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## QUANTUM-CHEMICAL CONCEPTS: ARE THEY SUITABLE FOR SECONDARY STUDENTS?

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**ABSTRACT:** Quantum-chemical theories of atomic and molecular structure are now part of the upper secondary curriculum in many countries, despite the fact that many educators are against their use in basic chemistry courses. In this paper, we first summarise the main findings of previous work on chemistry students' knowledge and understanding of atomic orbitals, molecular orbitals and related concepts. We then report results of a study with twelfth-grade Greek students. A test was used that required critical thinking, and aimed to find whether students had acquired a deep understanding of the relevant concepts. The findings indicate that such understanding was missing from most students. Students did not have a clear understanding of orbitals, and especially their probabilistic rather than deterministic nature; for many, the orbitals represent a definite, well-bounded space; they did not realise the approximate nature of atomic orbitals for many-electron atoms; the inadequacy of the carbon-atom, ground-state, electron configuration to account for its valency of four was not evident. Implications for instruction and the curricula are discussed. [*Chem. Educ. Res. Pract. Eur.*: 2002, 3, 129-144]

**KEY WORDS:** *quantum chemical concepts; orbitals; misconceptions; conceptual difficulties; upper secondary chemistry*

### INTRODUCTION

Quantum-chemical theories of atomic and molecular structure are taught in general chemistry or introductory inorganic chemistry courses in chemistry and other science departments. Besides, atomic and molecular orbitals are part of the upper secondary curriculum in many countries. There are, however, many educators who are against the use of the orbital and related quantum chemical concepts in basic chemistry courses (Bent, 1984; Berry, 1986; Ogilvie, 1990; Gillespie, 1991a; Hawkes, 1992; Shiland, 1995), while a few argue for them (*e.g.*, Morwick, 1979). Supporters of the use of orbitals maintain that it is scientifically and pedagogically incorrect to teach old-fashioned, and mostly invalid theories, which will later have to be replaced or unlearned. Critics of the use of orbitals, on the other hand, consider these concepts highly abstract and involved, and therefore beyond reach for many students.

A number of researchers have addressed the difficulties with current sophisticated models of the atom and the molecule. For a comprehensive review see Taber (2001) in this Journal. In Italy, Cervellati and Perugini (1981) reported confusion among secondary-school students about orbitals; they attributed this to both the teachers - especially the non-chemists - and to bad books; on the other hand, some of their first-year university students identified orbitals with energy levels, and others thought they were electron trajectories. In France,

Cross and colleagues (Cross *et al.*, 1986), found that the mechanistic model of fast moving electrons in definite orbits was the dominant one among undergraduates. Similar findings were reported by Mashhadi (1994) for English students studying physics at A-level. Shiland (1997) examined a number of secondary chemistry textbooks and concluded that they did not provide a sufficient basis for the rational replacement of the Bohr model of the atom with the quantum mechanical model. Taber (1997a) reported that some U.K. A-level students treated the terms orbitals, shells, and orbits, interchangeably; furthermore, sub-shells and energy levels were confused with shells, sub-shells and orbitals, while orbital probability envelopes were considered to be orbital boundaries. Confusion between electron shells and electron clouds has been reported by Harrison & Treagust (2000). Mechanistic thinking (“electrons move around the nucleus in definite orbits” “the electron is always a particle”, “electrons move along wavy orbits around the nucleus”) was found among first and second year undergraduate physics students in England before starting the quantum mechanics course (Ireson, 2001). Finally, a classical-physics worldview was found to be held by upper secondary students in Norway with respect to the wave-particle duality (Olsen, 2001).

Turning to concepts of molecular structure, Taber’s students (Taber, 1997a) became confused between the mathematical modelling (LCAO) of molecular orbital formation, and the orbitals themselves, referring to ‘linear orbitals’. In addition, they confused molecular orbitals with atomic orbitals, suggesting electrons in bonds in molecules were in orbitals they designated as ‘s’ or ‘p’, or confusing sets of hybridised molecular orbitals (e.g.,  $sp^3$  hybrids) with molecular orbitals. According to Taber, “learning the abstract scheme for atomic orbital occupation ( $1s^1$ ;  $1s^22s^2$ ;  $1s^22s^22p^3$ ; etc) requires some considerable effort, and once the scheme is acquired it acts as an example of a pedagogic learning impediment, tending to ‘come to mind’ more readily than ideas about molecular orbitals”. The resonance concept and  $\pi$ -bonds are other difficult concepts:  $\pi$ -bonds are considered by some students as two bonds, one above and the other below the plane of a molecule such as benzene, while resonance is taken to mean an alternation between the canonical forms, rather than something intermediate to them. Tan and Treagust (1999) reported that some learners believe that in such structures as graphite, it is atoms that are delocalised, rather than electrons. Finally, Coll and Treagust (2001) (see also Coll and Taylor, 2002 – this Issue) examined the [advanced (upper secondary, undergraduate, and graduate) students’] mental models of chemical bonding. They found that despite the participants’ competence in the description and use of more abstract models (especially when simple models had inadequate explanatory power), these learners preferred simple models, and relate to more abstract models only in the context of tests or examinations. Based on this finding, the authors recommended that “tertiary-level instructors consider limiting the teaching of complex models of chemical bonding until the advanced levels of the undergraduate degree”.

### **THEORETICAL BACKGROUND: CHEMISTRY STUDENTS’ MISCONCEPTIONS AND CONCEPTUAL DIFFICULTIES**

A basic question, which arises, is whether chemistry graduates have a deep and precise understanding of modern concepts of atomic orbitals (AOs), molecular orbitals (MOs) and related concepts. Tsaparlis (1993, 1997b) carried out an analysis of examination data from the compulsory, undergraduate, quantum-chemistry course, and reported that students arrive at this course carrying with them from previous instruction a number of misconceptions and incomplete knowledge about quantum-chemical concepts. This was attributed mainly to the elementary, imprecise and mostly pictorial coverage of the relevant concepts.

The following topics were studied: The definition of an atomic orbital (AO); the real mathematical versus the complex mathematical forms of the AOs; the representation of AOs (AO shapes); the approximate nature of AOs for many-electron atoms; Slater determinants; the definition of a molecular orbital (MO) and the nature of the chemical bond; and, finally, other related topics. Here we will discuss only those concepts and topics that are relevant to general-chemistry and secondary school courses. Note that in the investigation only students who were successful in (i.e. passed) the undergraduate compulsory quantum chemistry course were included.

### Definition of atomic and molecular orbital

Most students failed to provide an exact definition for an atomic orbital, such as "a one-electron, well-behaved function that can describe - more or less successfully - the behaviour of an electron in an atom". 17% of the students avoided answering the question, while for 19% of the students, an AO was understood as or connected with "*a region in space inside which there exists a given probability, for example 90%, for an electron to be encountered.*" This is a definition that can be found in some textbooks (e.g. Buttle *et al.*, 1981; Miller & Augustine, 1975; Sherman & Sherman, 1983). Furthermore, from the elementary courses, students also become familiar with *hydrogenic* (or *hydrogen-like*) orbitals only, that is, exact solutions of the Schrödinger equation for the hydrogen atom or the hydrogen-like (monoelectronic) atoms. In quantum-chemical calculations of many-electron atoms and molecules, however, one uses as a rule basis *functions*, which are not solutions of any Schrödinger equation (Szabo & Ostlund, 1982).

The correct definition of a molecular orbital (MO) is similar to that of an AO. Performance in a relevant question was, however, much poorer. A significant proportion (40%) of the students identified an MO only with a linear combination of atomic orbitals, a misconception which arises from the *Linear Combination of Atomic Orbitals - Molecular Orbital* (LCAO-MO) approximation. 23% avoided answering the question, while only 4% (just two students) connected an MO to '*the probability of an electron to be encountered somewhere in space*'.

### Real versus complex mathematical forms of atomic orbitals

From elementary courses, students are familiar mostly with real mathematical forms of AOs. The actual solutions of the Schrödinger equation are, however, complex functions, except for the *s*-type orbitals. This is another cause of confusion. Real mathematical forms of AOs are constructed by taking linear combinations of complex mathematical forms of AOs having the same energy (*degenerate*). Students were asked whether the complex or the real mathematical forms of AOs provide a better description of atomic structure: 27% answered correctly, almost half (46%) did not answer the question, while 20% thought the real AOs are superior because they arise through a linear combination of the complex forms. The remaining 7% opted for the superiority of the complex orbitals because they result directly as solutions to the Schrödinger equation.

### Representing atomic orbital shapes

The most important finding was misinterpretation of the figure eight "*p*-type AO", familiar from previous instruction. This is a cross-section of the graph of the squared spherical harmonic,  $Y^2(\theta, \phi)$ , for the  $p_z$  AO; it *does not* give the shape of a  $p_z$  orbital, as some

elementary texts say (e.g. Boikess & Edelson, 1978; Buttle *et al.* 1981). We see again that incomplete and imprecise or even wrong previous instruction may develop in students' deeply rooted misconceptions, which cannot easily be corrected by later more advanced instruction. In addition, note that only 16% of the students recognised the *equal-probability contour* (or *boundary surface*) for a  $p_y$  orbital.

### The approximate nature of atomic orbitals for many-electron atoms

In many-electron atoms, the Schrödinger equation cannot be solved exactly, so approximations must be made. The simplest and crudest approximation is to neglect entirely electron-electron interactions (repulsions) and electron spin. In this way, hydrogenic orbitals are found as solutions. Into these orbitals we then place the electrons, according to the *aufbau principle*, and thus derive electron configurations, for example, for the oxygen atom  $1s^2 2s^2 2p^4$ . More sophisticated methods are available that take into account, in an approximate fashion, the electron-electron interactions. All these involved details are not dealt with adequately in introductory courses, and cause confusion for many students.

### The nature of the chemical bond

The standard chemistry text which had been used by all students before they came to university (Sakellarides, 1985) gave a (dated) wrong explanation of the nature of the chemical bond, offering the opportunity to check its effect on students' views. The text explained the chemical bond in terms of the opposing magnetic fields, created by the spinning pair of electrons that form the bond, an explanation that goes back to G.N. Lewis (Stranges, 1981). Thus, the chemical bond was assumed to be of an electromagnetic nature, opposing the current quantum mechanical view according to which bonding is attributed to the lowering of energy caused by the simultaneous attraction of the electrons to *all* the nuclei of the molecule. Note that the above magnetic fields do exist, but they are too weak to account for the strong chemical bond (McWeeny, 1970); besides, a chemical bond can be formed by a single electron alone as in the  $H_2^+$  molecule. Students were supplied with the relevant excerpt from the high-school book, and invited to comment on it, in the light of their quantum-chemistry background. The result was disappointing as far as the effectiveness of the quantum-chemistry instruction was concerned (mean achievement 1.6%). The authority of the high-school book was commanding. "It must be true. It was in the book!"

## THE PRESENT STUDY WITH SECONDARY STUDENTS

### Method and subjects

Quantum-chemical concepts have been introduced recently (1999-2000) into the Greek upper-secondary level (*lykeion*), at twelfth grade (final school year). The relevant chemistry course is a compulsory one for all students taking the '*positive direction*' of studies leading to science, engineering, medicine, and agro-science tertiary education departments. In the final examination, a common paper for all Greece is set by the Greek Ministry of Education. Because achievement in this examination is crucial for students' selection for higher education, they study seriously and hard for that course.

During the 1999-2000 school year, and some time after students had completed in their schools the study of the relevant concepts and material, a test was administered, with

questions different from the standard simple recall or application questions set in the examinations and having been practised by the students. The questions intended to test for deep understanding and critical thinking. A first draft of the test was judged for content validity independently by four teacher-chemists. Their feedback was taken into account, and the final questionnaire was prepared.

Although students had been instructed to revise the relevant material from their textbook in advance, they were allowed to use their textbooks during testing. There was one and the same textbook used by all students, published by the Greek Ministry of Education and distributed free to the students (Mavromoustakos *et al.*, 1999). Note that neighbouring in class students did not answer the same test, but some variation both in order and content existed. A total of 119 high school students from upper secondary schools in the town of Ioannina participated.

The same test was also administered to first-year undergraduate students ( $N = 62$ ) of the *Department of Biological Applications and Technologies* of the *University of Ioannina* at the beginning of the academic year 2000-2001. These students came from upper secondary schools all over Greece. Their knowledge about the subject was based upon what they had learned during the previous year in school (twelfth grade); that is, these students had the same background as the high-school students. Note, however, that a time of over four months had elapsed from their last contact with high-school chemistry; in addition, these students did not use any textbooks during testing. What is of great interest is that all these students were among the high achievers in the National Entrance Examinations to Greek universities. It must also be added that these students answered the test with great interest and care, so their achievement data are highly reliable.

Marking of the answers was carried out by one of the researchers (GP) as follows: two marks were given for each correct answer; one mark for partially correct answers; and zero marks for wrong or no answers. In the results that follow, we report indexes of discrimination for each question. These values were derived by dividing our whole sample into three sections, each with about equal numbers of students: The top section included the top third in achievement in the whole test, and similarly for the middle and bottom sections. An index of discrimination was calculated for each question on the basis of the top and the bottom sections:

$$ID = \frac{1}{2} [(\text{mean achievement on the question of top section}) - (\text{mean achievement on the question of bottom section})].$$

## Results

Tables 1-3 show the questions, together with the following information: discrimination values for each question, student performance, plus representative answers, including correct answers. In all cases, two results as percentage of respective students are given: the first number refers to twelfth-grade students, and the second number to first-year university students (see above). All questions that test the same concept have been grouped. Questions A1-A7 refer to the atomic-orbital concept (Table 1). Questions B1-B3 cover the approximate nature of atomic orbitals for many-electron atoms (Table 2). Finally Table 3 has question C1 on electron configurations and bonding plus question D1 on molecular orbitals. Note that some questions (the two forms of question A2, or questions A3 and A4, or questions B1, B2, B3) test exactly the same idea; for this reason these questions were answered by different students.

In addition to the questions included in Tables 1-3, some other questions were asked. Two of them asked for knowledge, which was outside the curriculum, so performance on



**TABLE 1.** Questions and student performance on the atomic orbital concept. In each case, the first number refers to twelfth-grade students, and the second number to first-year university students (see text).

**A1.** Is it possible for the hydrogen-atom electron in its ground state to be found outside the space that is defined as 1s orbital? Explain. [ID (index of discrimination): 0.41]

No answer: 3% / 3%	Correct: 19% / 26% [YES, there is some possibility (e.g. 5%) to be found outside]*	Other: 65% / 66% (YES, in excited state / NO, it would be in excited state)
Other: 9% / 5% (NO, the space of 1s orbital refers to the first shell, that is the ground shell / NO, hydrogen has only one electron.)		

\* The definition of the space defined as an 'orbital' takes into account a lower than 100% probability (e.g. 99 or 95%) for the electron to be encountered within that space (i.e. the orbital). A 100% probability (i.e. certainty) would have required the whole space for the orbital.

**A2.** Observe the Figures 1 and 2 that show the electron clouds in the 1s and a 2p orbital respectively (taken from the students' textbook: Mavromoustakos et al. 1999, pp. 7 & 8). While in Fig. 1 there are sparse dots far away from nucleus, in Fig. 2 such dots do not exist. Do you think there is an error in either or in both of the figures? [ID: 0.14 - An equivalent question in which the added information of the second sentence was missing had a higher discriminating power: ID: 0.26]

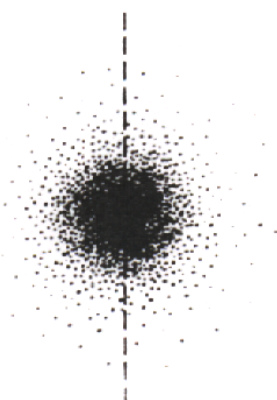


Fig. 1

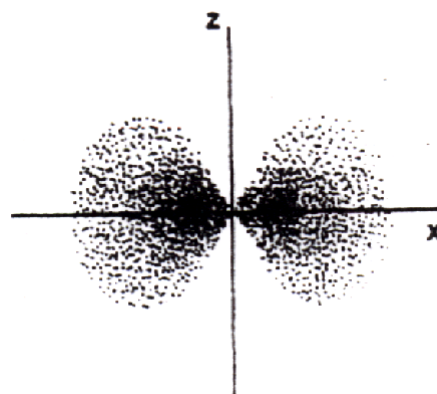


Fig. 2

No answer: 13% / 0%	Correct: 11% / 11% (In Fig. 2 there should also be sparse dots away from nucleus, as in Fig. 1)
Other: 76% / 89% (There is no error, p orbital is more stable / There is no error, in the first one we have an s orbital while in the second one we have a p orbital.) (One student stated that it could not be false, because it was written in the book)	

Table 1 continued on next page

Table 1 continued

**A3.** In your textbook it is stated that atomic orbitals are represented by spheres inside which the probability of encountering the electron is 95%. How is the other 5% shown in the orbital shape (diagram)? [ID: 0.35]

No answer: 24% / 7%	Correct: 45% / 53% (By dots outside the orbital, as in Fig. 1 above)	Other: 31% / 40% (It is not possible to be shown / It is represented as empty space)
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**A4.** In your textbook it is stated that the exact size of an orbital cannot be shown ... the orbital does not become zero even in large distances away from the nucleus. How is this or should be shown in the shapes of the orbitals? [ID: 0.61]

No answer: 25% / 8%	Correct: 21% / 75% (see answer to question A3)	Other: 54% / 17% (It should be shown with an asymptotic curve in a co-ordinate axis system;* it should be shown as spheres) * This statement is not wrong, but it does not directly answer the question, which is about the <i>shapes</i> of the orbitals.
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**A5.** If you could take a photo of the electron as it moves around the nucleus, how could you construct the picture of the electron cloud? (HINT 1: The picture of the cloud is stable - still. -HINT 2: A camera takes still pictures. HINT 3: Photos can be either prints or transparencies.) [ID: 0.45]

No answer: 16% / 16%	Correct: 15% / 34% (Take a large number of photos at different times. Print photos as transparencies. Place transparencies on top of each other. View the composite picture)	Other: 69% / 50% (Electron cloud is drawn / I would take many photographs)
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**A6.** It is given that the  $2p_z$  atomic orbital corresponds to triad (2,1,0) for the first three quantum numbers, while the  $2p_x$  and  $2p_y$  atomic orbitals result by adding and subtracting the orbitals with triads (2,1,+1) and (2,1,-1) respectively. Use these facts to comment whether the third quantum number shows the orientation of each of the  $2p_z$ ,  $2p_x$ , and  $2p_y$  orbitals. [ID: 0.00]

No answer: 51% / 44%	Correct: 0% / 0% [For $p_z$ , $m_l = 0$ , so shows orientation (along the z-axis). For $p_x$ and $p_y$ , $m_l$ is not defined (it is not a good quantum number), so it does not show orientation.]	Other: 40% / 42% [YES, it shows orientation, $2p_x$ and $2p_y$ correspond to triads (2,1,+1) and (2,1,-1) respectively*] * Such a statement appeared in some Greek 'informal' student texts!
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**A7.** In the final analysis, which one of the following two is the case? (a) an electron creates an orbital or (b) the electron is placed in an pre-existing orbital? [ID: 0.23]

No answer: 5% / 0%	Correct: 18% / 29% [(a) is correct: without electrons, orbitals do not exist]	Other wrong: 73% / 66% [(b) is correct]
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them was very low. One question asked for the reason why the energy of the 2s and 2p orbitals is the same for the hydrogen atom, but different for all other atoms; the other question asked why the third quantum number is named 'magnetic quantum number'. Another question asked for the most probable distance of the 1s electron from the nucleus through the use of a relevant graph. Caution should be taken in using such graphs because two different graphs are used, one giving  $|\psi|^2$ , the other  $4\pi r^2 |\psi|^2$  as a function of distance  $r$  from nucleus; thus, while the second graph becomes zero at the nucleus (because of the  $r^2$  factor), the first graph gives a maximum value at the nucleus. Note that it is only the second graph that gives the probability of finding the electron at distance  $r$  from nucleus.

As expected, in many cases, the university students had higher (and in fewer cases much higher) achievement than the general sample of the high-school students. This is explainable of course if we take into account that these were very able students (see above). Yet, in the most demanding questions, even these students did not fair better than the general sample. In the comments that follow, we concentrate on the performance of the high-school students, because these are representative of the general Greek school population.

## Comments

*A. The atomic-orbital concept.* Leaving aside question A6, we had correct answers ranging from 11 to 45% for the six relevant questions. However, many students continued to think in terms of the old quantum theory, assuming that the term 'orbital' is another word for (that is, is synonymous to) an 'orbit', and that the electrons rotate around the nucleus like the planets around the sun. In addition, a number of them considered that orbitals are unique and represent a definite, well-bound space. All these students then failed to realise the probabilistic nature of AOs; instead they seemed to subscribe to a deterministic perspective.

Question A6 was indeed a very difficult one. As a result we had 51% no answers and 0% correct answers, and zero discriminating power. Note that this issue is not treated at all in general chemistry books. Question A7 had also small discriminating power, revealing its conceptual difficulty.

*B. The approximate nature of atomic orbitals for many-electron atoms.* Correct answers were few here (3-18% for the three relevant questions), while many students did not answer at all. The discriminating power of these questions was subsequently low. Students had the misconception that the hydrogenic orbitals are exact for many-electron atoms. Many students did not understand the precise meaning of the electron configurations, which however they did not find difficult to write down. This set of questions proved very hard for the students, because it was not treated at all in the lessons. This partly explains also the lack of difference in achievement between high school and university students; but the latter students had fewer no answers, and consequently more partially correct or insufficient answers.

*C. Electron configurations and bonding.* Here we had just one question that dealt with the inadequacy of the carbon-atom, ground-state, configuration to account for the valency of four, as well as the equivalency of the four bonds. Only a small number of partially correct answers (6%) were found, while many students (64%) did not answer at all.

*D. Molecular orbitals.* Only one question dealt with molecular orbitals. Few students (13%) gave correct answers, while more students (26%) gave partially correct answers. Note that the student book mentioned only the bonding character of MOs, but not the existence of antibonding and non-bonding MOs.



**TABLE 2.** Questions and student performance on the approximate nature of atomic orbitals for many-electron atoms. First numbers refer to twelfth-grade students, second numbers to university students (see text).

**B1.** The electron configuration of H:  $1s^1$  is an exact configuration. The electron configurations of all other atoms, e.g. He:  $1s^2$ , O:  $1s^2 2s^2 2p^4$  are approximate. Do you know the reason why this is the case?

[ID (index of discrimination): 0.13]

No answer: 36% / 26%	Correct: 3% / 3% [Orbitals 1s, 2s, 2p etc. derive from the exact solution of the Schrödinger equation for a one electron-atom, such as hydrogen. For many-electron atoms, the Schrödinger equation cannot be solved exactly because of the presence of the electron-electron interaction (repulsion) energy terms. Hydrogenic orbitals 1s, 2s, 2p etc. can be found for many-electron atoms only if we omit the electron-electron interactions (a crude approximation).]
Partially correct: 19% / 37% (Hydrogen has only one electron)	Other: 42% / 34% (They have more electrons so it is more possible to get excited / Scientists like Bohr and Rutherford studied only the hydrogen atom, they found its exact configuration and then they found the other atoms' configurations according to hydrogen's configuration.)

**B2.** Between the ground-state electron configurations:  $1s^1$  for H and:  $1s^2$  for He, there is a fundamental difference. (Apart from the fact that hydrogen has one proton in its nucleus while helium has two, as well as apart from the fact that hydrogen has one electron while helium has two. Also, apart from the fact that in hydrogen the electron is unpaired, while in helium the two electrons are paired with opposite spins.) The difference we are after is related to the 1s orbital that is used in both cases. Which is this fundamental difference? [ID: 0.17]

No answer : 52% / 27%	Correct: 7% / 0% (See answer to question B1)
Other: 41% / 73% (The He 1s orbital is smaller or bigger than the H 1s orbital / The orbitals of the other atoms are hybridised / The fundamental difference has to do with the energy of the two atoms)	

**B3.** The Schrödinger equation can be solved exactly for the hydrogen atom, but only approximately for all other atoms. Do you know for which reason the equation cannot be solved in the case of the other atoms? [ID: 0.17]

No answer: 18% / 8%	Correct: 18% / 17% (Because of the electron-electron repulsion term)	Other partially correct: 28% / 75% (Because there are more electrons in the case of all other atoms)
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**TABLE 3.** Questions and student performance on (i) electron configurations and bonding and (ii) on molecular orbitals. First numbers refer to twelfth-grade students, second numbers to university students (see text).

**C1.** Is the ground-state electron configuration  $2s^2 2p_x^1 2p_y^1$  for the valence shell of the C atom consistent with the fact that C forms four covalent bonds, e.g. in  $\text{CH}_4$ , as well as with the tetrahedral arrangement of these bonds? Explain. [ID (index of discrimination): 0.24]

No answer: 64% / 40%	Correct: (0% / 0%) (NO, it is inconsistent because it has only two unpaired electrons, not allowing formation of four equivalent bonds; in addition, it does not predict the tetrahedral arrangement (e.g. $p_x$ and $p_y$ form an angle of $90^\circ$ .)	
Other partially correct: 6% / 25% (NO, it is not consistent; if it were, carbon should form two bonds, not four)	Other wrong: 30% / 35% (YES, it is consistent)	

**D1.** A molecular orbital forms by the combination-overlap of two atomic orbitals. Mathematically, this combination is equivalent to addition of the two atomic orbitals. In your opinion, would it be possible to subtract one atomic orbital from the other? If yes, which would be the consequences of that subtraction for the electron density in the space between the two nuclei as well as for the chemical bond? [ID: 0.37]

No answer: 31% / 16%	Correct: 13% / 19% (YES, it would be possible; electron density would be smaller or zero. Hence chemical bond would be weaker or broken)	Other partially correct: 26% / 35% (Partially correct answers refer either to the electron density or to the chemical bond: YES, but electron density would be lower)
Other: 30% / 30% (YES, but electron density would be larger because of smaller available space / This is not possible)		

## DISCUSSION AND IMPLICATIONS

The present study has revealed upper-secondary students' difficulty in understanding deeply quantum-chemical concepts that are taught to them. Although there is good reason to accept that these concepts are highly abstract and complicated for students (see below), we must also take note of a major source of difficulty in dealing not just with the quantum-chemical concepts, but actually with any concepts. It is known that chemistry teachers place great emphasis on equipping students through extensive practice with chemical skills, such as numerical problem solving, the placing of electrons in shells or atomic orbitals, the balancing of chemical equations, etc. It seems that teachers subscribe to the view that such mastery presupposes, hence is equivalent to, conceptual understanding of chemistry. Numerous studies have demonstrated that this is not so (Nakhleh, 1993; Nakhleh & Mitchell, 1993; Niaz & Robinson, 1993; Niaz, 1995; Zoller *et al.*, 1995; Zoller & Tsaparlis, 1997). Nakhleh and Mitchell confirmed that "it does not seem that presenting an algorithm and demonstrating the myriad of problems that can be solved by that algorithm facilitate understanding of the underlying concept." The same must be true of questions on the atomic and molecular structure: the ability, for instance, of students to write down electron configurations for atoms does not guarantee conceptual understanding of the underlying concepts. On the other hand, we must accept that the need to cover a lot of material of an ever-expanding science such as

chemistry, coupled with the limited teaching time allocated to chemistry (at least in Greece), makes it imperative for teachers to rush through the material.

But there is more to the quantum-chemical concepts than the above limitations. Pauling and Wilson (1935, p. iii) stated over sixty years ago that

*“Quantum mechanics is essentially mathematical in character, and an understanding of the subject without a thorough knowledge of the mathematical methods involved and the results of their application cannot be obtained.”*

And as Coulson (1974, p. 17) has put it:

*“Mathematics is now so central, so much ‘inside’, that without it we cannot hope to understand our chemistry ... These (quantum-chemical) concepts have their origin in the bringing together of mathematics and chemistry.”*

It is then quite understandable why without the necessary mathematical machinery, the relevant concepts cannot be properly grasped. On the other hand, the mathematical disguise that is characteristic of quantum-chemistry courses makes both teachers and students pay more attention to the complexities of the mathematics (the tools, the trees) and lose the physics (*the actual world*, the forest).

The physics of quantum chemistry is complicated and different from classical physics. It has been argued (Castro & Fernandez, 1987) that thinking abilities beyond Piagetian formal operations may be of major importance for an adequate understanding of quantum-mechanical (and relativistic) issues. These *post-formal operations* include what has been termed nearly sixty years ago as *quantum logic* (Birkhoff & von Newmann, 1936). Although one can derive the Schrödinger equation with entirely classical arguments (Fong, 1962; see also Tsaparis, 2001) (with Planck’s constant  $h$  serving as the bridge between classical and quantum mechanics), one has to admit that quantum mechanics has brought a new way of thinking about the physical world at the subatomic level.

Quantum theory suggests that, strictly speaking, “atomic orbitals can no longer be said to physically ‘exist’ in anything except one-electron systems; many-electron orbitals are ontologically redundant” (Scerri, 2001). And yet, we know that chemists are very comfortable in using orbitals everywhere. The extensive use of electronic configurations of atoms in chemistry textbooks (with a lot of relevant practice questions), reinforces further the impression about the fundamental nature of orbitals and configurations (Scerri, 2000). This misconception is also extended by the modern visualisation of orbitals by means of computers (Scerri, 1998, 1999). On the other hand, we know that we must be aware that the way chemists see and use quantum mechanics is essentially different from that of physicists, with the result that the need for a ‘philosophy of chemistry’ has arisen (Scerri, 2000). Accordingly, the view that chemistry has been reduced to physics, or more specifically quantum mechanics, is mistaken according to Scerri (2001).

### Trying to overcome problems

Science education research has a lot to offer for overcoming the issues raised in this work. The problem of *instructor-driven misconceptions* (Bodner, 1991) that result from previous elementary, imprecise, incomplete and mostly pictorial instruction is very serious. Science education research on *concept learning* has shown that to change misconceptions is a very hard task. Students, even if they come close to realising the errors in their established thinking, revert very easily to their previous ideas, with which they are more comfortable

(Driver, 1983; Eylon & Linn, 1988). Traditional instruction cannot overcome these ideas. But some innovative strategies from science education research on *conceptual change* are promising (Eylon & Linn, 1988). Hewson and Hewson (1984) describe teaching strategies, which aim at linking ideas. One technique is *integration*, which attempts to link conceptions, for example AOs and MOs in our case. Another technique is *differentiation*, which tries to identify differences between related concepts, such as complex and real, or hydrogenic and non-hydrogenic orbitals. These two techniques can provide missing links among concepts and thus facilitate learning and overcome misconceptions.

We repeat that students are as a rule good at applying practised algorithmic rules, while they find hard to deal with conceptual questions. We need to focus on *meaningful learning*, discourage rote learning, and aim at *coherent understanding*, and anticipate pre-conceptions. These can be achieved only by integrated, in-depth coverage of the topics (Eylon & Linn, 1988). In this respect, general chemistry should stop playing the role of a ‘baby physical chemistry’, at least in courses for chemists.

What is more important is that the overall teaching methodology must change, for it may be that more and better content, taught in the old didactic way, is unlikely to improve the situation. A conceptual change constructivist pedagogy, not only in schools but also in colleges and universities, holds promise of being more effective (Stofflett & Stoddart, 1994). According to Shiland (1997), secondary chemistry textbooks should be revised to include the elements of conceptual change with respect to quantum mechanics: the limitation of the Bohr model should be stated explicitly to create dissatisfaction, quantum mechanics should be made more intelligible, and problems which actually use quantum mechanics should be included. *Co-operative learning* is another promising methodology that involves students in the active construction of quantum-chemical knowledge. To this end, we have already some positive results from an extension of the current study (see below, “prospects for further work”).

Finally, we must emphasise that although mathematics is essential for a deep understanding of quantum chemistry, the underlying physical picture and its connection with mathematics is equally important. AOs, MOs and related concepts derive from Schrödinger's wave mechanics, which is an approximation to nature. *"Orbital concepts are merely aspects of the best presently available model; they are not 'real' in the same sense that experimental observations are"* (Simons, 1991, p. 132). It goes without saying, of course, that chemical educators should have a deep understanding of quantum chemistry, including its historical routes (Tsaparlis, 2001); on the other hand, it is very important that they should be aware of the new philosophy of chemistry: “what theories, models and laws are in general and how they vary in nature among the basic sciences of physics, chemistry and biology” (Scerri, 2001).

### General chemistry and secondary education

The question, which naturally arises, is: *"Should quantum-mechanical concepts be censored from secondary education and even from general chemistry?"* Should we be content with, at least in secondary education, the historical ideas about atomic and molecular structure, with the emphasis placed on old quantum theory and the classical bonding theories (Lewis structures and VSEPR theory)? Although there are an increasing number of voices, which agree with such a drastic action, it is very likely that it will be hard for a lot of other people to accept this! What then should be said to the latter?

Both general chemistry and upper-secondary school chemistry must emphasise basic chemical principles and descriptive chemistry integrated with the principles (Gillespie,

1991a). According to Pauling (1992), beginning courses in chemistry should emphasise the simpler aspects of molecular structure in relation to the properties of substances; these concepts include, the electronic structure of atom, with emphasis on the noble-gas structure, the shared electron-pair bond, the tetrahedral carbon atom, the electronegativity scale, the partial ionic character of bonds, and the idea of resonance as applied to the benzene molecule; but molecular orbitals should be left out.

It is well known that on the whole, the concepts of atomic and molecular structure are very difficult for most students (Tsaparlis, 1997a). The modern quantum-chemical concepts present additional barriers, so they should be introduced, if and where they are necessary, with great care. A possible procedure may consist of the following components (Polydoropoulos, 1974):

1. A quick reference to some quantum-mechanical results, with emphasis on quantum numbers and the aufbau principle.
2. The careful introduction of the AO as a mathematical function describing an electron in an atom (and similarly for the MO). In particular, it may be better to avoid orbital shapes (e.g. Dunstan, 1968), with the sole exception of boundary surfaces, that is contours of equal probability (equal  $\psi^2$ , and hence equal  $|\psi|$ ) (Polydoropoulos, 1968; Cromer, 1968; Levine, 1974; Baughman, 1978; Kikuchi & Suzuki, 1985; Allendoerfer, 1990). Pictorial models must be built onto the mathematics to turn it into a useful intuitive tool.
3. An outline of the quantum-mechanical nature of the chemical bond: two electrons, not belonging to either atom but to the molecule, are placed into an MO (described by an MO).
4. The distinction between  $\sigma$  and  $\pi$  bonds. Equal probability contours are most useful here.

Serious consideration must, however, be given to alternative ways of teaching chemistry that avoid the orbitals. In a book for beginning school chemistry, Johnstone, Morrison and Reid (1981) do not discuss orbitals, but also avoid theories and principles such as the Bohr atom and the octet rule; further, they treat bonding by developing the concept of electrons trying to keep as far apart as possible. Very significant are the contributions of Gillespie: the VSEPR model (Gillespie & Nyholm, 1957; Gillespie, 1972; Laing, 1995; Gillespie & Matta, 2001), and the *electron domain* model (Gillespie, 1991b, 1992a, 1992b; Gillespie *et al*, 1994; Gillespie, 1995; Gillespie, Spencer, & Moog, 1996). According to Gillespie, Lewis structures and VSEPR are all that is required for secondary school, while the electron-domain model is sufficient for general chemistry. More emphasis should be placed on electron density rather than on orbitals (Gillespie & Matta, 2001).

### Prospects for further work

The results reported here constitute a preliminary report of on-going research. Based on the findings, a new improved questionnaire was designed and administered to a new sample of students at the beginning of 2001-02. The quantitative results guided us to extend our study to a qualitative one by monitoring through interviews students' deeper way of thinking about quantum-chemical concepts. In addition, we are using co-operative, constructivist-learning methodology. We shall report our findings in due course.

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