

Models, Mysteries and Magic of Molecules

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PREFACE

A century ago Chemistry was the queen of the sciences. Today Molecule is king.

Many of the exciting scientific theories of a hundred years ago originated with chemists such as Stoney, who postulated the existence of electrons, and those who formulated the periodic law of the elements. Van't Hoff, the father of stereochemistry, was also the first Nobel laureate. A chemist named van den Broek introduced the concept of atomic number, and another chemist named Harkins postulated the neutron and first mooted the idea of a mass defect as the origin of nuclear binding energy. Not only the chemists of the era but also the subject area of chemistry produced spectacular theoretical advances. The physicist Lord Rutherford, who is purported to have stated

“in science there is physics and stamp collecting”

must have been mortified to have his research recognized with a Nobel prize for chemistry.

A hundred years on, significant progress in chemistry arises only at the bench, through the synthesis of high T_c superconductors, nanomaterials, ‘bucky balls’ and other magical molecules, with little appreciation of the underlying theories. Chemistry is no longer a priority as a career option, and the emphasis is shifting constantly towards molecular sciences. Students, who vote with their feet, sense that, through lack of theoretical innovation, chemistry is becoming a sterile science. By comparison, models, mysteries and magic abound in molecular sciences.

It was demonstrated more than sixty years ago [1] that a major intramolecular migration of chiral groups, during Beckmann rearrangements, occurs with retention of chirality. A reasonable mechanism to account for this amazing effect has never been formulated; like the optical activity of chiral molecules, it is simply accepted as a fact of life, not deserving of further theoretical analysis. The reason for this indifference is not difficult to find. The models of chemical bonding, enthusiastically embraced during the twentieth century, might seem plausible, but they lack the authority to address fundamental issues. The soporific that stupefied chemistry is the lore of orbitals. By now it has been so thoroughly entrenched in the world's textbooks for undergraduate chemistry and in computational models, widely accepted as the ultimate in chemical theory, that it borders on the futile

to resist its use. A German-language text on Elementary Quantum Chemistry [2] laments (my translation),

1. “Modern quantum chemistry allows us to calculate bond energies (more correctly: dissociation energies) and bond lengths (more correctly: internuclear separations), but does not tell us what the chemical bond ‘actually’ is. We are not even sure whether it is stupid or intelligent to enquire into the nature of chemical bonding.
2. The definition or characterization of orbitals found in many textbooks for chemistry in secondary school is a scandal. It is an insult to our youth to confront them with such trash”.

Another expert [3] remarks

In reality, chemical bonding is a molecular property, not a property of atomic pairs.

The chemistry community finds itself burdened with an operational theory, based on outdated and discredited classical concepts, and without predictive power in the quantum world of the twenty-first century. Few fascinating observations documented in this volume can be explained convincingly in terms of orbital jargon. Topics such as polymorphism, nanomaterials and biopolymers are of immense commercial importance, but scientifically poorly understood. These phenomena are as mysterious as crystal growth or the structure of snow flakes, quasi crystals or viruses. To state that interactions responsible for biological modifications of life, the circadian clock or the colour of cooked lobster are of chemical origin is tantamount to an admission of complete ignorance. Models that feature in the description of chemically more familiar systems such as transition-metal complexes, host-guest interactions and solvation are largely empirical and rely on experimental results obtained with diffraction of X-rays and neutrons.

Aspects of all these various topics were discussed at the fifth international *Indaba* workshop of the International Union of Crystallography at Berg-en-Dal, Kruger National Park, South Africa, 20–25 August 2006. In most instances the analysis terminated before a fundamental interpretation of the results, because there is no fundamental theory of chemistry. As all chemical interactions are mediated by electrons it is clear that such a theory must be quantum-mechanical. The only alternative is a phenomenological simulation of chemical processes with empirical classical models. There is no middle ground.

The classical approach appropriately known as molecular mechanics has been used with conspicuous success to predict molecular geometries, chemical reactivities and even magnetic, electronic and spectral properties of molecular systems. Molecular mechanics functions with no intention or pretence to elucidate the essential nature of molecules; it applies concepts that pertain to the nineteenth-century classical model of the molecule, *i.e.*, bond length, bond order, force constant, torsional rigidity and steric congestion. Transferable numerical values are empirically

assigned to the corresponding parameters to ensure that minimization of steric energy converges to observed molecular structures. Any remaining discrepancies are assumed to arise from quantum-electronic effects, incorrectly simulated with a classical model. Additional parameters to compensate for particular effects such as planarity of aromatic rings or Jahn-Teller distortions are then introduced.

There is no evidence that any classical attribute of a molecule has quantum-mechanical meaning. The quantum molecule is a partially holistic unit, fully characterized by means of a molecular wave function, that allows a projection of derived properties such as electron density, quantum potential and quantum torque. There is no operator to define those properties that feature in molecular mechanics. Manual introduction of these classical variables into a quantum system is an unwarranted abstraction that distorts the non-classical picture irretrievably. Operations such as orbital hybridization, LCAO and Born-Oppenheimer separation of electrons and nuclei break the quantum symmetry to yield a purely classical picture. No amount of computation can repair the damage.

The previous statement does not imply that the computational chemistry of the previous half century is all wasted effort; it simply means that what became known as *quantum chemistry* is based on classical mechanics, without necessarily invalidating the useful results that flowed from this pursuit. This conclusion should not be read as an insult, but as an encouragement to renew the quest in a true spirit of quantum theory, which is bound to produce unthought-of new insights into the mysteries and magic of molecules. A modest start has been made [4] in recognizing the power of quantum potential to explain the stability and reactivity of atoms and molecules and of quantum torque as the agent responsible for molecular shape, torsional rigidity and optical activity. In principle, the same approach might produce a winning strategy to solve the mysteries of intramolecular rearrangement, photochemistry, protein folding and the unwinding of DNA.

The book is aimed at students of chemistry and general readers interested in molecular sciences, structural chemistry, the fundamental basis of the life sciences, and computational chemistry. Not only is it intended to highlight some of the many challenges in molecular science, but also it serves as an introductory text for students who might subsequently wish to specialize in any of these fascinating fields. Written at a level for advanced undergraduates and graduate students in chemistry, most concepts are expected to be familiar to readers with a first degree in chemistry and modest expertise in mathematics and physics.

The material is organized under four main headings. The first section includes specialized methods used in the study of molecules, followed by partially solved molecular mysteries and poorly understood phenomena with a magical quality. The final section treats various models that might contribute to an improved understanding of molecular behaviour. The confusion in chemistry is largely due to an indiscriminate mixing of classical and quantum concepts and the distortion of the latter by the science writers of the twentieth century, more interested in sensation than science. These Proceedings might assist to eliminate some confusion and show a new direction for theoretical chemistry.

I wish to express my sincerest appreciation to all authors for producing their contributions under serious temporal constraints, to J.F. Ogilvie for editing all texts under even greater constraint, and to Thereza Botha for organizing more than a workshop and the production of these Proceedings.

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4. J.C.A. Boeyens, New Theories for Chemistry, 2005, Elsevier, Amsterdam.

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