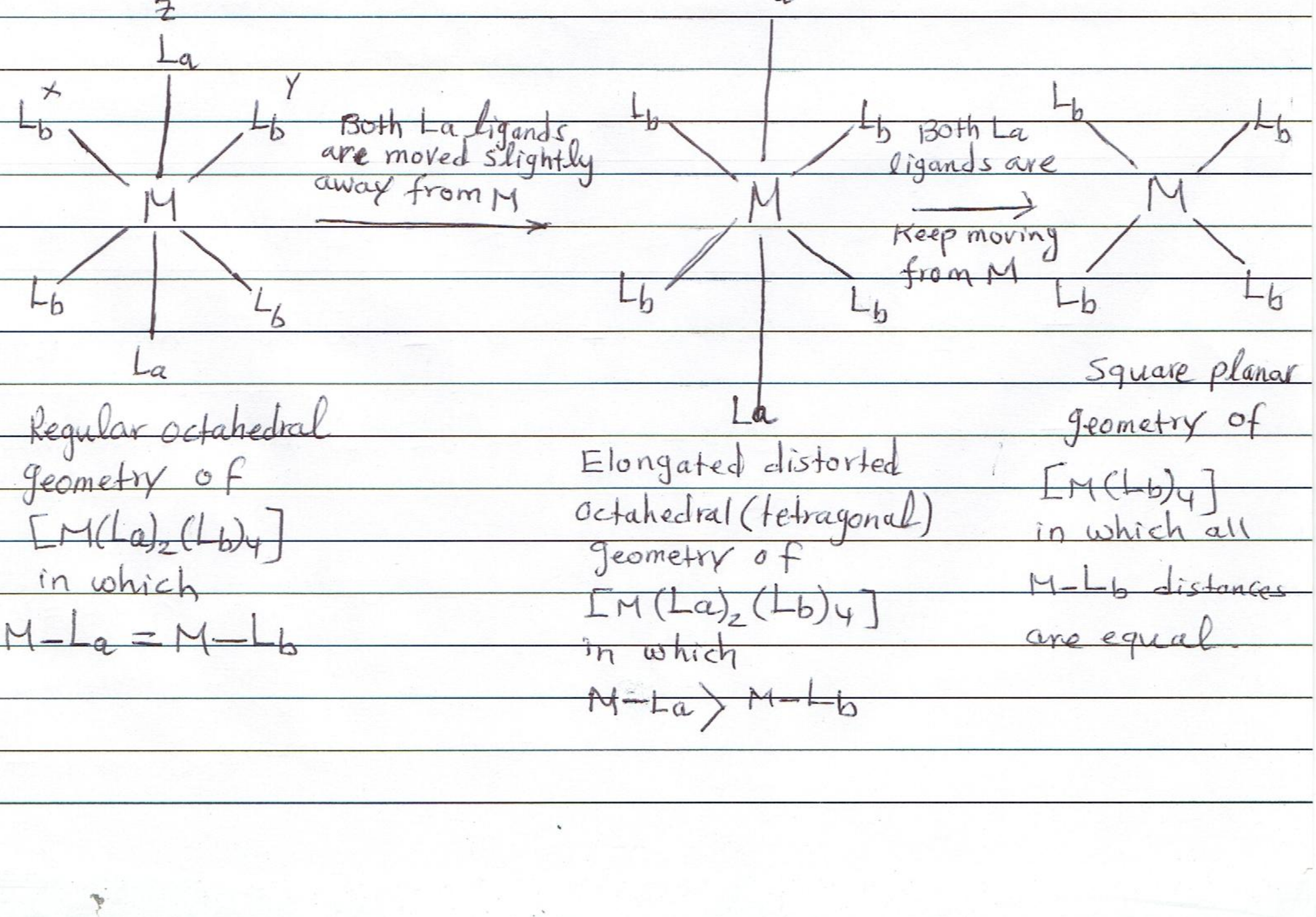
Crystal field Splitting of d-Orbitals in tetragonal and Square planar Complexes

If two trans ligands in an octahedral ML_6 Complex (for example those along the Z axis) are moved either towards or away from the metal ion, the resulting Complex is called tetragonally distorted Complex. Ordinarily, such distortions are not favored since they result in a net of loss of bonding energy. In certain situation, however, such a distortion is favored due to Jahn-Teller effect.

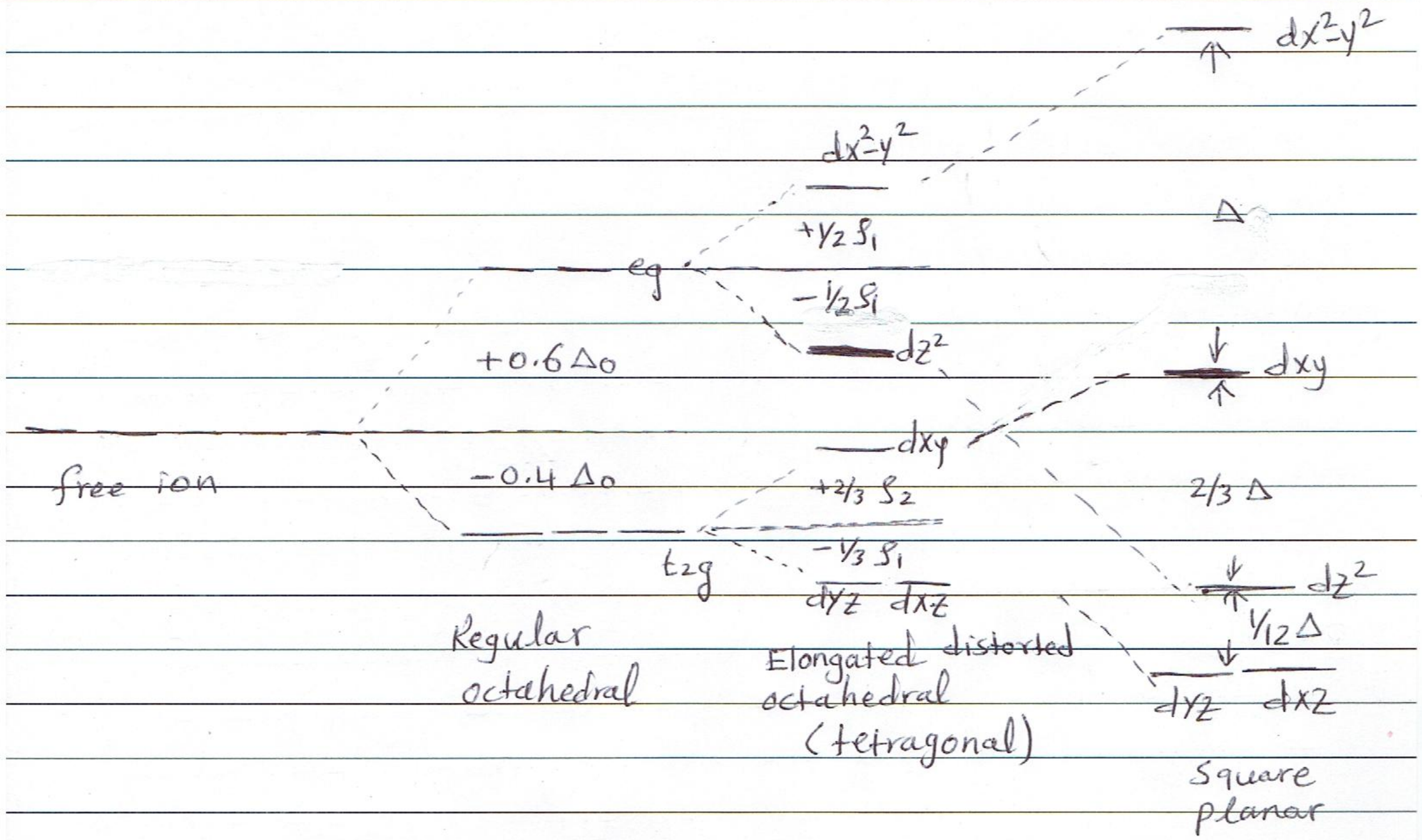
A Complex of general formula trans-MA_2B_4 also will have tetragonal symmetry. For now, we will merely Consider the limiting case of tetragonal elongation, a square planar ML_4 Complex, for the purpose of deriving its d orbital splitting pattern.



Regular octahedral geometry of $[M(L_a)_2(L_b)_4]$ in which $M-L_a = M-L_b$

Elongated distorted octahedral (tetragonal) geometry of $[M(L_a)_2(L_b)_4]$ in which $M-L_a > M-L_b$

Square planar geometry of $[M(L_b)_4]$ in which all $M-L_b$ distances are equal.



The square planar geometry is favored by metal ions having a d^8 configuration in the presence of a strong field. This combination gives low spin complexes with the eight d-electrons occuping the low energy dxz, dyz, dz^2 and dxy orbitals, while the high energy dx^2-y^2 orbital remain unoccupied. The stronger the surrounding field, the higher the dx^2-y^2 orbital will be raised. As long as this level is unoccupied, however, the overall effect on the complex will be stabilization because the lower occupied orbitals will be drop in energy by corresponding amount.

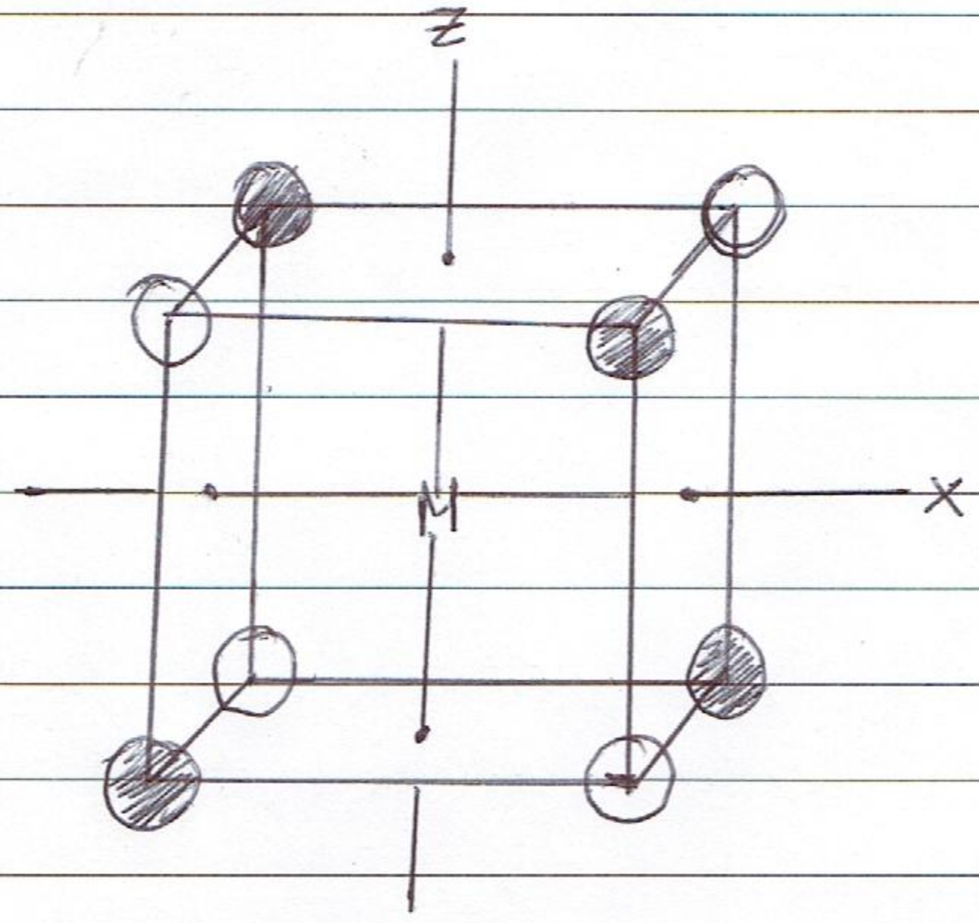
Typical low spin square planar complexes are:

$[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$, and $[AuCl_4]^{-}$,

all are d^8 species.

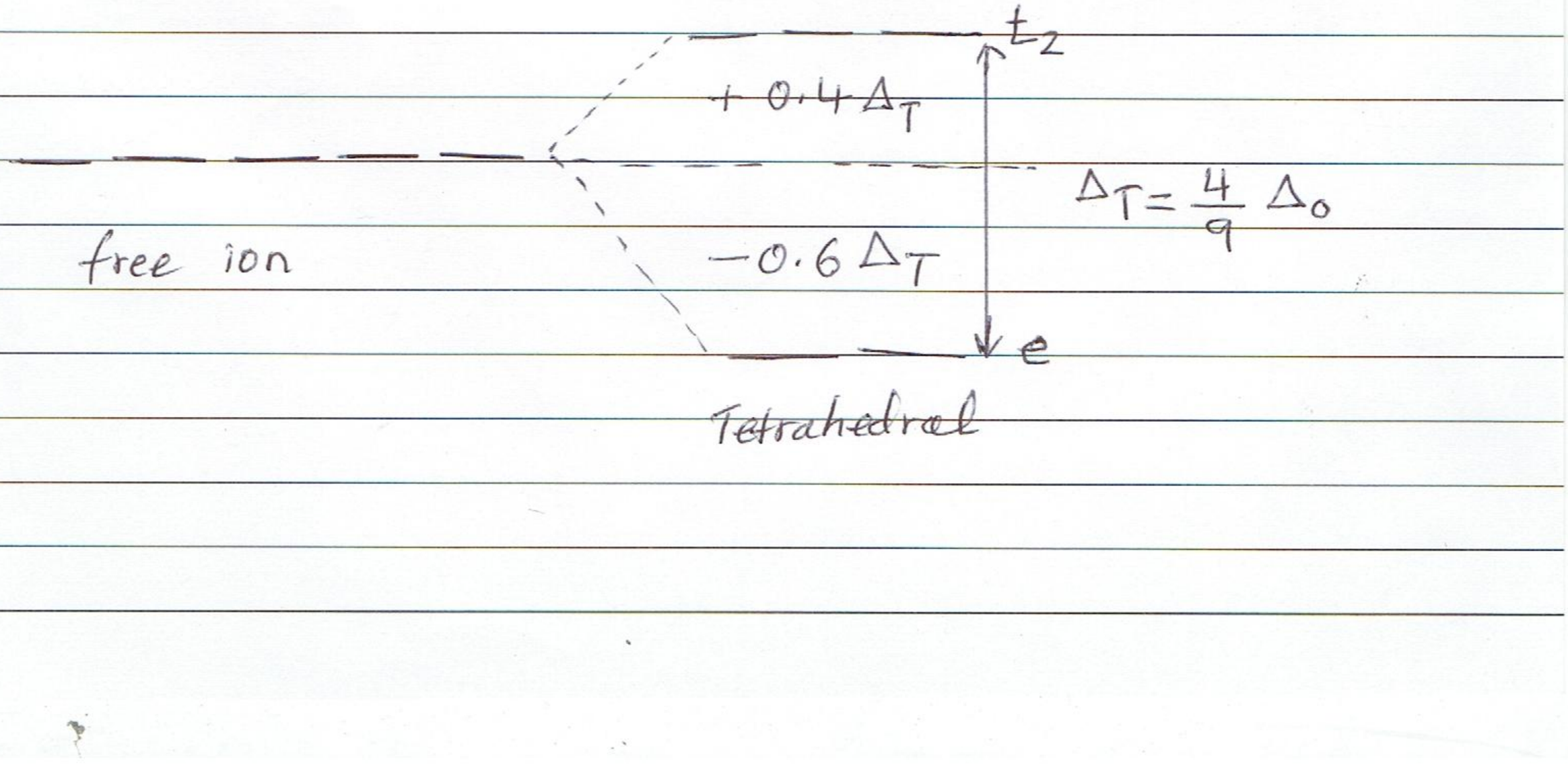
Crystal field Splitting of d-orbitals in Tetrahedral Complexes

The procedure used to determine the Crystal field Splitting of the d orbitals in an octahedral Complex may be applied similarly to tetrahedral Complexes. In this case, the process is perhaps simplest to understand if the ligand electron density is first localized from a spherical shell to the Corners of a Cube, as shown below:



In the set of Coordinates used, the dz^2 and dx^2-y^2 orbitals are oriented towards the Centers of the faces of the Cube, while the dxy, dxz and dyz orbitals are oriented towards the Centers of the edges. Simply, the distance between the metal ion (M) and the Centres of the edges of the Cube is apparently shorter than that between the metal ion (M) and the Centres of the faces. It might be expected from this simple geometric Consideration that the repulsive force between the ligand electron density and electrons in the dz^2 and dx^2-y^2 orbitals will be smaller than for the dxy, dxz and dyz orbitals.

Thus, in both of cubic and tetrahedral structures, the d_{z^2} and x^2-y^2 orbitals will move to lower energy, and the dxy, dxz and dyz orbitals to higher energies. As the barycenter of the system must remain unchanged, so the dxy, dxz and dyz orbitals will rise in energy by 0.4 of the splitting, and dZ^2 and dx^2-y^2 orbitals will drop in energy by 0.6 of the splitting. In order to derive a tetrahedral field from the cubic arrangement, it is simply necessary to alternately remove four regions of electron density. The resulting splitting of the sets of dZ^2 and dx^2-y^2, and the dxy, dxz, and dyz orbitals is known as Δ_T and, for the same ligand L, calculations show the magnitude of Δ_T for tetrahedral $[ML_4]$ is (4/9) of Δ_o for octahedral. Because the magnitude of Δ_T is less than half of that of Δ_o, tetrahedral coordination compounds are essentially all high spin with some few and rare exptional cases.



Limitations of CFT

1. CFT Considers only the metal ion d-orbitals, and gives no consideration to other metal orbitals like s, P_x, P_y, and P_z, and also for π-orbitals. CFT gives no consideration for the formation of π-bonding in complexes.

2. CFT is unable to account satisfactory for the relative strength of ligands. Bearing in mind that CFT is an ionic model based on the electrostatic effect of the ligands on the energies of the metal ion d orbitals, it is surprising to find that anionic ligands such as Br^-, F^-, and OH^- should be weaker-field than neutral ligands such as NH_3, NR_3, and CO. This anomaly arises because the simple CFT does not take account of covalency in metal-ligand bonding.

3. According to CFT, the bond between the metal and ligand is purely ionic. It gives not account of the partly covalent nature of metal-ligand bonds.