Theoret. chim. Acta (Berl.) 10, 337—341 (1968)

Ligand Field Splitting for a Diffuse Charge Model

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Received December 19, 1967

The simple electrostatic point charge model of the ligand field theory is extended by representing each ligand by N fractional point charges. The special cases $N=6$, 18, and 62 are considered. A spherical charge distribution gives results similar to those of the point charge model. The splittings for non-spherical charge distributions are found to depend strongly on the orientation of the ligand charge.

Das in der Ligandenfeldtheorie übliche einfache elektrostatische Punktladungsmodell wird erweitert, indem jeder Ligand durch N Teilpunktladungen ersetzt wird. Untersucht wurden die Fälle $N=6$, 18 und 62. Eine kugelsymmetrische Ladungsverteilung gibt Ergebnisse, die mit denen des einfachen Punktladungsmodells vergleichbar sind. Bei nicht kugelsymmetrischer Ladungsverteilung hängt die Aufspaltung sehr stark von der Richtung der Ligandenladungen ab.

Le modèle électrostatique simple à charge ponctuelle de la théorie du champ des ligandes est étendu, en réprésentant chaque ligand par N charges ponctuelles fractionnaires. On considère les cas particuliers N = 6,18, et 62. Une distribution de charge sphérique donne des résultats semblables à ceux du modèle à charge ponctuelle. Les séparations obtenues avec des distributions de charge non sphériques s'avèrent dépendre fortement de l'orientation de la charge des ligands.

Introduction

When a transition metal ion is enclosed in the electrostatic field of ligands a splitting of d-orbitals occurs. In the calculations the ligand field is usually approximated by the field due to point charges situated at the center of ligand atoms. We wish to elaborate this simple model by considering the effects of replacing the single point charge by several charged points, thus simulating a diffuse charge distribution for ligands. By increasing the number of points which represent a ligand we will approach the charge distribution of the real complexes in a more satisfactory manner.

To find the splitting of d-orbitals in a complex we have to solve a secular determinant

$$|H_{ik}-E\delta_{ik}|=0\,,$$

where

$$-2\leqq i,\ k\leqq +2$$

with

$$H_{ik}\equiv\langle\chi_i|V|\chi_k\rangle\,.$$

V is the electrostatic potential originating from the point charges representing the ligands. The explicit formulae for the ligand field matrix elements for point charges in general positions are given by Hartmann and König [1, 2]. We reproduce here the expressions for the elements H_{22}, H_{11}, H_{00}, and $H_{2,-2}$, which, later on we require in an application:

$$\langle 2|V|2\rangle = Ze^2\sum_i\{G_0-\tfrac{2}{7}(\tfrac{3}{2}\cos^2\theta_i-\tfrac{1}{2})G_2+\tfrac{1}{21}(\tfrac{35}{8}\cos^4\theta_i-\tfrac{15}{4}\cos^2\theta_i+\tfrac{3}{8})G_4\}\,,$$

$$\langle 1|V|1\rangle = Ze^2\sum_i\{G_0+\tfrac{1}{7}(\tfrac{3}{2}\cos^2\theta_i-\tfrac{1}{2})G_2-\tfrac{1}{21}(\tfrac{35}{8}\cos^4\theta_i-\tfrac{15}{4}\cos^2\theta_i+\tfrac{3}{8})G_4\}$$

$$\langle 0|V|0\rangle = Ze^2\sum_i\{G_0+\tfrac{2}{7}(\tfrac{3}{2}\cos^2\theta_i-\tfrac{1}{2})G_2+\tfrac{2}{7}(\tfrac{35}{8}\cos^4\theta_i-\tfrac{15}{4}\cos^2\theta_i+\tfrac{3}{8})G_4\}\,,$$

$$\langle 2|V|-2\rangle = Ze^2\sum_i\tfrac{5}{24}\sin^4\theta_i e^{\pm 2i\phi_i}G_4\,.$$

The summation is over all point charges (representing individual ligands). The coordinates θ_i, ϕ_i are given by the position of a ligand, while the coordinate r_i enters the radial integrals G_n.

To proceed with the calculations we have now to sum over the contributions of the simple charge points. The choice of the wave function and the selection of fractional point charges will depend on the complex considered and on the accuracy with which the problem is investigated. In the following we will apply the proposed model to an octahedral complex.

Calculations

Spherical Charge Distributions

We will consider the complex $[Cr(H_2O)_6]^{3+}$. For $3d$ radial function of chromium we take the function of a double zeta form, given by Richardson [3]:

$$R_{3d}(r) = c_1\chi(\zeta_1) + c_2\chi(\zeta_2),$$

where $\chi(\zeta_i)$ are normalized Slater-type orbitals with $\zeta_1 = 4.95$ and $\zeta_2 = 2.20$, while $c_1 = 0.5460$ and $c_2 = 0.5822$. For the Cr–O distance we take the value of 1.97 Å, as taken by Tanabe and Sugano in their more detailed computation on this complex [4].

We will consider several approximations for this complex: $N = 6$, 18, 62 (N denoting the number of fractional point charges of each ligand). For simplicity in all the cases the fractional charge will be located on a sphere of constant radius, i.e. all new points representing ligand will be at the same distance from the center of the ligand, which is given by the covalent radius of oxygen (0.74 Å). We have still to decide on the geometrical distribution of these points in the space. We assumed in case $N = 6$ the points to form an octahedron, and when $N = 18$ the additional 12 points are in between each pair of the initial 6 points (i.e. above the sides of the octahedron). The octahedron is oriented so that its axis are parallel to the axis of the octahedron representing the complex. With a large number of

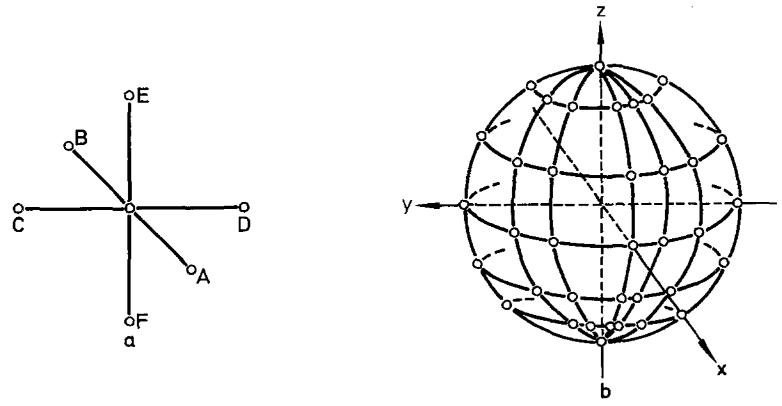

Fig. 1. a Octahedral complex with labbeling of ligands. b Ligand charge replaced by 62 fractional point charges

points it is better to abandon regular polyhedra and simply devide the sphere into sections introducing polar coordinates for each sphere and distribute the points accordingly. This is illustrated in Fig. 1b. Each set of 12 points lie on a circle of the sphere, and there are in all five such parallel circles (at $\theta_C = 30°, 60°, 90°, 120°$, and $150°$ measured from the internal z-axis, which is pointed towards the central atom), and in addition there are two points on the axis ($\theta_C = 0°$ and $180°$) for each ligand.

In the case $N = 6$ or 18 each point is carrying the charge Q/N. (Without loss of generality we may assume $Q \cdot e = 1$, i.e., we measure the charge in units of the effective interaction charge.) In the case $N = 62$ we simulate a uniform charged shell by normalizing the charge of each point in such a way that the charge density ϱ on the sphere is constant. We write $q_i/P_i =$ constant for the points on the z-axis of each ligand (poles), and $12q_i/P_i =$ constant for the remaining set of points, 12 points being on each of the five bands of the sphere. Here P_i is an area of the ith section of the sphere, $i = 1, 2, \ldots$ 7 ($i = 1$ and $i = 7$ correspond to the poles of the sphere). In this way a uniform charge density on the shell is achieved, and so defined q_i, which become $q_1 = q_7 = 0.03349$, $q_2 = q_6 = 0.01042$, $q_3 = q_5 = 0.01804$ and $q_4 = 0.02083$, are used to obtain the results in Table 2.

Now we evaluate the radial integrals G_0, G_2, and G_4 which enter the expressions for the matrix elements. In the case $N = 6$ there are three distances for which the G_n integrals have to be evaluated: 1.23 Å, 2.1044 Å and 2.71 Å. For $N = 18$ only two additional intermediate distances appear (1.5584 Å and 2.5476 Å), and for $N = 62$ we need to calculate G_n integrals for seven different distances. The values of radial integrals which are required are given in Table 1.

Performing now the summation over all fractional point charges we obtain the matrix elements. The numerical values of the H_{ik} elements, and the magnitude of the splitting ΔE is given in Table 2. The magnitude of H_{ik} (and the splitting ΔE)

Table 1. *Radial integrals G_n for various distances R of the fractional point charges from the central metal atom*

R (a.u.)		G_0	G_2	G_4
G_n values for point charge model $N = 1$:				
3.7228	G	0.26862	0.02990	0.00735
G_n values for the case $N = 6$:				
2.3244	G^{I}	0.42790	0.11048	0.05143
3.9768	G^{II}	0.25147	0.02458	0.00536
5.1212	G^{III}	0.19528	0.01153	0.00154
Additional G_n values for the case $N = 18$:				
2.9072	G^{IV}	0.34365	0.06115	0.02226
4.8143	G^{V}	0.20773	0.01387	0.00209
Additional G_n values for the case $N = 62$:				
2.6071	G^{VI}	0.38263	0.08230	0.03422
3.2570	G^{VII}	0.30694	0.04424	0.01364
4.5847	G^{VIII}	0.21813	0.01606	0.00266
4.9831	G^{IX}	0.20069	0.01251	0.00176

oscilate somehow irregularly with N. However, already a change from $N=18$ to $N=62$ makes smaller alternations than the change from $N=6$ to $N=18$. It is interesting to notice that the difference between $N=1$ and $N=62$ is not so large. This result explains why the simple electrostatic point charge model gives so surprisingly good results in spite of its crude features.

Non-Spherical Charge Distributions

In the following we will consider the effects of non-spherical charge distributions in the approximation of a single shell. As an example we will try to simulate a charge cloud due to a p-orbital. Several orientations are possible and firstly we consider the case when the lobes of p-orbital are oriented towards the central atom.

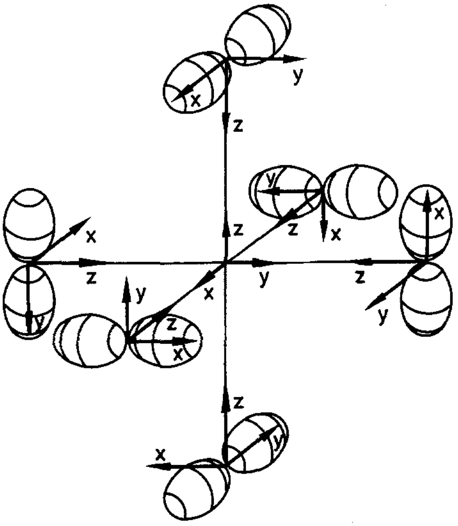

Fig. 2. Octahedral complex with p-shaped charge distribution which simulate ligand charge in complexes like $Co(NO_2)_6^{4-}$

From the uniform distribution we can obtain the axial distribution of a p-orbital by multiplying charge q_i at each point by $\cos^2\theta_i$, where θ_i is measured for each ligand from the axis pointed toward the central atom. We obtain for new charges (after they have been renormalized so that $q_i=1$): $q_1=0.00769$, $q_2=0.02154$, $q_3=0.01244$ and $q_4=0$. The splitting ΔE is given in Table 2, and as expected it is larger than for the spherical charge distribution, since p-orbitals of ligands oriented towards the central metal atom are more efficient in perturbing the free atom d-shell.

If p-orbitals are oriented perpendicular to the metal-ligand bond several different cases, all of a reduced symmetry result. Of some interest is the orientation of axial charge shown in Fig. 2. Such a charge distribution corresponds to a charge of NO_2 groups found in $Co(NO_2)_6^{4-}$ [5]. However, we do not wish to imply that NO_2 contributes to the ligand field only through its p-like charge. There is also a σ-component, which will play a dominant role. In the following we are interested only in the part of the ligand field produced by various orientations of p-like

Table 2. *The numerical values for the ligand field matrix elements and the splitting of d-orbitals for the models considered*[a]

N	$\langle 0\|V\|0\rangle$	$\langle 1\|V\|1\rangle$	$\langle 2\|V\|2\rangle$	$R_e\,\langle 2\|V\|-2\rangle$	$\Delta=(E_1-E_5)$
1	1.61906	1.60682	1.61294	0.00612	0.01224
6	1.63951	1.62209	1.63080	0.00871	0.01742
18	1.62028	1.60896	1.61462	0.00566	0.01132
62	1.62896	1.61736	1.62316	0.00580	0.01160
62	1.41143	1.39853	1.40498	0.00645	0.01290
62	0.79228	0.79008	0.79118	0.00110	0.00220

[a] The first $N=62$ case correspond to a spherical charge distribution, the second to a *p*-shaped axial charge oriented along the metal-ligand bond, and the last case to a *p*-shaped charge oriented perpendicular to the metal-ligand bonds, as in $Co(NO_2)_6^{4-}$.

charges. To simulate the axial charge distribution shown in Fig. 2 we have to weight the charges q_i by $\sin^2\theta_i\cos^2\phi_i$ for ligands at A, C, E, and by $\sin^2\theta_i\sin^2\phi_i$ for ligands at B, D, F. The total charge is again renormalized. The renormalization factors are: $N_2=0.00694$; $N_3=0.02083$; $N_4=0.02778$. The matrix elements and the splitting of *d*-orbitals are given in Table 2.

Conclusion

It is shown that a diffuse spherical charge distribution gives results, at least for the example we considered, similar to those of the point charge model. However, by introducing a large number of points a ligand non-spherical charge distribution may be simulated, which the simple model was unable to consider. By further increasing the number of fractional point charges (which may be located at different distance from the ligand also), one may investigate more realistically the effect of charge perturbation in complexes. A further work in this direction may be problematical with regard to its ability to reproduce the experimental results, since, as is well known, the calculations with a good charge distribution have led to false predictions (compare e.g. [6, 7]). As has been said, the electrostatic model of the ligand field is in disagreement with several types of experimental facts [8]. However, we believe that the refined model will give better insight in the factors influencing the accuracy of the electrostatic model, all possibilities of which have not been fully investigated.

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