Simple model for Crystal Field Theory

Francisco M. Fernández

INIFTA (UNLP, CCT La Plata-CONICET), División Química Teórica
Blvd. 113 S/N, Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina

April 4, 2016

Abstract

We investigate a simple model for the prediction of the splitting of the $3d$ orbitals of a metal ion in the environment of ligands. The electrons are considered to be independent and their interaction with the ligands is represented by the Dirac delta function in three dimensions. We discuss several cases where the model is successful and a few ones where it is not.

1 Introduction

The crystal field theory (CFT) developed by Bethe long ago was utilized by physicists to explain magnetic properties and absorption spectra of transition metals and other compounds. This theory is commonly discussed in specialized textbooks as well as in standard books on inorganic chemistry.

CFT treats the interaction between the metal ion and the ligands as a purely electrostatic problem in which the ligand atoms or molecules are considered to be mere point charges (or point dipoles). In spite of this oversimplification CFT provides a very simple and easy way of treating numerically many aspects of the electronic structure of complexes.

The purpose of this paper is to investigate an even simpler CFT model were the electrostatic repulsion between the $3d$ electrons (assumed to be noninteract-
ing) and the ligands is represented by a Dirac delta function in three dimensions centered at the ligand positions. Although this extremely short-range interaction may appear to be rather too unrealistic at first sight some of the results are surprisingly reasonable.

In section 2 we develop the model that we later apply to some examples in section 3. We consider cases where the model is successful and others in which it fails. Finally we summarize the main results and draw conclusions in section 4.

2 The model

The model takes into account only 3d electrons that are considered to be independent. It is further assumed that in the absence of ligands each electron can be described by an effective hydrogen-like Hamiltonian

$$H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r},$$

where $Z$ is an effective core charge. The effect of $M$ negative ligands around the central metal ion is taken into account by means of a perturbation Hamiltonian of the form

$$H' = V_0 \sum_{k=1}^{M} \delta(r - r_k),$$

where $V_0 > 0$ is the strength of the electrostatic interaction between a $d$ electron and the ligands and $\delta(r - r_k)$ is the well known Dirac delta function in three dimensions. In the absence of ligands the 3d hydrogen-like orbitals

$$\{ \varphi_j, j = 1, 2, \ldots 5 \} = \{ \varphi_{d_{2z}}, \varphi_{d_{xz}}, \varphi_{d_{x^2-y^2}}, \varphi_{d_{yz}}, \varphi_{d_{xy}} \},$$

are degenerate.

In order to calculate the splitting of the 5-fold degenerate 3d level we resort to perturbation theory. The perturbation corrections of first order to the orbital energies are given by the roots $\epsilon'_n, n = 1, 2, 3, 4, 5$ of the secular determinant

$$|H' - \epsilon' I| = 0,$$
where the elements of the perturbation matrix $H'$ are

$$H'_{ij} = \langle \phi_i | H' | \phi_j \rangle = V_0 \sum_{k=1}^{M} \phi_i(\mathbf{r}_k) \phi_j(\mathbf{r}_k).$$

(5)

Note that the calculation reduces to obtaining the values of each $3d$ orbital at the locations of the ligands.

The calculation is greatly simplified if we write the $3d$ real orbitals as

$$\varphi_j(x, y, z) = f(\rho) u_j(x, y, z)$$

$$f(\rho) = \frac{\sqrt{2}}{81 a_0^2 \sqrt{\pi}} (\frac{Z}{a_0})^{3/2} e^{-\rho/3},$$

(6)

where $a_0$ is the Bohr radius and the form factors $u_j(x, y, z)$ read

$$\begin{align*}
\text{Orbital} & | d_z^2, x^2-y^2 | dxz | dyz | dxy \\
\varphi & | 1/\sqrt{12} (2z^2-x^2-y^2) | 1/2 (x^2-y^2) | xz | yz | xy
\end{align*}$$

(7)

In this way, the matrix elements (5) can be written in the simpler form

$$H'_{ij} = \lambda \frac{L^4}{5} \sum_{k=1}^{M} u_i(x_k, y_k, z_k) u_j(x_k, y_k, z_k),$$

$$\lambda = V_0 f(ZL/a_0)^2 L^4,$$

(8)

where $L$ is the distance between each one of the ligands and the metal nucleus.

For the time being we assume that all such distances are equal in order to simplify the presentation.

It follows from the Hellmann-Feynman theorem

$$\frac{d\epsilon}{dV_0} = V_0^{-1} \langle \psi | H' | \psi \rangle = \sum_{k=1}^{M} \epsilon(\mathbf{r}_k)^2 \geq 0,$$

(9)

that $\epsilon(V_0) \geq \epsilon(0)$. Therefore, the matrices constructed in the way just indicated do not satisfy the so called center of gravity rule [3, 4]. Although this rule is irrelevant for our purposes we can build matrices that satisfy it within present simple model. For example, the modified perturbation matrix

$$H'_{cg} = H' - \frac{1}{5} \text{tr}(H') I,$$

(10)

where $\text{tr}$ denotes the trace of a matrix and $I$ is the $5 \times 5$ identity matrix, already satisfies the center of gravity rule.
3 Examples

In what follows we test the predictive power of the model outlined in the preceding section on several complexes of various geometries.

3.1 Tetrahedral complex

In the case of four ligands at the vertexes of a tetrahedron we have

\[ r_s = \frac{L}{\sqrt{3}} \begin{pmatrix}
1 & 1 & 1 \\
-1 & -1 & 1 \\
-1 & 1 & -1 \\
1 & -1 & -1
\end{pmatrix}, \tag{11} \]

where each row of the structure matrix \( r_s \) is one of the ligand position vectors \( r_k \) with modulus \( |r_k| = L \). A straightforward calculation leads to the following diagonal perturbation matrix:

\[ H' = \lambda \begin{pmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 4/9 & 0 & 0 \\
0 & 0 & 0 & 4/9 & 0 \\
0 & 0 & 0 & 0 & 4/9
\end{pmatrix}. \tag{12} \]

We appreciate that the model predicts the widely accepted splitting of the energy levels \( \epsilon(d_{z^2}) = \epsilon(d_{x^2-y^2}) < \epsilon(d_{xz}) = \epsilon(d_{yz}) \) \[\geq \epsilon(d_{xy})\] with the energy interval \( \epsilon(T_2) - \epsilon(E) = \Delta_T = 4\lambda/9. \)
3.2 Octahedral complex

The octahedral structure matrix

\[ \mathbf{r}_s = L \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & -1 \end{pmatrix}, \]  

(13)

describes four ligands located on the \( xy \) plane at the vertexes of a square and two more at opposite sides on the \( z \) axis. It leads to the diagonal perturbation matrix

\[ \mathbf{H}' = \lambda \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \]  

(14)

that exhibits the well known splitting of the energy levels \( \epsilon (d_{xz}) = \epsilon (d_{yz}) = \epsilon (d_{xy}) < \epsilon (d_{x^2-y^2}) \). In this case the energy interval is \( \epsilon (T_{2g}) - \epsilon (E_g) = \Delta_O = \lambda \). The most interesting feature of present simple model is that it correctly predicts the ratio between the tetrahedral and octahedral splittings \( \Delta_T = \frac{4}{9} \Delta_O \) that is commonly obtained by more elaborate methods [2]. This ratio is valid provided that all the model parameters in \( \lambda (Z, L, V_0) \) are exactly the same for both complexes.
3.3 Cubic complex

From the structure matrix that represents eight ligands on the vertes of a cube

\[ r_s = \frac{L}{\sqrt{3}} \begin{pmatrix} 1 & 1 & 1 \\ -1 & 1 & 1 \\ -1 & -1 & 1 \\ 1 & -1 & 1 \\ 1 & -1 & -1 \\ -1 & 1 & -1 \\ -1 & 1 & -1 \\ -1 & -1 & -1 \end{pmatrix}, \quad (15) \]

we easily obtain the diagonal perturbation matrix

\[ H' = \lambda \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 8/9 & 0 & 0 \\ 0 & 0 & 0 & 8/9 & 0 \\ 0 & 0 & 0 & 0 & 8/9 \end{pmatrix}, \quad (16) \]

that predicts the well known splitting \( \delta (d_{xz}) = \epsilon (d_{x2-y2}) < \epsilon (d_{yz}) = \epsilon (d_{xy}) \) and the energy difference \( \delta (T_{2g}) - \epsilon (E_g) = \Delta_C = \frac{8}{9} \lambda \). Besides, the model predicts the correct ratio between the magnitudes of the cubic and octahedral splittings \( \Delta_C = \frac{8}{9} \Delta_O \) obtained by means of more elaborate methods [2]. Note that the ratios \( \frac{8}{9} \Delta_T = \Delta_O = \frac{8}{9} \Delta_C \) are mentioned in most textbooks on the field [2-4] but explicitly calculated in a few of them [2]. Undoubtedly, present calculation is far simpler.

3.4 Square antiprismatic complex

If we rotate the four ligands on one of the cube faces perpendicular to the \( z \) axis by an angle \( \pi/4 \) about that axis we obtain the structure matrix for a square
antiprismatic complex

\[
\mathbf{r}_s = \frac{L}{\sqrt{3}}\begin{pmatrix}
0 & \sqrt{2}/2 & 1 \\
-\sqrt{2}/2 & 0 & 1 \\
0 & -\sqrt{2}/2 & 1 \\
\sqrt{2}/2 & 0 & 1 \\
1 & -1 & -1 \\
1 & 1 & -1 \\
-1 & 1 & -1 \\
-1 & -1 & -1
\end{pmatrix},
\]

(17)

A straightforward calculation yields

\[
\mathbf{H}' = \lambda\begin{pmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 4/9 & 0 & 0 & 0 \\
0 & 0 & 8/9 & 0 & 0 \\
0 & 0 & 0 & 8/9 & 0 \\
0 & 0 & 0 & 0 & 4/9
\end{pmatrix},
\]

(18)

that predicts the correct splitting \(\epsilon(d_{xz}) < \epsilon(d_{x^2-y^2}) = \epsilon(d_{xy}) < \epsilon(d_{xz}) = \epsilon(d_{yz})\).

### 3.5 Trigonal bipyramidal complex

The structure matrix describing three ligands on the vertexes of an equilateral triangle on the \(xy\) plane and two more on the \(z\) axis is given by

\[
\mathbf{r}_s = L\begin{pmatrix}
1 & 0 & 0 \\
-1/2 & \sqrt{3}/2 & 0 \\
-1/2 & -\sqrt{3}/2 & 0 \\
0 & 0 & 1 \\
0 & 0 & -1
\end{pmatrix}.
\]

(19)
From it we obtain the diagonal perturbation matrix
\[
H' = \lambda \left( \begin{array}{cccccc}
11/12 & 0 & 0 & 0 & 0 \\
0 & 3/8 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 3/8 \\
\end{array} \right),
\]
(20)
that predicts the well known orbital splitting \( \epsilon(d_{xz}) = \epsilon(d_{yz}) < \epsilon(d_{x^2-y^2}) = \epsilon(d_{xy}) < \epsilon(d_z) \).

### 3.6 Pentagonal bipyramidal complex

If 5 ligands are located at the vertexes of a pentagon on the \(xy\) plane and two more on the \(z\) axis the resulting structure matrix
\[
r_s = L \left( \begin{array}{cccccc}
1 & 0 & 0 & 0 & 0 \\
\sqrt{\frac{5-1}{4}} & \sqrt{\frac{\sqrt{5}+5}{8}} & 0 & 0 & 0 \\
-\sqrt{\frac{5-1}{4}} & \sqrt{\frac{\sqrt{5}-5}{8}} & 0 & 0 & 0 \\
-\sqrt{\frac{5+1}{4}} & -\sqrt{\frac{\sqrt{5}-5}{8}} & 0 & 0 & 0 \\
\sqrt{\frac{5-1}{4}} & -\sqrt{\frac{\sqrt{5}+5}{8}} & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & -1 \\
\end{array} \right),
\]
(21)
leads to the diagonal perturbation one
\[
H' = \lambda \left( \begin{array}{cccccc}
13/12 & 0 & 0 & 0 & 0 \\
0 & 5/8 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 5/8 \\
\end{array} \right),
\]
(22)
that predicts the correct orbital splitting \( \epsilon(d_{xz}) = \epsilon(d_{yz}) < \epsilon(d_{x^2-y^2}) = \epsilon(d_{xy}) < \epsilon(d_z) \).
3.7 Square complex

If there are four ligands at the vertexes of a square on the $xy$ plane the structure matrix reads

$$r_s = L \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}. \quad (23)$$

The symmetry elements of this complex are those of the point group $D_{4h}$ and its character table predicts that the degeneracy of the $d$ orbitals should be $\{d_{z^2}\}, \{d_{x^2-y^2}\}, \{d_{xy}\}, \{d_{xz}, d_{yz}\}$ [6]. Present oversimplified model leads to a somewhat greater degeneracy as shown by the diagonal perturbation matrix

$$H' = \lambda \begin{pmatrix} 1/3 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (24)$$

Note that the $d_{xy}$ orbital remains degenerate with $\{d_{xz}, d_{yz}\}$ in spite of the fact that the former and latter are bases for the $B_{2g}$ and $E_g$ irreducible representations, respectively [6]. Present model also fails if we distort the octahedral complex along the $z$ axis leading to either $D_{4h}$ or $C_{4v}$ symmetry [6]. The reason is that the three orbitals $d_{xy}$, $d_{xz}$ and $d_{yz}$ vanish at all ligand locations and are not affected by the distortion. We conclude that the Dirac delta interaction appears to be unsuitable for the description of these complexes.

4 Conclusions

The model developed in this paper for the splitting of the 3$d$ orbitals of a metal ion in a ligand environment is extremely simple and easy to apply because it only requires the calculation of the values of the $d$ orbitals at the ligand positions in
space. It provides the well known order of energy levels in most of the cases and even yields the relative magnitudes of the splittings. Although it fails to predict the splitting of the orbitals in distorted octahedral complexes we think that it is an interesting model for the qualitative (and even semi quantitative) discussion of such molecules, particularly because the standard approach is considerably more difficult to apply [2].

References

[1] H. A. Bethe, Termaufspaltung in kristallen, Ann. Physik 3 (1929) 133-208.

[2] C. J. Ballhausen, Ligand Field Theory, McGraw-Hill Book Company, New York, 1962).

[3] R. G. Burns, Mineralogical Applications of Crystal Field Theory, Second (Cambridge University Press, Cambridge, 1993).

[4] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience Publishers, New York, 1972).

[5] H. Eyring, J. Walter, and G. E. Kimball, Quantum Chemistry, John Wiley & Sons, New York, 1944).

[6] F. A. Cotton, Chemical Applications of Group Theory, 3rd ed. (John Wiley & Sons, New York, 1990).