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INVITED LECTURE BY DR MICHAEL JEWESS

The old quantum theory to quantum mechanics and chemical bonding in the first half of the twentieth century

(mainly in small molecules)

Chemists during the nineteenth century, above all after the International Chemical Congress in Karlsruhe of 1860, developed pictures of many molecules that are still regarded as correct today. They elucidated the topologies of molecules (which atoms were bonded to which), for instance Kekulé's ring structure of benzene. Even geometries in three dimensions were elucidated, such as tetrahedral geometries surrounding carbon atoms in many molecules. Chemists' results and those of physicists using the kinetic theory of gases overlapped to a modest degree, for instance in relation to the atomicity of molecules in gases and vapours.

In the early twentieth century, significant advances in physics and chemistry became more closely related, as indicated by the foundation of the Faraday Society in the UK and of the *Journal of Chemical Physics* in the USA. Understanding of the (electronic) nature of the bonds that combined atoms into molecules was a common endeavour of the two sciences.

The Bohr "planetary" model of the hydrogen atom and his electronic structures for atoms formed a basis for investigating the nature of the bonding between atoms within molecules; these structures included structures for the inert gases helium to radon, which had been isolated and characterised from 1894 onwards. The fact that the majority of molecules had an even number of electrons stimulated the concept of the electron pair shared between atoms to form a bond between them. In many molecules the bonding achieved for the participating atoms the stability of electronic structures identical with those of the inert gases, with two electrons in the case of helium and otherwise an outer octet. Detailed electronic structures of molecules were devised for a wide range of molecules culminating in Sidgwick's *The electronic theory of valency* of 1927 ("valency" meaning the capacity of an atom to form bonds with other atoms), which has been described as "a masterpiece of the old quantum theory", and many of the ideas in which survive in 2025. A significant problem had arisen with molecules for which a special form of electron pair bond[1] had to be devised if the outer octets were to be formed. To validate this special form, Sidgwick, following Sugden, made use of an unusually constructed and nowadays mostly forgotten molecular property, the "parachor". The expression for the parachor includes molecular weight, liquid surface tension, and liquid and vapour phase densities, with the surface tension term raised to the power ¼.

Also in 1927, Heitler and London presented a quantum-mechanical theory of the electron-pair bond. Pauling and others in the 1930s reinforced many earlier concepts of chemical bonding by quantum-mechanical calculation, and furthermore explained away some

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[1] The "dative" or "coordinate" bond: these terms from the 1920s are still in use in 2025. Pauling accepted the existence of these bonds physically but did not use this terminology.

of its anomalies. In 1939, Pauling presented quantum mechanical results without their proofs for the generality of chemists in his large and influential book *The nature of the chemical bond*. Pauling in 1939 had available far more physical data to support his conclusions than was available to Sidgwick in 1927 – from spectroscopy, dipole moment measurements, electron diffraction, and X-ray diffraction; the parachor had outlived its usefulness.

Pauling primarily considered a molecule in terms of electron-pair bonds between pairs of atoms, subject as necessary to “quantum mechanical resonance” (so that, for instance, if there were two equivalent ways of arranging the bonds, the real molecule would be represented by a linear equal combination of two respective hypothetical wave functions). This became known as the “valence bond” (VB) approach. Contemporarily, others developed the molecular orbital (MO) approach. Orbitals for the entire molecule were generated by linear combination of atomic orbitals, and the available electrons were allocated to these; this built in the possibility of bonding being delocalised over more than two atoms. By mid-century, the value of the MO approach was recognised, especially in relation to the treatment of molecules such as benzene. An important experiment supporting the treatment was made in 1954 at the privately-funded, short-lived Hickrill Chemical Research Foundation in the USA.