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Mimicking the Two-Dimensional Spectrochemical Series Using Density Functional Computations

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With tetragonal distortions of tetrahedral d^2 complexes as examples, nonadditive and additive ligand fields are compared computationally, using Kohn–Sham density functional theory (KS–DFT) and ligand-field theory to obtain 45 linear, parametrical equations. For each complex, a "data" reduction from three nonadditive-field parameters to two parameters of the additive field occurs. The complexes VX_4^- and CrX_4 (where X = F, Cl, Br, I) provide the two-dimensional spectrochemical series of the σ and π AOM parameters, which are known semiempirically for the halide ligands. The same parametrical results can be obtained from the Kohn–Sham orbital energies of the "average of configuration" computation.

Introduction

The success of density functional theory (DFT) in handling transition-metal systems has spurred an interest in bridging between DFT and ligand-field theory (LFT).[1]

In three previous papers,[2] our ambition was to mimic LFT. We focused on the dominating submodels of LFT, which consist of the one-electron operator model of the ligand field (LF) itself and the two-electron operator model of the interelectronic repulsion (R) between the electrons of the partially filled shell. The sum of these two models (LFR) comprises quantitative LFT.

Because a mimicking of LFR was our focus, we constrained the Kohn–Sham density functional theory (KS–DFT), using a so-called "average of configuration" (AOC) computation[3] to define all orbitals. The AOC computation is based on the occupation numbers that represent an even distribution of electrons upon the 10 spin–orbitals of the partially filled shell corresponding to the d shell of LFT. These fixed AOC orbitals are used throughout the mimicking process, and in this way, KS–DFT is not used optimally for any state in particular.

Previously, we found that our method confirmed the qualitative molecular orbital interpretation of LFT that is inherent in the angular overlap model (AOM).[4,5]

Our first contribution[2a] was concerned with atomic ions of all the transition metals whose complete d^q spectra had been observed and assigned by the atomic spectroscopists. Our concern was the interelectronic repulsion, which was parametrized by the Slater–Condon–Shortley model (SCS). Note that the SCS model, which is based on spherical symmetry, is that conventionally used in LFR, although the symmetry of the LF component is taken as the molecular symmetry group. It turns out that these computations were better than those of the Hartree–Fock model.

Our second and third contributions[2b,c] were concerned with ligand-field systems and, in particular, d^2 systems of the type VX_4^- and CrX_4 (X = F, Cl, Br, I), where the symmetry of the AOC computation is T_d. Almost all the prerequisites for the present paper were discussed in detail in these two papers, which both have in common with the present paper that symmetry restrictions require the LF eigenorbitals to be the usual real d orbitals. These orbitals, which simultaneously

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(1) (a) Deeth, R. J. *J. Chem. Soc., Dalton Trans.* **1991**, 1895. (b) Daul, C. A. *Int. J. Quantum Chem.* **1994**, *52*, 867. (c) Atanasov, M.; Daul, C. A.; Rauzy, C. *Chem. Phys. Lett.* **2003**, *367*, 737. (d) Deeth, R. J. *Faraday Discuss.* **2003**, *124*, 379. (e) Deeth, R. J. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, U.K., 2004; Vol. 2, pp 643–650.

(2) (a) Anthon, C.; Schäffer, C. E. *Coord. Chem. Rev.* **2002**, *226*, 17. (b) Anthon, C.; Bendix, J.; Schäffer, C. E. *Inorg. Chem.* **2003**, *42*, 4088. (c) Anthon, C.; Bendix, J.; Schäffer, C. E. *Struct. Bonding (Berlin)* **2004**, *107*, 207.

(3) Baerends, E. J.; Branchadell, V.; Sodupe, M. *Chem. Phys. Lett.* **1997**, *265*, 481.

(4) Schäffer, C. E.; Jørgensen, C. K. *Mol. Phys.* **1965**, *9*, 401. (b) Schäffer, C. E. *Inorg. Chim. Acta* **2000**, *300–302*, 1035.

(5) The only group known to us who uses the same constrained KS–DFT procedure as described here is that of Atanasov, Daul, and co-workers. See, for example: (a) Atanasov, M.; Daul, C. A.; Rauzy, C. *Struct. Bonding (Berlin)* **2004**, *106*, 97. (b) Atanasov, M.; Daul, C. A.; Rauzy, C. *Chem. Phys. Lett.* **2003**, *367*, 737. (c) Mineva, T.; Goursot, A.; Daul, C. *Chem. Phys. Lett.* **2001**, *350*, 147.

belong to the two symmetry hierarchies

$$D_{\infty h} \supset D_{4h} \supset D_{2h} \tag{1a}$$

and

$$O_h \supset D_{4h} \supset D_{2h} \tag{1b}$$

can be individually recognized by symmetry in the partially filled shell of the AOC computation. The complete set of LF states are generated here by collecting together all the Pauli-allowed pairs of d-like molecular spin−orbitals, requiring them to have unit occupation numbers (uon).[6] Thus, a one-to-one correspondence between KS−DFT uon pairs and LF determinants that contain the pairs of corresponding d orbitals is established for all 45 states of the partially filled shell. The KS−DFT energies of all these states can now be computed by our constrained use of KS−DFT, and the energies of the corresponding LF states can be expressed in terms of a linear combination of LF parameters and interelectronic repulsion parameters. By equating corresponding energies, the result is 45 linear equations in the parameters of the ligand field plus repulsion model (LFR).

Note that the states we have described here are not eigenstates. What we have computed are expectation values for the energies of 45 states, which are molecular orbital KS−DFT states, whereas the corresponding LFR states are the diagonal elements of a full LFR description, which are mutually orthogonal by symmetry. Thus, if there are a sufficient number of equations[6] to determine all the parameters, the LFR model provides the nondiagonal elements as well, and, therefore, by diagonalization, the eigenenergies of the constrained KS−DFT mimicking of the LFR.

Common to all our previous papers is our use of mutually orthogonal[7,8] conglomerate LFR operators, which each consists of a product of a parameter and its corresponding coefficient operator. To represent the two−parameter Slater−Condon−Shortley model in this way,[8] we used Jørgensen's spin pairing energy parameter (D) and its complementary parameter (E). These two parameters were used in our first two papers.[2a,b]

In our latest paper,[2c] we extended the SCS model orthogonally to the parametrical multiplet term model, which has the consequence that the energetic SCS constraints on the d^2 configuration are loosened and only the symmetry consequence of the splitting into five multiplets remains. This is achieved by splitting D into D^S and D^ν (where the

superscripted indices refer to total spin and seniority) and E into E^1 and E^0 (where the indices refer to S = 1 and S = 0, respectively. Using this two-electron operator model, the variances of the parametrical fitting of the 45 computed energies were substantially decreased. However, only ∼1% of the information contents—that is, the variance—had to be regarded as useless for our LF−SCS parametrization purposes. The PMT model allowed the classification of the nonparametrizable "errors", either as systematic (deviations from the SCS model), spatial (symmetry-based), or random.

Our classes of one-electron operators and two-electron operators are, by definition, bary-centered and orthogonal to each other. Moreover, because of our hierarchically defined orbitals, our two-electron basis belongs to all the strong-field subconfigurations of eq 1, and, thus, the ligand-field part of our LFR matrices is diagonal. This means that the ligand-field operators are mutually *diagonally orthogonal* in this basis, and also diagonally orthogonal to the two-electron operators. Therefore,[2c] the values of the ligand-field parameters can be determined individually and without the codetermination of any of the two-electron parameters. However, the standard deviations of all the parameters are dependent, of course, critically on the assembly of operators used.

For the ligand field, efforts of bridging between KS−DFT and LFT have concentrated on nonadditive parametrizations.[2b,2c,5] Here, we extend previous studies to encompass homoleptic tetragonally distorted tetrahedral systems. This choice of model systems provides important insight in the mapping of KS−DFT onto the ligand field plus repulsion model (LFR). It allows for the analysis in terms of an additive two-parameter ligand-field model and thereby may provide the two-dimensional spectrochemical series[9] computationally. It does so in a manner especially faithful to the AOM method by avoiding radial distortions, and finally, it does so for systems where purely symmetry-based (nonadditive) ligand-field parametrizations represent an overparametrization of the AOM. Thereby, this choice of model systems imposes a check on the two assumptions of the conventional AOM: the additivity of ligand contributions (not to be confused with the transferability) and the treatment of the halide ligands as linearly ligating.[10]

Symmetry-Based and Angular Overlap Model (AOM) Parametrizations

A holistic view of the ligand field does not take the ligands into account individually.[11] The symmetry of the nonadditive field determines the number of independent parameters[12] that can be determined and also provides a clue[13] to the choice of these parameters.

For a tetrahedral metal complex, it is a symmetry property that the d orbitals belong to the irreducible representations t_2 and e of the point group T_d, and the only ligand-field

(6) Ziegler, T.; Rauk, C. *Theor. Chim. Acta* **1977**, *43*, 261.

(7) The usefulness of mutually orthogonal operators was illustrated in several previous papers; see, for example: (a) Schäffer, C. E. *Physica A* **1982**, *114A*, 28. (b) Brorson, M.; Damhus, T.; Schäffer, C. E. *Comments Inorg. Chem.* **1983** *3*, 1. (c) Bendix, J.; Brorson, M.; Schäffer, C. E. *Inorg. Chem.* **1993**, *32*, 2838.

(8) Brorson, M.; Schäffer, C. E. *Inorg. Chem.* **1988**, *27* (7), 2522.

(9) McClure, D. S. In *Advances in the Chemistry of the Coordination Compounds*; Kirschner, S., Ed.; The Macmillan Company: New York, 1961; p 498.

(10) (a) Schäffer, C. E. *Struct. Bonding (Berlin)* **1968**, *5*, 68. (b) Schäffer, C. E. *Struct. Bonding (Berlin)* **1973**, *14*, 69.

(11) Bendix, J.; Schäffer, C. E.; Brorson, M. *Coord. Chem. Rev.* **1989**, *94*, 181.

(12) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, U.K., 1961.

(13) Schäffer, C. E. In *Wave Mechanics—The First Fifty Years*; Price, W. C., Chissick, S. S., Ravensdale, T., Eds.; Butterworths: London, 1973.

observable is the energy difference between these two orbital sets, which may be chosen as the parameter Δ. For tetrahedral systems, a KS−DFT mimicking of the nonadditive model, leading to a computationally based spectrochemical series of halide ligands, was recently[2b,2c,5b] demonstrated.

The present mimicking of the ligand fields in distorted systems, here distorted tetrahedral systems, has not been attempted previously.

As opposed to nonadditive parametrizations based on a holistic view and on the global symmetry, the additive view regards the ligands as individual perturbers and the additive field is the sum of these perturbations, which is dependent on the symmetries of the individual metal−ligand bonds.

Since the rotation group O of the octahedron and the tetrahedral point group T_d are isomorphic, and the same applies to their respective tetragonal subgroups (D_4 and D_{2d}), the nonadditive field provides the same parametrical discussion of the tetragonal distortion for MX_6 and MX_4 systems, because of its dependence solely on symmetry.

However, geometrically, a tetragonal distortion of an octahedron requires a distinction between equatorial and axial ligands, whereas such a distortion of a tetrahedron allows indistinguishable ligands that angularly move to form the bisphenoidal D_{2d} geometry:
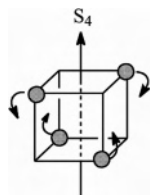
For an octahedral chemical system, one may consider either substitutional tetragonality or tetragonality caused by radial distortion, that is, by changes of the metal-to-ligand distances. Both types of tetragonality may lead to AOM concepts such as σ- or π-elongation or compression, and, in the case of substitutional tetragonality, a system may be simultaneously σ-elongated and π-compressed, as found[14] in the case of *trans*-$[Cr(NH_3)_4Cl_2]^+$, where $e_{\sigma Cl} < e_{\sigma N}$ and $e_{\pi Cl} > e_{\pi N}$.

Our previous choice of systems, which belonged to the cubic symmetry class T_d, resulted in the fact that $\Delta(T_d)$ was the only piece of ligand-field parametrical information involved. Thus, the spectrochemical series could be said to be one-dimensional. In the present paper, we impose a tetragonal distortion upon our chemical systems and yet keep all the orbital symmetry advantages of our previous choice so that the one-to-one relationship between our KS−DFT and LFR models remains.

When using the holistic or nonadditive ligand field, the cubic field parameter Δ must, in D_{2d} symmetry, be supplemented with the parameters Δt_2 and Δe, representing the tetragonal splittings of the t_2 and e orbital levels. Thus, from a computation on a tetragonally distorted complex, exactly
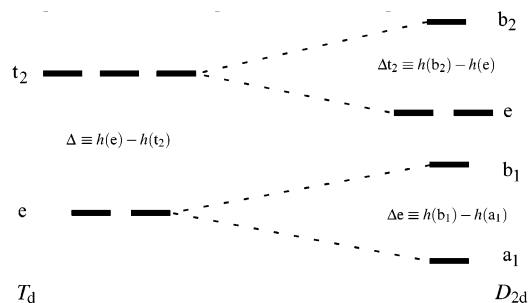

Figure 1. Splitting diagram corresponding to tetragonal compression of a homoleptic tetrahedral complex.

three one-electron parameters may be extracted. The associated coefficient operators are orthogonal because they act on subspaces that belong to different symmetry species of T_d. The signs of the parameters are shown in Figure 1 and are defined in analogy with the octahedrally[13,14] derived case.

We now use the ligand-field AOM that partitions the ligand field into components associated with the individual ligands using an additive description of the nonspherical part of the field.[10b,13] Because the four halides remain equivalent in the tetragonal symmetry group D_{2d}, and because we use the conventional AOM assumption that halides are linearly ligating,[15] the two LF parameters e_σ and e_π are common to all the ligands of a given complex. This means that, when going from the nonadditive to the additive ligand field, there will be a reduction in the number of LF parameters and, thereby, a computational test of the concept of linear ligation. The parameters of these data reductions are dependent on the acute angle θ between the S_4 axis and the radius vector of a halide ligand. In all of the present systems, $\theta = 60°$ and the valence angles containing the S_4 axis become $120°$, while the other four angles are, accordingly, $104.5°$. Thus, the atomic configuration is between that of the tetrahedron and the square. The parametrical relationships are

$$[\Delta]_{AOM} = \frac{123}{128}\left(-\frac{4}{9}\right)(3e_\sigma - 4e_\pi)$$

$$[\Delta t_2]_{AOM} = \left(\frac{9}{16}\right)e_\sigma - \left(\frac{1}{4}\right)e_\pi \quad \text{(valid for } \theta = 60°) \quad (2)$$

$$[\Delta e]_{AOM} = \left(-\frac{1}{16}\right)e_\sigma + \left(\frac{3}{4}\right)e_\pi$$

where $-^4/_9(3e_\sigma - 4e_\pi)$ is the AOM expression for $\Delta(T_d)$ obtained for $\theta = \theta(T_d) = 54.74°$ and the pre-factor ($^{123}/_{128}$) may be conceived as a geometrical distortion factor.

Note that the coefficient operators associated with the AOM parameters are nonorthogonal.

Results and Discussion

Table 1 contains the results of our modeling for the particular distorted tetrahedra of the VX_4^- and CrX_4 complexes.

The first pair of rows of Table 1 contains the values of the parameters that describe the tetrahedral parts of the LF

(14) (a) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399. (b) Glerup, J.; Schäffer, C. E. *Proceedings of the 11th ICCC*; Cais, M., Ed.; 1968; p 500.

(15) It should be emphasized that, although linear ligation is a symmetry requirement for a ligator participating in regular tetrahedral coordination, this is, not even for mono-atom ligands, the case in a tetragonally distorted tetrahedral coordination environment.
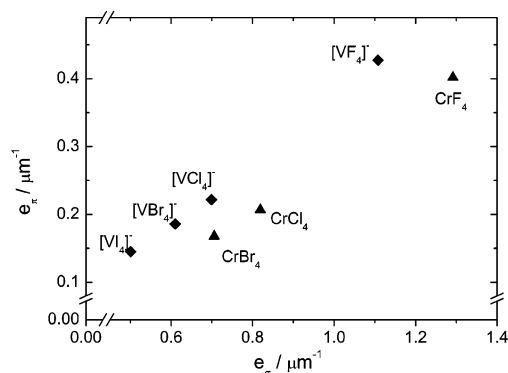
Figure 2. Halide components of the two-dimensional spectrochemical series computed by Kohn−Sham density functional theory (KS−DFT). For the four halide ligands, the two series are qualitatively identical.

Table 1. Computed Values of Ligand-Field Parameters

		F	Cl	Br	I
		Nonadditive Model			
Δ (μm^{-1})	V^{III}	−0.693(7)	−0.513(8)	−0.459(8)	−0.388(9)
	Cr^{IV}	−0.972(6)	−0.693(7)	−0.613(7)	
Δe (μm^{-1})	V^{III}	0.263(11)	0.111(12)	0.086(12)	0.054(11)
	Cr^{IV}	0.234(9)	0.092(11)	0.064(12)	
Δt_2 (μm^{-1})	V^{III}	0.504(10)	0.349(11)	0.312(10)	0.269(11)
	Cr^{IV}	0.613(8)	0.420(10)	0.373(10)	
		Additive Model in the Form of the AOM with Linear Ligation			
e_σ (μm^{-1})	V^{III}	1.108(18)	0.699(19)	0.610(19)	0.501(22)
	Cr^{IV}	1.292(15)	0.819(18)	0.706(19)	
e_π (μm^{-1})	V^{III}	0.427(13)	0.222(14)	0.186(14)	0.145(16)
	Cr^{IV}	0.402(11)	0.207(13)	0.168(14)	
		Spectrochemical Parameter $[\Delta]_{AOM}$ Calculated from e_σ and e_π			
$[\Delta]_{AOM}$ (μm^{-1})	V^{III}	−0.690	−0.516	−0.464	−0.394
	Cr^{IV}	−0.969	−0.696	−0.618	

splittings and, thus, exhibits the spectrochemical series of the nonadditive model,

$$I^- < Br^- < Cl^- \ll F^- \qquad (3)$$

based on the tetragonal complexes.

The second and third pairs of rows contain the values of the tetragonal parameters Δe and Δt_2, which are uncorrelated in the nonadditive model.

The fourth and fifth pairs of rows of Table 1 provide the so-called two-dimensional spectrochemical series (the σ-series and the π-series; see Figure 2), which, for the halides, both coincide with the usual spectrochemical series of eq 3. These series also agree qualitatively with those obtained semiempirically for substitutionally[14] tetragonal octahedral Cr^{III} complexes.

Note that, although the values of the parameters Δt_2 and Δe are dependent on the size of the distortion, those of the AOM parameters e_σ and e_π are chemically based and, within certain limits, are distortion-independent.

The sixth pair again provides the same spectrochemical series like that of eq 3; however, this time, the values have been derived from the AOM. The two sets of Δ values are identical, within one standard deviation.

The four parameters of the two-electron operators of the PMT model (not included in the table), and the three one-electron parameters of the nonadditive model explain 99.62% of the variance in calculating the average energy alone from

Table 2. Comparison of Values of the Symmetry-Based Tetragonal Ligand-Field Parameters for VCl$_4^{-a}$

	Δ (μm^{-1})	Δe (μm^{-1})	Δt_2 (μm^{-1})
nonadditive	−0.513	0.111	0.349
AOM	−0.516	0.123	0.338
AOC	−0.499	0.114	0.332

a The first row is obtained from the nonadditive model by direct fitting, and the second row is obtained using the e_σ and e_π values of Table 1, applying eq 2. The values in the last row are derived from the Kohn−Sham orbital energies of the "average of configuration" (AOC), using the definitions in Figure 1.

Table 3. $\Delta(T_d)$ Determined Directly from a KS−DFT Computation in T_d Symmetry (From ref 2c)

	F	Cl	Br	I
V^{III}	−0.675	−0.502	−0.449	−0.377
Cr^{IV}	−0.968	−0.682	−0.601	

the 45 computed energies. In the first two rows of Table 2, the values of the nonadditive model are compared to those obtained from the AOM by eq 2. This representative set, which is valid for VCl$_4^-$, shows that the AOM assumption of linear ligation is nicely fulfilled for this increase of ∼10° in the bisphenoidal angle θ.

In Table 3, the computed values of $\Delta(T_d)$ for the genuine[2b,c] tetrahedral complexes are given. The AOM model predicts a geometrical distortion factor of $\Delta/\Delta(T_d) = {}^{123}/_{128}$, in agreement with the intuitive statement that the magnitude of the cubic part Δ of the ligand-field should be decreased by the angular tetragonal distortion. However, by comparison of Tables 1 and 3, it is observed that this statement is weakly violated.

Kohn−Sham Density Functional Theory (KS−DFT) Orbital Energy Differences within the Partially Filled Shell

Instead of using the energies of the 45 individually computed two-electron states to determine the three LF orbital energy differences of Figure 1, the corresponding one-electron energy differences can alternatively be calculated from the Kohn−Sham orbital energy differences of the single AOC computation. The parameter values thereby obtained are those for the representative system VCl$_4^-$, given in the last row of Table 2. The agreement between the AOC set of values and those obtained using the energies of the full set of states is most remarkable. (The data for the remaining systems are given as Supporting Information.)

Conclusions

This paper has illustrated how Kohn−Sham density functional theory (KS−DFT) can be used to provide a computational supplement, when experimental ligand-field results are unobtainable. The primary point here is that no experimental method is available to create the well-defined distortions that are described here. Thus, no direct comparison with experiment is possible. However, on comparison of the computed values for the ligand-field parameters with those expected on the basis of the regularities found in the past, the present results are very satisfactory. In particular, the two-dimensional spectrochemical series is in agreement

with the σ- and π-series that is known from octahedral[14] Cr^{III} complexes of the *trans*-dihalido tetrammine class.

Supporting Information Available: Computed AOC values of the ligand-field parameters of bisphenoidally distorted tetrahedral complexes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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