Origin of accidental degeneracy in ligand-field splittings of substituted octahedral complexes

S K BOSE*, B M DEB** and D MUKHERJEE†
*Department of Chemistry, University College of Science, Calcutta 700 009
**Department of Chemistry, Indian Institute of Technology, Bombay 400 076
†Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032

Abstract. Accidental degeneracy seems to be the rule rather than an exception amongst the d orbital energies of substituted octahedral complexes of d^1 configuration. By using symmetry and physical arguments, in conjunction with first-order and second-order degenerate perturbation theory, it is shown that such accidental degeneracies arise in crystal-field theory due to the choice of an inflexible basis set of metal orbitals which neglects the polarisation of metal orbitals by the ligand charges.

1. Introduction

Ligand-field splittings of d-orbital energies in substituted octahedral complexes of transition metals are of considerable interest because, apart from the gradual spectral changes due to progressive substitution, *they display perhaps the most frequent occurrence of accidental degeneracy in a series of compounds.* Although such accidental degeneracies have been noted before (see e.g. Krishnamurthy and Schaap 1969, 1970; Larsen and La Mar 1974), we have not come across a satisfactory explanation of this interesting feature. We have constructed the correlation diagram in figure 1 by crystal-field calculations, done in the usual manner (Ballhausen 1962; Figgis 1966) for complexes of d^1 configuration. One can also readily construct this diagram by *purely qualitative* arguments using the well-known pictorial concept of electrostatic repulsions between metal d orbitals and ligand charges. However, we would not present these arguments here.

One notices the curious fact that in figure 1, accidental degeneracy seems to be the rule rather than an exception. All C_{2v} complexes exhibit two-fold degeneracy while the C_{3v} complex exhibits three-fold degeneracy. Therefore, the question arises: *Do such accidental degeneracies arise because of some inherent limitation in crystal-field theory or is crystal-field theory being applied wrongly?* We shall now show, by considering a simpler example of a pair of square-planar MY_4 and MY_2X_2 complexes, that such accidental degeneracies arise, due to the use of crystal-field theory, or degenerate first-order perturbation theory (DFOPT), with an *inflexible basis set* of metal orbitals.
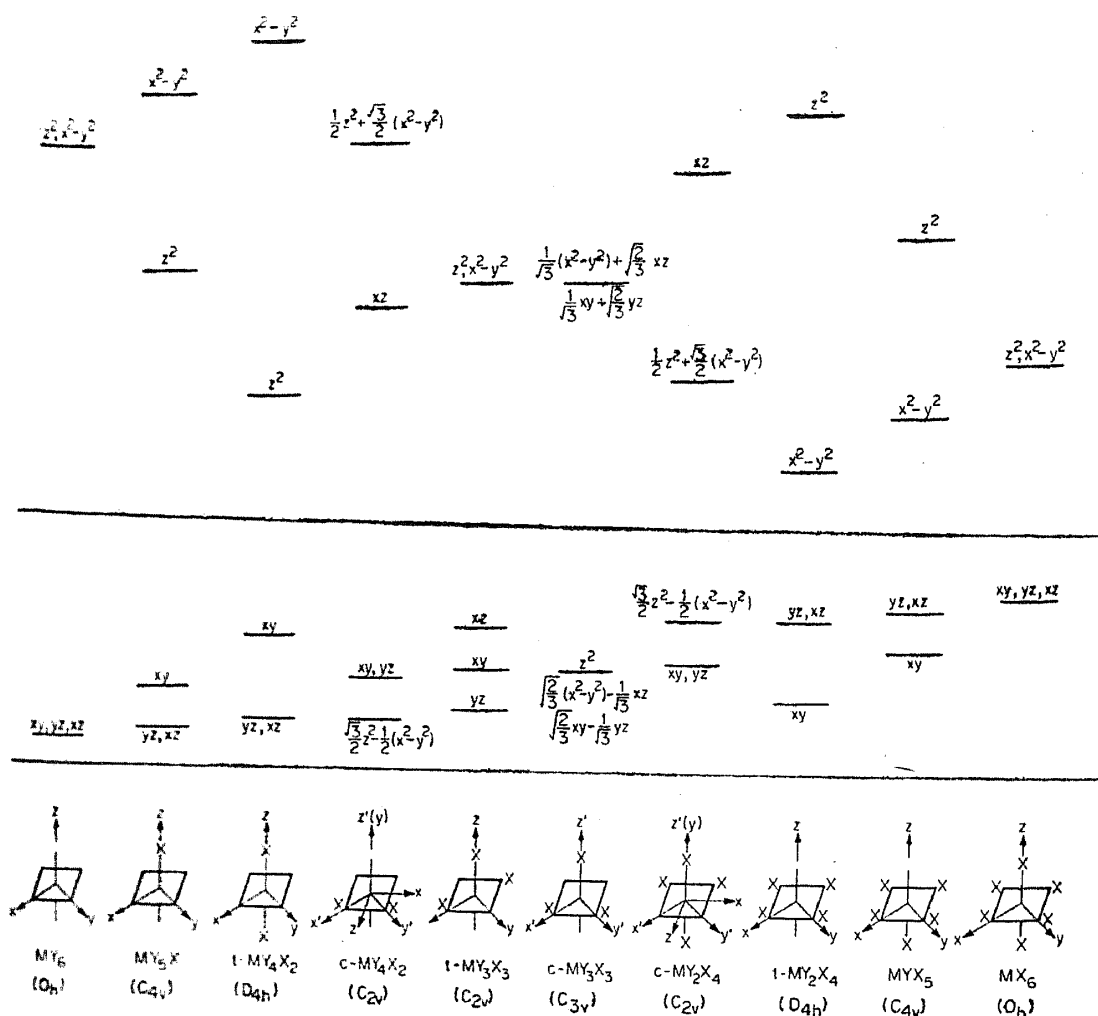
**Author to whom correspondence should be addressed.

x^2-y^2

x^2-y^2

z^2,x^2-y^2

$\frac{1}{2}z^2+\frac{\sqrt{3}}{2}(x^2-y^2)$

z^2

xz

z^2

z^2,x^2-y^2 $\frac{1}{\sqrt{3}}(x^2-y^2)+\sqrt{\frac{2}{3}}xz$

xz $\frac{1}{\sqrt{3}}xy+\sqrt{\frac{2}{3}}yz$

z^2

$\frac{1}{2}z^2+\frac{\sqrt{3}}{2}(x^2-y^2)$ z^2,x^2-y^2

z^2

x^2-y^2

x^2-y^2

xy xz $\frac{\sqrt{3}}{2}z^2-\frac{1}{2}(x^2-y^2)$ yz,xz yz,xz xy,yz,xz

xy xy,yz xy z^2 xy,yz xy

yz $\sqrt{\frac{2}{3}}(x^2-y^2)-\frac{1}{\sqrt{3}}xz$

x,yz,xz yz,xz yz,xz $\frac{\sqrt{3}}{2}z^2-\frac{1}{2}(x^2-y^2)$ $\sqrt{\frac{2}{3}}xy-\frac{1}{\sqrt{3}}yz$ xy

MY_6 MY_5X $t-MY_4X_2$ $c-MY_4X_2$ $t-MY_3X_3$ $c-MY_3X_3$ $c-MY_2X_4$ $t-MY_2X_4$ MYX_5 MX_6
(O_h) (C_{4v}) (D_{4h}) (C_{2v}) (C_{2v}) (C_{3v}) (C_{2v}) (D_{4h}) (C_{4v}) (O_h)

Figure 1. Geometries, axial systems and d-level schemes for substituted octahedral complexes of d^1 configuration. The z-axis is chosen along the principal symmetry axis of a molecule. The magnitude of the negative charge on the ligand X is half that on Y, i.e. $10Dq_X = 1/2\,(10Dq_Y)$. The C_{3v} and C_{2v} complexes show *accidental degeneracy*.

2. Origin of accidental degeneracy

Let the central-atom px and py orbitals constitute the basis set. The shifts in their orbital energies are given by the secular equation:

$$\begin{vmatrix} (V_L^{4h})_{xx} - E & (V_L^{4h})_{xy} \\ (V_L^{4h})_{yx} & (V_L^{4h})_{yy} - E \end{vmatrix} = 0, \qquad (1)$$

where V_L^{4h} is the perturbing potential arising from the ligands in figure 2a and $(V_L^{4h})_{xy} = \langle px\,|\,V_L^{4h}\,|\,py\rangle$. The two orbital energies would be the same if (i) the off-diagonal elements vanish, and (ii) the diagonal elements are identical. For the D_{4h} complex
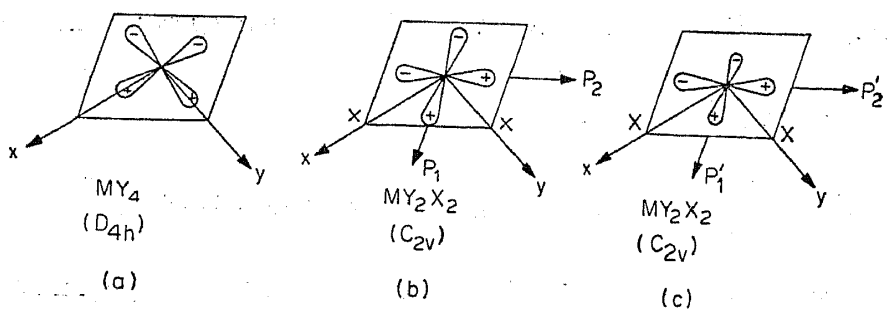
Figure 2. Axial systems and p-type basis functions for square-planar complexes. a. MY_4, of D_{4h} symmetry, and b. c. MY_2X_2, of C_{2v} symmetry. In **c** an s orbital has mixed with a p orbital.

both conditions are satisfied by symmetry. Of course, a mere look at figure 2a also indicates that the two orbitals are in identical ligand environments and will have identical energies.

For the C_{2v} complex MY_2X_2 the symmetry-adapted basis functions are (figure 2(b))

$$p_1 = (1/\sqrt{2})\,(px+py),\tag{2}$$

$$p_2 = (1/\sqrt{2})\,(px-py).$$

The secular equation now becomes

$$\begin{vmatrix} (V_L^{2v})_{11} - E & (V_L^{2v})_{12} \\ (V_L^{2v})_{21} & (V_L^{2v})_{22} - E \end{vmatrix} = 0.\tag{3}$$

One can readily show that the off-diagonal elements in (3) vanish, and

$$(V_L^{2v})_{11} = (V_L^{2v})_{22} = (V_L^{2v})_{xx} = (V_L^{2v})_{yy}.\tag{4}$$

Thus, the energy levels are not changed at all by transforming the basis (px, py) into the basis (p_1, p_2). The new basis functions are still in identical ligand environments and will remain degenerate, although their energy is different from the D_{4h} complex (this is also qualitatively apparent from figure 2b). The above conclusion can be reached in another way that will be useful later:

Let $$q_X = q_Y + \delta\,q_Y.\tag{5}$$

In expressing V_L^{2v} in terms of the ligand charges q_X and q_Y, one finds that this is a superposition of V_L^{4h} coming from the four q_Y, and U_L^{2v} coming from the δq_Y charges, i.e.

$$V_L^{2v} = V_L^{4h} + U_L^{2v}.\tag{6}$$

Remembering that V_L^{4h} has even parity, and V_L^{2v} has *no definite parity*,[*] one can write

$$V_L^{2v} = U_L^{\text{even}} + U_L^{\text{odd}}. \tag{7}$$

Then $\quad (V_L^{2v})_{12} = (U_L^{\text{even}})_{12} + (U_L^{\text{odd}})_{12} = 0 + 0, \text{ by symmetry,} \tag{8}$

and $\quad (V_L^{2v})_{11} = (V_L^{2v})_{22} = (U_L^{\text{even}})_{11} + (U_L^{\text{odd}})_{11} = (U_L^{\text{even}})_{11}, \text{ by symmetry,}$

$$= \tfrac{1}{2}\,[(U_L^{\text{even}})_{xx} + (U_L^{\text{even}})_{yy}] = (U_L^{\text{even}})_{xx} = (U_L^{\text{even}})_{yy}. \tag{9}$$

Thus, as long as DFOPT is employed in the above manner, as is generally done in crystal-field theory, accidental degeneracies will persist. Evidently, one must carry the perturbation through to second order (DSOPT).

The SOP energies are of the form

$$\sum_i \frac{|\langle p_j | U_L^{\text{even}} + U_L^{\text{odd}} | \phi_i \rangle|^2}{E_{pj} - E_i}, \tag{10}$$

$$j = 1, 2; \; E_{pj} \neq E_i,$$

where the ϕ_i's are *other* orbitals of the metal atom. For (10) to be non-zero, ϕ_i's must be of even parity (e.g. s or d) or odd parity (e.g. p). In view of this, one may now construct new basis functions (p'_1, p'_2) and apply FOPT as before:.

Case I:

Let $\quad p'_1 = p_1 + \phi^{\text{even}},$

$$p'_2 = p_2 + \phi^{\text{even}}, \tag{11}$$

Then $\quad (V_L^{2v})_{1'2'} = (U_L^{\text{even}})_{1'2'} + (U_L^{\text{odd}})_{1'2'} = \langle \phi^{\text{even}} | U_L^{\text{even}} | \phi^{\text{even}} \rangle$

$$+ 2 \langle p_1 | U_L^{\text{odd}} | \phi^{\text{even}} \rangle \neq 0. \tag{12}$$

Thus, even if $(V_L^{2v})_{1'1'} = (V_L^{2v})_{2'2'}$, the two-fold degeneracy will split.

Case II:

Let $\quad p'_1 = p_1 + \phi^{\text{odd}}$

$$p'_2 = p_2 + \phi^{\text{odd}} \tag{13}$$

---

[*]In general, U^{2v} may have odd-parity or even-parity *plus* odd-parity terms.

Then $\quad (V_L^{2v})_{1'2'} = (U_L^{even})_{1'2'} + (U_L^{odd})_{1'2'},$

$$= \langle \phi^{odd} | U_L^{even} | \phi^{odd} \rangle + 2 \langle p_1 | U_L^{even} | \phi^{odd} \rangle$$

$$\neq 0.$$

Again, the degeneracy will be split. Similar arguments hold for d and f basis functions in a ligand field of given symmetry.

What has been done in equations (11) and (13) amounts physically to taking care of polarisation of metal orbitals by ligand charges when one chooses basis functions. For example, one may conceive of a symmetry-adapted basis set $(p_1 + s, p_2)$ as in figure 2c. Obviously these two functions would have different energies in the C_{2v} ligand environment.

Acknowledgement

References

Ballhausen C J 1962 *Introduction to Ligand Field theory* (New York: McGraw-Hill)
Figgis B N 1966 *Introduction to Ligand Fields* (New York: Wiley-Interscience)
Krishnamurthy R and Schaap W B 1969 *J. Chem. Educ.* **46** 799;
Krishnamurthy R and Schaap W B 1970 *J. Chem. Educ.* **47** 433
Larsen E and La Mar G N 1974 *J. Chem. Educ.* **51** 633