles—were taken from the literature (the corresponding references are given in the tables).

The  $U_{dd}$  and  $\beta^{M-L}$  parameters determining the value of one-electron splitting parameter  $10Dq$  in the  $d$ -shell and the spectrum of the  $d-d$ -transitions were fitted so that the best agreement of calculated and experimental values of  $10Dq$  and of the excitation energies is achieved. The values of  $U_{dd}$  for each metal of the considered V, Cr, Fe, and Co series

were modified so that the positive values of  $\Delta E_{dj}$  and  $\Delta E_{jd}$  Eq. (13) are guaranteed to ensure the stability of the system with respect to electron transfer between the subsystems. After that the  $\beta^{M-L}$  parameters have been fitted to reach a required agreement between the calculated and experimental values of the splitting parameters and calculated and experimental excitation energies.

The calculated  $10Dq$  values, the ionic and covalent contributions to them, and the respective experimental values are given in Table I. The fitted values of the parameters  $U_{dd}$  and  $\beta^{M-L}$  for the trivalent ions, the respective parameters for the divalent ions, and also bond length differences between the di- and trivalent cations complexes (in those cases when the corresponding data for both complexes are available) are given. Also the Slater exponents for the valence  $4s$ -,  $4p$ -, and  $3d$ -orbitals of the trivalent ions are given. These quantities, chosen in accordance with the Burns rules [25] accepted in the

TABLE II

Parameters  $\beta^{M-L}$ ,  $U_{dd}$  (eV), Slater exponents for the valence  $4s$ -,  $4p$ -, and  $3d$ -orbitals and difference of metal-donor atom separations for complexes of doubly and triply charged transition metal cations.

		V	Cr	Mn	Fe	Co
F	2	—	—	1.225	1.431	1.826
	3	1.051	1.825	—	1.244	1.664
$\Delta r_{23}$		—	—	—	0.308	0.1444
Cl	2	0.975	—	1.250	1.339	1.588
	3	—	1.020	0.765	1.60([MCl <sub>4</sub> ] <sup>-</sup> )	—
$\Delta r_{23}$		—	—	0.228	0.059	—
O	2	0.985	1.400	1.325	1.825	1.838
	3	1.180	1.004	—	1.484	2.540
$\Delta r_{23}$		0.133	0.153	—	0.14	0.011
N	2	—	—	—	1.505	1.505
	3	—	1.002	—	—	1.470
$\Delta r_{23}$		—	—	—	—	0.146
C	2	—	—	—	1.263	—
	3	—	0.728	—	0.995	0.940
$\Delta r_{23}$		—	—	—	-0.037	—
$U_{dd}$	2	-56.42	-73.04	-92.49	-107.49	-129.79
	3	-47.0	-70.0	-90.0	-105.0	-125.0
$\zeta_s$	2	1.200	1.325	1.450	1.575	1.700
	3	1.325	1.450	1.575	1.700	1.825
$\zeta_p$	2	0.750	0.825	0.900	0.975	1.050
	3	0.825	0.900	0.975	1.050	1.125
$\zeta_d$	2	2.501	2.650	2.935	3.152	3.369
	3	2.650	2.935	3.152	3.369	3.586

$$\Delta r_{23} = r(M^{2+} - L) - r(M^{3+} - L), (\text{\AA})$$

original ECF method [14], are less diffuse than the respective orbitals of the divalent ions. It should be noted that the  $U_{dd}$  values for the trivalent ions are smaller (by the absolute value) by only a few electronvolts (or a few percent) than the values of the same parameters employed previously to describe their divalent analogs. The parameters  $\beta^{M-L}$  for the trivalent cations are as a rule smaller than those for the divalent ones with the exception of hexahydrate complexes of  $V^{3+}$  and  $Co^{3+}$ . One also may note that the values  $\beta^{M-L}$  for all the donor atoms  $L$  are systematically smaller for the trivalent ions but increase with the atomic number of the metal as for the divalent ions. Because we considered only one complex of Mn, we had to take the  $U_{dd}$  value by a few percent smaller than the absolute value for the divalent manganese ion by analogy with Cr, Fe, and Co.

We note also that the fitted values of the parameters are close to the respective values for the divalent ions, an additional proof of consistency of the ECF method permitting a comparatively simple extension to a new class of objects—complexes of

trivalent cations. Covalent interactions in the considered complexes of the trivalent cations contribute about 80% to the  $d$ -states splitting as in the case of the divalent cation complexes.

In Tables II–VI the results of calculations on octahedral complexes of the transition metal trivalent cations are given. Such complexes as  $[VF_6]^{3+}$ ,  $[V(H_2O)_6]^{3+}$ , and  $[CoF_6]^{3+}$  are the Jahn–Teller complexes. Our assumption that these complexes possess an octahedral symmetry adds an additional uncertainty to the calculated transition energies, so one may expect somewhat a larger difference between the calculated and experimental transition energies for these complexes.

Values of the Racah parameters  $B$  and  $C$  describing the electron interaction in the  $d$ -shell cited in the literature were used in our calculations. But, where such data were absent in the original works we used the Racah parameters given in the tables in Ref. [15].

Despite all the sources of uncertainty mentioned above, we succeeded in fitting the  $\beta^{M-L}$  parameters so that the correct ground-state term symmetry and

**TABLE III**  
**Calculated and experimental excitation energies**  
**(cm<sup>-1</sup>) of transition metal fluorocomplexes.**

Transition	E (theor)	E(exp)
[VF <sub>6</sub> ] <sup>3-</sup> , ground state <sup>3</sup> T <sub>1g</sub> [23, 26] B = 648, C = 3815		
<sup>3</sup> T <sub>1g</sub> → <sup>1</sup> T <sub>2g</sub>	9225	10200
→ <sup>1</sup> E <sub>g</sub>	9374	10200
→ <sup>3</sup> T <sub>2g</sub>	16098	14800
→ <sup>1</sup> A <sub>1g</sub>	20279	—
→ <sup>3</sup> T <sub>1g</sub>	24508	23000
→ <sup>1</sup> T <sub>2g</sub>	26578	—
→ <sup>1</sup> T <sub>1g</sub>	28874	—
[CrF <sub>6</sub> ] <sup>3-</sup> , ground state <sup>4</sup> A <sub>2g</sub> [27, 28] B = 643, C = 4133		
<sup>4</sup> A <sub>2g</sub> → <sup>2</sup> E <sub>g</sub>	10980	—
→ <sup>2</sup> T <sub>1g</sub>	11597	—
→ <sup>4</sup> T <sub>2g</sub>	15329	15200
→ <sup>2</sup> T <sub>2g</sub>	16778	—
→ <sup>4</sup> T <sub>1g</sub>	21680	21800
→ <sup>2</sup> A <sub>1g</sub>	24201	—
→ <sup>2</sup> T <sub>2g</sub>	26229	23000
→ <sup>2</sup> T <sub>1g</sub>	26621	—
→ <sup>2</sup> E <sub>g</sub>	27853	—
→ <sup>2</sup> T <sub>1g</sub>	31077	—
→ <sup>4</sup> T <sub>1g</sub>	33951	35000
→ <sup>2</sup> T <sub>2g</sub>	35720	—
→ <sup>2</sup> A <sub>2g</sub>	37061	—
[FeF <sub>6</sub> ] <sup>3-</sup> , ground state <sup>6</sup> A <sub>1g</sub> [23, 28] B = 835, C = 4800		
<sup>6</sup> A <sub>1g</sub> → <sup>1</sup> T <sub>1g</sub>	13700	14200
→ <sup>2</sup> T <sub>2g</sub>	14843	—
→ <sup>4</sup> T <sub>2g</sub>	18938	19700
→ <sup>4</sup> A <sub>1g</sub>	25050	25400
→ <sup>4</sup> E <sub>g</sub>	25050	25400
→ <sup>2</sup> A <sub>2g</sub>	25374	—
→ <sup>2</sup> T <sub>1g</sub>	25570	—
→ <sup>2</sup> T <sub>2g</sub>	27239	—
→ <sup>4</sup> T <sub>2g</sub>	28153	28800
→ <sup>2</sup> E <sub>g</sub>	29041	—
→ <sup>4</sup> E <sub>g</sub>	30895	30200
→ <sup>2</sup> T <sub>1g</sub>	33298	—
→ <sup>2</sup> A <sub>1g</sub>	35251	—
→ <sup>2</sup> T <sub>2g</sub>	36649	—
→ <sup>2</sup> E <sub>g</sub>	36740	—
→ <sup>4</sup> T <sub>1g</sub>	36964	—
→ <sup>2</sup> T <sub>2g</sub>	38640	—
[CoF <sub>6</sub> ] <sup>3-</sup> , ground state <sup>5</sup> T <sub>2g</sub> [23, 29] B = 787, C = 10000		
<sup>5</sup> T <sub>2g</sub> → <sup>1</sup> A <sub>1g</sub>	6622	—
→ <sup>3</sup> T <sub>1g</sub>	8977	—
→ <sup>3</sup> T <sub>2g</sub>	12932	11800, 14400
→ <sup>5</sup> E <sub>g</sub>	13114	—
→ <sup>1</sup> T <sub>1g</sub>	17656	—
→ <sup>3</sup> T <sub>1g</sub>	20129	—
→ <sup>1</sup> E <sub>g</sub>	20686	—
→ <sup>3</sup> T <sub>2g</sub>	21249	—
→ <sup>3</sup> E <sub>g</sub>	23068	—
→ <sup>3</sup> T <sub>1g</sub>	23589	—
→ <sup>1</sup> T <sub>2g</sub>	25510	—
→ <sup>3</sup> T <sub>2g</sub>	26834	—

the values of optical electron transitions were obtained with high accuracy (in most cases up to a few hundred cm<sup>-1</sup>). The calculated values of 10Dq are in good agreement with the experimental data with the precision of 200–400 cm<sup>-1</sup>. An exception is the Jahn–Teller vanadium aquacomplex, but even in this case the difference does not exceed 1000 cm<sup>-1</sup>, accurate enough.

Comparison of the transition energies in the *d–d*-spectra, calculated by the ECF method with the

**TABLE IV**  
**Calculated and experimental excitation energies**  
**(cm<sup>-1</sup>) of transition metal chlorine complexes.**

Transition	E (theor)	E (exp)
[CrCl <sub>6</sub> ] <sup>3-</sup> , ground state <sup>4</sup> A <sub>2g</sub> [30, 31] B = 918, C = 4133		
<sup>4</sup> A <sub>2g</sub> → <sup>2</sup> E <sub>g</sub>	9700	—
→ <sup>2</sup> T <sub>1g</sub>	10148	—
→ <sup>4</sup> T <sub>2g</sub>	13206	13100
→ <sup>2</sup> T <sub>2g</sub>	14796	—
→ <sup>4</sup> T <sub>1g</sub>	18272	18700
→ <sup>2</sup> A <sub>1g</sub>	21206	—
→ <sup>2</sup> T <sub>2g</sub>	22810	—
→ <sup>2</sup> T <sub>1g</sub>	23086	—
→ <sup>2</sup> E <sub>g</sub>	24210	—
→ <sup>2</sup> T <sub>1g</sub>	26613	—
→ <sup>4</sup> T <sub>1g</sub>	28845	—
[MnCl <sub>6</sub> ] <sup>3-</sup> , ground state <sup>5</sup> E <sub>g</sub> [30, 32] B = 965, C = 4450		
<sup>5</sup> E <sub>g</sub> → <sup>3</sup> T <sub>1g</sub>	5317	—
→ <sup>1</sup> T <sub>2g</sub>	16656	—
→ <sup>1</sup> E <sub>g</sub>	16812	—
→ <sup>5</sup> T <sub>2g</sub>	17552	17540
→ <sup>3</sup> E <sub>g</sub>	19687	—
→ <sup>3</sup> T <sub>1g</sub>	20728	—
→ <sup>3</sup> T <sub>2g</sub>	21591	—
→ <sup>3</sup> A <sub>2g</sub>	23140	—
→ <sup>3</sup> A <sub>2g</sub>	23712	—
→ <sup>1</sup> A <sub>1g</sub>	24743	—
→ <sup>3</sup> E <sub>g</sub>	26665	—
→ <sup>1</sup> A <sub>2g</sub>	29828	—
[FeCl <sub>4</sub> ] <sup>-</sup> , ground state <sup>6</sup> A <sub>1g</sub> [23, 31] B = 550, C = 220		
<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub>	15356	15600
→ <sup>4</sup> T <sub>2g</sub>	16500	16300
→ <sup>4</sup> A <sub>1g</sub> , <sup>4</sup> E <sub>g</sub>	19192	18800
→ <sup>4</sup> A <sub>1g</sub> , <sup>4</sup> E <sub>g</sub>	19192	18800
→ <sup>4</sup> T <sub>2g</sub>	20350	20100
→ <sup>4</sup> E <sub>g</sub>	22229	22400

**TABLE V**  
**Calculated and experimental excitation energies**  
**(cm<sup>-1</sup>) of transition metal aquacomplexes.**

Transition	E (theor)	E (exp)
[V(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> , ground state <sup>3</sup> T <sub>1g</sub> [23, 34] B = 862, C = 3815		
<sup>3</sup> T <sub>1g</sub> → <sup>1</sup> T <sub>2g</sub>	11457	—
→ <sup>1</sup> E <sub>g</sub>	11657	—
→ <sup>3</sup> T <sub>2g</sub>	16149	17100
→ <sup>1</sup> A <sub>1g</sub>	24453	—
→ <sup>3</sup> T <sub>1g</sub>	26023	25200
→ <sup>1</sup> T <sub>2g</sub>	29096	—
[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> , ground state <sup>4</sup> A <sub>2g</sub> [23, 35] B = 750, C = 3300		
<sup>4</sup> A <sub>2g</sub> → <sup>2</sup> E <sub>g</sub>	15168	15000
→ <sup>2</sup> T <sub>1g</sub>	15799	—
→ <sup>4</sup> T <sub>2g</sub>	17407	17400
→ <sup>2</sup> T <sub>2g</sub>	22749	—
→ <sup>4</sup> T <sub>1g</sub>	24508	24600
→ <sup>2</sup> A <sub>1g</sub>	30167	—
→ <sup>2</sup> T <sub>2g</sub>	32430	—
→ <sup>2</sup> T <sub>1g</sub>	32857	—
→ <sup>2</sup> E <sub>g</sub>	34640	—
→ <sup>2</sup> T <sub>1g</sub>	37836	—
→ <sup>4</sup> T <sub>1g</sub>	38437	37800
[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> , ground state <sup>6</sup> A <sub>1g</sub> [23, 36] B = 1010, C = 4800		
<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub>	13661	12600
→ <sup>2</sup> T <sub>2g</sub>	14767	—
→ <sup>4</sup> T <sub>2g</sub>	18904	18500
→ <sup>4</sup> A <sub>1g</sub> , <sup>4</sup> E <sub>g</sub>	25050	24300, 24600
→ <sup>2</sup> A <sub>2g</sub>	25335	—
→ <sup>2</sup> T <sub>1g</sub>	25532	—
→ <sup>2</sup> T <sub>2g</sub>	27203	—
→ <sup>4</sup> T <sub>2g</sub>	28150	27500
→ <sup>2</sup> E <sub>g</sub>	29005	—
[Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> , ground state <sup>1</sup> A <sub>1g</sub> [23, 37] B = 615, C = 3085		
<sup>1</sup> A <sub>1g</sub> → <sup>3</sup> T <sub>1g</sub>	9649	—
→ <sup>5</sup> T <sub>2g</sub>	10347	—
→ <sup>3</sup> T <sub>2g</sub>	13486	—
→ <sup>1</sup> T <sub>1g</sub>	16227	16500
→ <sup>1</sup> E <sub>g</sub>	19213	—
→ <sup>1</sup> T <sub>2g</sub>	24051	24950
→ <sup>3</sup> T <sub>1g</sub>	25928	—
→ <sup>3</sup> T <sub>2g</sub>	26718	—
→ <sup>3</sup> E <sub>g</sub>	28474	—
→ <sup>5</sup> E <sub>g</sub>	28503	—
→ <sup>3</sup> T <sub>1g</sub>	28990	—

parameterization cited in Table VII, with the experimental absorption band energies demonstrates that calculation with the fitted parameters leads to results that are in good agreement with experimental data. The divergences are in the range of 1000 cm<sup>-1</sup> except for cyanocomplexes. The calculated transition energies in the latter case differ from the experimental energies by up to 2000 cm<sup>-1</sup>. However, two experimental works concerning iron(III) hexacyanide [23, 24] give for the same states energy values differing by about 1000 cm<sup>-1</sup>. Thus, one may conclude that the accuracy of the ECF method with the given parameterization is comparable with the accuracy of the spectral methods themselves.

Figures given in Table VII concerning the differences of the metal–donor atom separations between the complexes of di- and trivalent cations show some regularities. In all cases, with the exception of the pair of iron hexacyanocomplexes where the Fe–C distance increases by 0.037 Å, the metal–

**TABLE VI**  
**Calculated and experimental excitation energies**  
**(cm<sup>-1</sup>) of transition metal aminocomplexes.**

Transition	E (theor)	E (exp)
[Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> , ground state <sup>4</sup> A <sub>2g</sub> [23, 38] B = 918, C = 4133		
<sup>4</sup> A <sub>2g</sub> → <sup>2</sup> E <sub>g</sub>	15283	15300
→ <sup>2</sup> T <sub>1g</sub>	15882	—
→ <sup>4</sup> T <sub>2g</sub>	21538	21550
→ <sup>2</sup> T <sub>2g</sub>	23398	—
→ <sup>4</sup> T <sub>1g</sub>	28984	28500
→ <sup>2</sup> A <sub>1g</sub>	34298	—
→ <sup>2</sup> T <sub>2g</sub>	36645	—
→ <sup>2</sup> T <sub>1g</sub>	36986	—
→ <sup>2</sup> E <sub>g</sub>	38771	—
[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> , ground state <sup>1</sup> A <sub>1g</sub> [23, 39] B = 615, C = 3085		
<sup>1</sup> A <sub>1g</sub> → <sup>3</sup> T <sub>1g</sub>	14287	13000
→ <sup>3</sup> T <sub>2</sub>	18350	—
→ <sup>5</sup> T <sub>2g</sub>	19559	—
→ <sup>1</sup> T <sub>1g</sub>	20815	21200
→ <sup>1</sup> E <sub>g</sub>	24046	—
→ <sup>1</sup> E <sub>g</sub>	24046	—
→ <sup>1</sup> T <sub>2g</sub>	29075	29550
→ <sup>3</sup> T <sub>1g</sub>	35148	—
→ <sup>3</sup> T <sub>2g</sub>	35919	—
→ <sup>3</sup> T <sub>2g</sub>	35919	—
→ <sup>3</sup> E <sub>g</sub>	37759	—
→ <sup>3</sup> T <sub>1g</sub>	38354	—



**TABLE VII**  
**Calculated and experimental excitation energies**  
**(cm<sup>-1</sup>) of transition metal cyanocomplexes.**

Transition	E (theor)	E (exp)
[Cr(CN) <sub>6</sub> ] <sup>3-</sup> , ground state <sup>4</sup> A <sub>2g</sub> [23, 40] B = 550, C = 1900		
<sup>4</sup> A <sub>2g</sub> → <sup>2</sup> E <sub>g</sub>	10013	—
→ <sup>2</sup> T <sub>1g</sub>	10417	—
→ <sup>2</sup> T <sub>2g</sub>	16076	—
→ <sup>4</sup> T <sub>2g</sub>	26833	26700
→ <sup>4</sup> T <sub>1g</sub>	32946	32600
→ <sup>2</sup> A <sub>1g</sub>	34733	—
→ <sup>2</sup> T <sub>2g</sub>	36673	—
→ <sup>2</sup> T <sub>1g</sub>	36799	—
→ <sup>2</sup> E <sub>g</sub>	37904	—
[Fe(CN) <sub>6</sub> ] <sup>3-</sup> , ground state <sup>2</sup> T <sub>2g</sub> [41, 42] B = 1015, C = 4800		
<sup>2</sup> T <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub>	25131	—
→ <sup>4</sup> T <sub>2g</sub>	29008	—
→ <sup>2</sup> A <sub>2g</sub>	32156	30700
→ <sup>2</sup> T <sub>1g</sub>	32325	30700
→ <sup>2</sup> T <sub>2g</sub>	33846	33000
→ <sup>2</sup> E <sub>g</sub>	34912	35000
→ <sup>2</sup> T <sub>1g</sub>	38689	38000
→ <sup>2</sup> T <sub>2g</sub>	40035	—
→ <sup>2</sup> A <sub>1g</sub>	41755	—
→ <sup>6</sup> A <sub>1g</sub>	43294	—
→ <sup>2</sup> E <sub>g</sub>	47327	—
[Co(CN) <sub>6</sub> ] <sup>3-</sup> , ground state <sup>1</sup> A <sub>1g</sub> [41, 43] B = 400, C = 2000		
<sup>1</sup> A <sub>1g</sub> → <sup>3</sup> T <sub>1g</sub>	26860	—
→ <sup>3</sup> T <sub>2g</sub>	29823	—
→ <sup>1</sup> T <sub>1g</sub>	30997	31800
→ <sup>1</sup> E <sub>g</sub>	33571	—
→ <sup>1</sup> T <sub>2g</sub>	36944	38700

donor atom distances decrease by 0.1–0.3 Å. However, in the pair of hexaaquacomplexes of cobalt an essentially smaller difference (0.011 Å) is observed. We also note that for the majority of cations the complexes of the trivalent ones possess total spin values that are smaller than those for their divalent counterparts. If a complex of a divalent cation has a low spin, the corresponding complex of a trivalent cations also has a low spin and vice versa. The only exception is provided by the aquacomplexes of Co. This anomaly in the experimental data can be reflected in the ECF calculations only if the regularity in the  $\beta^{M-L}$  parameter variation along the row is

broken. In the case of the cobalt hexaaquacomplexes pair the difference of  $\beta^{M-L}$  values is abnormally large (0.7, essentially higher than the difference typical for all other complexes: 0.2–0.4). This fact requires that we perfect our approach, for example, by adjusting a larger number of parameters. Nevertheless, in the case of the iron hexacyanocomplexes the difference of  $\beta^{M-L}$  appears to be regular despite the anomalous difference of the metal–donor atom separation.

In the present work the ECF method [14] is employed for calculations of the complexes of trivalent ions of the first row transition metals. It is demonstrated that the description of the *d-d*-excitation spectra of the trivalent ion complexes is possible with the same high accuracy as in the case of the complexes of respective divalent ions, provided the parameters of the resonance interactions between the *d*-shell and ligands are respectively adjusted.

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