Visualizing, rather than deriving Russell-Saunders terms: a classroom activity with quantum numbers

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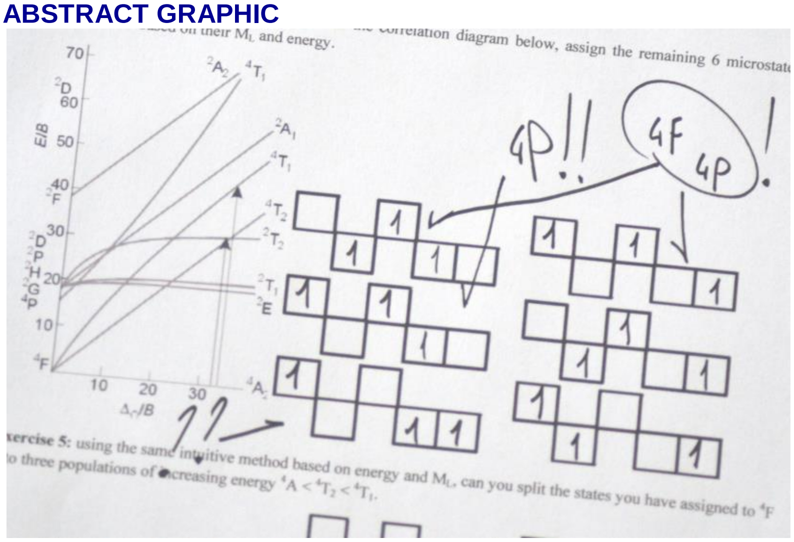
ABSTRACT

A one hour classroom activity is presented, aimed at consolidating the concepts of microstates and Russell-Saunders energy terms in transition metal atoms and coordination complexes. The unconventional approach, based on logic and intuition rather than rigorous mathematics, is designed to stimulate discussion and enhance familiarity with quantum numbers in classes of Chemistry undergraduate students.

ABSTRACT GRAPHIC



KEYWORDS

Inorganic chemistry, physical chemistry, problem solving/decision making, collaborative/cooperative learning, spectroscopy, coordination compounds, second-year undergraduate, upper-division undergraduate.

INTRODUCTION

Teaching and learning modern Chemistry implies an elementary understanding of quantum physics.[1] While the derivation of quantum mechanics equations is beyond the scope of a degree course in Chemistry, familiarity with the meaning of quantization, quantum numbers and their operations is essential to understand atomic and molecular structure, as well as spectroscopy.[2,3] Recent studies, supporting years of practice, suggest the use of analogies and methods to visualize concepts is an effective way to engage students in active learning.[4-6] Conventionally, teaching the concepts of spin multiplicity and atomic energy terms (Russell-Saunders terms) involves deriving the combinations of n-electrons in d-orbitals (microstates), using factorial formulas. Once the number of microstates in a system is defined, Russell-Saunders coupling of the individual electrons quantum numbers produces a numerical table of microstates.[7-11] A mathematical elimination process yields the assignment of energy terms, which are given capital letters S, P, D, F etc. to reflect their combined quantum number L. The atomic terms are then correlated to molecular symmetry terms, without an attempt to visualize them, given that neither textbooks nor software packages offer this option.[12] While the process is formally correct and allows derivation of the full energetic picture in multi-electron d-metal orbitals, it is an abstract way to represent combinations of electrons in orbitals.[13-15] In the author's experience, feedback from students criticize the approach as it does not contextualize S, P, D, F energy terms and does not make clear how these differ from s, p, d, f orbitals. The elimination process can be unpopular, as unique microstates of the same M_L are assigned to an energy term without a rationale.

The counter argument is the assignment of a microstate to a defined energy term is only obvious in a limited number of cases, where the symmetry is obvious by lack of degeneracy (A molecular energy terms). However, the process of rationalizing a microstate assignment is of great help to familiarize students with quantum numbers operations as well as symmetry and helps understanding the significance of energy states and the electronic transitions between them.

The activity hereby discussed aims at providing students and tutors with a method to visualize combinations of electrons in orbitals (microstates) and assign them to an atomic or molecular energy term using a set of meaningful criteria. The treatment of microstates throughout the process is not trivialized and therefore the activity is best suited to an undergraduate level workshop, aimed at consolidating the material covered in the course. Although students can work alone on the supplied activity sheet, the solution of the problems as group activity is encouraged to promote discussion and sharing of ideas. For group activities, the use of laminated d-orbital diagrams combined with non-permanent markers is also advised.

The entry level requires familiarity with the n, l, m_L and m_s quantum numbers, notions of point group symmetry and an understanding of the octahedral crystal field energy split of d-orbitals.

METHODOLOGY

Rarely discussed in textbooks, but obvious to the naked eye, it is possible to subdivide the five d-orbitals into one symmetry A orbital, and two pairs of symmetry E orbitals in a C_{5v} point group.[16,17] We can assign a defined angular momentum to any of the five d-orbitals, based on their extension relative to the axes. Using an analogy to compare an atom to a planet, if the vertical (polar) axis z of a spherical atom is taken as the reference, then magnetic quantum number m_l =0 is assigned to the dz^2 orbital, that has mainly pole-to-pole extension. This orbital transforms with symmetry A. Orbitals dxy and dx^2-y^2 of symmetry E_2 will be assigned to m_l + 2 and -2 respectively, to account for their larger angular momentum and equatorial direction. The pair transforms into each other by rotation of 45° about a C_8 axis. Angular quantum numbers m_l +1 and -1 will be assigned to orbitals dzx and dyz of symmetry E_1, as the polar and equatorial components balance out. These will be referred to as the "tropical" orbitals, to maintain the analogy with a planet. The pair also transforms into each other, but with a 90° rotation about a C_4 axis. The assignment of + and – sign to the angular momentum of the E pairs is arbitrary, but consistent throughout the activity (see figure 1).

-2	-1	0	+1	+2
x^2-y^2	yz	z^2	zx	xy

Figure 1. Assignment of a quantum number m_l to individual d-orbitals.

ACTIVITY 1: THE GROUND STATE TERMS

This simple exercise introduces the use of letters and numbers to define Russell-Saunders terms. Given that Hund's rule assigns lowest energy to the highest spin configurations, the populated ground state configurations of atoms will be those of the greatest multiplicity. Therefore, one way to simplify the treatment of microstates and Russell-Saunders terms is to consider only electron configurations of the highest spin multiplicity. The argument for this is that they are sufficient to rationalize the electronic spectra of many common coordination complexes, such as those of d^1 –d^3 metal ions, as well as the low-field high-spin complexes of d^4-d^5 metal ions. For those complexes, low spin transitions are not observed in the absorption spectra and therefore the relevant electronic states are somewhat less important. This activity involves finding the combination of electrons with the highest spin and the highest angular momentum, by adding up the individual m_s and m_l of every electron (Russell-Saunders coupling) in a set of d^1-d^5 atoms, to obtain M_S and M_L. The next step is to convert the M_S into multiplicity by using the simple formula 2S +1 and to convert a population of M_L into the relevant L terms (0,1,2,3,4,5 = S,P,D,F,G,H). Maximum combined angular momentum M_L means lowest repulsions between electrons, which in turn mean lower energy of the system, also pointing at the highest L term as the ground state one (see figure 2).

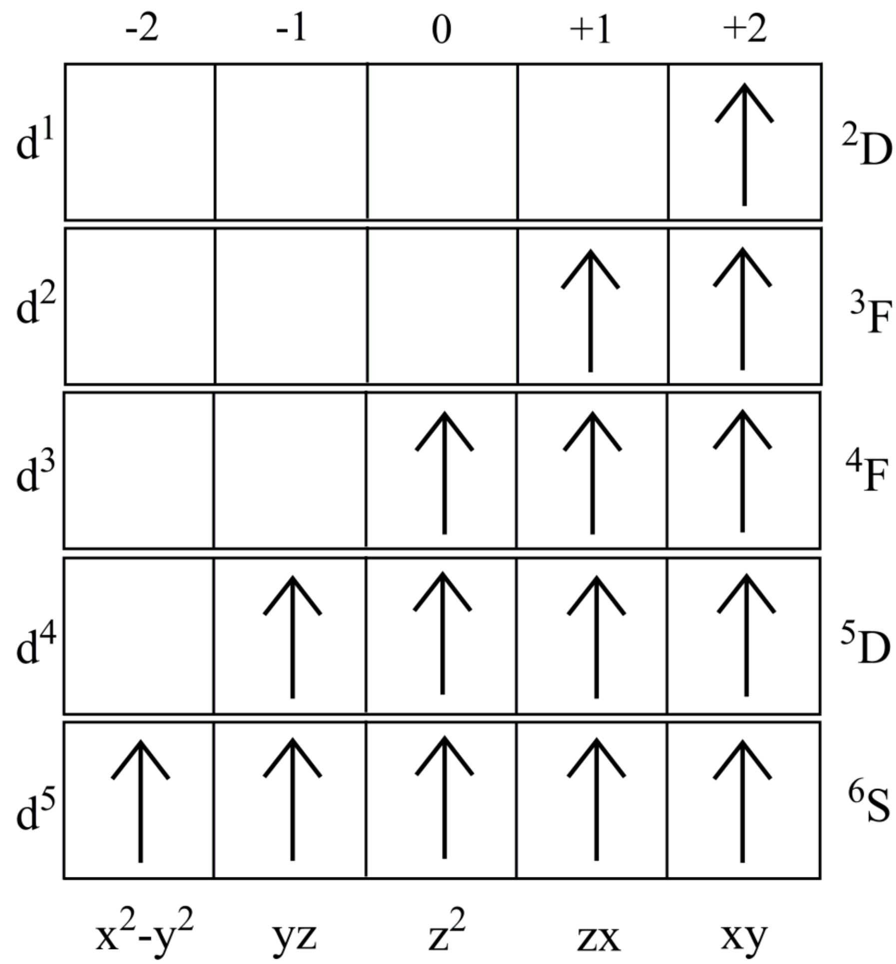


Figure 2. Activity 1 solution.

ACTIVITY 2: THE MICROSTATES

In line with the previous activity, the students are required to concentrate only on the microstates that satisfy the Hund's rule of maximum spin multiplicity. Those microstates represent the electronic configurations of the ground state and those of the spin allowed excited states in a d^2 ion and the transitions between them are those detected in a UV-visible absorption spectrum of a d^2 metal complex in solution. Upward pointing arrows will be used for consistency. The number of such combinations (*N*) is predictable, using the simple formula below (see equation 1), where *d* is the number of orbitals and *n* is the number of electrons. Each combination can exist and is called "microstate".

$$(1) \quad N = \frac{d!}{n!(d-n)!}$$

The students are asked to work out the M_L of each combination of electrons, as a sum of the m_l assigned to each occupied orbital, as shown in figure 1 (-3,-2,-1,-1,0,0,+1,+1,+2,+3). The presence of a population of seven M_L values from -3 to +3 of "triplet" multiplicity implies the existence of the term L = ^3F, which will contain one microstate per possible value of M_L, by definition. The remaining microstates with M_L -1, 0, +1 can only be assigned to a term L = ^3P. The ten microstates can be divided into two families: ^3F and ^3P, which are called energy terms. In the previous activity ^3F was found to be the ground state energy term, implying that those microstates belonging to ^3P are higher in energy. While d-orbitals are degenerate in a set, combinations of singly occupied orbitals might differ in energy in view of electron-electron repulsions: if the electrons are closer to each other, we expect them to form a higher energy microstate, so in this case, one belonging to ^3P. Those four microstates with M_L -3,-2, +2, +3 can be unequivocally assigned to the term ^3F at this stage (see figure 3). The remaining six microstates could belong to each of the two terms. In order to assign the remaining microstates to a given term, it is helpful to observe what happens when the d^2 atom is placed in an octahedral ligand field, or in other words when we form a coordination complex, which is the scope of the following activity.

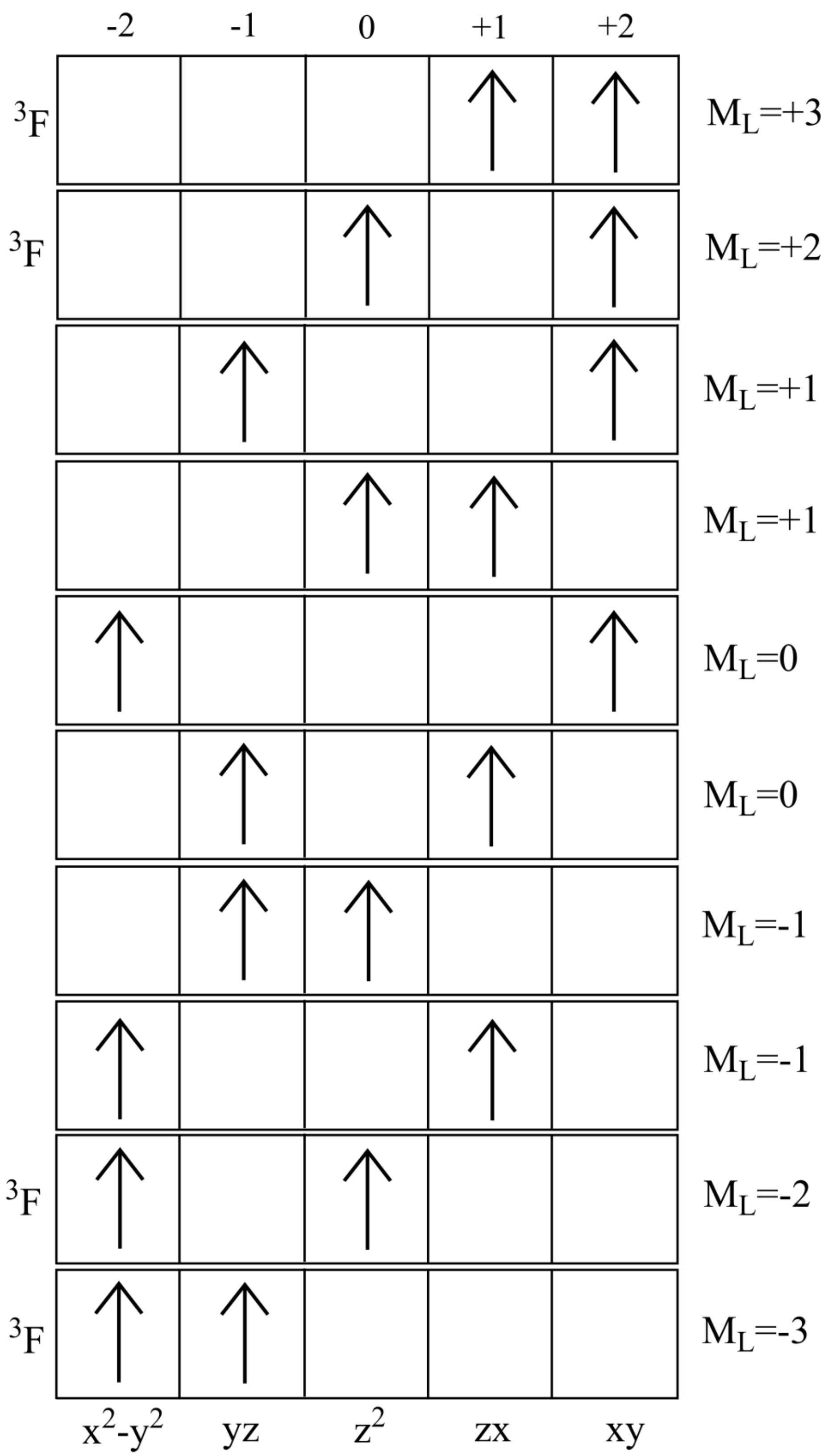

-2
-1
0
+1
+2
3F
M_L=+3
3F
M_L=+2
M_L=+1
M_L=+1
M_L=0
M_L=0
M_L=-1
M_L=-1
3F
M_L=-2
3F
M_L=-3
x2-y2
yz
z2
zx
xy

Figure 3. Activity two solution.

ACTIVITY 3: ASSIGNMENT BY ENERGY AND SYMMETRY

In this activity, the d-orbitals are split in an octahedral ligand field, where the dz^2 and the dx^2-y^2 orbitals form a pair of high energy orbitals, with symmetry e_g and the remaining orbitals form a triplet degenerate, low energy set of label t_{2g}. In keep with the m_L assignment in figure 1, the ligand field produces the diagram shown in figure 4.

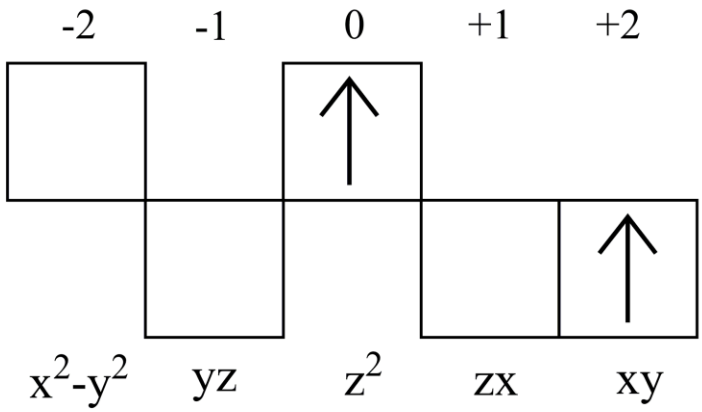


Figure 4. Energy split of d-orbitals, ordered by increasing m_l.

The students are introduced to a correlation between the d^2 atom and a d^2 octahedral complex (figure 5). The diagram shows how the same microstates exist in both the atom and the complex, but the ligand field results in the splitting of the F term into three populations of microstates: A + T + T.

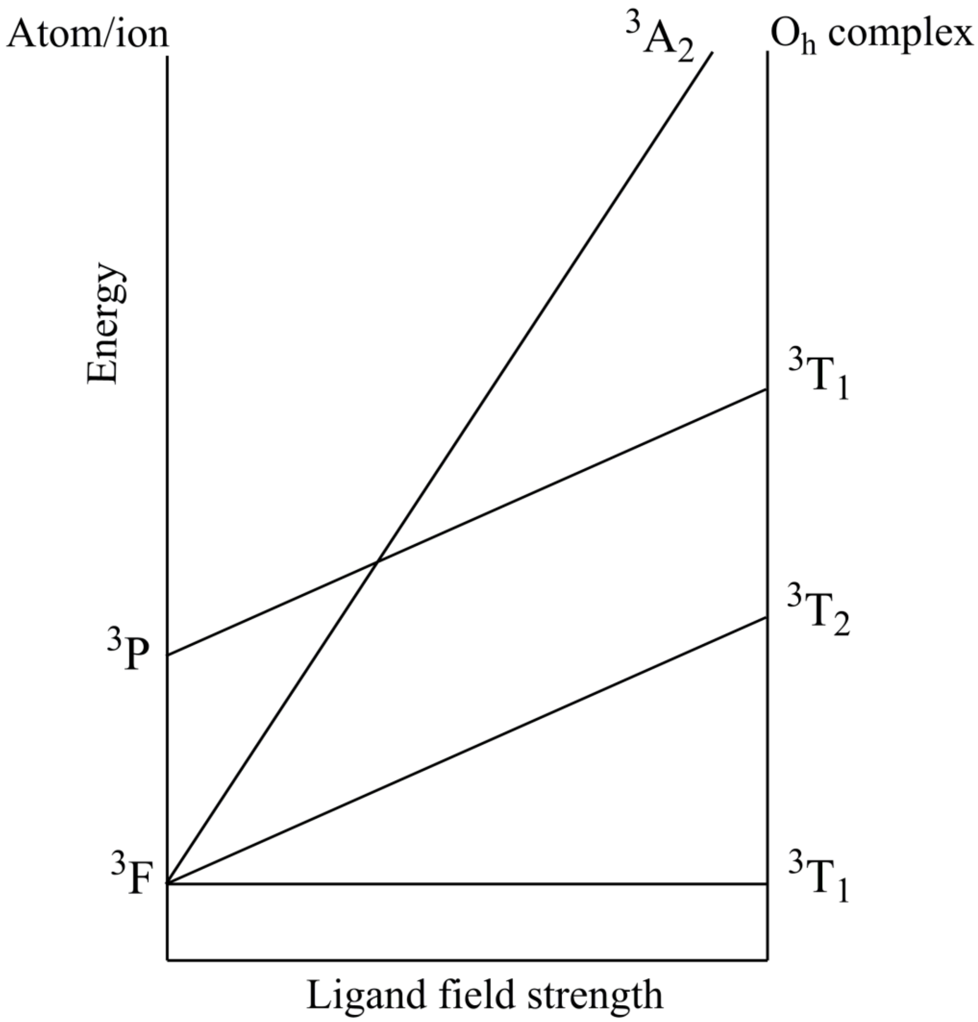


Figure 5. Simplified correlation diagram between triplet multiplicity atomic terms and the corresponding molecular terms in an octahedral ligand field.

The ligand field-induced split can be used by students to assign the remaining microstates to their energy term. Four states have already been assigned to ^3F, based on their M_L being unique of a ^3F term. In view of the octahedral ligand field split, the three microstates with both electrons in lower energy orbitals (t_{2g}) unequivocally belong to a $^3T_1$ ground state term, correlating with ^3F in the diagram. The only microstate with both electrons in higher energy orbitals (e_g) can be assigned to high energy $^3A_2$, also correlating with ^3F from figure 5. Following these assignments, only one set of M_L = 0 and +1 is left and they have to be assigned to a $^3T_1$ term correlating with ^3P. The two microstates with one electron in t_{2g} and one in e_g, having M_L = 2 and -3 can be safely assigned to a $^3T_2$ term correlating with ^3F, as on balance they will be higher than $^3T_1$ and lower than $^3A_2$ in a O_h ligand field. The latest assignment, only leaves two microstates, both having M_L = -1 that cannot be distinguished either by combined energy, or by their M_L. This method goes as far as assigning eight out of ten microstates of triplet multiplicity (see figure 6).

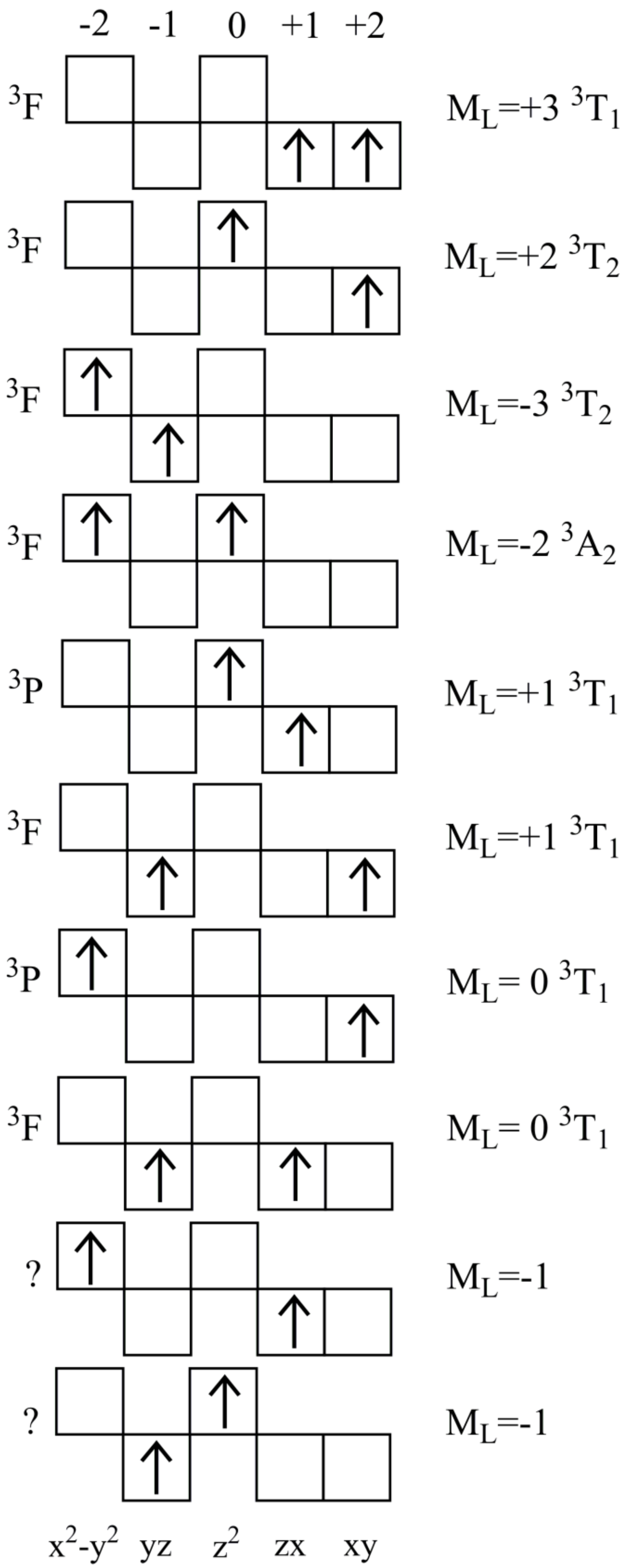

-2 -1 0 +1 +2
3F
ML=+3 3T1
3F
ML=+2 3T2
3F
ML=-3 3T2
3F
ML=-2 3A2
3P
ML=+1 3T1
3F
ML=+1 3T1
3P
ML= 0 3T1
3F
ML= 0 3T1
?
ML=-1
?
ML=-1
x2-y2 yz z2 zx xy

Figure 6. Activity 3 solution.

Electron repulsions offer an alternative method students can use to assign combinations of electrons in orbitals to a given term. From figure 6, there are six microstates with one electron in t_{2g} and one electron in e_g. From figure 5, these belong to the two triplet degenerate terms $^3T_2$ and $^3T_1$ of intermediate energy (remember we have already assigned the remaining four microstates to the lowest and the highest energy term in the O_h complex).

The spatial extension of the occupied orbitals can be broken down into three components, representing the x, y and z axes (see table 1). One set of three microstates extend along all three axes: xyz = 121 ($dyz + dx^2-y^2$); 211 ($dx^2-y^2 + dzx$); 112 ($dxy + dz^2$) and one set extends along two axes only: xyz = 103 ($dzx + dz^2$); 013 ($dyz + dz^2$); 220 ($dxy + dx^2-y^2$). Only the latter is a complete set of quantum numbers, with M_L = -1, 0, +1, as from figure 1 assignment.

Orbital/extension	x	y	z
dz^2	0	0	2
dzx	1	0	1
dyz	0	1	1
dxy	1	1	0
dx^2-y^2	1	1	0

Table 1. Orbitals spatial extension along the three axes.

It is reasonable to conclude that they not only belong to the same symmetry label, but they can be unequivocally assigned to ^3P (see figure 7). This assignment is consistent and completes the one discussed previously. The other set can be assigned to $^3T_2$ correlating to the term ^3F by exclusion. As discussed in activity 2, the microstates assigned to ^3P should be higher in energy, in the absence of a ligand field. Our assignment means that the two electrons in those microstates are confined in a restricted region of space, which is consistent with the notion of higher energy as a result of increased electron-electron repulsions.

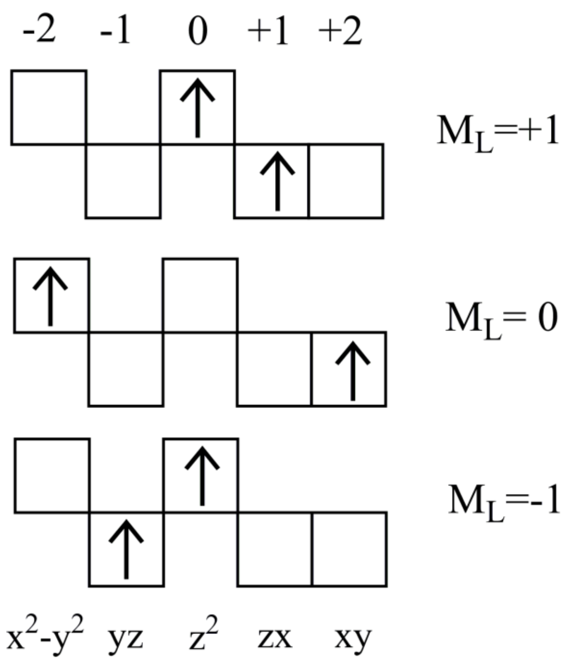


Figure 7. Activity 4. Assignment to ^3P by symmetry comparison. All three microstates have spatial distribution of electrons in two directions only, according to table 1.

Ultimately, students need to be able to perceive a value in their assignments and relate them to the theory learned and the laboratories practical experiments. The four populations of microstates correspond to three possible families of electron transitions from the ground state, which reflect the bands observed in the UV-visible spectra of d^2

octahedral complexes in the practical laboratories. The $^3A_2 \leftarrow {}^3T_1$ transition is the only one that involves relocation of two electrons and therefore, when visible, it is generally a very weak band in the UV absorption spectrum. Visualization of the individual microstates shows the double excitation very clearly.

It is possible to assign in similar fashion the ten quartet microstates in a d^3 ion and the five quintet microstates in a d^4 metal ion, the latter assignment being particularly easy and could be used as a “warm-up” exercise (see supplementary material).

The activity was trialed as part of a year two module in transition metals chemistry at Warwick. The activity was broken in three parts, giving small groups of three students ten minutes to solve each part. Each activity was then commented by the tutor, prior to moving to the next. The understanding, based on clickers responses, went from 43% for activity one, to 57% for activity two, to 72% for the final activity. Overall, out of 48 students, 81% found it useful to help understanding microstates and quantum numbers.

CONCLUSIONS

In conclusion, a method to consolidate the concepts of “microstate” and “energy term”, complementary to the textbook treatment, is presented in the form of an activity for undergraduate students. The activity allows students to correlate atomic microstates with molecular equivalents and rank them by energy. The main feature is that a different approach is used as compared to the lectures, based on logic and intuition rather than abstract mathematics. The activity is best suited to a group workshop of one hour.

ASSOCIATED CONTENT

Supporting Information

Supporting information includes: a description of the activities, an activity sheet, printouts of d-orbital boxes in degenerate and non-degenerate form for lamination and assignment of microstates for d^3 and d^4 atoms.

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