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## PREFACE

One year ago (Vol. 2, No. 2, May 2001), *CERAPIE* published the first theme issue on structural concepts with invited contributions. The promise was then given that a second theme issue on the same theme would follow one year later. There were two reasons for this issue: one was to cover areas of structural concepts that were not covered in the previous issue (organic chemistry, crystal chemistry, NMR spectroscopy, and chemical kinetics); another reason was to have, in addition to invited, independently submitted, peer-reviewed contributions. This Preface should be taken as an addition (literally be incorporated) to the Preface in last year's theme issue (Tsaparlis, 2001).

### SPECIAL SECTION ON STRUCTURAL CONCEPTS IN ISSUE 3, VOLUME 2

At this point, we must mention three more papers on structural concepts that were included in Issue 3 of Volume 2 (October 2001). The first paper, by **Peter G. Nelson** was Part 2 of his modified Lewis theory. In it, the author extended the theory to molecules containing coordinate bonds. A further modification to the theory was proposed to make it applicable to molecules containing nonintegral bonds (e.g.,  $B_2H_6$ ).

The second paper, by **Rick Toomey**, **Ed Depierro** and **Fred Garafalo**, aimed at helping students at the introductory college level to make inferences about the atomic realm by delaying the presentation of atomic structure. The authors criticised the early introduction in such courses of the topics of atomic and molecular structure, despite being far removed from direct experience, and historically having been elucidated relatively late in the history of chemistry. The paper described a freshman chemistry curriculum, in which the topic of atomic structure is delayed until the second semester. Concept development is linked to the observable behaviour of matter, while the submicroscopic and symbolic realms are introduced by engaging students in some of the 'detective work' that established the relative atomic masses of the elements and formulae of simple compounds. In addition, a brief review of literature on relevant history and educational research was included.

In the third paper, **Georgios Tsaparlis** studied the physical and mathematical evidence that make the Schrödinger equation plausible. First, an approach from the historical perspective was made in which the methods of the pioneers Schrödinger, Heisenberg, and Dirac were studied. Then, numerous heuristic introductions to quantum mechanics were reviewed, and a synthesis of the various methods into a coherent and meaningful whole was suggested.

## THIS ISSUE

This theme issue contains eleven papers, of which three are invited and eight are reviewed contributions. At the outset, I thank very much all contributors.

In the first paper (by *P. Laszlo*), the widely used practice of using curled arrows in reaction mechanisms (especially in organic chemistry) is criticised. Then follows a quantum-chemistry paper (by *P. Karafiloglou*), that in one way is relevant to Laszlo's paper: it connects molecular orbital theory with valence bond theory, expressing electronic transfer through resonance structures. The following three papers (one paper by *G. Tsaparlis* and *G. Papaphotis*, and two papers by *K.S. Taber*) deal with quantum chemical concepts (atomic orbitals, molecular orbitals and related concepts) from the science-education research perspective. Another paper (by *R.S. Coll* and *N. Taylor*) examines mental models for chemical bonding held by senior secondary students, undergraduates and postgraduates. Then follows a paper (by *H.-D. Barke* and *H. Wirbs*) that proposes sphere packings and crystal lattices as structural models of inorganic solids. A review of a research program in the first and the second year of chemical education (age 14-15) in the Netherlands is presented by *J.H. Van Driel*. The programme aimed at teaching corpuscular conceptions in the context of chemical equilibrium and chemical kinetics. The science education part of the issue is concluded with a proposal (by *P.G. Nelson*) of a progressive teaching of introductory chemistry, starting from substances, and then moving to atoms and molecules, and finally to electrons and nuclei. Finally, two papers take us in deep scientific waters, providing links to advanced studies and applications of structural concepts. In the first paper, *I. Gerathanassis*, *A. Troganis*, *V. Exarchou*, and *C. Barbarossou* propose a sequence for teaching NMR spectroscopy at the undergraduate level, and describe traditional and modern applications of NMR. In the second paper *R. Kapral* and *S. Consta* provide us with the state-of-art of classical, quantum, and mixed quantum-classical theory used for studying chemical rate constants in condensed phases.

### Contributions from science (I)

#### *Describing (especially organic) reactivity with structural formulae and curved arrows*

**Pierre Laszlo** deals with the widespread practice, in the classroom, of the paper tool of reaction mechanisms, taught with Lewis structural formulae, using curved arrows to denote motions of electrons - a practice which he himself has used too in his long teaching of mechanistic organic chemistry at many famous Universities. According to the author, while this practice improves upon the rational understanding of chemical reactions and their underlying logic, it has many of the features of slang with respect to more thoughtful and dignified speech. Electron-pushing with curved arrows and the VSEPR rationale for molecular geometry view electronic density as a static distribution around each atomic nucleus, ignoring that electrons are mobile and delocalised over the entire molecule. Laszlo emphasises that when we write any reaction mechanism, what we are truly doing is to replace a dynamic phenomenon, which we little understand, with a stroboscopy of a succession of instantaneous successive static structures. On the other hand, the study of any reaction mechanism is experimental in nature: it is hard work, using a large number of diverse tools. The intention of the author is to influence colleagues who teach to non-chemists (and I should add here upper-secondary school curriculum planners and textbook authors): "to use mechanistic language on such a public is to do them a disservice because they are not future chemists and they do not need to master the language of the specialists".

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*Delocalisation and hyperconjugation in terms of (covalent and ionic) resonance structures*

The article by **Padeleimon Karafiloglou** is an exercise in quantum chemistry and is in some way relevant to the position paper of Laszlo. It builds bridges between valence bond and molecular orbital theories, expressing electronic transfer through resonance structures. Electron transfer (from bonding to anti-bonding orbitals) effects, as delocalisation and hyperconjugation, are translated into a language referring to resonance structures of covalent and ionic components of bonds. ‘Structural multiplication tables’ are introduced as a pedagogical tool, allowing one to generate resonance structures in a pictorial manner. It is shown that the transfer of one electron from a bonding orbital,  $\omega_{i,j}$  (donor), to an anti-bonding one,  $\omega_{k,l}^*$  (acceptor), creates an odd (an unpaired) electron in region (i,j) and another odd electron in region (k,l); the coupling of these two odd electrons provides the necessary covalent component(s) of the new bond(s) between the donor and the acceptor.

**Contributions from science education***Quantum-chemical concepts in secondary education*

**Georgios Tsaparis** and **Georgios Papaphotis** report results of a study with twelfth-grade Greek students. They used a test 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; in addition, they did not realise the approximate nature of atomic orbitals for many-electron atoms. The inadequacy of the ground-state carbon-atom electron configuration to account for its valency of four was not evident. The authors also summarise the main findings of previous work on chemistry students' knowledge and understanding of atomic orbitals, molecular orbitals and related concepts. Finally, they discuss implications for instruction and the curricula.

*Student understanding of atomic and molecular orbitals*

In two connected papers, **Keith S. Taber** presents and discusses data relating to student understanding of the orbital concept and related ideas at college level (i.e. between secondary and university level education). The data derives from in-depth research into the thinking of a small sample of U.K. students. Interview extracts provide insights into the students' attempts to make sense of these unfamiliar and abstract ideas. It is suggested that this is an area where there is a genuine pedagogic problem: capable and motivated students struggle to learn from experienced and knowledgeable teachers. The first paper describes how students conceptualised these key aspects of atomic orbitals. In the subsequent paper, the author considers the students' understanding of the molecular orbital concept. It is suggested that when learners are introduced to ideas about molecular orbitals before they have mastered ideas about atomic systems, then their learning difficulties may be ‘compounded’ in the more complex context. For example, it was found that students often identified the orbitals involved in two-centre bonds as atomic orbitals. Representations of delocalised bonds invoked various alternative interpretations: but were seldom

conceptualised as implying many-centred molecular orbitals. These findings suggest that students are not given sufficient time to construct acceptable models of atoms and molecules as ‘quanticles’

### *Mental models of chemical bonding*

Using an interview protocol that included the use of a variety of common substances and focus cards, **Richard K. Coll** and **Neil Taylor** examined New Zealand senior secondary students, undergraduates and postgraduates’ mental models for chemical bonding. They found that the learners’ mental models were simple and realist in nature, in contrast with the sophisticated and mathematically complex models they were exposed to during instruction. When their models proved inadequate to explain macroscopic events, the students used concepts from other models.

### *Sphere packings and crystal lattices as structural models of inorganic solids*

For many years now **Hans-Dieter Barke** carries out work related to the use of crystal structural models in secondary education and the related spatial ability of the students. Some of this work has been published in this Journal. In this Issue, with **Hilde Wirb** they propose the use of sphere packings and crystal lattices as structural models of inorganic solids: students can develop images of chemical structures and will differentiate between molecules and giant structures; in addition, unit cells can be introduced as smallest units of giant structures. In a research study with students at the eighth grade in Germany, the authors found that students of the treatment group were able to recognise unit cells of cubic structures and to determine empirical formulae from the used models.

### *Corpuscular conceptions in the context of chemical equilibrium and chemical kinetics*

**Jan H. Van Driel** reviews a research program in the first and the second year of chemical education in The Netherlands which aimed to develop 14-15 years-old students’ ideas of macroscopic chemical phenomena together with their views of the particulate nature of matter. The program was initiated with the work of *Wobbe De Vos*, who has developed an educational approach for the introduction of fundamental chemical ideas to secondary school children in Grade 9. Starting from the initial and often naive corpuscular conceptions of the students, an attempt was made to develop these conceptions by letting students perform chemical experiments, and inviting them to explain their observations in corpuscular terms. In the first year, students were introduced to the concepts of ‘chemical substance’ and ‘chemical reaction’. In the second year, the program focused on the introduction of the concepts of ‘chemical equilibrium’ and ‘chemical kinetics’. The results of the empirical investigation of students’ conceptions and reasoning revealed that students of this age have limited abilities to reason in corpuscular terms. However, there were students who used a simple model of colliding and moving particles to explain chemical phenomena in the areas of chemical equilibrium and chemical kinetics. This and similar evidence led to the conclusion that students can gradually learn to become more proficient in using corpuscular models as explanatory tools.

## A contribution from science and science education

### *From substances, to atoms and molecules, to electrons and nuclei*

**Peter G. Nelson** has published numerous studies in which he suggests methods for connecting the world of molecules, atoms, electrons etc. with macroscopic concrete phenomena. In this Issue, he draws upon his previous work to propose a progressive teaching of introductory chemistry. He starts by pointing out that in most current chemistry courses, students are introduced to atoms, molecules, ions, and electrons early in the course, and have to accept the teacher's word that these exist. A better method is to teach chemistry progressively, starting with observations at the macroscopic or bulk level (level one), interpreting these at an atomic and molecular level (level two), and then at an electronic and nuclear level (level three).

## Return to advanced science

### *NMR spectroscopy: Principles and applications*

It is well-known that Nuclear Magnetic Resonance (NMR) spectroscopy constitutes now an integral part in undergraduate chemistry education, while in recent years, its applications have been extended to biology and medicine. Concentrating on the structure of matter, NMR has made an invaluable contribution to the identification and structural studies of complex biomolecules, such as proteins, in the liquid (aquatic) phase. On the other hand, conceptually, NMR is a very demanding subject to teach and learn, requiring both basic and advanced concepts and methods of physics. In their contribution, **Ioannis Gerothanassis**, **Anastassios Troganis**, **Vassiliki Exarchou**, and **Climentini Barbarossou** present a student-oriented approach, which enhances the ability of students to comprehend the basic concepts of NMR spectroscopy and the NMR spectra of various nuclei. The origin of chemical shifts, coupling constants, spin relaxation and the nuclear Overhauser effect (NOE) are discussed, and their relation to molecular structure is provided. In addition, a wide range of applications of NMR spectroscopy is presented, including exchange phenomena, structural studies of complex biomolecules in solution and in the solid state, applications to food analysis, clinical studies, and NMR as a microscope and magnetic tomography.

### *The time dimension in chemistry at the electrical level: Quantum chemical kinetics*

In the preface to last year's theme issue (Tsaparlis, 2001), mention was made of Jensen's (1998) scheme for the logical structure of chemistry. According to the author, the most complicated area of theoretical chemistry is the treatment of chemical kinetics at the electrical level. Of great importance is the study of reaction rates in condensed phases, since the majority of chemical and biochemical reactions take place in the liquid phase. The theoretical-computational treatment of reaction rate constants in condensed phases is a field of active research, to which **Raymond Kapral** and his research group have contributed greatly. In this issue, with **Styliani Consta**, they review this conceptually and mathematically complex theory. First they visit the topic of treating rate coefficients with classical mechanics. Condensed-phase reactions have been often been dealt with in classical terms: an interesting application of aqueous droplets loaded with several sodium ions is provided. There are reactions, such as the conformational changes of the ammonia molecule (due to the tunnelling effect) or the proton and electron transfer processes, where quantum mechanics

must be applied. A lot of research then is devoted to the study of quantum rate coefficients. On the other hand, there are very important reactions in solution (especially for biological systems), occurring by proton or electron transfer and the hydrogen bond, that strictly should be treated quantum mechanically, that is, by solving the time-dependent Schrödinger equation for the entire system (solvent and reacting system). This is not practical due to the large number of degrees of freedom. A mixed approach is then used in which the system is separated into two subsystems, the one treated quantum mechanically, the other classically.

### REFERENCES

- Jensen, W.B. (1998). Logic, history, and the chemistry textbook. I. Does chemistry have a logical structure? *Journal of Chemical Education*, 75, 679-687.
- Tsaparlis, G. (2001). Molecules and atoms at the centre stage (Preface to the first theme issue on structural concepts). *Chemistry Education: Research and Practice in Europe*, 2, 57-64.  
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