Calculation of Spin-Orbit Coupling Within the LFDT: Applications to \([\text{NiX}_4]^{2-}\) (X=F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\))

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ABSTRACT: Spin-orbit coupling has been introduced into our newly developed ligand field density functional theory (LFDT), using the zero-order regular approximation as implemented into the Amsterdam density functional (ADF) code. Application of the formalism to a series of \([\text{NiX}_4]^{2-}\) (X=F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\)) compounds shows the increasing importance of intra-ligand spin-orbit coupling across the F, Cl, Br, I series, to lead to sign reversal (in the case of Br\(^-\) and I\(^-\)) of the spin-orbit splitting within the \(t_2\)-orbitals manifold of \(\text{Ni}^{2+}\). Symmetry lowering from \(T_d\) to \(D_{2d}\), due to the Jahn–Teller coupling for the \(e^4t_2^4\) configuration of \([\text{NiX}_4]^{2-}\), is used to manifest further the effect of bonding changes on the sign and magnitude of the spin-orbit constant. Ligand field and spin-orbit coupling matrices are found to be correlated, with the higher extent of antibonding being accompanied by lower values of the spin-orbit coupling constant. In cases of little or no symmetry, this leads to situations in which ligand field and spin-orbit coupling cannot be neatly separated in the mathematical description. Using these results, the electronic energy levels of this series of compounds are predicted to be in good agreement with available spectral and magnetic data from literature.

Key words: spin-orbit coupling; density functional theory; ligand field theory; Jahn–Teller effect; zero field splitting

1. Introduction

Spin-orbit coupling is an essential constituent of the Hamiltonian for electronic states originating from \(d^n\)-configurations of transition metals in ligand fields (LF). It governs the fine structure of the electronic multiplets and, for the ground state it is mainly responsible for the zero-field splitting and the anisotropy affecting the spectroscopic and magnetic behavior of TM compounds with open \(d\)-shells. Recently, we proposed a ligand field density functional theory [1, 2] (LFDT), which is a DFT-based method to determine ligand field parameters. Modern functionals, which are all based

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2. Spin-Orbit Coupling

Spin-orbit coupling cannot be ignored when ions or molecules contain heavy elements. The effect is not very large for first-row elements and is more pronounced in their magnetic properties. However, for second- and third-row transition metals, as well as for the f-elements, even qualitative accounts of electronic absorption spectra cannot neglect spin-orbit effects. Similarly, for molecular orbitals calculations in which ligands play an important role, spin-orbit coupling due to ligands, e.g., iodide or bromide, must be considered.

2.1. THEORETICAL DESCRIPTION

The nature and origin of spin–orbit coupling have been discussed by many investigators [7]. Misetich and Buch [8] have shown that the spin-orbit Hamiltonian of a molecule can be approximated reasonably well as

\[ \hat{H}_{SO} = \sum_{N,i} \zeta_{N} \cdot \hat{I}_{i,j} \cdot \hat{s}_{i} = \sum_{i} \tilde{u}_{i,j} \cdot \hat{s}_{i,\mu} \]  

(1)

where \( \zeta_{N} \), the spin-orbit coupling constant of nucleus \( N \), is incorporated into the molecular operator \( \tilde{u}_{i} \) for electron \( i \).

To carry out a spin-orbit calculation, it is necessary to relate the resultant splitting of many electron states and also the interaction of different states to one-electron spin-orbit coupling matrix elements. This can be done most conveniently on the basis of micro-states (single determinants), as shown in Refs. [1, 2, 9] for the calculation of multiplets, using Slater’s rules. Indeed, the calculation of matrix elements of one- and two-electron operators between determinantal N-electron wave functions is straightforward. For the spin-orbit interaction, only one-electron operators are involved. Calculation of the corresponding matrix elements is described next.

The spin-orbit operator in Eq. (1) enables the expression of matrix elements of spin-orbit coupling in and between subshells in terms of molecular orbitals. Thus, any arbitrary one-electron spin-orbit coupling matrix element can be written as:

\[ \langle s m_{i,\mu} | \hat{H}_{SO} | s m'_{\nu} b \beta \rangle = \langle s m_{i,\mu} | a a | \hat{s} | s m'_{\nu} b \beta \rangle \]

\[ = \sum_{k=x,y,z} \langle s m_{i} | s_{k} | s m'_{\nu} \rangle \times \langle a a | u_{i} | b \beta \rangle, \]  

(2)

where \( s \) is the spin of a single electron with component \( m_{s,\mu} \), and \( a \) and \( b \) are the irreducible representa-
tions (irrep.) of the molecular orbitals; and \( \alpha \) and \( \beta \) are the corresponding components in the case of degeneracy. The first term on the right-hand side of Eq. (2) is no more than the Pauli matrices and the second term can be further reduced using Wigner–Eckhardt’s theorem:

\[
\langle a|a|b\rangle = \langle a|a|b\rangle (a||b|b), \quad (3)
\]

where \( \langle a|a|b\rangle \) are coupling coefficients for the tetrahedral group and \( \langle a|a|b\rangle \) are reduced matrix elements. Combining Eqs. (2) and (3) enables us to express any arbitrary spin-orbit matrix element as a product of symmetry coefficients and reduced matrix elements:

\[
\langle s_m, a|a|b\rangle |s_m, b\rangle = \langle a|a|b\rangle \sum_{k=x,y,z} (s_m|s_m|b) \times (a|a|b, t, k). \quad (4)
\]

To estimate the still unknown reduced spin-orbit coupling matrix elements \( \langle a|a|b\rangle \), we shall map Eq. (4) onto a ZORA-DFT calculation and adjust the reduced matrix elements to reproduce the calculated ligand field levels as done previously in LF-DFT. This task requires a symmetry adaptation of the K-S molecular orbitals to the double-group \( T_d \), i.e.,

\[
e \otimes \Gamma_6(\alpha, \beta) = \Gamma_6;
\]

\[
|\Gamma_6(e) : \kappa\rangle = -|e\rangle, \beta\rangle;
\]

\[
|\Gamma_6(e) : \lambda\rangle = |e\rangle, \alpha\rangle;
\]

\[
|\Gamma_6(e) : \mu\rangle = -|e\rangle, \beta\rangle;
\]

\[
|\Gamma_6(e) : \nu\rangle = |e\rangle, \alpha\rangle;
\]

\[
t_2 \otimes \Gamma_6(\alpha, \beta) = \Gamma_6;
\]

\[
|\Gamma_6(t_2) : \kappa\rangle = \frac{1}{\sqrt{6}} |t_2\rangle, \alpha\rangle - \frac{i}{\sqrt{6}} |t_2\rangle, \beta\rangle + \frac{2}{\sqrt{6}} |t_2\rangle, \alpha\rangle;
\]

\[
|\Gamma_6(t_2) : \lambda\rangle = -\frac{1}{\sqrt{2}} |t_2\rangle, \beta\rangle + \frac{i}{\sqrt{2}} |t_2\rangle, \beta\rangle;
\]

\[
|\Gamma_6(t_2) : \mu\rangle = \frac{1}{\sqrt{2}} |t_2\rangle, \alpha\rangle + \frac{i}{\sqrt{2}} |t_2\rangle, \beta\rangle;
\]

\[
|\Gamma_6(t_2) : \nu\rangle = -\frac{1}{\sqrt{6}} |t_2\rangle, \beta\rangle - \frac{i}{\sqrt{6}} |t_2\rangle, \beta\rangle + \frac{2}{\sqrt{6}} |t_2\rangle, \alpha\rangle;
\]

\[
|\Gamma_6(t_2) : \alpha\rangle = |t_2\rangle, \beta\rangle + \frac{1}{\sqrt{3}} |t_2\rangle, \alpha\rangle;
\]

\[
|\Gamma_6(t_2) : \beta\rangle = \frac{1}{\sqrt{3}} |t_2\rangle, \beta\rangle - \frac{1}{\sqrt{3}} |t_2\rangle, \beta\rangle.
\]

where the notation of the double-group representation is according to Bethe, and their components are Griffith’s [10]. Using this basis transformation along with spin-orbit coupling elements (Appendix 1), the one-electron spin-orbit coupling and LF matrix reduces to:

\[
\begin{array}{ccc}
\Gamma_6(e) & \Gamma_6(t_2) & \Gamma_6(t_2) \\
\hline
\Gamma_6(e) & h_{cc} & -\frac{3}{2} \xi_{x}^{t_2} \\
\Gamma_6(t_2) & \frac{3}{2} \xi_{x}^{t_2} & h_{t_2} \\
\Gamma_6(t_2) & 0 & 0
\end{array}
\]

(6)

where \( h_{cc} \) and \( h_{t_2} \) are the one-electron ligand field matrix elements, the \( h_{t_2} \) difference being the cubic field splitting \( \Delta \), and \( \xi_{x}^{t_2} \) and \( \xi_{y}^{t_2} \) the reduced matrix elements:

\[
\xi_{x}^{t_2} = \langle e|\xi_{x}^{t_2}(t_2)|t_2\rangle
\]

\[
\xi_{x}^{t_2} = \langle e|\xi_{y}^{t_2}(t_2)|t_2\rangle
\]

which we derive in a form to be directly compared with the free Ni\(^{2+}\) spin-orbit coupling constant (630 cm\(^{-1}\)). Section 3.3 describes a procedure of obtaining these parameters from ZORA-DFT calculations.

The \( ^{3}T_1 \) ground state of Ni\(^{2+}\) (d\(^{8}\)) in a tetrahedral \( (T_d) \) ligand field is Jahn–Teller unstable and distorts toward tetragonal \( D_{4d} \) symmetry with elongation along the \( S_4 \) axis of the tetrahedron. For this point group, the symmetry species \( t_2(\xi, \eta, \zeta) \) and \( e(\theta, \phi) \) split into \( e(\xi, \eta) + b_2(\xi) \) and \( a_1(\theta) + b_1(\phi) \), respec-
We note that in $D_{2h}$ symmetry the cubic quantities $\xi_{21,1}^c$ and $\xi_{1,2}^c$ split into three and two different reduced matrix elements, respectively. Symmetry adaptation of the K–S molecular orbitals to the $D_{2h}$ double group yields

$$a_1 \otimes \Gamma_6(\alpha, \beta) = \Gamma_6:$$

$$|\Gamma_6(a_1), \alpha'\rangle = |a_1, \alpha\rangle$$

$$|\Gamma_6(a_1), \beta'\rangle = |a_1, \beta\rangle$$

$$e \otimes \Gamma_6(\alpha, \beta) = \Gamma_6:$$

$$|\Gamma_6(e), \alpha'\rangle = \frac{1}{\sqrt{2}} |e\xi, \beta\rangle - \frac{i}{\sqrt{2}} |e\eta, \beta\rangle$$

$$|\Gamma_6(e), \beta'\rangle = \frac{1}{\sqrt{2}} |e\xi, \alpha\rangle + \frac{i}{\sqrt{2}} |e\eta, \alpha\rangle$$

$$b_1 \otimes \Gamma_6(\alpha, \beta) = \Gamma_7:$$

$$|\Gamma_7(b_1), \alpha''\rangle = -|b_1, \beta\rangle$$

$$|\Gamma_7(b_1), \beta''\rangle = |b_1, \alpha\rangle$$

where again double-group representations are according to Bethe. Using this basis transformation along with the spin-orbit coupling matrix elements (Appendix 1), we obtain the spin-orbit coupling and LF matrix for this symmetry

$$b_2 \otimes \Gamma_6(\alpha, \beta) = \Gamma_7:$$

$$|\Gamma_7(b_2), \alpha''\rangle = |b_2, \xi, \beta\rangle$$

$$|\Gamma_7(b_2), \beta''\rangle = |b_2, \xi, \alpha\rangle$$

$$e \otimes \Gamma_6(\alpha, \beta) = \Gamma_7:$$

$$|\Gamma_7(e), \alpha''\rangle = \frac{1}{\sqrt{2}} |e\xi, \alpha\rangle - \frac{i}{\sqrt{2}} |e\eta, \alpha\rangle$$

$$|\Gamma_7(e), \beta''\rangle = -\frac{1}{\sqrt{2}} |e\xi, \beta\rangle + \frac{i}{\sqrt{2}} |e\eta, \beta\rangle,$$

where $h_{a1,1}, h_{a2,2}, h_{b1,1}, h_{b1,2}$ are the (diagonal in this case as well) one-electron ligand field matrix elements and $\xi_{ij}^c$ are the reduced matrix elements:

$$\xi_{a1}^c = \langle a_1, \|\hat{\sigma}\rangle |e\rangle \langle e|$$

$$\xi_{a2}^c = \langle b_1, \|\hat{\sigma}\rangle |b_2\rangle \langle b_2|$$

$$\xi_{b1}^c = \langle b_1, \|\hat{\sigma}\rangle |e\rangle \langle e|$$

$$\xi_{b2}^c = \langle e, \|\hat{\sigma}\rangle |a_2\rangle \langle a_2|$$

$$\xi_{b2}^c = \langle b_2, \|\hat{\sigma}\rangle |e\rangle \langle e|.\] (10)

We note that in $D_{2h}$ symmetry, the cubic quantities $\xi_{b1,1}^c$ and $\xi_{1,2}^c$ split into three and two different reduced matrix elements, respectively, yielding a total of five independent parameters. In LF studies, thus far the variation of spin-orbit coupling between the various symmetries of the involved LF-orbitals have been approximated in terms of orbital reduction factors. In the next section, we derive a rigorous procedure that allows us to deduce these quantities from DFT-ZORA calculations.

### 3. Computational Procedure

The DFT calculations have been performed with the aid of the ADF program code (release 2003.01) [6]. For the exchange-correlation functionals, both
the local density approximation (LDA, for geometry optimizations) and the generalized gradient approximation (GGA) (for energies of electronic states) have been used. For LDA, we adopt an Xα functional for exchange ($α = 0.7$) [11] and Vosko, Wilk, and Nusair functional for correlation [12]. The GGA has been introduced in the form given by Perdew–Wang [13]. The frozen-core approximation was used for inner core electrons. The orbitals up to $3p$ for Ni, $1s$ for fluorine, $2p$ for chlorine, $3d$ for bromine, and up to $4d$ for iodine were kept frozen. The valence shells were described by triple zeta plus one polarization function (TZP basis set). Spin-restricted relativistic ZORA calculations have been done by adopting the ZORA basis set (TZP) [14].

The valence shells were described by triple zeta plus one polarization function (TZP basis set). Spin-restricted relativistic ZORA calculations have been done by adopting the ZORA basis set (TZP) [14]. Using basis functions of increasing quality from TZP to TZ2P to TZ2P+ does not change results significantly (see Section 4.4).

3.1. GEOMETRY OPTIMIZATIONS

Geometry optimizations of the NiX$_2^-$ species have been done in nonrelativistic spin-unrestricted ($M_s = 1$) formalism, using the LDA-only functional, which we know from experience [2] to yield TM–ligand bond distances in good agreement with experiment. To study the Jahn–Teller activity within the $^3T_1$ ground state, separate optimizations imposing a $D_{2d}$ geometry have been carried out following the guidelines of accounting for the Jahn–Teller effect within DFT [15]. It should be noted that, as a single determinant method, DFT is unable to yield optimized geometries in the case in which two or more configurations mix with each other. This is the case in our study, where two $^3A_2$ states (originating from $^3T_1$ in tetrahedral symmetry), corresponding to the ground configuration ($e^4t_{2g}^2$) and to the excited configuration ($e^4t_{2g}^4$), mix and reduce the extent of the structural distortion and of the Jahn–Teller stabilization ($E_{JT}$) [16]. A procedure to solve this problem is briefly outlined in Appendix 2 and is used here to obtain ground-state $D_{2d}$ geometries for all NiX$_2^-$ species.

3.2. LF-DFT CALCULATIONS

The LF-DFT method is well documented [1, 2]. In short, the following steps are considered. Having chosen a reference geometry (see Section 3.1), an average of configuration spin-restricted (AOC) calculation is performed with eight electrons distributed evenly over the five $3d$-molecular orbitals. The latter are identified as such, according to their dominant metal character, inspecting the K–S eigenvectors. Constraining the electron density to this distribution of charge, the energies of all 45 Slater determinants are calculated in a spin-unrestricted way. Using the two $5 \times 5$ matrices of K–S 3d-eigenvalues (diagonal matrix) and their MO coefficients along with the energies of the SD our formalism (implemented into a MATLAB script) yields the parameters of interelectronic repulsion $B$ and $C$ and the $5 \times 5$ LF matrix, which in our case takes a diagonal form with two different energies ($e$ and $t_2$) for $T_d$ and four different energies ($h_{t_1a}, h_{t_1b}, h_{h_2a},$ and $h_{h_2b}$) for $D_{2d}$ (MATLAB 6.1 scripts and programs written for each system can be obtained from the authors on request.) At the same time, the program yields the energies of all 45 electronic states in an LF multiplet calculation. This corresponds to a CI procedure within the DFT formalism.

3.3. CALCULATION OF REDUCED MATRIX ELEMENTS OF SPIN-ORBIT COUPLING FROM ZORA-DFT

Let us consider the K–S eigenvalues in the basis of the double group symmetry adapted fragment orbitals (SFO) and the symmetry adapted fragment spin-orbitals [see Eqs. (5) and (8)]. To be more specific let us take as an example NiCl$_2^-$. Focusing on the $T_d$ complex, the 5$1t_1$, 16$2t_2$, and 8$e$ spin-orbitals give rise to a total of 29$1\Gamma_8$ and 16$1\Gamma_7$ K–S-orbitals, from which we identify the 6$1\Gamma_8$, 7$1\Gamma_8$, and 4$1\Gamma_7$ ones with dominant 3$d$ character. We correspondingly occupy these evenly in the ZORA input with occupation numbers and ZORA eigenvalues taken from the output listed in Eq. (11). We further find from the table of the SFO, 8, 5, and 16 species of $E$, $T_1$, and $T_2$ symmetry, yielding a total of 29 basis functions for $1\Gamma_8$ and 16 $T_2$ species, giving rise to the same number of $1\Gamma_7$ species. These yield the coefficients of the 6$1\Gamma_8$, 7$1\Gamma_8$, and 4$1\Gamma_7$ K–S–ZORA eigenvectors. We thus obtain truncated ZORA-K–S eigenvectors and (diagonal) eigenvalues matrices $U$ and $\Lambda$ [Eqs. (11)]:

$$
\begin{align*}
\begin{bmatrix}
6\Gamma_8 & 7\Gamma_8 & 4\Gamma_7 \\
6\Gamma_8 & 2.940 & 0.0 & 0.0 \\
7\Gamma_8 & 0.0 & 3.458 & 0.0 \\
4\Gamma_7 & 0.0 & 0.0 & 3.509
\end{bmatrix}
\end{align*}
$$

$$
U = \begin{bmatrix}
-0.842 & -0.135 & 0.0 \\
-0.104 & 0.789 & 0.0 \\
0.0 & 0.0 & -0.816
\end{bmatrix}
$$

$$
\Lambda = \begin{bmatrix}
6\Gamma_8 & 2.940 & 0.0 & 0.0 \\
7\Gamma_8 & 0.0 & 3.458 & 0.0 \\
4\Gamma_7 & 0.0 & 0.0 & 3.509
\end{bmatrix}
$$

$$
S = U \cdot U^T
$$
The spin-orbit coupling elements listed in Table II. Thus, from a single ZORA calculation, both the ligand field and spin-orbit coupling matrices are obtained. To facilitate the analysis of the ADF output, a series of MATLAB scripts are used as interfaces.

4. Applications, Results, and Discussion


NiX$_4^2$– (X=Cl$^-$, Br$^-$, I$^-$) are well studied structurally [17, 18] and/or spectroscopically [19–22] and found to exist as slightly distorted (NiCl$_4$) or almost regular tetrahedra (NiBr$_4$ and NiI$_4$). NiF$_4^2$– remains unknown, Ni$^{2+}$–F$^-$ complexes tending invariably to adopt a regular octahedral geometry. In line with these observations, our geometry optimizations (Table I) show, that the extent of the Jahn–Teller elongation (Fig. 1) and the stabilization energy is strongly reduced due to mixing between the $e^3t^2_2$ and $e^1t^2_2$ configurations (cf. Appendix 2), the latter configuration being Jahn–Teller stabilized by a $D_{2h}$ compression. In this respect, the $e^3t^2_2$ configuration resembles very much the Jahn–Teller activity in Cu$^{2+}$ with a single hole in the $t_2$-shell, which readily explains the different stereochemistries of these two ions [16]. Table I (square brackets) also lists geometries and $E_{JT}$ values of NiX$_4^2$– neglecting the $e^3t^2_2$–$t_2^2$ mixing. It is this geometry, with more pronounced distortions, that we use to explore the effect of symmetry lowering on the anisotropy of spin-orbit coupling. However, in the discussion of electronic transitions and comparison with the experiment, we make use of the correct geometry.

After manipulations as described in Eqs. (12) and (13), we obtain the one-electron Hamiltonian matrix [Eq. (14)]. The comparison with Eq. (6) yields directly the reduced matrix elements $e_{ij}$ and $h_{ij}$ as well as the cubic ligand splitting $\Delta$ (333, 487, and 4,166 cm$^{-1}$, respectively). In a similar way, the matrices of the spin-orbit coupling plus the LF for NiCl$_4^2$– in $D_{2h}$ symmetry are derived from matrix 15. Using definition Eq. (10), this yields the LF and}

\[
\begin{align*}
\Gamma_{\delta}(a_1) & : 2.991 
0.072i 
0.0 
0.0 
0.0 \\
\Gamma_{\delta}(e) & : -0.072i 
3.582 
0.0 
0.0 
0.0 \\
\Gamma_{\gamma}(b_1) & : 0.0 
0.0 
2.950 
-0.063i 
-0.040i \\
\Gamma_{\gamma}(b_2) & : 0.0 
0.0 
0.063i 
3.301 
-0.029 \\
\Gamma_{\gamma}(e) & : 0.0 
0.0 
0.040i 
-0.029 
3.623 \\
\end{align*}
\]

(15)
While spin-orbit coupling leads to splitting of levels, whose ZORA energies we plot in Figure 2.

**4.2. SPIN-ORBIT COUPLING IN Td SYMMETRY**

The \((\alpha, \beta)\)-e, \(t_2(3d)\) spin-orbit coupling in \(T_d\) symmetry gives rise to \(\Gamma_8(e)\) and \(\Gamma_8 + \Gamma_7(t_2)\) spinor levels, whose ZORA energies we plot in Figure 2. While spin-orbit coupling leads to splitting of \(t_2(\alpha, \beta)\) in first order, it causes a mixing of \(\Gamma_8(t_2)\) and \(\Gamma_8(e)\) to second order. LF splitting \(\Delta(T_d)\) is calculated in the range of 4370 (NiF\(_4^{2-}\)) to 3395 (NiI\(_4^{2-}\)) and dominates over the spin-orbit coupling: \(\xi(\text{Ni}^{2+}) = 630\) cm\(^{-1}\); this is accounted for in Figure 2, where dominant contributions from \(e\) and \(t_2\) are underlined. We notice that when moving from NiF\(_4^{2-}\) to NiCl\(_4^{2-}\), the \(\Gamma_8(t_2 + e) - \Gamma_7(t_2)\) energy separation, which equals \(3/2\) \(\xi_{t_2}^{\text{t}2\text{t}2}\) [see Eq. (6)], becomes smaller and is lowered further, going to NiBr\(_4^{2-}\) and NiI\(_4^{2-}\). It is important to observe that the sign of the splitting changes in the latter two complexes. The analysis of the energy levels (Fig. 2) in terms of the parameters \(h_{t_2t_2}^{\text{t}2\text{t}2}, h_{\text{t}2\text{t}2}^{\text{t}2\text{t}2}\), and \(\xi_{t_2}^{\text{t}2\text{t}2}\) [cf. Eq. (6)] calculated values are listed in Table II] shows indeed that \(\xi_{t_2}^{\text{t}2\text{t}2}\) becomes negative in the case of NiBr\(_4^{2-}\) and NiI\(_4^{2-}\). As has been pointed out previously [22], ligand spin-orbit coupling (as large as 5,000 cm\(^{-1}\) for \(\Gamma_7(t_2)\)) in combination with the metal (3d)–ligand \((np)\) mixing can strongly modify the effective spin-orbit coupling constant; this contribution can be of different sign and can even outweigh the spin-orbit coupling due to the 3d electrons; this turns the sign of the \(\Gamma_8(t_2 + e) - \Gamma_7(t_2)\) splitting. Our ZORA calculations lend full support of this proposition, initially observed by MCD data on NiI\(_4^{2-}\) [22]. Contrary to earlier interpretations [23], our results indicate that spin-orbit coupling undergoes a stronger decrease with increasing metal–ligand covalency than Stevens’s orbital reduction factors in the magnetic moment operator (amenable from a fit to magnetic susceptibilities). Indeed, with increasing covalency from F\(^-\) to Cl\(^-\) to Br\(^-\) to I\(^-\), \(\xi_{t_2}^{\text{t}2\text{t}2}\) and \(\xi_{t_2}^{\text{t}2\text{t}2}\) show a much stronger reduction than deduced from orbital reduction factors as the squared MO coefficients \(\zeta_{3d}^{\text{t}2\text{t}2}\) for \(3d\) in the \(e\) and \(t_2\) MOs and their combinations \(0.82, 0.72, 0.68, 0.66 \) (\(e\)) and \(0.75, 0.63, 0.60, 0.56 \) \((t_2)\) for F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\) complexes, respectively. The order of values for the reduced matrix elements in a given complex \(\xi_{t_2}^{\text{t}2\text{t}2} > \xi_{t_2}^{\text{t}2\text{t}2}\) (obeyed for all cases in Table I) reflects also subtle changes in the metal–metal interactions over the spin-orbit coupling:

\[ \text{TABLE II} \]

| Ligand field (diagonal) matrix elements and reduced spin-orbit coupling matrix elements for \(T_d\) and elongated \(T_d \rightarrow D_{2d}\) (in square brackets) DFT optimized (spin-unrestricted, LDA-functional) [NiX\(_4^{2-}\) \((X=F^-, Cl^-, Br^-, I^-)\) geometries from ZORA (spin-restricted, LDA + PW91 functional) calculations. |
| \(T_d\) | \([D_{2d}]\) | \([\text{NiF}_4^{2-}]\) | \([\text{NiCl}_4^{2-}]\) | \([\text{NiBr}_4^{2-}]\) | \([\text{NiI}_4^{2-}]\) |
| \(T_d\) | \([D_{2d}]\) | \(T_d\) | \([D_{2d}]\) | \(T_d\) | \([D_{2d}]\) | \(T_d\) | \([D_{2d}]\) |
| \(h_{eo}\) | \([h_{e,o}^{\text{t}2\text{t}2}] \) | \([-2622\] | \([-1904\]) | \([-2500\] | \([-2410\]) | \([-2277\] | \([-2310\]) | \([-2037\] | \([-2150\]) |
| \(h_{\text{t}2\text{t}2}\) | \([h_{\text{t}2\text{t}2}^{\text{t}2\text{t}2}] \) | \([-2990\] | \([-3600\]) | \([-3247\] | \([-2736\]) | \([-2526\] | \([-2386\]) | \([-2259\] | \([-2151\]) |
| \(\xi_{t_2}^{\text{t}2\text{t}2}\) | \([\xi_{t_2}^{\text{t}2\text{t}2}] \) | \([588\] | \([576\]) | \([488\] | \([474\]) | \([373\] | \([337\]) | \([375\] | \([222\]) |
| \(\xi_{t_2}^{\text{t}2\text{t}2}\) | \([\xi_{t_2}^{\text{t}2\text{t}2}] \) | \([518\] | \([516\]) | \([332\] | \([326\]) | \([-242\] | \([-242\]) | \([-832\] | \([-824\]) |
ligand overlap (differential covalency) being larger for the more strongly \((\sigma + \pi)\)-antibonding \(t_2\) compared with the only weakly \((\pi)\)-antibonding \(e\) orbital.

### 4.3. SPIN-ORBIT COUPLING IN \(D_{2d}\) SYMMETRY

Going to the \(D_{2d}\) distorted \(T_d\) complex, the \(e(d_{z^2}, d_{x^2-y^2})\) and \(t_2(d_{xy}, d_{xz}, d_{yz})\) orbitals split into \(a_1(d_{z^2}) + b_1(d_{x^2-y^2})\) and \(b_2(d_{xy}) + e(d_{xz}, d_{yz})\) species and the ligand field matrix becomes fully defined in terms of 10 \(D_q\) plus the \(t_2\) and \(e\) splitting parameters \(\delta_t\) and \(\Delta e\), respectively. This is illustrated in Figure 3 with parameter values pertaining to \(\text{NiCl}_4^{2-}\). In parallel with this increase in the level of parameterization, the matrix of spin-orbit coupling becomes dependent on five reduced matrix elements [Eq. (9)]. Figure 5 shows their variation with the angular geometry for \(\text{NiCl}_4^{2-}\), changing the \(\theta\)-angle in wide range from elongated to compressed \(D_{2d}\) structures. It is striking that the variations of the spin-orbit coupling parameters \(\xi_{ij}\) follow the same trends as the energies of the correspondingly involved \(i\) and \(j\) orbitals (Figs. 4 and 5); the stronger the extent of antibonding (increasing the energy of the involved \(i\) and \(j\) orbitals), the stronger the \(\xi_{ij}\) reduction. Thus, in an attenuated way, the \(\xi_{ij}\) parameters reflect the angular dependence of the LF matrix. In classical LF theory, the parameter \(\zeta\) has been deemed to have an atomic nature, being scaled by some reduction factor, occasionally accounting for axial anisotropy as well. In view of our results, we suggest that such treatments are incomplete. The strong interre-

---

**FIGURE 3.** Orbital level splittings and notations for a symmetry based description of the \(D_{2d}\) distorted (elongated) \(\text{NiCl}_4^{2-}\) complex for a geometry obtained without correction for \(^3T_1(e^{a_1})\)\(^3T_1(e^{b_2})\) missing.

**FIGURE 4.** Reduced matrix elements of the spin-orbit coupling operator from ZORA-ADF calculations in the \(T_d\) and \(D_{2d}\) geometries of the \(\text{NiCl}_4^{2-}\) and their dependence in the geometrical angle \(\theta\) (see Fig. 1).

**FIGURE 5.** Dependence of Kohn–Sham orbital energies from nonrelativistic calculation with average-of-configuration occupancies (\(T_d\): \(e^{a_1.2b_1.6a_1.6e^{a_3.2}}\); \(D_{2d}\): \(a_1.6b_1.6a_1.6e^{a_3.2}\)) on the geometric angle \(\theta\) for \(\text{NiCl}_4^{2-}\) (\(R = 2.29\ \text{Å}, \text{PW91-functional, TZP basis}\)). Orbital energy expressions on the right-hand side refer to the limiting case of a compression–square planar geometry and angular overlap model expressions (see Section 4.4).
TABLE IV

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>$[D_{2d}]$</th>
<th>$\text{[NiF}_4^{2-}]$</th>
<th>$\text{[NiCl}_4^{2-}]$</th>
<th>$\text{[NiBr}_4^{2-}]$</th>
<th>$\text{[NiI}_2^{2-}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_{ee}$</td>
<td>$[h_{d,a}(d_{x^2-y^2})]$</td>
<td>$-2494$</td>
<td>$-2482$</td>
<td>$-2274$</td>
<td>$-2034$</td>
</tr>
<tr>
<td></td>
<td>$[h_{d,p}(d_{x^2-y^2} + y)]$</td>
<td>$-1696$</td>
<td>$-2320$</td>
<td>$-2321$</td>
<td>$-2266$</td>
</tr>
<tr>
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<td>$[h_{d,p}(d_{x^2-y^2})]$</td>
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<td>$1619$</td>
<td>$1516$</td>
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</tr>
<tr>
<td></td>
<td>$[h_{ee}(d_{x^2} + d_{y^2})]$</td>
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<td>$146$</td>
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<td>$445$</td>
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<td>$[B]$</td>
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<td>$521$</td>
<td>$462$</td>
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<tr>
<td>$C$</td>
<td>$[C]$</td>
<td>$2732$</td>
<td>$2136$</td>
<td>$1944$</td>
<td>$1804$</td>
</tr>
</tbody>
</table>

4.4. LIGAND FIELD PARAMETERS, GROUND AND EXCITED STATES ENERGIES OF NiX$_4^{2-}$ ($X$=Cl$^-$, Br$^-$, I$^-$) AND COMPARISON WITH EXPERIMENTAL DATA

A list of LF parameters, the (diagonal) LF matrix and the $B$ and $C$ values for NiX$_4^{2-}$ halide complexes in $T_d$ and $D_{2d}$ symmetry, is presented in Table III. There is a good agreement between the LFDF calculation and the experimental data. These results are consistent with the use of more sophisticated basis functions, such as a quadruple 3d basis for Ni$^{2+}$ (TZ2P+) does not alter the values of $\xi$ [causing an increase in $\xi$ (Table II) by 3–4%]. Excited state energies (Table V) for geometries, corresponding to the $T_d$ and $D_{2d}$ energy minima [in this case taking $^{3}T_1(e^4f^2) \rightarrow ^{5}T_1(e^4f^2)$ mixing into account] shows good agreement between LFDF and experimental values for the energies of the transitions $^{3}T_1 \rightarrow ^{3}T_2$ and $^{3}T_1 \rightarrow ^{3}A_2$, while the energies of the spin-forbidden transitions to $^1T_2$, $^1E$, and $^1T_2$, $^1T_1$, $^1A_1$, as well as the spin-allowed one to $^3T_1$ are found to be by $\sim 4,000$ cm$^{-1}$ and $5,500$ cm$^{-1}$ smaller than the experimental ones. This is in accordance with the smaller $B$ and $C$ values and the stronger dependence of the energies of the mentioned states on $B$ and $C$.

It is interesting that LF matrices from a non-relativistic LFDF calculation and from ZORA differ from each other. These are compared in Table VI, taking the $b_1 \rightarrow a_1$, $b_1 \rightarrow b_2$, and $b_1 \rightarrow e$ energy differences. It can easily be shown, when taking the angular geometry into account, that these differences can be translated into an angular overlap parameterization to yield values of 10 Dq for NiCl$_4^{2-}$ (4,150 cm$^{-1}$) and the one deduced from a direct fit to the spectrum (3,500 cm$^{-1}$) [19] referred to hereafter as “experimental”). However, values of $B$ and $C$ are, correspondingly, 64% and 68% off from the experimental ones (810 and 3,150 cm$^{-1}$, respectively) [19]. This can be traced back to the functionals in use that overestimate 3d-electron delocalization.
The Fermi contact terms [H9260] have a notable effect on elongated [Ni \text{Cl}_4]^2- \text{ and Br}^- \text{ geometries [DFT geometry optimizations taking mixing between } ^3T_1(e^4_{\text{td}}) \text{ and } ^3T_1(e^2_{\text{td}}) \text{ into account] in comparison with experimental data from literature.}

**TABLE VI**

| Multiplet energies (in kK = 10^3 \text{ cm}^{-1}) for NiX_2^- (X=Cl', Br', I') complexes from LDFDT calculations (zero spin-orbit coupling) in their T_d and D_{2d}-elongated geometries [from DFT geometry optimizations taking mixing between } ^3T_1(e^4_{\text{td}}) \text{ and } ^3T_1(e^2_{\text{td}}) \text{ into account] in comparison with experimental data from literature.} |
|-----------------|-----------------|-----------------|-----------------|
| Electronic state | NiCl_2^-         | NiBr_2^-        | NiI_2^-         |
| T_d(D_{2d})     | LDFDT           | Exp. [21]       | LDFDT           | Exp. [20]       | LDFDT           | Exp. [22]       |
| ^3T_1(1A_2, 3E) | 0.0 (0.0, 1.87)  | 0.0 (0.0, 1.65) | 0.0 (0.0, 1.24) |
| ^3T_1(1E, 1B_2) | 3.48 (4.20, 6.21)| 3.84–4.76       | 3.28 (3.86, 5.80)| 2.93 (3.39, 4.99)|
| ^3A_2(1B_1)    | 7.53 (9.03)      | 6.90            | 7.06 (8.41)      | 6.40            | 6.32 (7.47)      |
| ^1T_1(1B_2, 1E) | 7.64 (7.67, 9.40)| 11.69           | 6.89 (6.92, 8.44)| 6.22 (6.34, 7.46)|
| ^1E(1B_1, 1A_1) | 7.99 (7.80, 10.08)| 12.22           | 7.19 (7.03, 9.02)| 6.47 (6.44, 7.98)|
| ^3T_1(1E, 1A_1) | 10.74 (11.44, 13.57)| ~14.70           | 9.69 (10.32, 12.01)| 8.49 (9.09, 10.19)|
| ^1T_1(1E, 1A_1) | 12.69 (13.61, 15.10)| 18.18           | 11.50 (12.26, 13.75) (16.50, 17.44)| 10.30 (10.94, 12.22)|
| ^1A_1(1A_1)     | 14.01 (14.55, 17.06)| 19.48           | 12.71 (13.23, 15.24)| 18.13           | 11.35 (11.97, 13.28) (13.60, 14.64)|
| ^1E(1B_1, 1A_1) | 14.38 (17.78, 18.09)| 22.08           | 14.99 (16.25, 16.42)| 19.00           | 13.43 (14.59, 14.66) (15.75, 15.62)|
| ^1A_1(1A_1)     | 30.12 (31.55)    | —               | 27.29 (28.56)    | 24.58 (25.89)    |

The effect of elongated [Ni \text{Cl}_4]^2- \text{ and Br}^- \text{ geometries [from DFT geometry optimizations taking mixing between } ^3T_1(e^4_{\text{td}}) \text{ and } ^3T_1(e^2_{\text{td}}) \text{ into account] in comparison with experimental data from literature.}

**TABLE VI**

| Orbital interpretations of ligand field energies from LDFDT and ZORA calculations in terms of the AOM parameterization scheme (e_{\sigma}, e_{\pi}, e_{\text{sd}}) along with values of 10 Dq and the t_2-splitting 3\delta_2 for tetragonally (D_{2d}) elongated [NiX_4]^2- (X=F, Cl', Br', I`). |
|-----------------|-----------------|-----------------|-----------------|
| E(b_1 \rightarrow a_1) | 1832             | 1696             | 346             | 326             | 42             | 76             | -194            | 10             |
| E(b_1 \rightarrow b_1) | 2629             | 2610             | 2812            | 2831            | 2610           | 2564           | 2477            | 2461           |
| E(b_1 \rightarrow e) | 6639             | 6847             | 5086            | 5262            | 4581           | 4645           | 3938            | 4096           |
| e_{\sigma}               | 6488             | 6688             | 4980            | 5350            | 4457           | 4735           | 3734            | 4231           |
| e_{\pi}                  | 2612             | 2690             | 1594            | 1857            | 1379           | 1622           | 1012            | 1397           |
| e_{\text{sd}}             | 2277             | 2529             | 3402            | 4094            | 3910           | 4382           | 4359            | 4562           |
| 10 Dq                    | 4353             | 4597             | 4155            | 4289            | 3903           | 3913           | 3548            | 3550           |
| 3\delta_2                | 4110             | 4237             | 2274            | 2431            | 1971           | 2081           | 1461            | 1635           |

The parameters for \sigma- and \pi-bonding and for mixing of d_z^2 and 4s (which, being of the same symmetry, i.e., a_1, in D_{2d} can mix with each other), yielding e_{\sigma}, e_{\pi}, and e_{\text{sd}}, respectively. Remarkably, ZORA results reflect a distinctly larger extent of \sigma- and \pi-antibonding and e_{\text{sd}}-mixing compared with the nonrelativistic LDFDT result. The effect of sd-mixing has a crucial influence via the Fermi contact terms \kappa on the hyperfine structure tensor A. This is the topic of a separate study [25]. We also notice that the value of the parameter \xi_{1,2} for NiCl_2^- we deduce from the ZORA results (332 cm^{-1}, Table II) is found in excellent agreement with the one deduced from a fit to magnetic susceptibility data (380 cm^{-1}) [23]. It is this parameter (in combination with the \delta_{1,2} (ground-state Jahn–Teller activity, see Appendix 2), that affects the \delta_{1,2} ground-state splitting. These are shown in Figure 6 for NiX_4^- (X=Cl', Br', and I`). In accordance with the large negative \xi_{1,2} value for NiI_2^- an inverted zero-field splitting pattern for the ground state is calculated with a \delta_{1} ground state and an \delta_{2} excited state 33 cm^{-1} higher in energy. In NiBr_2^- an intermediate coupling scheme is realized with an \delta_{2} ground state and \delta_{1} next in energy. A D_{2d} distortion leads to an \delta_{1} ground state, as is the case in NiCl_2^-. However, it originates from the tetrahedral \delta_{1}.
rather than from the tetrahedral \( A_1 \) state as in \( \text{NiCl}_4^2^- \). It follows that the sign and magnitude of the parameter \( \beta_1 \) is of crucial importance for the ground state splitting. This, as well as the Jahn–Teller activity in the \( 3T_1 \) ground state, is a further experimental challenge for these systems. For more conclusive results, these compounds should be studied with more modern tools, such as resonance Raman and high-field–high-frequency EPR. We hope this study will motivate further experimental work in this direction.

5. Conclusions

In this work we extended our LF DFT proposed recently [1–4] with spin-orbit coupling, developing a procedure allowing one to extract spin-orbit coupling matrix elements from spin-restricted ZORA calculations. Using symmetry analysis, we show that a set of spin-orbit coupling parameters, rather than a single value or values scaled for anisotropy using (Stevens) orbital reduction factors are needed for a proper description of a realistic situation. In particular, highly covalent ligands such as \( \text{Br}^- \) and \( \text{I}^- \) and their own spin-orbit coupling contributions can lead to unexpected, unprecedented splitting patterns of the ground state (zero-field splitting), which deserve further theoretical justification and testing and motivates further experimental work. In subsequent contributions, we will extend the formalism to systems with lower or no symmetry, calculating zero-field splitting for systems well characterized by EPR, thus extending the applicability of our LF DFT approach to fine structure tensor and hyperfine coupling effects.

References

Appendix 1: Spin-Orbit Coupling Matrix Elements in $T_d$ and in $D_{2d}$ Symmetry

\[
\begin{align*}
(a_1 e | s \tilde{u}(e) | e [t_2]) &= \xi_{a,e} \quad (b_1 e | s \tilde{u}(e) | e [t_2]) = \xi_{b,e} \\
(b_1 e | s \tilde{u}(a_2) | b_2 [t_2]) &= \xi_{b,e}^{a_2} \quad (e [t_2] | s \tilde{u}(a_2) | e [t_2]) = \xi_{a,e}^{a_2} \\
(b_2 [t_2] | s \tilde{u}(e) | e [t_2]) &= \xi_{b,e} \quad (b_2 [t_2] | s \tilde{u}(e) | e [t_2]) = \xi_{b,e}^{a_2}
\end{align*}
\]

Symmetry notations for the real $3d$ orbitals in $D_{2d}$ are written on the left-hand side along with conventions for the $e$-components given in the ADF code. For $T_d$ symmetry, one has to take

\[
\begin{align*}
&\langle e | s \tilde{u}(t_1) | t_2 \rangle = \xi_{e,t} = \xi_{a,t} = \xi_{b,t} = \xi_{b,t}^{a_2} \\
&\langle t_2 | s \tilde{u}(t_1) | t_2 \rangle = \xi_{t,t} = \xi_{b,t}^{a_2}.
\end{align*}
\]

\[
\begin{array}{cccccc}
\xi^+(d_{xy}^+) & \eta^+(d_{yz}^+) & \xi^+(d_{xz}^+) & \epsilon^+(d_{xy}^{+2}) & \theta^+(d_{xz}^+) & \xi^-(d_{xy}^-) \\
\xi^-(d_{yz}^-) & \eta^-(d_{xy}^-) & \xi^-(d_{xz}^-) & \epsilon^-(d_{yz}^{+2}) & \theta^-(d_{xz}^-) & \epsilon^-(d_{xy}^{+2}) \\
b_2^+ \xi^+(d_{xy}^+) & i \xi_{b,b_2}^{a_2} & & & & -i \frac{\epsilon_{b_2}}{2} - \frac{\eta_{b_2}}{2} \\
\frac{-\eta_{b_2}}{2} & i \frac{\epsilon_{b_2}}{2} & \frac{\xi_{b_2}}{2} & \frac{-\eta_{b_2}}{2} & \frac{\epsilon_{b_2}}{2} & \frac{-\eta_{b_2}}{2} \\
e^+ : 2^+ \eta^+(d_{xy}^+) & & & & & \\
3 \frac{\epsilon_{b_2}}{2} & \frac{-\xi_{b_2}}{2} & \frac{\xi_{b_2}}{2} & \frac{-\eta_{b_2}}{2} & \frac{\epsilon_{b_2}}{2} & \frac{-\eta_{b_2}}{2} \\
erg^+ : 1^+ \xi^+(d_{yz}^+) & & & & & \\
\frac{i \epsilon_{b_2}}{2} & \frac{-\xi_{b_2}}{2} & \frac{\xi_{b_2}}{2} & \frac{-\eta_{b_2}}{2} & \frac{\epsilon_{b_2}}{2} & \frac{-\eta_{b_2}}{2} \\
a_1^+ \theta^+(d_{xz}^+) & & & & & \\
\frac{-i \xi_{b_2}}{2} & \frac{-i \epsilon_{b_2}}{2} & \frac{-\xi_{b_2}}{2} & \frac{-i \epsilon_{b_2}}{2} & \frac{i \xi_{b_2}}{2} & \frac{-i \epsilon_{b_2}}{2} \\
b_2^- \xi^-(d_{xy}^-) & & & & & \\
\frac{-i \epsilon_{b_2}}{2} & \frac{-i \xi_{b_2}}{2} & \frac{-\xi_{b_2}}{2} & \frac{-i \epsilon_{b_2}}{2} & \frac{i \xi_{b_2}}{2} & \frac{-i \epsilon_{b_2}}{2} \\
e^- : 2^- \eta^- (d_{yz}^-) & & & & & \\
\frac{\eta_{b_2}}{2} & \frac{\xi_{b_2}}{2} & \frac{-\xi_{b_2}}{2} & \frac{\eta_{b_2}}{2} & \frac{\xi_{b_2}}{2} & \frac{-\xi_{b_2}}{2} \\
eg^+ : 1^- \xi^- (d_{xy}^-) & & & & & \\
\frac{-i \epsilon_{b_2}}{2} & \frac{-i \xi_{b_2}}{2} & \frac{-\xi_{b_2}}{2} & \frac{-i \epsilon_{b_2}}{2} & \frac{i \xi_{b_2}}{2} & \frac{-i \epsilon_{b_2}}{2} \\
b_2^- \epsilon^- (d_{yz}^-) & & & & & \\
\frac{-i \xi_{b_2}}{2} & \frac{i \epsilon_{b_2}}{2} & \frac{-\xi_{b_2}}{2} & \frac{i \epsilon_{b_2}}{2} & \frac{i \xi_{b_2}}{2} & \frac{-i \epsilon_{b_2}}{2} \\
a_1^- \theta^- (d_{xz}^-) & & & & & \\
\frac{-i \xi_{b_2}}{2} & \frac{i \epsilon_{b_2}}{2} & \frac{-\xi_{b_2}}{2} & \frac{i \epsilon_{b_2}}{2} & \frac{i \xi_{b_2}}{2} & \frac{-i \epsilon_{b_2}}{2}
\end{array}
\]

Appendix 2: DFT Treatment of Jahn–Teller Activity in the Case of Mixing of Electronic States

The Hamiltonian of the $^3T \otimes e$ Jahn–Teller problem in a linear approximation

\[
H = (1/2) K_e (Q_a^2 + Q_e^2) \cdot I + V_e Q_e \cdot C_\alpha + V_e Q_e \cdot C_e
\]

(A2.1)

where $I$ is the identity matrix and $C_\alpha$ and $C_e$ are $3 \times 3$ matrices taken on the basis of the $T_1 \alpha, \beta,$ and $\gamma$ wavefunctions:

\[
C_\alpha = \begin{bmatrix}
\frac{1}{2} & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{bmatrix} \quad C_e = \begin{bmatrix}
-\frac{\sqrt{3}}{2} & 0 & 0 \\
0 & \frac{\sqrt{3}}{2} & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

(A2.2)
TABLE A2.1
Mixing coefficients $c_1$ and $c_2$ of $3T_1(e^4t_2^2)$ and $3T_1(e^2t_2^2)$ in the $3T_2$ ground-state function, DFT optimized angles $\delta \theta^o = \theta^o - \theta_{x^2}$ and $E_{JT}$ values for $3T_1(e^4t_2^2)$, force field constants, and vibronic coupling parameters $K_\sigma^e$, $V_\sigma^e$, $K_\sigma^e$, $V_\sigma^e$ and $K_\sigma$ of $3T_1(e^4t_2^2)$, $3T_1(e^2t_2^2)$ and the $3T_1$ ground state (taking mixing into account) for NiX$_4^{2-}$ ($X = F^-$, Cl$^-$, Br$^-$, I$^-$).*

<table>
<thead>
<tr>
<th>Species</th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$\delta \theta$</th>
<th>$E_{JT}$</th>
<th>$K_\sigma^e$</th>
<th>$V_\sigma^e$</th>
<th>$K_\sigma^e$</th>
<th>$V_\sigma^e$</th>
<th>$K_\sigma$</th>
<th>$V_\sigma$</th>
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<tbody>
<tr>
<td>NiF$_4^{2-}$</td>
<td>-0.944</td>
<td>0.330</td>
<td>34.48</td>
<td>-8655</td>
<td>12792</td>
<td>14883</td>
<td>22234</td>
<td>-6049</td>
<td>21206</td>
<td>-3770</td>
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<tr>
<td>NiCl$_4^{2-}$</td>
<td>-0.953</td>
<td>0.303</td>
<td>15.58</td>
<td>-2599</td>
<td>13721</td>
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<td>10549</td>
<td>-2334</td>
<td>10840</td>
<td>-1344</td>
</tr>
<tr>
<td>NiBr$_4^{2-}$</td>
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<td>0.297</td>
<td>13.36</td>
<td>-1907</td>
<td>11948</td>
<td>6752</td>
<td>7686</td>
<td>-1747</td>
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<tr>
<td>NiI$_4$</td>
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<td>5360</td>
<td>2122</td>
<td>-453</td>
<td>2921</td>
<td>43</td>
</tr>
</tbody>
</table>

* For values of $\delta \theta^o$ and $E_{JT}$ for the $3T_1(e^4t_2^2)$ DFT optimized single determinant energy, see the entries in square brackets in Table I. $K_\sigma$, $V_\sigma$, and $E_{JT}$ parameters have been expressed in cm$^{-1}$, Å$^{-2}$, and Å$^{-1}$, respectively. $\delta \theta$ in °.

$Q_\sigma$ and $Q_\alpha$ are the higher and lower symmetric components of the $e$-vibration, which distorts the tetrahedron into $D_{2d}$ and $D_2$ geometries, respectively. If we restrict ourselves to distortions of the $Q_\sigma$ type and define $Q_\alpha$ as being positive for tetragonal compression, Eq. (A2.1) simplifies to Eq. (A2.3) for the nondegenerate ground state ($^3A_2$ in $D_{2d}$) and to Eq. (A2.4) for the degenerate higher energy state ($^3E$). Minimization of Eq. (A2.3)

$$3A_2: E(T_1, \gamma) = (1/2) K_\sigma Q_\sigma^2 - V_\sigma Q_\sigma$$

(A2.3)

$$3E: E(T_1, \alpha, \beta) = (1/2) K_\sigma Q_\sigma^2 + (1/2) V_\sigma Q_\sigma$$

(A2.4)

with respect to $Q_\sigma$ yields the equilibrium geometry $Q_\sigma^0$ and the Jahn–Teller stabilization energy $E_{JT}$:

$$Q_\sigma^0 = V_\sigma/K_\sigma$$

(A2.5)

$$E_{JT} = -(1/2)V_\sigma^2/K_\sigma.$$  

(A2.6)

If we take $\theta$ (in °) to be the angle between the $S_4$ axis and the TM–ligand bond (for the tetrahedron we have $\theta_{x^2} = 54.73°$). $Q_\sigma^0$ (in radians · Å) can be calculated from Eq. (A2.7):

$$Q_\sigma = R(\theta^o - \theta_{x^2})(\pi/180).$$

(A2.7)

In tetrahedral NiX$_4^{2-}$ complexes, the $3T_1$ wave function $\psi(3T_1)$ is given by:

$$\psi(3T_1) = c_1 \psi(3T_1, e^4t_2^2) + c_2 \psi(3T_1, e^2t_2^2),$$

(A2.8)

where $c_1$ and $c_2$ (Table A2.1) are given by the ground state eigenvector diagonalizing the matrix

$$3T_1(e^4t_2^2) \rightarrow 3T_1(e^2t_2^2)$$

$$\begin{bmatrix}
0 & 6B \\
6B & 9B + 10Dq
\end{bmatrix}.$$  

(A2.9)

The $3T_1(e^4t_2^2)$ and $3T_1(e^2t_2^2)$ states before the mixing are described by single determinants and their equilibrium geometries (elongation, Table I and compression, Table A2.1) and energies $E_{JT}$ can be calculated from separate DFT geometry optimizations to yield corresponding parameters $K_\sigma$, $V_\sigma$, $K_\sigma$, $V_\sigma$, respectively. Then $K_\sigma$ and $V_\sigma$ after mixing are given by:

$$K_\sigma = c_1^2K_\sigma^e + c_2^2K_\sigma^e$$ 

(A2.10)

$$V_\sigma = c_1^2V_\sigma^e + c_2^2V_\sigma^e.$$ 

(A2.11)

Substitution into Eq. (A2.5) yields the equilibrium distortion $Q_\sigma^0$ and using Eq. (A2.7) we get the equilibrium angle $\theta^o$. This is given in Table I. Parameter values summarizing the logical steps of this procedure are listed in Table A2.1.