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

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Abstract. Accidental degeneracy seems to be the rule rather than an exception amongst the d orbital energies of substituted octahedral complexes of $d^4$ 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.

Keywords. Ligand-field splitting; accidental degeneracy; degenerate perturbation theory; symmetry; octahedral complexes.

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 $d^4$ 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 $MY_3X_2$ 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.

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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:

\[
\begin{vmatrix}
(V_L^{4h})_{xx} - E & (V_L^{4h})_{xy} \\
(V_L^{4h})_{xy} & (V_L^{4h})_{yy} - E
\end{vmatrix} = 0,
\]

where \(V_L^{4h}\) is the perturbing potential arising from the ligands in figure 2a and \((V_L^{4h})_{xy} = \langle px \mid V_L^{4h} \mid py \rangle\). 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,
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Figure 2. Axial systems and p-type basis functions for square-planar complexes. a. \(MY_2\), 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))

\[
P_1 = (1/\sqrt{2}) (px + py),
\]

\[
P_2 = (1/\sqrt{2}) (px - py).
\]

The secular equation now becomes

\[
\begin{vmatrix}
(V^{2p}_L)_{11} - E & (V^{2p}_L)_{12} \\
(V^{2p}_L)_{21} & (V^{2p}_L)_{22} - E
\end{vmatrix} = 0.
\]

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

\[
(V^{2p}_L)_{11} = (V^{2p}_L)_{22} = (V^{2p}_L)_{xx} = (V^{2p}_L)_{yy}.
\]

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 \(q_X = q_Y + \delta q_Y\).

In expressing \(V^{2p}_L\) in terms of the ligand charges \(q_X\) and \(q_Y\), one finds that this is a superposition of \(V^{4h}_L\) coming from the four \(q_Y\), and \(U^{2s}_L\) coming from the \(\delta q_Y\) charges, i.e.

\[
V^{2p}_L = V^{4h}_L + U^{2s}_L.
\]
Remembering that $V^4_L$ has even parity, and $V^{2\sigma}_L$ has no definite parity, one can write

$$V^{2\sigma}_L = U^\text{even}_L + U^\text{odd}_L.$$  \hfill (7)

Then

$$ (V^{2\sigma}_L)_{12} = (U^\text{even}_L)_{12} + (U^\text{odd}_L)_{12} = 0 + 0, \text{ by symmetry},$$ \hfill (8)

and

$$ (V^{2\sigma}_L)_{11} = (V^{2\sigma}_L)_{22} = (U^\text{even}_L)_{11} + (U^\text{odd}_L)_{11} = (U^\text{even}_L)_{11}, \text{ by symmetry},$$

$$= \frac{1}{2} [(U^\text{even}_L)_{xx} + (U^\text{even}_L)_{yy}] = (U^\text{even}_L)_{xx} = (U^\text{even}_L)_{yy}.$$ \hfill (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

$$\sum_j \frac{|\langle p_j | U^\text{even}_L + U^\text{odd}_L | \phi_i \rangle|^2}{E_{2j} - E_i},$$ \hfill (10)

where the $\phi_i$'s are other orbitals of the metal atom. For (10) to be non-zero, $\phi_i$'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

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

$$p'_2 = p_2 + \phi^\text{even};$$ \hfill (11)

Then

$$ (V^{2\sigma}_L)_{1'1'prime} = (U^\text{even}_L)_{1'1'prime} + (U^\text{odd}_L)_{1'1'prime} = \langle \phi^\text{even} | U^\text{even}_L | \phi^\text{even} \rangle + 2 \langle p_1 | U^\text{odd}_L | \phi^\text{even} \rangle \neq 0.$$ \hfill (12)

Thus, even if $(V^{4\sigma}_L)_{1'1'prime} = (V^{2\sigma}_L)_{2'2'prime}$, the two-fold degeneracy will split.

**Case II:**

Let

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

$$p'_2 = p_2 + \phi^\text{odd};$$ \hfill (13)

*In general, $U^{2\sigma}$ may have odd-parity or even-parity plus odd-parity terms.*
Then \( (V_L^2)_{\alpha' \alpha} = (U_L^{\text{even}})_{\alpha' \alpha} + (U_L^{\text{odd}})_{\alpha' \alpha} \),

\[
\langle \phi_{\text{odd}} | U_L^{\text{even}} | \phi_{\text{odd}} \rangle + 2 \langle p_3 | U_L^{\text{even}} | \phi_{\text{odd}} \rangle 
\neq 0.
\]

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 \((p_3 + s, p_3)\) as in figure 2c. Obviously these two functions would have different energies in the \( C_{2v} \) ligand environment.

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References