The Theories of Chemistry

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Preface

At the end of the nineteenth century chemistry was at the cutting edge as a theoretically well-founded experimental science. The most advanced and controversial physical theories of the day had their origin in chemical research, which concerned itself with all aspects related to the nature and constitution of matter. The theories of electrons (*sic*), atoms and molecules were the working models of practising chemists. Optical activity, like other forms of spectroscopy in its infancy, was the pursuit of analytical chemistry.

The theoretical chemistry of a hundred years ago comes across as an exciting, vibrant activity, hotly disputed at the laboratory benches of the leading research schools. By comparison, present-day chemistry has very little by way of an innate theory to stimulate the experimentalist. Instead, the necessity of specialization dictates that theoretical pursuits be performed elsewhere and stimulate chemical research by some two-way flow of information. This cross-fertilization however, has dwindled gradually until it finally disappeared during the latter half of the twentieth century. That is why it is not uncommon today, to find synthetic chemists designing new advanced materials such as nano-structures or superconductors, in blissful ignorance of the basic theories that determine the behaviour of these systems.

Symmetry is another example. Its importance is constantly emphasized, but rarely examined beyond the concepts of point-group symmetry, applied to molecules and orbitals. The implications of translational symmetry and continuous symmetry groups in chemical contexts, are simply ignored, and the fundamental significance of conservation (or non-conservation) laws never appreciated. Consequently, chemical thermodynamics remains a sterile recycling of yesterday's formulae. It embodies nothing more challenging than distinguishing between equivalent energy functions, without the guidance of basic theory.

Reaction mechanisms are formulated strictly in terms of time-like events, while the rest of the scientific world marvels at the wonders of non-local correlations and teleportation. Interpretative chemistry still operates in terms of empirical concepts such as electronegativity and molecular shape, commonly said to be without theoretical underpinning. Admittedly, there are those who pontificate against the use of such classical concepts, while remaining singularly unsuccessful themselves to account for the predictive powers of these ideas, or to provide alternatives that are theoretically more soundly based.

Despite a lot of posturing the electron of chemistry is still the electron of Lewis [1], untouched by quantum electrodynamics. The lip service paid to wave mechanics and electron spin does not alter the fact that the curly arrow of chemistry signifies no more than an inductive redistribution of negative charge. A fundamental theory of electrode processes is still lacking. The working theories are exclusively phenomenological and formulated entirely in terms of ionic distributions in the vicinity of electrode interfaces. An early incomplete attempt [2] to develop a quantum-mechanical theory of electrolysis based on electron tunnelling, is still invoked and extensively misunderstood as the basis of charge-transfer. It is clear from too many statements about the nature of electrons[1] that the symbol e is considered sufficient to summarize their important function. The size, spin and mass of the electron never feature in the dynamics of electrochemistry.

Instead of a theory to elucidate the important unsolved problems of chemistry, theoretical chemistry has become synonymous with what is also known as *Quantum Chemistry.* This discipline has patently failed to have any impact on the progress of mainstream chemistry. A new edition of the world's leading Physical Chemistry textbook [4] was published in the year that the Nobel prize was awarded to two quantum chemists, without mentioning either the subject of their work, nor the names of the laureates. Nevertheless, the teaching of chemistry, especially at the introductory level, continues in terms of handwaiving by reference to the same quantum chemistry, that never penetrates the surface of advanced quantum theory.

The natural enabling theories behind chemistry have been left dormant for so long that they are no longer recognized as part of the discipline. It is rarely appreciated that the theories of relativity, quantum phenomena and

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[1]From a modern textbook [3]: Electrons are too weak in energy to climb the potential-energy hill at the metal-solution interface. Nevertheless, their quantum qualities permit the electrons to sneak through the barrier in ghostlike fashion provided there are hospitable acceptor states for the electron, *i.e.*, welcoming vacant energy levels in hydrated hydrogen ions.

fields, are as fundamental to chemistry as to physics. Like the elementary particles of physics, the objects of chemistry are best defined in terms of gauge fields, symmetry breaking and the structure of space-time manifolds.

It is futile to hope for physicists to apply their modern views to chemical phenomena, or even expect these concepts to emerge in user-friendly form. It is incumbent on the chemists themselves to incorporate the ideas of advanced quantum mechanics, relativity and field theory into the canon of chemistry. This procedure requires recasting of the formalisms in different terms; into the language of chemistry.

The theme of this book is not a reformulation of theoretical physics, but an attempt to identify the theoretical ideas fundamental to chemistry and recast them in more familiar style. There is no doubt but, that the chemist of this century will have to be familiar with the concepts that appear to be new, even alien, at present. The philosophy that inspires this work is that specialization in science is detrimental in the long term. Specialization may well stimulate productivity in the short term, but this productivity becomes sterile in the absence of innovation, that depends on cross-pollenation, or the adoption of new theoretical models.

The subject area of chemistry is substances and their interaction or evolution, which means a study of matter and time. A clear understanding of time avoids the necessity of statistical arguments when applying mechanics directly to microsystems in chemistry. Delving into the nature of matter brings into focus chemically active substances such as molecules, atoms and electrons, ranging from classical to quantum-mechanical objects. To probe their interaction requires insight into the nature of fields and photons. These issues, approached from a chemical perspective and with emphasis on understanding rather than simulation, will be addressed in a future volume.

The sequence in which to introduce the range of topics presents a problem. To end up with a theory of chemistry based on relativity and quantum mechanics a minimum background in physical chemistry, mechanics and electromagnetism is essential, which in turn requires a knowledge of vectors, complex numbers and differential equations. The selection of material within the preliminary topics is strictly biased by later needs and presented in the usual style of the parent disciplines. Many readers may like to avoid some tedium by treating the introductory material only for reference, as and when required.

The book contains very little original material, but reviews a fair amount of forgotten results that point to new lines of enquiry. Concepts such as *quaternions, Bessel functions, Lie groups, Hamilton-Jacobi theory, solitons, Rydberg atoms, spherical waves* and others, not commonly emphasized in chemical discussion, acquire new importance. To prepare the ground, the book has been designed as a self-contained summary of the essential theoretical background on which to build a modern theory of chemistry.

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