TEACHING CHEMICAL BONDING THROUGH PROJECT-BASED LEARNING. II. WEIGHTING “KNOW HOW” AND “KNOW WHY” WITHIN THE PROJECTS

Departamento de Química Física, Universidade de Vigo (SPAIN)

Abstract

In previous issues we have reported some experiences with project-based learning. All of them were carried out by us when teaching fundamental concepts of Quantum Chemistry in a course placed in the second year of the Chemistry Degree. Introducing project-learning has worked really well avoiding the usual disconnection of many students from the mathematical deductions presented (using the expositive method), or proposed as homework. Nevertheless, we have noticed that our projects have not changed that our students tend to be more interested in acquiring solving skills (know how) they can use in front of an examination problem, than about reasoning which causes and/or first principles are behind what they are doing (know why).

We identify this as a shortcoming in our teaching method, certainly shared by other methods, and even rooted within the philosophy basing some predominant trends in contemporary education. Students are clearly oriented by the way they are evaluated. In fact, for years we have noticed that many of them really learn how to pass the course. A clear example in our subject is: many students gain the ability to write (and solve) secular determinants implementing the Hückel treatment for π-delocalized systems. They solve the problem correctly, but they are unable to answer what is a secular determinant and why it appears there. We believe this kind of facts point to a new strategy. The projects given to students, and examinations too, should be designed weighting: i) technical abilities; and ii) rigorous reasoning from basic concepts. A comparative analysis of chemical bonding in two small cations has been the first project where we have included diverse theoretical questions preventing from routine and prompting students for searching which scientific reasons are behind the treatment they are employing. As in previous projects, the whole mathematical formalism behind chemical bond is applied. Thus, motivation for acquiring stronger abilities in solving numerical problems is guaranteed. When the results are presented in a seminar, the teacher plays a more significant role, highlighting the questions on fundaments and monitoring explanations.

Keywords: Project-based learning, evaluation, highlighting “know why”, chemical bond, Hückel calculations.

1 INTRODUCTION

It has been said that promotion of Project-Based Learning (PBL) follows a radical change about the sense on university teaching. According to it, the main objective does not remain any longer on teachers’ efforts, but on students’ attainments. Within this context, the attention and effort paid by teachers on learning plays a substantial role and could be directly related with educational results [1].

We have been making use of PBL method for teaching chemical bond during several courses [2]. Our main objective was replacing classroom long-time consuming mathematical deductions by personal (or group) work done by the students and tutored by us. The improvement in the educational results was apparently clear: rather demotivating lectures attended by passive students were transformed into encouraging challenges. In fact, the response of many students was to face up the project actively. As a consequence, evaluation results improved and, more important than that, we noticed the concepts worked through PBL were firmly acquired by a larger amount of students. We could even expect those concepts became part of their future chemical background.

Being really pleased by the results obtained with our PBL experience, we extended it to other parts of our subject. Thus, we selected a different issue, placed far from chemical bonding in our quantum chemistry course. Taking into account that calculation with Hückel molecular orbital (HMO) method [3,4] are usually included in the exams, and this epigraph is placed around the middle of the course, it seemed to fulfil requirements for becoming the second PBL section in the course. Not surprisingly, this issue put forward what we see as a serious shortcoming in contemporary education: we are more
concerned with promoting practical abilities than about understanding basic concepts behind them. This is not a specific problem of PBL method. Nevertheless, particular strategies for solving the problem, should be designed within the context of PBL.

2 METHODOLOGY

Kilpatrick introduced the PBL method for early childhood education in 1918 [5]. Since then, this method has been regarded as an educational option where the teacher’s behaves as a guide helping students along their learning affair. Moreover, he/she has to encourage their interest in this learning process motivating them throughout the challenge of solving real problems. In Kilpatrick’s words: PBL “emphasizes the factor of action, preferably wholehearted vigorous activity”.

PBL has been long applied to teach chemistry courses of diverse levels. Scenarios for particular projects have been usually taken from socially interesting chemical phenomena or from research papers. Thus, a wide set of examples can be easily found in educative chemical literature for secondary and high school. In contrast, PBL examples are more scarce for university level [6].

Our particular task is teaching to Chemistry students an introductory course on “Quantum Chemistry and Molecular Spectroscopy”. The topics covered in the course include: chemical applications of group theory, chemical bonding (mostly, molecular orbital theory), computational chemistry, light-matter interaction, and molecular spectroscopy (rotational, vibration-rotation, electronic, photoelectronic, and NMR). This course is placed in the fourth semester within a 4-year curriculum for obtaining the Chemistry degree. It comprises 26 classroom hours, complemented by 26 additional hours devoted to solve numerical exercises. We think that, under these circumstances, it is absolutely impossible to teach the whole course according to PBL method. Nevertheless, we can take advantage of PBL characteristics in some parts of the course. As we have already said, chemical bond theory seems to suit particularly well for our purposes, replacing hard to follow lessons by student active work. The second topic where we have operated with PBL has not worked out so well. On first thoughts this could be surprising. For years we have observed that most of our students learn to employ HMO to describe the electronic structure of simple organic molecules bearing π-delocalized systems. So, which is the problem in letting them taking the initiative? Our reflection is the problem was not taking the initiative or follow directions marked in class. The point is what the students expect to find in the exam: a numerical problem asking for molecular orbital expressions and energies, or even atomic π-electron populations, bond orders or delocalization energies. That is, “know how”, “produce numbers” without rigorous reasoning.

3 RESULTS

Here we outline two projects were we have tried to weight “know how” and “know why” capacities. We consider the first one has basically reached all our desired formative objectives, whereas the second case still needs to be improved.

3.1 A Successfully Weighted Project: Chemical Bonding in H_3^{2+} and H_3^{+} Cations

3.1.1 Project Wording

The stability of the single electron species trihydrogen dication, H_3^{2+}, has been the objective of many theoretical and experimental investigations. In fact, at least 14 papers published between 1964 and 2008 have addressed this point [7]. Currently, it is considered unstable, experiencing spontaneous dissociation into two protons and one hydrogen atom. Nevertheless, it has been experimentally detected in the presence of highly intense magnetic fields (B > 10^8 G). One of the structures proposed for the species was an equilateral triangle. Using this geometry, group symmetry theory considerations, and the molecular orbital method with a minimal basis set formed by three 1s HTO functions, one of them centered on each of the nuclei, answer the following questions:

a) How many electronic states can be described for this system?

b) Which symmetry or symmetries are displayed by them?

c) How many different electronic energy levels can be calculated?

d) Write mathematical expressions for the normalized wave functions obtained.
e) Which are the energy limits for the following dissociation processes:

\[ \text{H}_3^{2+} \rightarrow 2 \text{H}^+ + \text{H} \]
\[ \text{H}_3^{2+} \rightarrow \text{H}_2^+ + \text{H}^+ \]

f) Deduce an expression for each of the energy levels in terms of overlap, \( S \), Coulomb, \( j \), resonance, \( k \), and tricentric, \( t \), integrals. Making use of the expressions of \( S \), \( j \) and \( k \) integrals and the table of values of \( t \) integral, you should:

\[ \text{g) Plot the evolution of the electronic energy of the totally symmetric state with the triangle side, } R. \text{ Verify the presence (or not) of a minimum for the electronic energy.} \]
\[ \text{h) Plot how the electronic energy for another electronic state evolves with } R. \]
\[ \text{i) Calculate the variation of the electronic energy displayed by the ground electronic state when the side of the triangle reduces from 1.200 to 1.000 Å.} \]
\[ \text{j) Calculate the energy gap between the ground and first excited electronic states when the triangle side is 2.000 au.} \]

Now, let's consider a 2-electron system: \( \text{H}_3^+ \).

k) Write an approximated wave function (Slater determinant) for its ground electronic state. To this end, employ the 1-electron wave functions obtained for \( \text{H}_3^{2+} \) as MOs for \( \text{H}_3^+ \).

l) Write also an approximated wave function for the first electronically excited state of \( \text{H}_3^+ \).

m) Obtain expressions for the energy of the ground and first electronically excited state. These expressions should be in terms of monoelectronic and bielectronic integrals.

Data: 1 au = 0.529177 Å; \( D_{\text{explt}}(\text{H}_2^+) = 2.79 \text{ eV} \); 1 au = 27.2116 eV;

\[ 1_{s_{H_3^+}}(\vec{R}_{d1}) = \frac{e^{-R_{d1}}}{\sqrt{\pi}} \]
\[ S_{dR} = e^{-R} \left( \frac{R^2}{3} + R + 1 \right) \]
\[ j = e^{-2R} \left( 1 + \frac{1}{R} \right)^{-\frac{1}{R}} \]
\[ k = -e^{-R} \left( 1 + R \right) \]

\[
\begin{array}{cccccccccccc}
R/\text{au} & 0.5 & 0.6 & 0.7 & 0.8 & 0.9 & 1.0 & 1.1 & 1.2 & 1.3 & 1.4 & 1.5 & 1.6 & 1.7 \\
R/\text{au} & 1.8 & 1.9 & 2.0 & 2.1 & 2.2 & 2.3 & 2.4 & 2.5 & 2.6 & 2.7 & 2.8 & 2.9 & 3.0 \\
100·t/\text{au} & 2.213 & 1.834 & 1.517 & 1.253 & 1.034 & 0.852 & 0.702 & 0.577 & 0.474 & 0.389 & 0.319 & 0.261 & 0.214 \\
\end{array}
\]

3.1.2 Results obtained

The achievement of educational objectives of this project was tested introducing a set of similar questions in the corresponding exam. These similar questions were those reported in 3.1.1 as epigraphs d), f), k), l) and m), but the latter related only to ground state, and were performed for another combination of 1- and 2-electrons systems, specifically: HHe^{2+} and HHe^+. We notice exam systems were obviously more simple for the sake of time.

It has to be said that delivering the reports of the project was not compulsory for the students. We only received 42 reports from students that were also present in the examination. 23 students which did not deliver reports were also in the exam. Table 1 summarizes the results obtained for these epigraphs and for an additional question, not included in the project, represented by \( \alpha \). This question asked the students to demonstrate that molecular orbital wave functions give equivalent weights to covalent and ionic dissociation. It can be observed that the results obtained in this question were, as expected, significantly worse. In contrast, those questions worked in the project were much better solved by those students who had delivered the corresponding report. Moreover, the results obtained in project report and exam display a good correlation. Finally, we also observe that the results obtained in question \( \alpha \) are better for the set of students delivering the project, what we believe is just a consequence of a larger presence of conscientious workers within this set.
Table 1. Percentages of students solving correctly certain epigraphs of project 3.1, P, and related questions in the exam, E1, and those present in the exam but without project reports, E2.

<table>
<thead>
<tr>
<th>Epigraph</th>
<th>d</th>
<th>f</th>
<th>k</th>
<th>l</th>
<th>m</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>88.1</td>
<td>76.2</td>
<td>73.8</td>
<td>59.5</td>
<td>69.0</td>
<td>-</td>
</tr>
<tr>
<td>E1</td>
<td>83.3</td>
<td>61.9</td>
<td>78.6</td>
<td>50.0</td>
<td>52.4</td>
<td>42.9</td>
</tr>
<tr>
<td>E2</td>
<td>56.5</td>
<td>43.5</td>
<td>47.8</td>
<td>26.1</td>
<td>39.1</td>
<td>17.4</td>
</tr>
</tbody>
</table>

3.2 A Project with a Weighting to be Improved: Hückel Molecular Orbital Study of Oxirene

![Figure 1. HF/6-31G** optimized molecular structure for oxirene.](image)

3.2.1 Project Wording

Oxirene, whose lowest-energy structure is shown on Fig. 1, is an unsaturated heterocycle which spontaneously decomposes at room temperature into ethane and oxygen. Bearing 2 double occupied \( \pi \) MOs in its ground electronic state, it is considered as an example of antiaromatic compound. A Hartree-Fock full geometry optimization carried out with for its ground electronic provided 1.491 and 1.260 Å for, respectively, C-O and C=C bond lengths and one imaginary frequency. For this molecule:

- a) Write the electrostatic Hamiltonian for the relative electronic movement making use of Born-Oppenheimer approximation.
- b) Obtain the symmetry adapted linear combinations for a minimal basis set of atomic orbitals (SALC-AOs) involved in its \( \pi \)-system and discuss which should be strictly the name of the \( \pi \)-system in a C\(_{2v}\) system.
- c) Which other symmetry species are obtained with the minimal basis set of AOs?
- d) How many basis functions are employed to describe the molecule in the HF/6-31G** calculation? Consequently, how many MO are obtained? How many of them are labeled as “occupied” and how many as “virtual”?
- e) How many basis functions are employed in the Hückel MO treatment of the \( \pi \)-system of this molecule. Does the HF/6-31G** calculation provide more “occupied” \( \pi \)-MOs? What about “virtual” \( \pi \)-MOs?
- f) What is the meaning of the imaginary frequency obtained in the HF calculation?
- g) Making use of the Hückel MO semiempirical method, compute the energy of all the \( \pi \) MOs in oxirene. To this end, employ the following data: \( \alpha_O = \alpha + 2\beta \) and \( \beta_{C-O} = 0.8 \beta \).
- h) Express the Hückel \( \pi \)-MO of lowest orbital energy as a linear combination of the basis functions considered with this method.
- i) Do the same for the remaining Hückel \( \pi \)-MOs you need to obtain the C-C and C-O bond orders and atomic \( \pi \)-electron populations.
- j) Estimate the electron delocalization energy or the system.
k) Accepting that HOMO and LUMO belong to the π system, analyze which electronic terms are contained in the first excited electronic configuration and write wave functions (Slater determinants or linear combinations of them) for each of their states.

l) Investigate if assumption made in question j) is corroborated or not by the HG/6-311G** calculation.

3.2.2 Results obtained

As done with project 3.1, we tested how the work done in the project had helped the students to learn about Hückel method. Thus, a set of similar questions were asked in the exam. As above, the system was changed, so oxirene was replaced by the s-trans conformer of butadiene (what could be named as a classic within the exercises of Hückel method). These similar questions were those reported in 3.1.2 as epigraphs b), f), g), i) and j). Once again, we added a couple of question not directly asked in the project. The first one, α, is not worked in the project, but had been previously worked when studying chemical bonding, and had been correctly answered by most of our students: Its was stated as follows:

α) “Normalize a certain σ-MO of butadiene given by the expression 0.75 [2s(C1) + 2s(C4)] - 0.25 [2s(C2) + 2s(C3)] assuming that all the overlap integrals between 2s AOs cantered on bonded atoms are equivalent and the remaining are negligible”.

The corresponding wording for β question was:

β) “Write the Fock matrix (in terms of basic functions) for the Hückel treatment of butadiene”.

Once again, delivering the reports of the project was not compulsory, and we received 34 reports from students present in the examination. 19 students which had not delivered reports for this project were also present. Table 2 summarizes the results obtained for the similar and additional questions

<table>
<thead>
<tr>
<th>Epigraph</th>
<th>b</th>
<th>f</th>
<th>g</th>
<th>i</th>
<th>j</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>73.8</td>
<td>73.8</td>
<td>71.4</td>
<td>69.0</td>
<td>54.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E1</td>
<td>66.7</td>
<td>61.9</td>
<td>59.5</td>
<td>59.5</td>
<td>38.1</td>
<td>19.0</td>
<td>21.4</td>
</tr>
<tr>
<td>E2</td>
<td>60.9</td>
<td>47.8</td>
<td>47.8</td>
<td>43.5</td>
<td>17.4</td>
<td>0.0</td>
<td>4.3</td>
</tr>
</tbody>
</table>

We observe that questions “repeated” in the examination, which are basically operational, do not display significant differences between both students sets. This difference becomes larger, and comparable to those observed in Table 1, when we look at the least operational question, “j”, concerning electronic terms. Finally, we highlight that, after studying Hückel method, students lose their ability to normalize wave functions considering overlap integrals, as they become used to assume they are negligible as stated by Hückel method approximations. This is revealed by the really bad results obtained in question α. Moreover, results obtained for question β reveal that most of the students continue looking at this topic as a merely exercises matter. They are able to write and solve secular determinants, but do not realise the secular determinant is just the way to diagonalize the Fock matrix. Though the results in β are better for students working project 3.2, they are not good enough, indicating the project has to be modified in order to work deeper “know why” points behind the “know how” details.

4 CONCLUSIONS

Exam-questions related to points worked in projects and not directly related to them have been employed to test the performance of projects to achieve learning objectives. We observe that reaching objectives related to deeper knowledge (“know why questions”) is more difficult than those related to operational abilities (“know how”). An adequate weighting of both kind of aspects seems to be crucial when designing projects for PBL strategies. Anyway PBL reveals as a successful technique to improve results obtained by our students.
Finally, the extension provided to Hückel MO method in introductory courses to Quantum Chemistry should be probably reconsidered as many students generalize peculiarities of this method to general cases.

ACKNOWLEDGEMENTS

We wish to thank all of our students for their valuable contribution to this experience. We especially thank those who motivate us, studying hard, delivering reports, attending lectures, making questions, and developing a critical mind.

REFERENCES