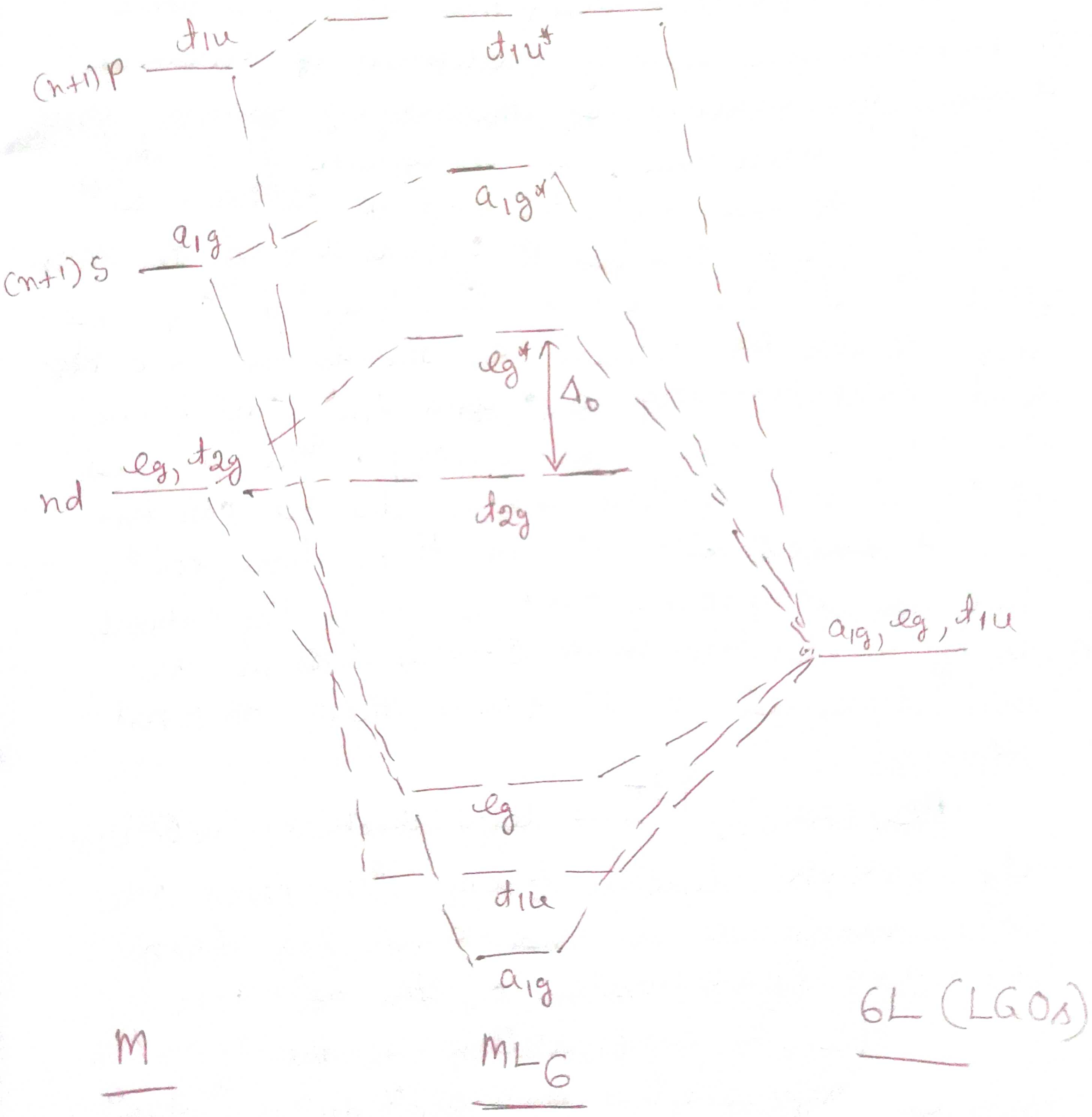
Molecular orbital of octahedral complex



A molecular orbital energy diagram for the σ bonds in an octahedral complex such as $[Co(NH_3)_6]^{3+}$ is shown in figure. There are several approximations involved and the diagram shown is only qualitatively accurate, even the ordering of the energy levels is somewhat uncertain. It is certain that the overlap of the metal 4s and 4p orbitals with ligand group orbitals is considerably better than that of the 3d orbitals. Consequently a_{1g} and t_{1u} molecular orbitals are the lowest in energy and corresponding a_{1g}^* and t_{1u}^* antibonding orbitals the highest in energy. The e_g and e_g^* orbitals arising from the 3d orbitals are displaced less from their barycentre because of poorer overlap. The t_{2g} orbitals being nonbonding in a σ-only system are not displaced at all from their original energy.

$[Co(NH_3)_6]^{3+} \longrightarrow$ total eighteen electrons to assign twelve from lone pairs on the ammonia ligand and six from the $3d^6$ configuration of the Co^{3+} ion. The electronic configuration of the complex can be represented as $a_{1g}^2 t_{1u}^6 e_g^4 t_{2g}^6$ or in a more abbrevation form as simply t_{2g}^6. Note that $[Co(NH_3)_6]^{3+}$ is diamagnetic because electrons pair in the t_{2g} level rather than enter higher energy e_g^* level.

If the energy difference between the t_{2g} and e_g^* level is small, as in $[CoF_6]^{3-}$ the electrons will be distributed $t_{2g}^4 e_g^{*2}$. Thus both molecular orbital theory and crystal field theory account for magnetic and spectral properties of octahedral complexes on the basis of two sets of orbitals separated by an energy gap Δ_0.

If energy gas is greater → low spin complex
" " " small → high spin complex.