Original Investigations

Linear Dependence of $X\alpha$ Eigenvalues on Occupation Number

Application to the Determination of the Ligand Field Integrals

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A linear relation between the $X\alpha$ eigenvalues and the occupation number of the ligand field states in $CrCl_4$ is established and used to calculate mono- and bimolecular integrals of ligand field interest. A formula for calculating $10\,Dq$ and Koide–Pryce's parameter (ε) from the $X\alpha$ eigenvalues is given. The method is generalized for any d^N system.

Key words: $CrCl_4$ – Electronic structure – SCFMS $X\alpha$ results – Ligand field integrals.

1. Introduction

Among the so-called strong ligand field models one may distinguish between different models that are more or less sophisticated. For cubic symmetries these are with decreasing complexity:

(i) the molecular strong field using ten coulomb parameters $a, b, \ldots, j$ [1].

(ii) the Koide and Pryce model [2].where the ten parameters are reduced to four, namely Racah's A, B, C and a covalency parameter ε which can be considered as a measure of the difference in expansion between t_2 and e orbitals.

Table 1. Connection between the Koide–Pryce and the molecular strong field parameters

Koide and Pryce model	Molecular orbital general approach
$(e, e) = (A - \frac{8}{3}B + \frac{4}{3}C)$	$(e - \frac{5}{3}f)$
$(e, t_2) = (1 - \varepsilon)(A - B + \frac{1}{2}C)$	$(d + c - \frac{1}{2}g - \frac{1}{2}h)$
$(t_2, t_2) = (1 - \varepsilon)^2(A - 2B + C)$	$\frac{1}{5}(a + 4b - 2j)$

The well-known connection between the two sets of parameters is given in Table 1; in tetrahedral symmetry, one has $n_{t_2} = 1 - \varepsilon$ and $n_e = 1$.

(iii) the ionic strong field model which is equivalent to the last one with $\varepsilon = 0$.

One should notice that, while ε equals at most a few percent, the difference in order between A (a few 10 eV) and B or C (fractions of 1 eV) makes the ε contribution an essential part in the parametrization. Evidently all models require also the crystal field parameter 10 Dq or Δ and if spin–orbit effects are not neglected, two or one spin–orbit parameters.

The purpose of this paper is not to develop a new method but to see what connections can be found between the crystal field and the MS $X\alpha$ models applied on transition metal complexes. As the MS $X\alpha$ method is a molecular one, it is obvious that the only crystal field model which can be compared is the Koide and Pryce one. In fact, the covalency is not taken into account in the ionic strong field model while the molecular strong-field method employs too large a set of parameters which cannot be accessible from a few $X\alpha$ calculations on different configurations.

For the sake of clarity, we will restrict the discussion to a d^2 configuration in tetrahedral symmetry (Fig. 1); later we will emphasize, when necessary, the results which are general for any configuration. In the following, like most authors [3], the 10 Dq parameter is defined as $10 \, Dq(1) = (t_2) - (e)$, the difference between the one electron energies, and not as the difference between triplets [4] like $10 \, Dq(2) = {}^3T_2 - {}^3A_2$ (see Fig. 1), which is directly obtained by experiment. In fact, one can connect the two definitions for d^2 system:

$$10 \, Dq(2) = {}^3T_2 - {}^3A_2 = 10 \, Dq(1) + d - c - g - 3h - e + 3f$$

according to the molecular strong field theory and

$$10 \, Dq(2) = 10 Dq(1) + \varepsilon (1 - \varepsilon) (A - 8B)$$

according to Koide and Pryce's model.

2. Determination of Mono- and Bielectronic Integrals From $X\alpha$ Calculations

Slater [5] showed that, for a given configuration, the $X\alpha$ total energy can be approximated by an expression identical to the HHF (hyper Hartree–Fock) total
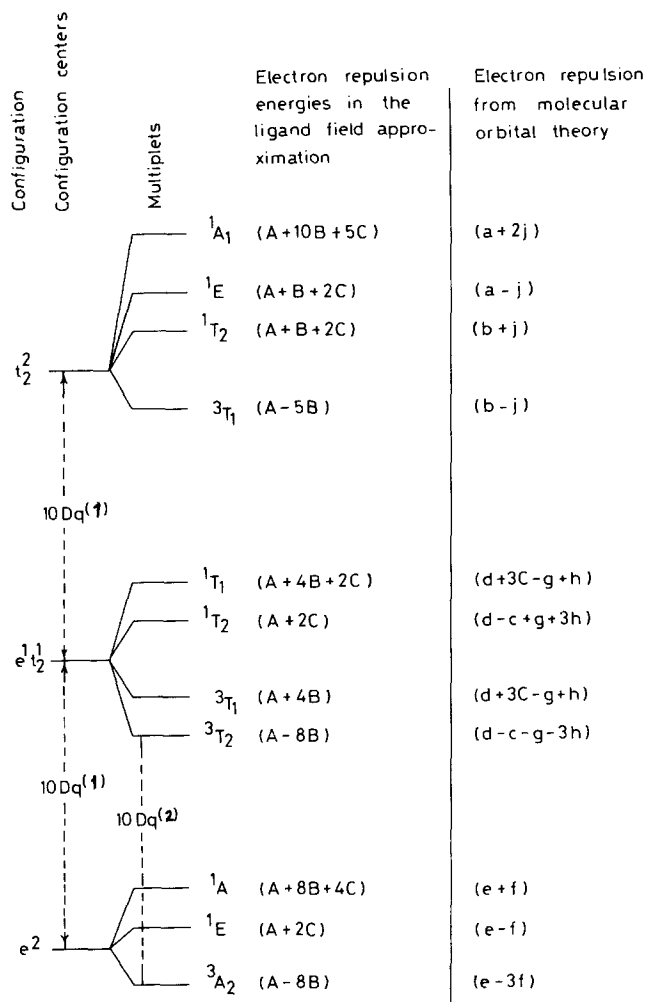
Configuration	Configuration centers	Multiplets		Electron repulsion energies in the ligand field approximation	Electron repulsion from molecular orbital theory
		$^1A_1$	$(A + 10B + 5C)$		$(a + 2j)$
		^1E	$(A + B + 2C)$		$(a - j)$
		$^1T_2$	$(A + B + 2C)$		$(b + j)$
t_2^2		$^3T_1$	$(A - 5B)$		$(b - j)$
		$^1T_1$	$(A + 4B + 2C)$		$(d + 3C - g + h)$
		$^1T_2$	$(A + 2C)$		$(d - c + g + 3h)$
$e^1 t_2^1$		$^3T_1$	$(A + 4B)$		$(d + 3C - g + h)$
		$^3T_2$	$(A - 8B)$		$(d - c - g - 3h)$
		^1A	$(A + 8B + 4C)$		$(e + f)$
		^1E	$(A + 2C)$		$(e - f)$
e^2		$^3A_2$	$(A - 8B)$		$(e - 3f)$

10 Dq(1)

10 Dq(1)

10 Dq(2)

Fig. 1. Multiplets of tetrahedral metal complex $N = 2$

energy, i.e., $\langle E_{X\alpha}\rangle \sim \langle E_{HHF}\rangle$. One has

$$\langle E_{X\alpha}\rangle = \sum_i n_i(i) + \frac{1}{2}\sum_i n_i(n_i - 1)(i, i) + \sum_{i \neq j} n_i n_j(i, j) \tag{1}$$

where (i) and (i, i) are mono- and bielectronic integrals, n_i occupation numbers. One knows that in $X\alpha$ formalism, the eigenvalues are given by $\varepsilon_i^{X\alpha} = \delta\langle E_{X\alpha}\rangle / \delta n_i$; consequently, if one considers that e and t_2 orbitals do not relax when their occupation numbers are varied, (which is easy to admit because no charge transfer occurs in the complex), one obtains

$$\varepsilon_i^{X\alpha} \sim \frac{\delta E_{X\alpha}(e^n t^m)}{\delta n_i} \qquad i = e, t_2 \tag{2}$$

or more explicitly

$$\varepsilon_e^{X\alpha}(n) = (e) + (n - \tfrac{1}{2})(e, e) + m(t_2, e) \tag{3}$$

$$\varepsilon_t^{X\alpha}(m) = (t) + (m - \tfrac{1}{2})(t_2, t_2) + n(e, t_2) \tag{4}$$

with $N = n + m$, total number of d electrons in the configuration d^N.

One obtains two linear relations:

$$\varepsilon_e^{X\alpha}(n) = a_e + b_e n, \qquad \varepsilon_t^{X\alpha}(m) = a_t + b_t m \tag{5}$$

which can be fitted from $X\alpha$ eigenvalues obtained in different configurations calculations. It is then easy to deduce from the four parameters set:

(i) The 10 Dq parameter:

$$10\,\mathrm{Dq}(1) = (t_2) - (e) = (a_t - a_e) + \tfrac{1}{2}(b_t - b_e). \tag{6}$$

(ii) The Koide and Pryce covalency parameter:
From Eqs. (4.5) and the method of average configurations [5, 6] we have

$$(e, e) - (t_2, e) = b_e = [A + \tfrac{4}{3}(C - 2B)] - (1 - \varepsilon)[A + \tfrac{1}{2}(C - 2B)] \tag{7}$$

$$(t_2, t_2) - (t_2, e) = b_t = [A + (C - 2B)](1 - \varepsilon)^2 - (1 - \varepsilon)[A + \tfrac{1}{2}(C - 2B)]. \tag{8}$$

As $A \gg B$, C and $\varepsilon \ll 1$, one obtains

$$(e, e) - (t_2, e) \simeq \varepsilon A + \tfrac{5}{6}(C - 2B)$$

$$(t_2, t_2) - (t_2, e) \simeq \tfrac{1}{2}(C - 2B) - \varepsilon A$$

so that

$$\varepsilon A \simeq \tfrac{1}{2}(3b_e - 5b_t) \tag{9}$$

leading to ε from a given value of the Racah parameter. One should note that in the ionic strong field model, $\varepsilon \sim 0$, then one has

$$(e, e) - (t_2, e) = 5/6(C - 2B), \qquad (t_2, t_2) - (t_2, e) = 1/2(C - 2B)$$

so that one always has $(e, e) > (t_2, t_2) > (t_2, e)$ which is not fulfilled if $\varepsilon \neq 0$ (see part 3).

The linear relations (3–4) can also be applied to ionization in which case one no longer has constant $n + m$, but n varying with constant m and vice versa. It should be noted that in this case orbital relaxation should occur and one could expect a deviation from linearity larger than in Eqs. (3, 4). In particular, if one considers the ionization of the $e^n t_2^0$ configuration one obtains

$$\varepsilon_e^{X\alpha}(n) \sim (e) + (n - \tfrac{1}{2})(e, e) \tag{10}$$

and simultaneously, for this same configuration

$$\varepsilon_t^{X\alpha}(m) \sim (t_2) - \tfrac{1}{2}(t_2, t_2) + n(t_2, e). \tag{11}$$

The linear fits give directly the (e, e), (e) and (t_2, e) integrals. It is then possible to obtain (t_2, t_2) and (t_2) from Eqs. (4) and (11), while (t_2, e) can alternatively

be obtained by Eqs. (3) and (10) and (10) Dq from the just calculated values of (t_2) and (e).

A general formula to obtain 10 Dq from any two different configurations $e^n t_2^m$ and $e^{n'} t_2^{m'}$ of $X\alpha$ calculations can be given:

$$(t_2) - (e) = [(2n' - 1)\varepsilon_e(n) - (2n - 1)\varepsilon_e(n') + (2m' - 1)\varepsilon_t(m)$$
$$- (2m - 1)\varepsilon_t(m')]/2(n' - n). \tag{12}$$

The "Sambe and Felton special configurations": It is evident from Eqs. (3) and (4) that one obtains directly

$$10 \, \mathrm{Dq} = (t_2) - (e) = \varepsilon_t^{X\alpha}(m^*) - \varepsilon_e^{X\alpha}(n^*) \tag{13}$$

for a particular configuration $e^{n^*} t_2^{m^*}$ if the other terms from Eqs. (3) and (4) can be annulled, i.e.:

$$(m^* - \tfrac{1}{2})(t_2, t_2) - (n^* - \tfrac{1}{2})(e, e) - (n^* - m^*)(t_2, e) = 0.$$

In ligand field formalism, this requires according to the $N = m^* + n^*$ relation that

$$\varepsilon[N(1 - \varepsilon) + 2n^* + n^*\varepsilon + (1 - \varepsilon/2)] = 0 \tag{14a}$$

to set to zero the Z coefficient and

$$\tfrac{1}{6}(3N - 8n^* + 1) + \varepsilon/2(2n^* - 3N + 1) + \varepsilon^2(N - n^* - 1) = 0 \tag{14b}$$

to set to zero the coefficient of $(C - 2B)$.

It is clear that in the ionic strong model ($\varepsilon = 0$), the "Sambe and Felton" [6] configuration $n^* = (3N + 1)/8$ allows the 10 Dq to be obtained directly from the difference in the t_2 and e eigenvalues. however, this is not true as soon as $\varepsilon \neq 0$. Consequently, the Sambe and Felton approximation should lead to a less precise value of 10 Dq than the other relations.

Spin polarized calculations of $CrCl_4$:

Similar results can be obtained in the spin polarized framework. For instance, Eqs. (10) and (11) become for $e_\uparrow^{n_0} t_\uparrow^{0} e_\downarrow^{0} t_{2\downarrow}^{0}$:

$$\varepsilon_{e\uparrow}^{X\alpha} = (e_\uparrow) - \tfrac{1}{2}(e_\uparrow, e_\uparrow) + n(e_\uparrow, e_\uparrow)$$
$$\varepsilon_{e\downarrow}^{X\alpha} = (e_\downarrow) - \tfrac{1}{2}(e_\downarrow, e_\downarrow) + n(e_\uparrow, e_\downarrow)$$
$$\varepsilon_{t\uparrow}^{X\alpha} = (t_{2\uparrow}) - \tfrac{1}{2}(t_{2\uparrow}, t_{2\uparrow}) + n(e_\uparrow, t_{2\uparrow}) \tag{15}$$
$$\varepsilon_{t\downarrow}^{X\alpha} = (t_{2\downarrow}) - \tfrac{1}{2}(t_{2\downarrow}, t_{2\downarrow}) + n(e_\uparrow, t_{2\downarrow}).$$

It is then possible to determine spin polarized integrals and one electron orbitals energies. However, these quantities cannot be connected easily to ligand field parameters because the ligand field theory is built on a restricted atomic scheme, i.e., the equality $(d_\uparrow, d_\uparrow)$, $(d_\downarrow, d_\downarrow)$ is assumed which is not the case in Eq. (15). Furthermore, as the molecular ligand field parameters (Griffith's parameters) do include more than is assumed by the theory (as is always the case in parametrized

calculations), difficulties should appear if one tries to obtain a linear dependence between Griffith's parameters and spin polarized (MS $X\alpha$) integrals. In fact, if one admits $(d_\uparrow, d_\uparrow) \sim (d_\downarrow, d_\downarrow)$ only two parameters, namely e and f, can be determined, as one gets to use the method of the average configuration in the polarized case [8]:

$$(e_\uparrow, e_\uparrow) = e - 3f, \qquad (e_\uparrow, e_\downarrow) = e - f, \tag{16a}$$

Some combinations of Griffith's parameters can also be obtained, namely $(c + d)$ and $(g + h)$, with

$$(e_\uparrow, t_{2\uparrow}) = (c + d) - (g + h), \qquad (e_\uparrow, t_{2\downarrow}) = (c + d) \tag{16b}$$

are evidently $(b - j)$ and $(a + 2b)$ with

$$(t_{2\uparrow}, t_{2\uparrow}) = (b - j), \qquad (t_{2\uparrow}, t_{2\downarrow}) = \tfrac{1}{3}(a + 2b). \tag{16c}$$

But, one has to remember that all these equations assume the unsatisfied equality $(d_\uparrow, d_\uparrow) = (d_\downarrow, d_\downarrow)$.

Numerical values on $CrCl_4$, presented in the next section, will point out the limitation of such equations.

3. Numerical Results of CrCl₄ Complex (d^2)

SCF MS $X\alpha$ calculations have been performed on $CrCl_4$ with the parameters set used in a previous work by Weber and Daul [7].

The linear dependence (3–5) of the $X\alpha$ eigenvalues on the occupation numbers is displayed on Table 2 and Fig. 2 while the corresponding fits are

$$\varepsilon_e^{X\alpha}(n) = -7.1464 + 0.1651n, \qquad \varepsilon_t^{X\alpha}(m) = -5.7929 - 0.1379m. \tag{5'}$$

According to Eq. (6), one obtains $10\,Dq = 1.202$ eV while the special configuration of Sambe and Felton ($n^* = 0.88$) gives from Eq. (13) $10\,Dq = 1.055$ eV (which are to be compared with ligand field parameter [7] $10\,Dq = 2.33$ eV).

Table 2. Energies of RSCF-$X\alpha$ excited configurations $e^n t_2^{(N-n)}$ for CrCl₄

Configuration	$\varepsilon_e^{X\alpha}$ (eV)	$\varepsilon_t^{X\alpha}$ (eV)	$\varepsilon_t^{X\alpha} - \varepsilon_e^{X\alpha}$ (eV)
$e^2 t_2^0$	−6.8138	−5.7913	1.0225
$e^{1.8} t_2^{0.2}$	−6.8458	−5.8176	1.0282
$e^{1.65} t_2^{0.35}$	−6.8729	−5.8401	1.0328
$e^{1.5} t_2^{0.5}$	−6.8996[a]	−5.8625	1.0371
$e^{1.25} t_2^{0.75}$	−6.9430	−5.8987	1.0443
$e^{1.0} t_2^{1.0}$	−6.9851	−5.9340	1.0511
$e^{0.88} t_2^{1.12}$	−7.0050[b]	−5.9500	1.055
$e^{0.5} t_2^{1.5}$	−7.0654[a]	−6.0012	1.0642
$e^0 t_2^{2.0}$	−7.1404	−6.0639	1.0765

[a]   Slater transition states.
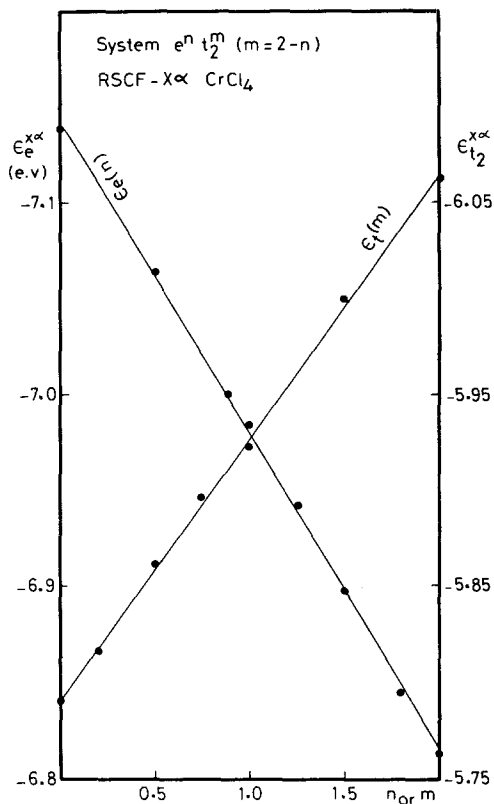[b]   Sambe and Felton special configuration for d^2.

Fig. 2. $CrCl_4 - e^n t_2^{2-n}$ – linear dependence of the $X\alpha$ eigenvalues

And also from Eq. (9) one obtains $\varepsilon A = 0.148$ eV. If one takes $A = 16.2$ eV [7] one obtains $\varepsilon \sim 0.009$ in good agreement with the usual values of this parameter. Notice that this value is sufficient to reverse the ionic ligand field theoretical order $(e, e) > (t_2, t_2) > (t_2, e)$ to the order $(e, e) > (t_2, e) > (t_2, t_2)$.

More precisely,

$$(e, e) - (t_2, e) = 0.165 \text{ eV}, \qquad (t_2, e) - (t_2, t_2) = 0.138 \text{ eV}.$$

for the ionization case the best fit of results from three configurations $e^2, e^{1.75}$ and $e^{1.5}$ (Table 3) are

$$\varepsilon_e^{X\alpha}(n) = -19.210 + 6.198n \tag{10'}$$

$$\varepsilon_t^{X\alpha}(m) = -17.878 + 6.044m. \tag{11'}$$

Table 3. RSCF-$X\alpha$ results for fractionally ionized $CrCl_4$

Configuration	Molecular charge	$\varepsilon_e^{X\alpha}$ (eV)	$\varepsilon_t^{X\alpha}$ (eV)
$e^{2.0}t_2^0$	0.0	-6.8138	-5.7913
$e^{1.75}t_2^0$	0.25	-8.3626	-7.2986
$e^{1.50}t_2^0$	0.50	-9.9131	-8.8135

From Eqs. (10–11) one obtains values of the integrals:

$(e, e) = 6.198$ eV, $(t_2, e) = 6.044$ eV, $(e) = -16.122$ eV

and from Eqs. (4) or (8) and (11) the other values:

$(t_2, t_2) = 5.906$ eV, $(t_2) = -14.926$ eV.

The (t_2, e) value obtained from Eqs. (3) or (7) and (10) is

$(t_2, e) = 6.033$ eV.

The 10 Dq value from the just calculated values of (t_2) and (e) is 10 Dq = 1.16 eV. This last value shows the self-consistency of the results.
We have calculated six different spin polarized configurations for $CrCl_4$ including the ground state, four excited states and one ionized state. The results are summarized in Table 4. The linearity relationship for the case of polarized SCF $X\alpha$ eigenvalues as a function of their occupation numbers is still confirmed from the study of the system $e_\uparrow^n t_{2\uparrow}^m$ (Fig. 3).

The integrals calculated from Eq. (15) are reported in Table 5. One could notice that the $(d_\uparrow, d_\uparrow) - (d_\downarrow, d_\downarrow)$ difference cannot be negligible in some cases; for instance, the relative difference is only 1% for (t_2, t_2), 2% for (e, e) but 10% for (e, t_2). This large discrepancy may induce large errors into an attempt to deduce Griffith's parameters from these integrals. For example, from (16a), one obtains

$e = \frac{1}{2}[3(e_\uparrow, e_\downarrow) - (e_\uparrow, e_\uparrow)] = 7.058$ eV

$f = \frac{1}{2}[(e_\uparrow, e_\downarrow) - (e_\uparrow, e_\uparrow)] = 0.400$ eV

but one also has

$f = \frac{1}{2}[(e_\uparrow, e_\downarrow) - (e_\downarrow, e_\downarrow)] = 0.320$ eV

which is numerically quite different.

Table 4. PSCF-$X\alpha$ results for $CrCl_4$

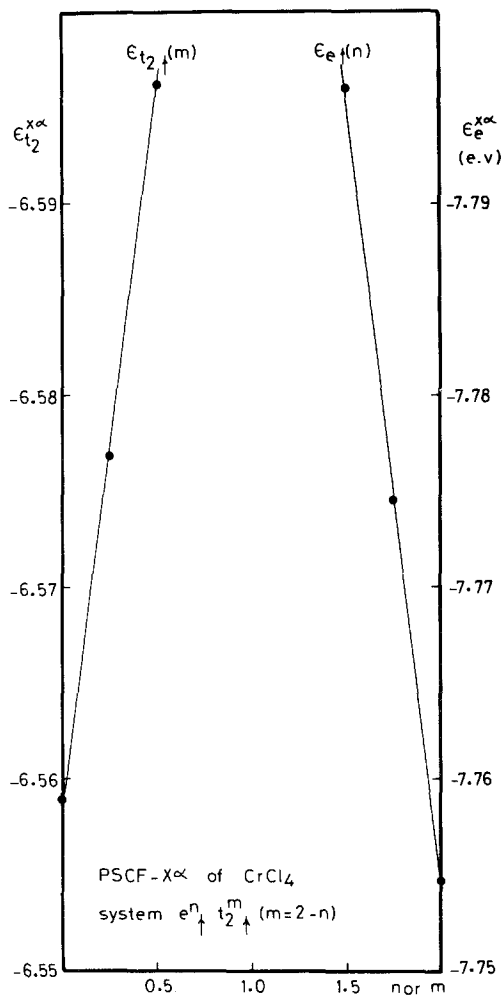|	$e_\uparrow$	$t_{2\uparrow}$	$e_\downarrow$	$t_{2\downarrow}$
Occupation	1.75	0.0	0.25	0.0
$-\varepsilon$ (eV)	7.555	6.391	6.055	5.180
Occupation	1.75	0.0	0.0	0.25
$-\varepsilon$	7.598	6.425	6.105	5.222
Occupation	2.0	0.0	0.0	0.0
$-\varepsilon$	7.755	6.559	5.896	5.047
Occupation	1.75	0.0	0.0	0.0
$-\varepsilon$	9.221	8.010	7.564	6.660
Occupation	1.75	0.25	0.0	0.0
$-\varepsilon$	7.776	6.577	5.938	5.081
Occupation	1.5	0.5	0.0	0.0
$-\varepsilon$	7.796	6.598	5.976	5.113

Fig. 3. Linear dependence of the PSCF $X\alpha$ eigenvalues

Table 5. PSCF-$X\alpha$ average electron repulsion parameters and one electron orbital energies (eV)

$(e_\uparrow, e_\uparrow) = 5.860$	$(t_{2\uparrow}, t_{2\uparrow}) = 5.702$
$(e_\uparrow, t_{2\uparrow}) = 5.778$	$(t_{2\uparrow}, t_{2\downarrow}) = 6.452$
$(e_\uparrow, e_\downarrow) = 6.659$	$(t_{2\downarrow}, t_{2\downarrow}) = 5.791$
$(e_\uparrow, t_{2\downarrow}) = 6.493$	$(e_\downarrow, t_{2\uparrow}) = 6.513$
$(e_\downarrow, e_\downarrow) = 6.018$	$(e_\downarrow, t_{2\downarrow}) = 5.270$
$(e_\uparrow) = -16.545$	$(e_\downarrow) = -16.203$
$(t_{2\uparrow}) = -15.266$	$(t_{2\downarrow}) = -15.143$
$(t_{2\uparrow}) - (e_\uparrow) = 1.279$	$(t_{2\downarrow}) - (e_\downarrow) = 1.060$

Table 6. Configuration centers energies (in cm^{-1}) relative to the ground state configuration $e_\uparrow^2$

Configuration	ΔE	Ref. [7]	Method used in the calculation
$e_\uparrow t_{2\uparrow}$	9 678	11 650	Slater transition state method
$e_\uparrow t_{2\uparrow}$	9 643	11 650	Linearity relation Eq. (17)
$e_\uparrow e_\downarrow$	9 203	8 134	Linearity relation Eq. (17)
$e_\uparrow t_{2\downarrow}$	16 460	14 196	Linearity relation Eq. (17)
$t_{2\uparrow}^2$	19 418	20 181	Linearity relation Eq. (17)
$t_{2\uparrow} t_{2\downarrow}$	26 160	25 378	From the known values of the two electron parameters of this configuration Table 5.

[a] Calculated from the Griffith parameters and 10 Dq given in Ref. [7].

However, we can calculate the configuration centers energies from any two configurations either by the transition state method or by using the linearity Eq. (5) or the more general one:

$$\varepsilon_t(m + \tfrac{1}{2}) - \varepsilon_e(n - \tfrac{1}{2}) = (a_t - a_e) + (m + \tfrac{1}{2})b_t - (n - \tfrac{1}{2})b_e.$$

The results are given in Table 6 and we notice that the configurations centers energies calculated from $X\alpha$ are in good agreement compared with that calculated from Griffith's parameters derived previously [7].

4. Conclusions

The MS $X\alpha$ method can be used to extract some useful ligand field parameters, utilizing the linear relation found between the $X\alpha$ eigenvalues of the ligand field states and their occupation numbers of the metal complex.

At least two different configurations of the type $e^n t_2^m$ are to be calculated by the SCF MS $X\alpha$ to evaluate 10 Dq and ε. It was found that the ligand field model after Koide and Pryce, is conveniently related to the $X\alpha$ method more than other models due to the spherical-like potential used in the $X\alpha$ scheme.

Although 10 Dq(1) cannot easily be related to experiment, the 10 Dq(2) can. The value of the latter is calculated through the expression

$$10\,Dq(2) = 10\,Dq(1) - \varepsilon(1 - \varepsilon)(A - 8B) = 8592\ cm^{-1}$$

which is in good agreement with the experimental value $10\,110\ cm^{-1}$ ($A = 130791$, $B = 835\ cm^{-1}$ from Ref. [7] and $\varepsilon = 0.009$).

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