Ligand Field Theory: An ever-modern theory

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Abstract: The Ligand Field (LF) model in molecular science or the Crystal Field model in condensed matter science has been introduced more than eighty years ago. Since then, this theory plays a central role each time that molecules containing d- and/or f-elements with open shells are addressed. No doubt, this fact is related to the dominant localisation of the frontier orbitals within the metal-sphere. This common feature enables us to describe approximately the electronic structure of these molecules using orbitals that are centred on a single atom and to treat their interaction with the chemical environment essentially as a perturbation. Another reason for the success of this simple theory is the fact that the more accurate molecular orbital theory does generally over-estimate covalence of transition metal atoms and thus yields wave functions that are too delocalized.

We give here a survey of the development of LF theory since its introduction simultaneously by Hans Bethe and John Hasbrouck van Vleck more than eighty years ago. Over the years, LF theory was a semi-empirical model with adjustable parameter until the end of last century when we introduced non-empirical LF theory that is based on DFT calculations. The results of this first-principle prediction are in very good agreement with the experimental observations. Sample calculations of tetrahedral and octahedral Cr-complexes and hexa-acquo Ni(II)-complexes are used to validate the new model and to analyse the calculated parameters.

Introduction

Hans Bethe and John Hasbrouck van Vleck have introduced the Ligand Field (LF) model more than eighty years ago simultaneously. It is a semi-empirical model with adjustable parameter. Twenty years later Christian Klixbüll Jorgensen and Klaus Erik Schäffer proposed the Angular Overlap Model (AOM) that is a revisited version of LF theory with more chemical insight, still using adjustable parameters, but also the angular geometry of the metal complex. About twenty years ago we proposed a new, non-empirical, Density Functional Theory (DFT) based Ligand Field model [1] based on a multi-determinantal description of the multiplet fine structure of the whole ligandfield manifold. We propose to call this model LFDFT. The key feature of this approach is the explicit treatment of near degeneracy correlation using ad hoc Configuration Interaction (CI) within the active space of Kohn-Sham (KS) orbitals with dominant d- or f-character. The calculation of the CI-matrices is based on a symmetry decomposition and/or on a ligandfield analysis of the energies of all single determinants (micro-states) calculated according to Density Functional Theory (DFT) for frozen KS-orbitals corresponding to the averaged configuration, eventually with fractional occupations, of the d- or f-orbitals. This procedure yields multiplet energies with an accuracy of a few hundred wave numbers and fine structure splitting accurate to less than a tenth of this amount. With this procedure we have been able to calculate all customary molecular properties e.g. Zero Field Splitting (ZFS) [2], Zeeman interaction [3], Hyper-Fine Splitting (HFS) [3], magnetic exchange coupling [4], shielding constants [5], etc. …

An LFDFT calculation involves two steps: (i) an Average Of Configuration (AOC), with equal occupation of the d- or f-orbitals is carried out, (ii) with these orbitals kept frozen, the energies of all Single Determinants (SD) within the whole LF-manifold is performed. These energies are then used to estimate all the Racah- and LF-parameters needed in a conventional LF-calculation. The results of this first-principle prediction are in very good agreement with the experimental values.

We will describe, next, briefly the LF and the AOM model followed by LFDFT. The final part of
Angular Overlap Model (AOM) and Ligand Field (LF) model

a) Ligand field model
We want to represent the action of the chemical environment through an electrostatic perturbation

\[ h = h_0 + v_{LF} \]

where \( h_0 \) is the Hamiltonian of the free ion and \( v_{LF} \) the electrostatic potential of ligand charge density at the metallic centre. If \( \rho(r) \) the charge density due to the ligands one obtains for the electrostatic potential

\[ v_{LF}(r) = -e \int \frac{\rho(R)}{|R-r|} dR \]

The symbols used are defined in the figure below and represent the charge of the electron.

Expand \( 1/|\mathbf{r}-\mathbf{R}| \) to obtain

\[ \frac{1}{|\mathbf{r}-\mathbf{R}|} = \frac{1}{R} \sum_{k=0}^{\infty} \left( \frac{r}{R} \right)^k P_k(\cos \omega) \]

where \( r_\text{<} = \min\{r,R\}, \ r_\text{>} = \max\{r,R\} \) and \( P_k(x) \) is a Legendre polynomial of order \( k \).

We suppose (van Vleck and Bethe, 1930) that: \( r < R \). With this hypothesis and writing: \( r_\text{<} = r \) and \( r_\text{>} = R \) we obtain

\[ \frac{1}{|\mathbf{r}-\mathbf{R}|} = \frac{1}{R} \sum_{k=0}^{\infty} \left( \frac{r}{R} \right)^k P_k(\cos \omega) = \frac{1}{R} \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \left( \frac{r}{R} \right)^k \sum_{m=-k}^{k} Y_{km}(\theta,\phi) Y_{km}(\Theta,\Phi) \]

That yields \( v_{LF} \) as
\[ v_{LF}(r, \theta, \phi) = \sum_{k=0}^{2l} \sum_{q=-k}^{+k} h_{kq}(r) Y_{kq}(\theta, \phi) \]

It is sometimes useful to represent \( v_{LF} \) in the basis of d- or f-orbitals:

\[ \langle lm | v_{LF} | lm' \rangle = \sum_{k=0}^{2l} \sum_{q=-k}^{+k} h_{kq} \langle lm | Y_{kq} | lm' \rangle \]

where the parameters \( h_{kq} \) are adjustable and describe the ligand field. The coefficients \( \langle lm | kq | lm' \rangle \) are simple coupling coefficients:

\[ \langle lm | kq | lm' \rangle = \int d\Omega Y_{lm}(\Omega) \cdot Y_{kq}(\Omega) \cdot Y_{lm'}(\Omega) \]

that can easily be calculated by numerical quadrature (vide infra). This theory is on the basis of the celebrated Tanabe-Sugano diagrams (cf. Fig. 1). An equivalent result can be obtained with the AOM discussed in the following section.

Fig. 1 Tanabe-Sugano diagram for \( d^3 \)

\[ b) \textbf{Angular Overlap Model (AOM)} \]

The AOM is based on the following four postulates:

- The LF acting on the open-shell electrons of a paramagnetic ion is the resultant of a sum of contributions coming from individual ligands in the molecule or crystal.
- Only contributions from the neighbouring ligands are taken into account.
- Each single ligand contribution in the sum is axially symmetric about the line joining its centre to that of the metal ion.
- Single-ligand contributions are dependent only on the nature of the ligand and its distance from the paramagnetic ion, and do not depend on other properties of the chemical environment or host crystal.

Consider the most common M-L interactions:

- no nodal plane: \( \sigma \)
- one nodal plane: \( \pi \)
- two nodal planes: \( \delta \) (only observed when the ligand is a metal complex)
E.g. the splitting of five d-orbitals due to a local M-L interaction is:

\[
\begin{array}{c}
\text{Définition de } e_\sigma \\
\text{Définition de } e_\pi
\end{array}
\]

A semi-quantitative physical interpretation of the parameters \( e_\sigma \) et \( e_\pi \) can be estimated as follows:

\[
e_\sigma \approx \langle \psi_M | h | \psi_M \rangle - \langle \psi_L | h | \psi_L \rangle \\
e_\pi \approx \text{const.} \langle \psi_M | \psi_L \rangle^2
\]

where \( h \) is an effective hamiltonian for the M-L entity and \( \psi \) represents respectively the orbitals of the metal M and of the ligand L, i.e. \( \sigma \) or \( \pi \).

If we suppose additivity and transferability of the AOM parameters we obtain for the ligand field

\[
v = \sum_L v_L
\]

The calculation of the elements \( \langle d_i | v | d_j \rangle \) in the basis of d-orbitals is illustrated below.

Let us first consider the interaction of a ligand L in axial z position with the d-orbitals, i.e. \( \langle d_i | v^z_L | d_j \rangle = v^z_{ij,L} \)

| \( v^z_L \) | \( z^2 \) | \( yz \) | \( xz \) | \( xy \) | \( x^2-y^2 \) |
|---|---|---|---|---|---|
| \( z^2 \) | 0 | \( \sigma_L \) | \( \pi_L \) | 0 | \( x^2-y^2 \) |
| \( yz \) | \( \sigma_L \) | 0 | \( \pi_L \) | 0 | \( x^2-y^2 \) |
| \( xz \) | \( \pi_L \) | 0 | 0 | 0 | 0 |
| \( xy \) | 0 | 0 | 0 | 0 | 0 |
| \( x^2-y^2 \) | \( x^2-y^2 \) | \( x^2-y^2 \) | \( x^2-y^2 \) | \( x^2-y^2 \) | \( x^2-y^2 \) |
Next consider the interaction of ligand L on an arbitrary position on an \((\theta, \phi)\) direction:

This involves simply a rotation in 3D using Eulerian angles \(\{\alpha, \beta, \gamma\}\). If one applies this transformation to the whole set of d-orbitals we obtain

\[
\begin{bmatrix}
T \\
D
\end{bmatrix} = d
\]

where the elements of \(T\) are nothing but the well-known Wigner Dstellungsmatizen:

\[
Y_{lm}(\theta,\phi) = \sum_{\sigma=-l}^{l} D^{l}_{m\sigma}(\alpha,\beta,\gamma) Y_{l\sigma}(\Theta,\Phi)
\]

where

\[
D^{l}_{m\sigma}(\alpha,\beta,\gamma) = \int Y_{lm}(\theta,\phi) Y_{l\sigma}(\Theta,\Phi) d\Omega
\]

Wigner’s matrices are most conveniently obtained using Lebedev’s quadrature. According to this quadrature rule, the surface integral of a function over the unit sphere:

\[
I(f) = \frac{1}{4\pi} \int d\Omega f(\Omega) = \frac{1}{4\pi} \int_{0}^{\pi} \sin(\theta) d\theta \int_{0}^{2\pi} d\phi f(\theta,\phi)
\]

is approximated in the Lebedev scheme as:

\[
\tilde{I}[f] = \sum_{i=1}^{N} w_i f(\theta_i,\phi_i)
\]

This formula is exact for linear combinations of spherical harmonics up to degree 2N-1! The nodes and weights in the formula above can be obtained from internet:

(http://www.ccl.net/cca/software/SOURCES/FORTRAN/Lebedev-Laikov-Grids/)
That is, in practice an AOM calculation is as follows:

(i) Calculate

$$R_L = \begin{bmatrix}
\cos \gamma \cos \beta \cos \alpha - \sin \gamma \sin \alpha & \cos \gamma \cos \beta \sin \alpha + \sin \gamma \sin \alpha & -\cos \gamma \sin \beta \\
-\sin \gamma \cos \beta \cos \alpha - \cos \gamma \sin \alpha & -\sin \gamma \cos \beta \sin \alpha + \cos \gamma \sin \alpha & \sin \gamma \sin \beta \\
\sin \beta \cos \alpha & \sin \beta \sin \alpha & \cos \beta
\end{bmatrix}$$

(ii) Calculate

$$D_{nm}^j (\alpha_L, \beta_L, \gamma_L) = \int d\Omega Y_{\mu}^* (R_L, \Omega) Y_{lm}^j (\Omega)$$

(iii) Calculate

$$V_{nm, l}^{(\alpha, \beta, \gamma)} = \sum_{k=\alpha, \pi_x, \pi_y} D_{mk}^j (\alpha_L, \beta_L, \gamma_L) e_k D_{m'k}^j (\alpha_L, \beta_L, \gamma_L)$$

(iv) Sum up

$$\langle lm | V_{LF} | l'm' \rangle = \sum_L V_{nm, l}^{(\alpha, \beta, \gamma)}$$

(v) Use this matrix to obtain the LF splitting of the full open shell manifold

**Density Functional Theory calculation of the Ligand-Field manifold (LFDFT)**

Ligand field theory has been used with success to describe ground and excited electronic states originating from d\(n\) or f\(n\) elements in their complexes. Both crystal/ligand field theory (LFT) and developments - the angular overlap model (AOM) parameterize the Hamiltonian in terms of one-electron (ligand field) parameters and two-electrons repulsion integrals within the manifold of d-electrons. The latter ones are treated as atomic-like, thus preserving spherical symmetry, while the former take full account for the lowering of symmetry when a spherical metal atom or ion is introduced in a complex. Thus, for a d\(n\) manifold in cubic symmetry, only one energy parameter 10Dq – the energy difference between the \(\sigma\) and \(\pi\), \(c_6\) and \(t_2g\) for octahedral field (or between the \(\sigma+\pi\) and \(\pi\), \(t_2\) and \(e\) orbitals for tetrahedral field) is introduced in addition to Racah’s inter-electronic repulsion parameters B and C. These three parameters are usually determined from a fit to electronic absorption spectra in high resolution. From these data, two general observations can be made:

i) Ligands order in a sequence of increasing values of 10Dq, called spectrochemical series, where negatively charged ligands such as I < Br < Cl < F possess smaller 10Dq values, than neutral molecules H\(_2\)O < NH\(_3\) < pyridine, CN\(^-\) and CO being the strongest ligand due to their ability for back bonding.

ii) B and C parameters in complexes are smaller than those for the free ions - the phenomenon being discovered by Schäffer and Jørgensen and rationalized in terms of the electronic cloud expansion of the \(d\)-orbitals when going from free TM ions to complexes (nephelauxetic effect). The more reducing and softer ligands show a stronger reduction than the more oxidizing and harder ones.

**Description of the method**

The LFDFT method, which has been recently proposed by Atanasov and Daul is briefly summarised here. Let us assume that we know the complex geometry, either from a first principle geometry optimisation or from X-ray data. The first step consists in a spin-restricted SCF DFT calculation of the average of the \(I^0\) configuration (AOC), providing an equal occupation \(n/(2l+1)\) on each MO dominated by the l-orbitals. The Kohn-Sham orbitals, which are constructed using this
AOC are best suited for a treatment in which, interelectronic repulsion is approximated by atomic-like Racah parameters $B$ and $C$. The next step consists in a spin-unrestricted calculation of the manifold of all Slater determinants (SD) originating from e.g. the $d^6$ shell, i.e. 45, 120, 210 and 252 SD for $d^{2,8}$, $d^{3,7}$, $d^{4,6}$ and $d^5$ metal ions, respectively. These SD energies are used in the third step to extract the parameters of the one-electron $5\times5$ LF matrix $h_{ab}$ as well as Racah’s parameters $B$ and $C$ in a procedure, which we describe below. Finally, we introduce these parameters as input for a LF program allowing to calculate all the multiplets using CI of the full LF manifold utilizing the symmetry as much as possible. We should note that in classical LF theory, it is only the LF $h_{ab}$ matrix, which carries information about the symmetry and the actual bonding in the complex, thus providing useful chemical information.

E.g. for octahedral complexes of a $d^n$ TM the LF matrix reduces to one parameter – $10D_q$. We, thus have, for each SD energy the simple linear expression in terms of $B$, $C$ and $10D_q$:

$$
E\left(\text{SD}_\mu^d\right) = E\left(\text{det}\left[d_{\mu,1}\sigma_{i(\mu,1)}d_{\mu,2}\sigma_{i(\mu,2)}\ldots d_{\mu,n}\sigma_{i(\mu,n)}\right]\right) = \sum_i \langle d_i | h_{\text{LF}} | d_i \rangle + \sum_{i<j} (J_{ij} - K_{ij}) \delta_{\sigma_i, \sigma_j} + \frac{3m_\mu - 2n_\mu}{5} 10D_q + \beta_\mu B + \gamma_\mu C + E_0
$$

The single determinants $\text{SD}_\mu^d$ are labelled with the subscript $\mu = 1, \ldots, \binom{10}{n}$ and with the superscript $d$ to refer to pure $d$-spinorbitals. The values of $m_\mu$ and $n_\mu$ specify the electronic configuration $t_{2g}^{m_\mu}e_{g}^{n_\mu}$, while the $\beta_\mu$ and $\gamma_\mu$ are coefficients obtained after substituting standard expressions for the Coulomb $J_{ij}$ and exchange $K_{ij}$ integrals in terms of $d$-only orbitals $d_i$ and spin functions $\sigma_i$. $E_0$ represents the gauge origin of energy.

Having obtained energy expressions for each $\text{SD}_\mu^d$: $10D_q$, $B$, $C$ and $E_0$ are estimated using a least-squares procedure. Using matrix notation, we thus obtain an overdetermined system of linear equations with the unknown parameters stored in $\mathbf{X}$ and given below.

$$
\mathbf{E} = \mathbf{A}X, \quad \text{i.e.} \quad \mathbf{X} = (\mathbf{A}^T\mathbf{A})^{-1}\mathbf{A}^T\mathbf{E}
$$

Comparing SD energies from DFT with those calculated using the LF parameter values, we can state for all considered cases, that the LF parameterization scheme is remarkably compatible with SD energies from DFT; standard deviations between DFT-SD energies and their LF-DFT values are generally between 0.01 and 0.05 eV as shown in Fig. 2 below:
Fig. 2: Predicted LF energies (o) and calculated DFT energies (*)
of the 120 micro-states of a d³ manifold.

This model can obviously be generalized allowing to treat systems with symmetry lower than cubic or even without any symmetry (C₁). Here we make use of the general observation that the KS orbitals and the set of SD considered in eq.(1) convey all the information needed to setup the LF matrix.

Following the effective Hamiltonian approach, let us consider the KS orbitals dominated by d-functions which result from an AOC dⁿ DFT-SCF calculation. From the components of the eigenvector matrix built up from such MOs one takes only the components corresponding to the d functions. Let us denote the square matrix composed of the new column vectors by \( \mathbf{U} \) and introduce the overlap matrix \( \mathbf{S} \):

\[
\mathbf{S} = \mathbf{U} \mathbf{U}^T
\]

Since \( \mathbf{U} \) is in general not orthogonal, we use Löwdin’s symmetric orthogonalisation procedure to obtain an equivalent set of orthogonal eigenvectors \( \mathbf{C} \):

\[
\mathbf{C} = \mathbf{S}^{-\frac{1}{2}} \mathbf{U}
\]

We identify now these vectors as the eigenfunctions of the effective LF Hamiltonian \( \mathbf{h}_{\text{eff}} \) sought, as

\[
\varphi_i = \sum_{\mu=1}^{5} c_{\mu i} d_{\mu}
\]
Thus, the fitting procedure described in the previous section will enable us to estimate
\( \langle \phi_i | H_{LF}^{\text{eff}} | \phi_i \rangle \) and hence the full representation matrix of \( H_{LF}^{\text{eff}} \) as
\[
H_{\mu \nu} = \langle d_\mu | H_{LF}^{\text{eff}} | d_\nu \rangle = \sum_{i=1}^{3} c_\mu c_\nu^* h_{\nu i}
\]

The next step is now to generalize the fitting procedure for the case of no or low symmetry. The energy of a single determinant becomes thus:
\[
E(\text{SD}_k^d) = E \left( \det \begin{pmatrix} \phi_{i(k,1)}^\sigma & \phi_{i(k,2)}^\sigma & \cdots & \phi_{i(k,n)}^\sigma \\ \phi_{i(1,1)}^\sigma & \phi_{i(1,2)}^\sigma & \cdots & \phi_{i(1,n)}^\sigma \\ \phi_{i(2,1)}^\sigma & \phi_{i(2,2)}^\sigma & \cdots & \phi_{i(2,n)}^\sigma \\ \cdots & \cdots & \cdots & \cdots \\ \phi_{i(n,1)}^\sigma & \phi_{i(n,2)}^\sigma & \cdots & \phi_{i(n,n)}^\sigma \end{pmatrix} \right) = \sum_i \langle \phi_i | H_{LF}^{\text{eff}} | \phi_i \rangle + \sum_{i<j} \left( f_{ij} - K_{ij} \delta_{\sigma_i \sigma_j} \right)
\]

Where \( \text{SD}_k^d \) is composed of the spinorbitals mentioned earlier.
In order to calculate the electrostatic contribution, it is useful to consider the transformation from the basis of \( \text{SD}_k^d \) to the one of \( \text{SD}_d^d \). Using basic linear algebra, we get:
\[
\left| \text{SD}_k^d \right> = \sum_{\mu} T_{k\mu} \left| \text{SD}_d^d \right>_{\mu}
\]

Where \( T_{k\mu} = \det \begin{pmatrix} c_{i(k,1),j(\mu,1)} & c_{i(k,1),j(\mu,2)} & \cdots & c_{i(k,1),j(\mu,n)} \\ c_{i(k,2),j(\mu,1)} & c_{i(k,2),j(\mu,2)} & \cdots & c_{i(k,2),j(\mu,n)} \\ \cdots & \cdots & \cdots & \cdots \\ c_{i(k,n),j(\mu,1)} & c_{i(k,n),j(\mu,2)} & \cdots & c_{i(k,n),j(\mu,n)} \end{pmatrix} \)

With the indices of the spinorbitals \( \phi_{i(k,1)}^\sigma, \phi_{i(k,2)}^\sigma, \cdots, \phi_{i(k,n)}^\sigma \) and \( \phi_{i(\mu,1)}^\sigma, \phi_{i(\mu,2)}^\sigma, \cdots, \phi_{i(\mu,n)}^\sigma \) respectively. Note that these indices are in fact a two-dimensional array of (number of SD) x (number of electrons or holes) integers. Finally the energy of a SD can be rewritten as
\[
E_k = E(\text{SD}_k^d) = \sum_i \langle \phi_i | H_{LF}^{\text{eff}} | \phi_i \rangle + \sum_{\mu,\nu} T_{k\mu} T_{k\nu} \langle \text{SD}_d^d_{\mu} | G | \text{SD}_d^d_{\nu} \rangle
\]

Where \( G = 1/r_{12} \) i.e. the electrostatic repulsion of all electron pairs in the LF manifold.

The matrix elements are readily obtained using Slater’s rules and the resulting electrostatic two-electron integrals \( <\text{abcd}> \) in terms of Racah or Slater-Codon parameters. Thus the final equation to estimate \( h_{\mu i} \), \( i = 1, \ldots, 5 \), \( B \) and \( C \) from the DFT energies \( E_k \) of all the SD within the LF manifold will be of the same shape as eqs.(4) and (5) where \( \chi = (h_{11}, \ldots, h_{55}, B, C) \) and \( A \) is calculated as indicated above.
Computational details

All DFT calculations have been performed using the ADF program package [6]. The approximate SCF KS one-electron equations are solved by employing an expansion of the molecular orbitals in a basis set of Slater-type orbitals (STO). All atoms were described through triple-ζ STO basis sets given in the program database (basis set IV) and the core-orbitals up to 3p for the TM and up to 1s (for O, N, C), 2p (Cl) and 3d (Br) were kept frozen. We used the local density approximation (LDA), where exchange-correlation potential and energies have been computed according to the Vosko, Wilk and Nusair’s (VWN) [7] parameterization of the electron gas data.

a) Calculated and experimental photophysical properties of Cs$_2$NaYCl$_6$:Cr$^{3+}$ and Cs$_2$NaYBr$_6$:Cr$^{3+}$

The ground and excited state properties of the Cr$^{3+}$ ion doped into the cubic host lattices Cs$_2$NaYCl$_6$ and Cs$_2$NaYBr$_6$ is studied using LF-DFT (vide supra). We calculate the energies of the multiplets $^4A_2g$, $^4T_2g$, $^2E_g$, and $^4T_1g$. The adiabatic energy surface of both ground state and excited states of the CrX$_6^{3-}$ cluster along the symmetry-adapted displacements (cf. fig. 3) of the six nearest halogen neighbours of the chromium impurity was calculated. The experimental Cr–X distance in the ground state can be reproduced to within 0.01 Å for both chloride and bromide systems. The calculated d – d excitation energies agree within 2'000 cm$^{-1}$. An energy lowering is obtained in the first $^4T_2g$ excited state when the octahedral symmetry of CrX$_6^{3-}$ is relaxed along the $e_g$ Jahn–Teller coordinate. The geometry corresponding to the energy minimum is in excellent agreement with the $^4T_2g$ geometry derived from high-resolution optical spectroscopy of Cs$_2$NaYCl$_6$:Cr$^{3+}$. It corresponds to an axially compressed and equatorially elongated CrX$_6^{3-}$ octahedron. An exhaustive analysis of the problem is given in ref. [8].
Fig. 4 below displays the contour plot of the $^4A_2$ potential energy surface as a function of both $Q_0$ and $Q_e$.

Fig. 4: Contour plot of the $^4A_2$ potential energy surface as a function of both $Q_0$ and $Q_e$. The asterisks indicate the position of the three equivalent excited states $^6T_2$ distorted geometries.
Fig. 5 below shows the contour plot of the $^4T_2$ potential energy surface as a function of both $Q_\theta$ and $Q_\varepsilon$.
Fig. 6 below represents the cross section through the $^4T_2$ potential energy surface along the Jahn-Teller active distortion $Q_0$. 

Fig. 6: Cross section through the $^4T_2$ potential energy surface along the Jahn-Teller active distortion $Q_0$. 

**Graph Details:**
- **Energy Value:** $E_{JT} = 1230 \text{ cm}^{-1}$
- **Distance:** $r_{JT} = 2.3 \text{ Å}$
- **Change:** $\Delta = 52 \text{ cm}^{-1}$
Fig. 7 below shows the cross section through the $^{4}T_2$ and $^{4}A_2$ potential energy surfaces along the Jahn-Teller active distortion $Q_0$:

![Cross section through the $^{4}T_2$ and $^{4}A_2$ potential energy surfaces along the Jahn-Teller active distortion $Q_0$.](image)

High-resolution absorption, MCD and luminescence spectra have been reported for Cs$_2$NaYCl$_6$:Cr$^{3+}$. Accurate values of the excited state energies are therefore known and included in Table 1 and 2. In particular, the region of $^{4}A_{2g} \rightarrow ^{4}T_{2g}$ electronic origins was investigated in detail [9]. As it can be seen from inspection of these tables, the agreement between observed and predicted data, is excellent.
Table 1. Calculated and experimental spectroscopic and structural properties for \( \text{Cs}_2\text{NaYCl}_6:\text{Cr}^{3+} \). Units are Å and cm\(^{-1} \).

|                      | VWN  | BP   | PW91 | Exp.  |
|----------------------|------|------|------|-------|
| Geometry \( ^4A_2 \) | d(Cr-Cl) [Å] | 2.382 | 2.462 | 2.401 | 2.44 |
|                      | d(Cr-Cl)(x,y) [Å] | 2.492 | 2.592 | 2.512 | 2.54 |
|                      | d(Cr-Cl)(z) [Å]  | 2.312 | 2.382 | 2.356 | 2.41 |
| Absorption Max. [cm\(^{-1} \)] | \( ^4A_2 \rightarrow ^4T_2 \) | 12550 | 9760 | 12600 | 12800 |
| Emission Max. [cm\(^{-1} \)] | \( ^4T_2 \rightarrow ^4A_2 \) | 11030 | 8382 | 10380 | 11000 |
| Stokes Shift [cm\(^{-1} \)] | \( ^4A_2 \rightarrow ^4T_2 \) | 1520 | 1378 | 2220 | 1800 |
| Jahn-Teller Energy [cm\(^{-1} \)] | \( ^4T_2 \) | 900 | 662 | 1230 |
| Absorption Max. [cm\(^{-1} \)] | \( ^4A_2 \rightarrow ^4T_1 \) | 15890 | 14650 | 17455 | 18200 |
| Absorption Max. [cm\(^{-1} \)] | \( ^4A_2 \rightarrow ^2E \) | 12320 | 11509 | 11850 | 14430 |

Table 2. Calculated and experimental spectroscopic and structural properties for \( \text{Cs}_2\text{NaYBr}_6:\text{Cr}^{3+} \). Units are Å and cm\(^{-1} \).

|                      | VWN  | BP   | PW91 | Exp.  |
|----------------------|------|------|------|-------|
| Geometry \( ^4A_2 \) | d(Cr-Br) [Å] | 2.525 | 2.615 | 2.579 | 2.60 |
|                      | d(Cr-Br)(x,y) [Å] | 2.635 | 2.755 | 2.694 | 2.75 |
|                      | d(Cr-Br)(z) [Å]  | 2.495 | 2.550 | 2.530 | 2.55 |
| Absorption Max. [cm\(^{-1} \)] | \( ^4A_2 \rightarrow ^4T_2 \) | 11590 | 9500 | 11800 | 12400 |
| Emission Max. [cm\(^{-1} \)] | \( ^4T_2 \rightarrow ^4A_2 \) | 10525 | 8055 | 9845 | 10200 |
| Stokes Shift [cm\(^{-1} \)] | \( ^4A_2 \rightarrow ^4T_2 \) | 1365 | 1445 | 1955 | 2200 |
| Jahn-Teller Energy [cm\(^{-1} \)] | \( ^4T_2 \) | 469 | 680 | 1000 |
| Absorption Max. [cm\(^{-1} \)] | \( ^4A_2 \rightarrow ^4T_1 \) | 14930 | 14550 | 15990 | 17700 |
| Absorption Max. [cm\(^{-1} \)] | \( ^4A_2 \rightarrow ^2E \) | 11390 | 11100 | 12100 | 13900 |
b) Tetrahedral \( d^2 \) \( \text{CrX}_4(g) \) where \( X = \text{Cl}^-, \text{Br}^- \)

Tetrahedral \( d^2 \) complexes possess a \( ^3A_2(e^2) \) ground state as well as \( ^3A_2 \rightarrow ^3T_2 \) and \( ^3A_2 \rightarrow ^3T_1, e \rightarrow t_2 \) singly excited states. They give rise to broad d-d transitions in the optical spectra. In addition, spin-flip transitions within the \( e^2 \) configuration lead to sharp line excitations. Multiplet energies from LDA agree within a few hundred cm\(^{-1}\) with experimental data. In particular the \( ^3A_2 \rightarrow ^3T_2 \) transition energy and thus 10Dq nicely agrees with experiment as is seen from inspection of table 3. Experimental transition energies for CrCl\(_4\) and CrBr\(_4\) as well as values of B, C and 10Dq deduced from a fit to experiment for CrCl\(_4\) are also listed.

**Table 3.** Electronic transition energies of \( \text{CrX}_4, X=\text{Cl} \) and \( \text{Br} \), with geometries optimized using LDA functional and calculated using values of B, C and 10Dq from least square fit to DFT energies of the Slater determinants according to the method described earlier.

| Term            | \( \text{CrCl}_4 \) | \( \text{LF-fit} \) | \( \text{Exp.}^a \) | \( \text{CrBr}_4 \) | \( \text{Exp.}^a \) |
|-----------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| \( ^3A_2(e^2) \) | 0                    | 0                    | 0                    | 0                    | 0                    |
| \( ^1E(e^2) \)   | 6542                 | 6089                 | -                    | 6373                 | 6666                 |
| \( ^1A_1(e^2) \)  | 11114                | 10586                | -                    | 10698                | 10869                |
| \( ^3T_2(e_1t_2) \) | 7008                 | 7010                 | 7250                 | 6163                 | -                    |
| \( ^3T_1(e_1t_2) \) | 10316                | 10440                | 10000                | 9269                 | -                    |
| \( ^1T_2(e_1t_2) \) | 13454                | 12991                | 12000                | 12434                | -                    |
| \( ^1T_1(e_1t_2) \)  | 15074                | 14718                | -                    | 14037                | -                    |
| \( ^1A_1(t_2^2) \)   | 32099                | 30599                | -                    | 30120                | -                    |
| \( ^1E(t_2^2) \)    | 21121                | 20716                | -                    | 19271                | -                    |
| \( ^3T_1(t_2^2) \)   | 16033                | 16229                | 16666                | 14424                | 13258                |
| \( ^1T_2(t_2^2) \)   | 21217                | 20822                | -                    | 19373                | -                    |
| \( \text{R(M-X)} \)  | 2.104                | -                    | -                    | 2.264                | -                    |
| B                | 355                  | 376                  | -                    | 347                  | -                    |
| C                | 1903                 | 1579                 | -                    | 1855                 | -                    |
| 10Dq             | 7008                 | 7250                 | -                    | 6162                 | -                    |
| Std Dev.         | 0.030                | -                    | -                    | 0.030                | -                    |

Optimized geometries correspond to stable minima in the ground state potential surface with harmonic frequencies of the \( \alpha_1, \epsilon, \tau_2(1) \) and \( \tau_2(2) \) vibrational modes of 359, 113, 126 and 464 cm\(^{-1}\) (for CrCl\(_4\)); 207, 63, 82 and 350 cm\(^{-1}\) (for CrBr\(_4\)); respectively; \(^a\) Studer P, Thesis, University of Fribourg, 1975.

c) Octahedral \( \text{Cr}^{III} d^6 \) complexes.

In Table 4 we list the predicted (this work), adjusted (LF fit to exp.) and observed (Exp.) multiplet energies for \( \text{CrX}_6^{3-} \) (\( X = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{CN}^- \)) complex ions. We used a LDA functional to calculate the \( \text{Cr}^{III} \)-X bond lengths and we compare these results with energies from a LF calculation utilizing values of B, C and 10Dq obtained from a best fit to the spectra. Bond lengths are too long while values of 10Dq are too small compared to experiment. The situation improves if instead of optimized, experimental bond lengths are taken for the calculation. Even in this case, spin-forbidden transitions come out by 3000-4000 cm\(^{-1}\) too low in energy compared to experiment. Clearly, in this example of highly charges species, our prediction is much less accurate. In order to
Table 4. Electronic transition energies of CrX₆³⁻, X = F⁻, Cl⁻, Br⁻ and CN⁻ molecules with geometries optimized using LDA functionals calculated using values of B, C and 10Dq from least square fit to DFT energies of the Slater determinants and to experiment. The values of (10Dq)orb as deduced from the eg-t₂g KS-orbital energy difference taken from the t₂g KS-energies are also listed. Experimental transition energies are also listed.

| Term | CrF₆³⁻ | CrCl₆³⁻ | CrBr₆³⁻ | Cr(CN)₆³⁻ |
|------|--------|---------|---------|-----------|
| 4A₂  | 0      | 0       | 0       | 0         |
| 2E   | 12497  | 15802   | 16300   | 10756     |
| 2T₁  | 13044  | 16461   | 16300   | 11180     |
| 2T₂  | 18628  | 23260   | 23000   | 15918     |
| 4T₂  | 13569  | 15298   | 15200   | 10911     |
| 4T₁  | 19443  | 22262   | 21800   | 15618     |
| 2A₁  | 24071  | 28709   | -       | 20056     |
| 2T₁  | 26348  | 31473   | -       | 21878     |
| 2T₂  | 25959  | 30970   | -       | 21568     |
| 2E   | 27819  | 33341   | -       | 23147     |
| 4T₁  | 30339  | 34636   | 35000   | 24375     |
| R(M-X) | 1.957 | 1.933   | 2.419   | 2.335     |
| B   | 605    | 734     | -       | 484       |
| C   | 2694   | 3492    | -       | 550       |
| 10Dq | 13598  | 15297   | -       | 10911     |
| SD  | 0.113  | -       | -       | 0.105     |
| (10Dq)orb | 13928 | -       | -       | 10775     |

Footnotes:
- a K₃CrF₆: Allen GC, El-Sharkawy AM, Warren KD (1971) Inorg. Chem. 10:2538
- b Cs₂NaYCl₃Br: Cr³⁺, Schwartz RW (1976) Inorg. Chem. 15:2817
- c Knox K, Mitchell DW (1961) J. Inorg. Nucl. Chem. 21:253
- d, e estimated for Cs₂NaCrCl₆ and Cs₂NaCrBr₆, Gilardoni F., Weber J., Bellafrouh K., Daul C., Journal de Chimie Physique et de Chimie de l'Air 99 (1996) 7623
- f Witzke H, Theoret. Chim. Acta 20:171 (1974)
- g Jagner S, Ljungström E, Vannerberg N-G (1974) Acta Chem. Scand. A28:623
- h This entry lists the KS-eigenvalue differences ε(eg) - ε(t₂g) for the sake of comparison.
improve the quality of the prediction we obviously need to consider the environment of the CrX₆³⁻ chromophore by adding an appropriate embedding potential to the KS-hamiltonian. Already the use of experimental bond lengths does significantly improve the precision of our calculation as mentioned before. A full analysis of this problem is given in ref. [10]. For the Cr(CN)₆³⁻ ion we note a value of 10Dq which is by 4000 cm⁻¹ higher than the experimental one. This is unusual and not expected: calculated and experimental Cr-C bond distances are indeed very close. We can conclude that for the latter system, existing DFT functionals do not perform properly. In addition the standard deviations are too high. More work is needed to better understand the phenomenon and to improve this.

d) Octahedral Hexaquo Ni(ii) d⁸ complexes.

In Table 5 we list the multiplet energies for the Ni(H₂O)₆²⁺ obtained according to the method outlined in section 2. The experimental electronic spectrum of Ni(ii) ion in aqueous solution exhibit three absorption peaks centered at 8'800cm⁻¹ (³A₂ → ³T₂), at 15'000cm⁻¹ (³A₂ → ³T₁) and at 25'500cm⁻¹ (³A₂ → ³T₁). The agreement with the predicted multiplets is perfect in this case.

| Degeneracy (Multiplicity) | Multiplet Energy [10³cm⁻¹] | S(S+1) | Spin-Orbit splitting [10³cm⁻¹] |
|---------------------------|---------------------------|--------|-------------------------------|
| 3                         | 0.0000000                 | 2.000  | 0.0000000 0.0001074 0.0001645 |
| 3                         | 8.8252743                 | 2.000  | 8.5714426 8.6014099 8.7127700 |
| 3                         | 8.8414083                 | 2.000  | 8.7298366 8.7386983 9.0699081 |
| 3                         | 8.8737000                 | 2.000  | 9.0847504 9.0917825 9.2288776 |
| 3                         | 14.5809908                | 2.000  | 13.9177850 14.1466476 14.1493461 |
| 3                         | 14.5921568                | 2.000  | 14.3609969 14.3613509 14.3698568 |
| 3                         | 14.5934211                | 2.000  | 15.0584802 15.0593531 15.0618965 |
| 1                         | 14.6214912                | 0.000  | 15.7200626 |
| 1                         | 14.6221451                | 0.000  | 15.7224490 |
| 1                         | 23.0538531                | 0.000  | 22.8226585 |
| 1                         | 23.0674913                | 0.000  | 22.8343287 |
| 1                         | 23.0966616                | 0.000  | 22.8599397 |
| 1                         | 23.5866071                | 0.000  | 23.7076105 |
| 3                         | 25.2933052                | 2.000  | 25.2187733 25.2277340 25.5319615 |
| 3                         | 25.3050996                | 2.000  | 25.5347498 25.5451571 25.5868215 |
| 3                         | 25.3063639                | 2.000  | 25.5873367 25.5920497 25.7705637 |
| 1                         | 27.5214320                | 0.000  | 27.6420000 |
| 1                         | 27.5214702                | 0.000  | 27.6420403 |
| 1                         | 27.5376041                | 0.000  | 27.6580624 |
| 1                         | 34.1878765                | 0.000  | 34.3128908 |
| 1                         | 34.2156132                | 0.000  | 34.3405845 |
| 1                         | 34.5899024                | 0.000  | 34.7083317 |
| 1                         | 34.5948335                | 0.000  | 34.7133008 |
| 1                         | 34.6084717                | 0.000  | 34.7269772 |
| 1                         | 60.3671270                | 0.000  | 60.5117478 |

From the spin-orbit splitting of the ³A₂ ground state it is possible to obtain the ZFS D-tensor using a conventional spin hamiltonian approach
\[ H_{\text{ZFS}} = \vec{S} \cdot \vec{D} \cdot \vec{S} = D \left( \hat{S}_z^2 - \frac{2}{3} \right) + E \left( \hat{S}_x^2 - \hat{S}_y^2 \right) \]

and equating the energies of the spin-orbit components of the \(^3\text{A}_2\) to the eigenvalues of this spin hamiltonian. The result is given below:

\[
\begin{bmatrix}
0.0000 \\
0.1074 \\
0.1645
\end{bmatrix} =
\begin{bmatrix}
-2/3 & 0 & 1 \\
1/3 & -1 & 1 \\
1/3 & 1 & 1
\end{bmatrix}
\begin{bmatrix}
D \\
E \\
C
\end{bmatrix}
\]

The solution of this set of three linear equations is: \(D = 0.1360 \text{ cm}^{-1}\) and \(E = 0.0285 \text{ cm}^{-1}\). The third parameter \(C\) describes the arbitrary energy origin. There are experimental measurements of the ZFS for \(\text{Ni(H}_2\text{O)}_{6}^{2+}\) in \(\text{NiSiF}_6\cdot6\text{H}_2\text{O}\) available. At 90K the ZFS is 0.17 cm\(^{-1}\). However, \(D\) is very sensitive on alteration of the temperature and pressure. Thus, an exhaustive description of the observed ZFS needs a dynamical study of the process which goes far beyond the goal of this work.

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