

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^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.

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^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.

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