Fact and fiction about the structure of molecules and matter

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Whether or not the shapes and structures of molecules and matter are formally included in the chemistry curriculum of secondary schools or colleges, it is important that a teacher of chemistry recognizes what is correct and what is myth in this subject that may be considered by educators of chemistry at the post-secondary level to be at the core of our discipline. As a result of the many qualitative ideas and concepts that have been developed over the years in relation to the nature of the chemical bond and to the structure of molecular matter, there is much material found in textbooks that is poorly understood, even by their authors. The objective of this article is to indicate what aspects of these ideas are truly correct, and thus acceptable in the modern contexts of chemistry in general and chemical education in particular.

The modern period of chemistry must be considered to begin with the atomic hypothesis of Dalton about 1807. The first enduring notions of molecular structure followed about a half century later. Thus was formed the classical idea of a molecule as a fairly rigid arrangement of atoms in three-dimensional space; between certain adjacent atoms a line was drawn to indicate a chemical bond, like a stick between balls. In the decade between 1910 and 1920, the first relatively accurate determinations of molecular and crystal

structure were achieved for comparatively simple substances, by means of infra-red spectroscopy and X-ray crystallography. Thus significant chemical structures were determined before the development of quantum mechanics.

When we consider quantum theories, we must bear in mind that many such theories exist. An important consequence of this plurality of theories is that any feature of a particular theory that is not directly observable must be regarded as an artefact of that particular approach, not a general truth.

Two enduring theories of quantum mechanics are known collectively as pioneer quantum mechanics. These are the matrix mechanics due to Heisenberg, Born and Jordan and the wave mechanics due to Schrodinger. As the name implies, the former is based on the properties of matrices, whereas the latter involves differential equations. The differential operators in these equations must have an operand; this is the wave function Ψ. The solutions to the differential equation for the system of the one-electron atom or one-electron molecule, which constitute the algebraic expressions (the values) of Ψ as a function of the spatial coordinates, are known as atomic or molecular orbitals respectively. Consistent with the rubric above, because these orbitals or wave functions need have no role in the solutions of the same systems according to matrix mechanics, then these orbitals must be considered as mathematical artefacts of one particular mathematical approach, specifically the calculation of the energy values of the given system within the Schrodinger theory.

A further consequence of quantum theory is that if an unnatural distinction between electrons and nuclei is not imposed, i.e. if all particles in an atom or molecule are treated equivalently according to either pioneer quantum theory, then there is no resulting molecular structure, because the integrations of the differential equations (in the commonly applied Schrodinger procedure) are

carried out over all coordinates. Thus according to rigorous quantum mechanics, a molecule has no extension in space or time. Therefore even to seek a quantum-mechanical explanation of molecular structure is logically inconsistent.

On the other hand, the quantum-mechanical procedures to "predict" molecular structure are well developed and currently achieve moderate accuracy in the best conditions. However in the practice of these procedures, certain experimental features are included implicitly. One must absolutely not be deluded into thinking that any present theory operates entirely from 'first principles'. In a thoughtful essay titled "The invincible ignorance of science", Pippard (1988) (Cavendish Professor of Physics in Cambridge University) has pointed out that even a single helium atom cannot be predicted purely mathematically from the starting point of two protons, two neutrons and two electrons.

Already we have two reasons that we should not state that methane has a tetrahedral structure because of sp^3 hybridisation, namely that s and p refer to orbitals which are artefacts of the wave-mechanical approach, and that in any case such an explanation would be a "quantum-mechanical" explanation of a molecular structure that is inconsistent with quantum mechanics. If any further reason is desired, although quite redundant, then we can understand that even within the wave-mechanical approach there are various computational procedures; two in particular are the so-called valence-bond theory and molecular-orbital theory. The sp^3 description is in fact an artefact of the valence-bond method. According to the molecular-orbital method; whether we initiate our calculation with four sp^3 hybrid orbitals on C, or three sp^2 orbitals plus a separate p orbital, or two sp orbitals plus two separate p orbitals, or even just (unhybridised) atomic s and three p orbitals, we obtain on completion of the calculation precisely the same structure (tetrahedral), with the same C--H bond lengths

(approximately correct by comparison with experiment) and the same energy. It is now generally understood by knowledgeable quantum chemists, although unfortunately not yet by authors of textbooks of general, inorganic and organic chemistry and by mere professors who teach such courses in universities, that hybridisation cannot explain the shapes of molecules (McWeeny, 1979; Murrell, Kettle and Tedder, 1978).

A further common fallacy in relation to molecular structure is that atoms exist within molecules. If we consider the picture of electron density obtained by means of X-ray diffraction experiments on crystals, or the corresponding electron diffration experiments on dilute gases, both being classical experiments in which no knowledge of the quantum states of the molecules is obtained, then it should be clear that there is a continuous distribution of electron density; there are no sharp discontinuities at the edge of one atom, or one ion in an ionic crystal such as NaCl. A molecule contains only nuclei and electrons, not atoms, and certainly not orbitals!

Because molecular structure is a classical concept, we might seek classical theories to describe it. One such theory was developed over the years by Sidgwick, Powell, Nyholm and Gillespie; it is commonly referred to by the initials of its name "Valence-Shell Electron-Pair Repulsion". Not only are the predictions of this theory prone to error, but also its basic premises of more or less equivalent localised electrons (as bonding pairs or lone pairs) are unjustified. After a quantitative assessment of the foundations of this theory, Roeggen (1986) concluded that "the VSEPR model can no longer be considered a valid framework for the discussion of molecular equilibrium geometries", that is, the [geometric] structure or shape.

In conclusion, we can understand that molecular structure is a classical concept, and that the structural properties of a given molecule may be determined experimentally or calculated according to

some empirically based procedures. Why does a given molecule have a certain structure? Why are there nine planets in our solar system? Such questions are theological, thus beyond the domain of science. What is more important for all chemists and students of chemistry to bear in mind is that chemistry is the study of chemical reactions and the chemical properties of matter. Apart from atmospheric gases, in most common materials the concept of an (isolated) molecule has little or no meaning. Think of salt crystals, liquid water or aqueous solutions, metals, natural wood and similar materials for instance. What makes chemistry the central science are not the molecules but the materials. Molecules and substances are categories of different logical types, as are also molecules and mathematical functions such as orbitals; a category fallacy is to treat such different types on a par. As a science of materials, chemistry is the basis of an industry. The chemical properties and reactions of materials, not molecules, are a proper subject of study because of the importance of this matter in our life.

References

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