

Magnetic orbitals of carbon and crystal field splitting in TM ions

Alessandro Vindigni

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Orbital wave function of two p electrons

The electronic configuration of carbon is $[\text{He}](2s)^2(2p)^2$, 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 $\hat{\mathbf{L}} = \hat{\mathbf{I}}_1 + \hat{\mathbf{I}}_2$ 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 $(2p)^2$ 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 $(2p)^2$ electrons being in a spin triplet state χ^T .

(see attached latex file)

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

(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

$$E_{x^2-y^2} = 6Dq - Dt + 2Ds$$

$$E_{z^2} = 6Dq - 6Dt - 2Ds$$

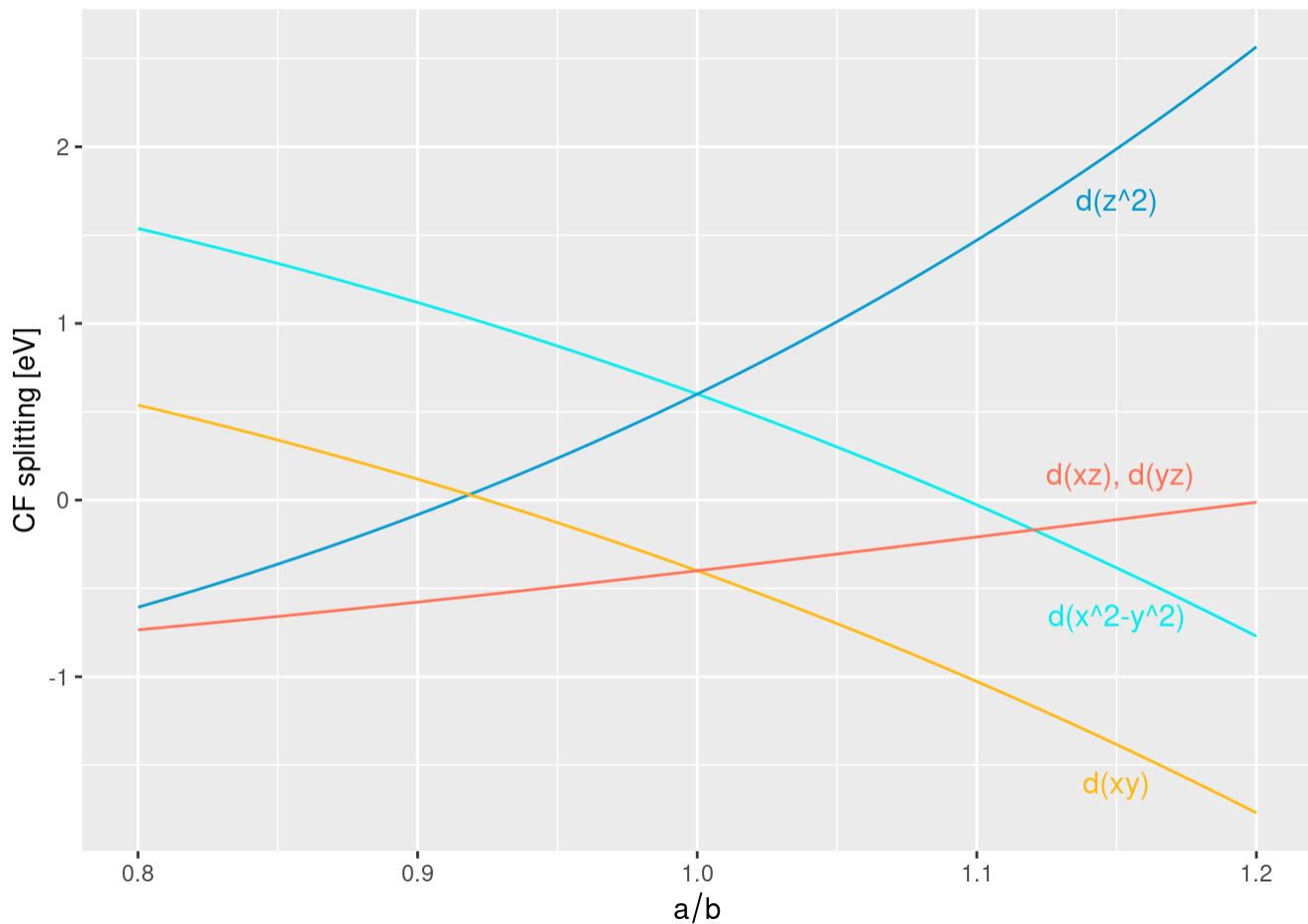
$$E_{xy} = -4Dq - Dt + 2Ds$$

$$E_{xz} = E_{yz} = -4Dq + 4Dt - Ds$$

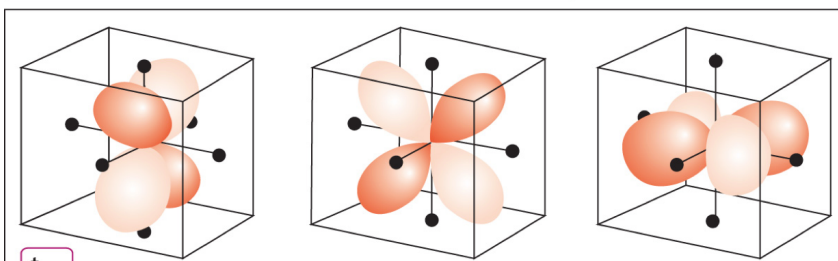
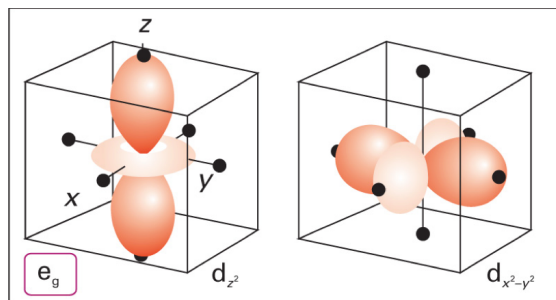
Following Lever and Solomon (see *CourseLibrary/BookChapters/Lever-Solomon_CF.pdf*), we will assume that the crystal-field strengths (Dq , Dt , Ds) can be parameterized as follows

$$D_s = D_{s0} \left(1 - \frac{a^3}{b^3} \right) \quad D_t = \frac{4}{7} Dq \left(1 - \frac{a^5}{b^5} \right)$$

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 $D_{s0} = 1$ 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.



INTRODUCTION TO MAGNETISM

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PD Alessandro Vindigni
vindigni@phys.ethz.ch

www.microstructure.ethz.ch

Laura van Schie
laura.vanschie@mat.ethz.ch

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 yields $1 + 3 + 5$ 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 function is the spin triplet χ^T (symmetric w.r.t. the exchange $1 \leftrightarrow 2$), the angular part of the wave function cannot be a state of the multiplet $L = 2$.
- For $L = 1$ multiplet, instead, using a Clebsch-Gordan coefficients table one can verify that

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

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

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

The spatial wave functions above are manifestly antisymmetric w.r.t. the exchange $1 \leftrightarrow 2$ and, therefore, 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

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

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 $\text{deg} = 1, 3, 5$. 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).