

## Does the nature of the chemical bond matter?

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There has been much recent discussion about not only the nature of the chemical bond but also of the relevance of this topic in chemical curricula of secondary schools and colleges, and even in tertiary institutions at introductory levels. These questions are indeed timely for we have now acquired much information from both experiment and theoretical calculations to enable the generation of a quantitative description of molecular phenomena to an extent previously impracticable. During this century, since the atomic nature of macroscopic matter became accepted by all reputable chemists and physicists, various theories and models of the chemical bond have in rapid succession followed, if not entirely replaced, one another, as sensitive techniques in the laboratory combined with the power of increasingly sophisticated and extensive calculations to yield new knowledge. Chemists have optimistically, if naively, interpreted this information in an endeavour to gain insight into the binding between atomic centres in molecules and crystals.

An early but enduring notable development was the putative role of a pair of electrons: four such pairs, whether shared jointly between two atomic centres or associated with a single centre, formed the basis of the octet of Lewis and Langmuir; even if their model is seldom taught explicitly, it lurks nevertheless in the background both within the context of the designation of Lewis acids and bases and in the distinction between ionic, covalent and coordinate-covalent bonds. As an alternative point of view of a double quartet instead of four pairs of electrons to comprise this magic shell of electronic stability yields enhanced insight into intramolecular and crystal structures,<sup>1</sup> even this well entrenched idea ought not to be regarded as sacrosanct.

Consistent with the nuclear atom demonstrated in Rutherford's experiments, Lewis's model of electron pairs appeared more realistic than that of sticks between balls according to the first tentative notions about molecular structure from Couper, Kekule, Dewar, van't Hoff and Le Bel during the third quarter of the nineteenth century. During the period 1924–1927, in which quantum mechanics appeared, a few chemists immediately sensed that this mathematical method might provide a means to define quantitatively the nature of chemical binding.<sup>2,3</sup>

One such person who exerted, and who continued to attempt to exert until the end of his long life, a major influence on the chemical interpretation of the interactions between atomic centres was Linus Carl Pauling (1901–1994); following his already significant research on the structure of crystals, Pauling was endowed with a mind prepared to absorb both the mathematical methods and some underlying physical principles for the purpose of a creative outburst that led within a few years to a series of papers and then a book,

'The more that we understand science, the more artificial become the traditional boundaries between chemistry and biology, chemistry and geology, chemistry and physics ... . The traditional boundaries within chemistry have become hopelessly irrelevant to the practice of chemistry in any but the most primitive or historical conditions.'

*The Nature of the Chemical Bond.*<sup>4</sup> Robert S. Mulliken, another pioneer in the application of quantum theory to chemical problems, described Pauling as a 'master salesman and showman';<sup>5</sup> since antiquity, such attributes have been associated with promoters of shoddy goods. If Pauling could cast a spell on his audience in the manner of an evangelist at a religious revival, similarly culminating in emotional conversion to a new faith, Mulliken was in contrast perhaps the worst lecturer (among notable scientists) that anybody would have suffered to hear; not only his verbal presentations but also his papers remain derisory models of obfuscation and circumlocution, despite the fact that some sensible content lies obscured beneath the scarcely penetrable surface of jargon. Pauling (and others) developed the valence-bond approach that even in 1992 he maintained to be worth retaining in the syllabus of general chemistry,<sup>6</sup> although he had no hesitation in deprecating for this purpose the method of molecular orbitals that Mulliken (among others) developed. These developments originated during the period 1930–1955, in which Europe was preoccupied with first political chaos, then war and recovery from the consequent general devastation; within this era, by default the schools of thought about chem-

ical binding from the United States became dominant. These ideas eventually diffused globally by means of textbooks from the US that effected the cultural domination of chemistry in (at least) the English-speaking world in the same way that, propelled by aggressive marketing, jazz and 'rock' infested 'popular' music; the influence was efficiently reflected in textbooks in other languages as uncomprehending authors and translators hastened to outdo each other in engraving and embellishing the concept of the chemical bond as the central theme of chemistry. The valence-bond and molecular-orbital pictures were pressed by their champions, teachers and professors at various levels, onto the hapless youth of developed and developing countries alike in about the same way that two major brands of cola beverages displaced less harmful drinks, serving to enrich the American authors and publishers practising this imperialism in science education as students everywhere were correspondingly deprived of the nourishment of practical chemical knowledge.

According to the existing paradigm, the most important content of chemistry courses must be the concept of chemical binding, presumed to be solidly founded on quantum mechanics in general and Schrödinger's equation in particular (implicitly or explicitly, depending on the level of the treatment). As the late Marshall McLuhan (University of Toronto) asserted in another context, the medium became the message. Despite the formal differences between valence-bond and molecular-orbital approaches, Schrödinger's equation was the essential common ingredient, like caffeine in the cola beverages. Only recently have some science educators recognized that there have always existed alternative forms of quantum mechanics; the wave function, known in some circumstances as an orbital, that is the solution of some Schrödinger equation, is entirely absent from matrix mechanics for instance. Because this wave function or orbital is an artifact of a particular mathematical method, namely, wave mechanics due to Schrödinger, it can never have a physical existence; in matrix mechanics one has instead a matrix of (in general) infinite order that in the appropriate calculation eventually produces abso-

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lutely equivalent values of some observable property, indeed arithmetically equal if the calculation is made at the same level to yield numerical results for a particular atomic or molecular system. First Schrödinger in a formal way, then Pauli, Dirac, von Neumann and others in increasingly precise treatments proved that wave mechanics and matrix mechanics are absolutely equivalent. Under these conditions, what sense does it make to claim that methane has a certain molecular structure — tetrahedral — because of an arbitrary collection of orbitals that might compose a basis set for some prospective mathematical calculation according to some arbitrarily selected method? For all but a few of the innumerable authors and professors who have unhesitatingly preached this heresy, the actual calculation is hypothetical.

Ironically, the chemists and physicists who pressed these and other fallacious ideas upon unsuspecting teachers and students of chemistry overlooked two further facts. One is that electrons are fundamentally indistinguishable. 'When this principle is taken into account it becomes nonsense to distinguish between K and L electrons, core and valence electrons and so on.'<sup>7</sup> The so-called Valence-state Electron-pair Repulsion theory perpetuates this fallacy. This theory is a mistaken attempt to avoid the orbital approach as an explanation of molecular structure; its proponents have unfortunately become trapped in the same pitfalls of their own rhetoric in claiming to be able to distinguish between electrons, to differentiate between bonding electrons, lone pairs, etc. Although this approach appears to have some success in 'predicting' the shape of simple molecules — actually the knowledge of that shape is crucial in deciding how to apportion the electrons between (for instance) bonding and lone pairs, an instance of circular reasoning — many examples of the failure of this VSEPR theory are documented.<sup>8</sup> In any case this approach lacks theoretical justification.<sup>9</sup>

The second mistake is the failure to recognize that according to rigorous quantum mechanics, a molecule, just like an atom, has extension in neither space nor time; it is merely a set of energy levels. To seek a quantum-mechanical basis for molecular structure is therefore illogical and inconsistent. Molecular structure is a classical concept, originating in chemical properties based on macroscopic experiments during the nineteenth century. Molecular structure may be introduced into — indeed imposed upon — quantum mechanics according to the prototypical treatment by

Born and Oppenheimer.<sup>10</sup> By this means we become enabled to undertake quantum-mechanical calculations of molecular structure. There appear to emerge from such computations, which reflect perhaps the raw speed and power of modern computers more than the beauty of the mathematical basis, striking predictions about structures of unknown molecular species. If we examine objectively these methods that are misleadingly described as *ab initio* (according to first principles), we find that the algorithms contain in significant number parameters that are either taken directly from experiment or have been assigned optimum values according to experimental criteria; these methods are fundamentally little more than sophisticated and complicated means of interpolation and extrapolation, even if there are already many practical applications of such calculations in design of pharmacologically active substances and routes of organic synthesis. No sensible chemical educator would dare to suggest that the underlying detailed quantal theories and their implementation in specific mathematical methods be learned by pupils in secondary schools or students of introductory chemistry in tertiary institutions. How can any educator seriously propose that young people in their first exposures to chemical science should take the presumed principles and methods on faith as a basis of comprehending the nature of chemical binding? The latter approach owes more to alchemy and superstition than to the scientific method. Another aspect of interest is that, although these molecular-orbital calculations *ab initio* appear fairly reliable near the equilibrium geometries of molecular structures, they become almost impracticable for larger internuclear distance characterizing the condition of bond breaking in the course of a chemical reaction; this region of breaking, and forming, of chemical bonds is the essence of chemistry — fundamentally the study of chemical change.

The more that we understand science, the more artificial become the traditional boundaries between chemistry and biology, chemistry and geology, chemistry and physics, and so on. The traditional boundaries within chemistry — analytical, inorganic, organic, physical and theoretical divisions — have become hopelessly irrelevant to the practice of chemistry in any but the most primitive or historical conditions. The importance of chemistry and its justification as a component of modern secondary education do not derive from its being a vehicle for logical thinking:

indeed the currently established presentation of chemistry as arising from Schrödinger's equation (first atomic orbitals and the aufbau principle as the basis of the periodic table, then molecular orbitals or hybridization as the basis of molecular structure) is fraught with logical fallacies, to which I have already alluded.

The justification of the study of chemistry in secondary schools and as supporting courses in post-secondary institutions is not the intrinsic value of chemistry but rather the inevitable relationships between chemical properties and reactions and every other aspect of human existence and activities. The chemical curriculum should reflect not merely a subject orientation but a career orientation and the importance of real chemical phenomena (not hybridization and electronegativity, for instance, but chemical reactions) in all aspects of our daily life. The method of teaching must be altered from being orientated to the convenience and interests of the teacher to what is truly useful and meaningful for the pupil and student in the context of their lives and communities. How many teachers find solubility and solubility products to be boring topics? These topics are extremely important in the processing of mineral deposits in South Africa, for instance. These same teachers are doubtless susceptible to endless fascination about orbitals (or the equivalent empty VSEPR concepts) and the shapes of molecules, but what good does that misinformation do to the pupil who faces the possibility of mixing incompatible commercial bleaching solutions for the purpose of cleaning domestic drains? The teaching aids are undergoing a process of transition, from chalk and black boards, which have unfortunately largely supplanted the practical classes and lecture demonstrations even in developed countries, to audio-visual materials and computer software. Among the first applications of the latter were unfortunately illustrations of 'shapes' of nonexistent atomic and molecular orbitals — under these unthinking computer programmers, the paradigm triumphed over the reality.

Chemistry is the field of basic science most strongly associated directly with an industry, the chemical industry, as well as being an essential component of many other industrial activities. Every citizen needs a basic chemical knowledge in order to make informed decisions about consumption of goods, about political choices in elections in relation to industrial development, and about simply the style of living in a finite world. This basic education

## Extinction of the river pipefish *Syngnathus watermeyerii* in the Eastern Cape Province, South Africa

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The river pipefish *Syngnathus watermeyerii* (Fig. 1) was first recognized as a species under threat in the 1987 South African Red Data Book on fishes.<sup>1</sup> That book described the status of *S. watermeyerii* as 'Indeterminate-Vulnerable' and recommended that an investigation be undertaken to 'establish the status and conservation of the river pipefish'. This species was known only from the Bushmans, Kariega and Kasuka estuaries (Fig. 2), usually in association with submerged aquatic macrophytes. The last known specimens were collected in 1963, which was also the year in which the species was described by Professor J.L.B. Smith.<sup>2</sup> The longnosed pipefish *Syngnathus acus* occurred sympatrically with *S. watermeyerii* in estuarine eelgrass (*Zostera capensis*) beds, with the former species still common within these habitats.<sup>3</sup>

Between 1989 and 1992 intensive searches were conducted in the Kariega, Bushmans and Kasuka estuaries to find surviving populations of *S. watermeyerii* but none was recorded.<sup>3</sup> According to the 1994 IUCN Red List of Threatened Animal,<sup>4</sup> *S. watermeyerii* is officially extinct (category Ex), but it should have been listed as extinct? (category Ex?) since 50 years have not elapsed since the last specimens were collected in the wild.

Can we identify any cause(s) which may have tipped the river pipefish into extinction? Although speculative, it would appear that changes in freshwater supplies to the estuaries may have been responsible

for this disturbing event. Catchment mismanagement within the Bushmans and Kariega systems, particularly the absence of environmental freshwater allocations from dams and other impoundments, has resulted in the estuaries becoming deprived of essential freshwater pulses.<sup>5</sup> These pulses provide nutrients which facilitate phytoplankton development within the estuaries and, together with particulate organic material brought down by the rivers, support the zooplankton community on which pipefish, especially the newly released larvae, depend for food. Marked reductions in zooplankton stocks, arising from depleted pelagic food resources, would have placed additional survival pressures on a fish species which was already exceedingly rare.

The available evidence from preserved specimens collected in 1963 suggests that *S. watermeyerii* was a spring breeder, which, based on historic rainfall patterns in the catchment areas of the Eastern Cape, would have coincided with pulses of fresh water entering the estuaries of the region. However, in recent decades this is precisely the season when increased evap-

oration and lack of freshwater pulses due to impoundments has caused hypersaline conditions ( $>40 \text{ g kg}^{-1}$ ) to develop in the upper reaches of both the Bushmans and Kariega estuaries.<sup>6</sup> It would appear therefore that the prolonged absence of river inflow, particularly during the breeding season when elevated food resources are required, may be directly or indirectly responsible for the extinction of *S. watermeyerii*.

Simberloff<sup>7</sup> distinguishes between processes that make populations rare in the first place (ultimate causes) and processes that finally cause the extinction once populations are already small (proximate causes). Frequently, the ultimate causes result in reduced species' ranges and make the remaining populations more vulnerable to the proximate causes.<sup>8</sup> In the case of *S. watermeyerii*, the ultimate cause(s) of its restricted distribution to three Eastern Cape estuaries is difficult to determine. It should be noted that similar habitats and environmental conditions are present in a number of other systems in the region (e.g. Swartkops and Krom) but the river pipefish has never been recorded beyond the confines of the Bushmans, Kariega and Kasuka estuaries. An indication of the suitability of the Swartkops and Krom estuaries for pipefish is provided by the fact that *S. acus* is relatively common in both systems.<sup>9,10</sup> The probable proximate cause of the extinction of ⇨

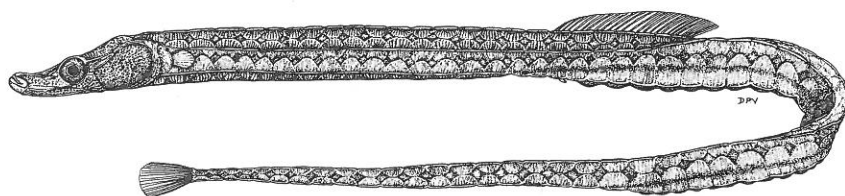


Fig. 1. The river pipefish *Syngnathus watermeyerii* Smith, 1963 (illustration by Dave Voorvelt).

⇨ in chemistry is the responsibility of the secondary schools, and any content of orbitals or kindred fallacies in their curriculum is not only wrong but also precludes attention to more meaningful and helpful material. Finally, chemistry is not separate or distinct from biology as anybody with a slight acquaintance of biochemistry and molecular biology must agree. Better than ever before, one can now recognize that chemistry is the central science: biological and geological processes reflect the basic underlying chemical phenomena, and all physical properties and phenomena at energies within the range of common experience are affected

or even dominated by the chemical nature of the materials. In the planning of science curricula for secondary or general post-secondary education, one is strongly recommended to think not of chemistry in its traditional isolation but of the science of materials and chemical processes that underpins every aspect of our scientific activity and daily life.

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