Magnetic orbitals of carbon and crystal field splitting in TM ions

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Orbital wave function of two p electrons

The electronic configuration of carbon is $[\text{He}](2\text{s})^2(2\text{p})^2$, meaning that both electrons in the outer shell have quantum numbers $n = 2$ and $l = 1$. Let $l_1 = l_2 = 1$ be the orbital angular momenta of those electrons and $\hat{\mathbf{L}} = \hat{\mathbf{l}}_1 + \hat{\mathbf{l}}_2$ the total angular momentum.

- Verify that the dimension of the Hilbert space obtained by the direct sum of all the multiplets $L = 0, 1, 2$ is equal to $(2l_1 + 1) \times (2l_2 + 1) = 9$.

(see attached latex file)

- Assuming that the spin part of the wave function of the $(2\text{p})^2$ electrons is the triplet state χ^{T} (consistently with the first Hund's rule), explain with your own words why the total angular momentum cannot be a state of the $L = 2$ multiplet (**hint**: look at a Clebsch-Gordan coefficients table on-line or in the file *CourseLibrary/Images/Clebsch-Gordan_coeff.pdf*).

(see attached latex file)

- With the help of a Clebsch-Gordan coefficients table, show that the multiplet $L = 1$ is, instead, compatible with the two $(2\text{p})^2$ electrons being in a spin triplet state χ^{T}.

(see attached latex file)

- Determine the eigenvalues of the operator $\hat{\mathbf{l}}_1 \cdot \hat{\mathbf{l}}_2$ and their degeneracy, using the relation $(\hat{\mathbf{L}})^2 = (\hat{\mathbf{l}}_1 + \hat{\mathbf{l}}_2)^2 = (\hat{\mathbf{l}}_1)^2 + 2\,\hat{\mathbf{l}}_1 \cdot \hat{\mathbf{l}}_2 + (\hat{\mathbf{l}}_2)^2$.

(see attached latex file)

Energy splittig in distorted octahedral environment

Verify (on your own) that the eigenvalues of the matrix in the table *CourseLibrary/Images/Table1-2.pdf* are

$$E_{x^2-y^2} = 6Dq - Dt + 2Ds$$
$$E_{z^2} = 6Dq - 6Dt - 2Ds$$
$$E_{xy} = -4Dq - Dt + 2Ds$$
$$E_{xz} = E_{yz} = -4Dq + 4Dt - Ds$$

Following Lever and Solomon (see *CourseLibrary/BookChapters/Lever-Solomon_CF.pdf*), we will assume that the crystal-field strengths (Dq, Dt, Ds) can be parameterized as follows

$$Ds = Ds_0 \left(1 - \frac{a^3}{b^3} \right) \qquad Dt = \frac{4}{7} Dq \left(1 - \frac{a^5}{b^5} \right)$$

where a indicates the distance of the ligand point charges lying on the xy plane from the nucleus of the transition metal and b indicates the distance of the ligand point charges lying on the z axis from the same nucleus (see lecture notes). The underlying script plots the four different eigenvalues written above as a function of the ratio a/b, assuming $Dq = 0.1$ eV and $Ds_0 = 1$ eV:
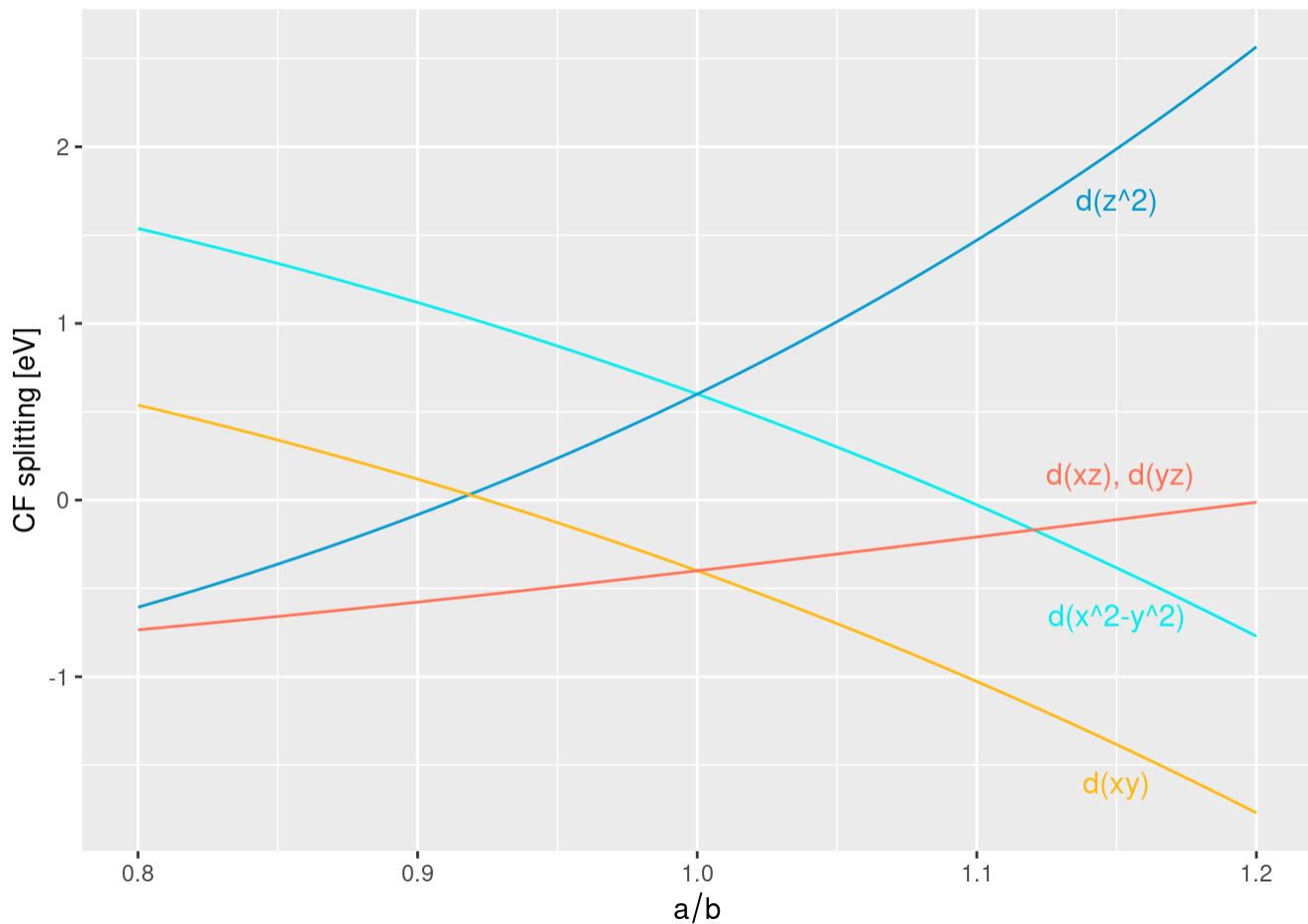
- Try to explain the features observed in the plot based on the spatial orientation of the real d orbitals given below and on electrostatic considerations.

t_{2g}	d_{zx}	d_{yz}	d_{xy}
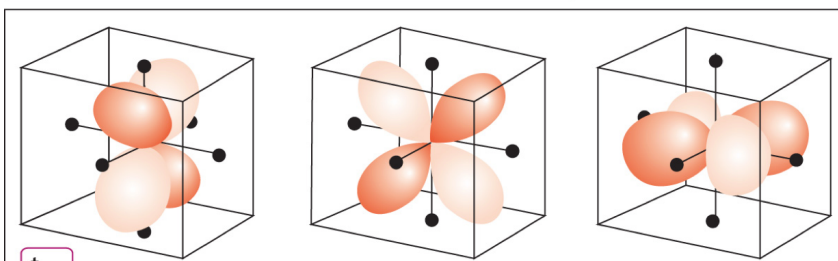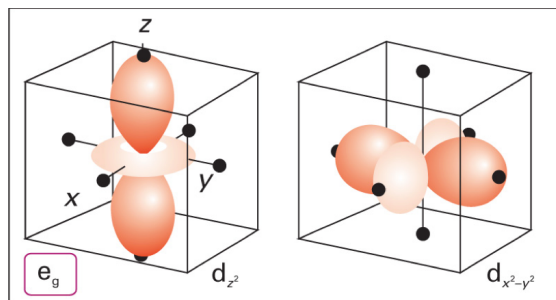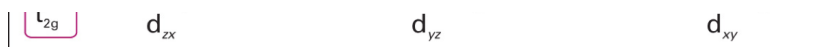
The lobes of the orbitals d_{z^2} (e_g multiplet), d_{zx} and d_{yz} (t_{2g} multiplet) have a sizable component pointing along the z axis; therefore, when charges lying on this axis are pulled away from the transition metal ($b > a$, elongation), the energy of those orbitals is reduced w.r.t. to that of other orbitals in the same multiplet. The opposite trend is observed when the octahedron of ligands is compressed ($b < a$).

- What happens when $a = b$?

When $a = b$ the perfect octahedral symmetry is realized associated with the group O_h. In all the other region of the diagram the underlying symmetry is D_{4h} (compressed or elongated octahedron).

square planar D_{4h}
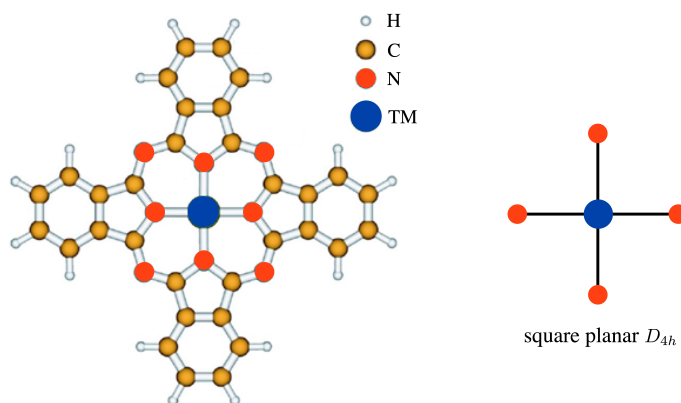
- Referring to the qualitative plot of the energy splitting as a function of a/b shown in the plot, which limit corresponds to a planar complex of TMPc (Transition-Metal Phthalocyanine) sketched above?

Nominally, it should correspond to $b \to \infty$ which gives the crystal field splitting produced by 4 negative point charges placed at the vertices of a square lying on the xy plane. In practice, this does not reproduce the observed splitting because reducing the effect of the 4 Nitrogen atoms (red dots) surrounding the transition metal (blue dot) to the coulomb repulsion of 4 point charges is an oversimplification. In fact, 3d orbitals also participate in the chemical bonding, which must lower the energy w.r.t. to the case of isolated atoms (otherwise the molecule would not be stable). This effect compensates for the ''energy penalization'' that one would naively infer from the crystal-field description.

Assignment 3

1. Orbital wave function of two p electrons

- The dimensionality of each multiplet of L is $2L + 1$; the direct sum of those subspaces yelds $1 + 3 + 5$ for $L = 0, 1, 2$ respectively.

- We know that the radial part of the spatial wave function is the same for both electrons $R_{2,1}(r_i)$ with $i = 1, 2$. As for the angular part, the state $|L = 2, M = +2\rangle = |m_1 = +1, m_2 = +1\rangle$, or in the of spherical harmonics representation $Y_{1,+1}(\theta_1, \phi_1)Y_{1,+1}(\theta_2, \phi_2)$, is symmetric w.r.t. the exchange of the two electrons. With the help of a Clebsch-Gordan coefficients table one can verify that the other 4 states in the $L = 2$ multiplet are symmetric w.r.t. the exchange of the two electrons as well. Knowing that the spin part of the wave fucntion is the spin triplet χ^{T} (symmetric w.r.t. the exchange $1 \leftrightarrow 2$), the angular part of the wave fucntion cannot be a state of the multiplet $L = 2$.

- For $L = 1$ multiplet, instead, using a Clebsch-Gordan coefficients table one can verify that

$$|L = 1, M = +1\rangle = \frac{1}{\sqrt{2}} \left[Y_{1,+1}(\theta_1, \phi_1)Y_{1,0}(\theta_2, \phi_2) - Y_{1,0}(\theta_1, \phi_1)Y_{1,+1}(\theta_2, \phi_2) \right]$$

$$|L = 1, M = 0\rangle = \frac{1}{\sqrt{2}} \left[Y_{1,+1}(\theta_1, \phi_1)Y_{1,-1}(\theta_2, \phi_2) - Y_{1,-1}(\theta_1, \phi_1)Y_{1,+1}(\theta_2, \phi_2) \right]$$

$$|L = 1, M = -1\rangle = \frac{1}{\sqrt{2}} \left[Y_{1,-1}(\theta_1, \phi_1)Y_{1,0}(\theta_2, \phi_2) - Y_{1,0}(\theta_1, \phi_1)Y_{1,-1}(\theta_2, \phi_2) \right]$$

The spatial wave functions above are manifestly antisymmetric w.r.t. the exchange $1 \leftrightarrow 2$ and, thereore, compatible with a symmetric spin wave function χ^{T}.

- Generally, the relation $(\hat{\mathbf{L}})^2 = (\hat{\mathbf{l}}_1 + \hat{\mathbf{l}}_2)^2 = (\hat{\mathbf{l}}_1)^2 + 2\,\hat{\mathbf{l}}_1 \cdot \hat{\mathbf{l}}_2 + (\hat{\mathbf{l}}_2)^2$ implies

$$\hat{\mathbf{l}}_1 \cdot \hat{\mathbf{l}}_2 = \frac{(\hat{\mathbf{L}})^2 - (\hat{\mathbf{l}}_1)^2 - (\hat{\mathbf{l}}_2)^2}{2}$$

from which it follows that

$$\langle L, M | \hat{\mathbf{l}}_1 \cdot \hat{\mathbf{l}}_2 | L, M \rangle = \frac{1}{2} \left[L(L+1) - l_1(l_1+1) - l_2(l_2+1) \right] = \frac{1}{2}L(L+1) - 2$$

when $l_1 = l_2 = 1$. Thus, the scalar product $\hat{\mathbf{l}}_1 \cdot \hat{\mathbf{l}}_2$ takes three different eigenvalues associated with the three possible values of the modulus $L = 0, 1, 2$ with the relative degeneracy deg $= 1, 3, 5$. As remarked at the first point of this assignment, the dimension of the Hilbert space is preserved passing from the basis $|l_1, m_1\rangle \otimes |l_2, m_2\rangle$ (3×3 basis kets) to $|L, M\rangle$ ($1 + 3 + 5$ basis kets).