



# The theoretical schism in foundational chemistry: Lewis vs. quantum

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Received: 26 August 2025 / Accepted: 5 November 2025  
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## Abstract

Chemical bonding, structure, and reactivity are routinely taught and understood using a combination of classical Lewis theory and quantum chemistry. Both approaches are highly successful at describing and explaining many of the phenomena of chemistry, but they are also mutually incompatible. The aim of this paper is to elucidate, illustrate, and explain the issues.

**Keywords** Bohr atom · Lewis theory · VSEPR · Reaction mechanisms · Quantum chemistry · Spectroscopy · Philosophy of chemistry

## Introduction

There is a *fissure* in theoretical chemistry that causes real difficulties for school and university students, post-graduates, high school teachers, university lecturers and educators, chemical researchers, philosophers of science, and crucially for those scientists and engineers in other disciplines who need to know *some* chemistry. The *schism* occurred soon after the introduction of the Bohr model of the atom (Bohr 1913).

- On one hand: In 1916, the UC Berkley chemist G.N. Lewis published his paper *The Atom and The Molecule* (Lewis 1916), and in 1923, his short but highly influential book: *Valence and the Structure of Atoms and Molecules* (Lewis, 1923). These works – which build directly on the semi-classical Bohr shell model – introduced and developed the idea of the ‘*shared electron-pair covalent chemical bond*’, double and triple covalent bonds, electron pair acceptor/donor reaction chemistry, and more.
- On the other hand, in the nineteen twenties, physicists were rapidly moving on from the old quantum theory to the modern quantum mechanics (QM) of Heisenberg, Born,

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Schrödinger, Dirac and others, as discussed and developed at the 5th Solvay Conference on Physics in October 1927 and later. By the 1930s, physicists were routinely thinking in terms of quantum field theories, specifically quantum electrodynamics (QED).

During the subsequent 100 years, the central chemical topics of *bonding, structure, and reactivity* have been taught and understood in terms of both classical Lewis theory with its particle-like electrons and in terms of quantum mechanics with wave-like electrons and distinct energy levels.

Our concern is pedagogical. We are not implying that students of chemistry are ‘*taught incorrectly*’, although this may be true in part, as some physicists may suggest. The problem is that there are two incompatible theoretical approaches to understanding much of the science of chemistry. In one approach, the electron is considered an object: a small, countable, classical particle. In the other, the electron is a smeared-out wave-packet with quantum spin that moves in mysterious ways. The twin approaches are used throughout chemistry and those sciences that rely on chemistry to provide their researchers with rational explanations.

As students, we are taught that “*methane, CH<sub>4</sub>, is tetrahedral because the four bonding pairs of electrons in the carbon’s valence shell repel each other*”. This valence shell electron pair repulsion, VSEPR, approach is a 100% classical idea derived from Lewis methodology. We are also told that “*the carbon atom has the atomic orbital structure: 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>2</sup>*”, a nomenclature derived from the four principal quantum numbers of quantum theory.

The following text, taken from a UK university entrance exam specification concerning electron configuration (AQA 2017):

[Understand and be able to answer exam questions about] electron configurations of atoms and ions up to Z=36 in terms of shells and sub-shells (orbitals) *s*, *p* and *d*.

The term “*shells*” in the above text refers to the semi-classical Bohr atom with its particle-like electrons, while “*s*, *p* and *d* sub-shells” are quantum mechanical concepts associated with wave-like electrons.

Writing about the problem of modelling chemical structure and bonding, Gilli and Gilli (Gilli and Gilli 2000) sum up the central issue of this paper:

*From a philosophical point of view chemistry differs widely from physics because of the large use it makes of chemical models or chemical theories not derived from more basic physicomathematical theories but directly inferred from the whole of experimental data. Examples of this chemical approach to reality are Lewis’ electron pair theory, Pauling’s electronegativity, hybridization and  $\sigma/\pi$ -separability, acid–base theory... and Gillespie’s VSEPR theories. While the epistemological relevance of chemical theories is always under discussion, there is little doubt about their usefulness, because they can predict fairly well structure, energetics and reactivity of most molecules of practical interest.*

But surely, the Lewis and quantum approaches cannot be correct at the same time? Can we really have alternative facts in science? As an American physicist colleague once said to me: “*At grad school we attended chemistry classes where we were told things that could not possibly be true*”... or as Lewis Carol’s Red Queen put it: “*Why, sometimes I’ve believed*

as many as six impossible things before breakfast". Science commentators constantly discuss the crisis in physics and cosmology where quantum theory is deemed incompatible with Einstein's classical general relativity explanation of gravity. Yet, the similar issue in chemistry is seldom mentioned even though many more scientists, engineers, medical professionals, etc. require a working knowledge of chemistry than they do of the expansion of the universe, the nature of dark energy or the difficulties in formulating quantum gravity.

So, the questions are:

- How and why did this situation arise?
- Does the dual approach cause confusion when teaching students?
- What are the successes and limitations of the Lewis vs. quantum approaches for chemistry?
- What are the overlaps between the Lewis and quantum methodologies?
- Does it matter if we understand chemical science with two incompatible theories? Should we be pragmatic and continue to '*mix and match*', as we have for decades?
- Should we tell students that we are employing conflicting theories? Textbooks currently present both the Lewis and quantum ideas, but they do not point out their mutual incompatibility.

## The Bohr atom

Bohr's atomic model, presented by Niels Bohr and Ernest Rutherford in 1913 (Bohr 1913), consists of a small, dense nucleus surrounded by '*orbiting*' electron particles. Initially, this was deemed to be somewhat analogous to the structure of the Solar System, but with electrostatic rather than gravitational attraction. The Rutherford-Bohr atomic model had three postulates:

1. The electrons populate certain stable or '*stationary*' orbits around the nucleus without radiating any energy, contrary to classical electromagnetic analysis.
2. Stationary orbits are found at distances for which the angular momentum of the electron is an integer multiple,  $n$ , times the reduced Planck constant:, where values of  $n = 1, 2, 3, \dots$
3. Electrons can only gain and lose energy by jumping from one allowed orbit to another, absorbing or emitting electromagnetic radiation with a frequency  $\nu$  determined by the energy difference of the levels according to the Planck relation:

$$\Delta E = \Delta E_1 - \Delta E_2 = h\nu$$

The Bohr model's first success lay in explaining Rydberg's 1890 formula for the hydrogen atom's spectral emission lines and thus providing a justification for the fundamental physical constants used in the Rydberg analysis. Over the next half dozen or so years, Bohr's atomic model evolved rapidly: Moseley's X-ray work led to an understanding of the importance of the atomic number,  $Z$ , and so reinforced the Rutherford-Bohr model; thanks to Kossel, Langmuir, Bury and X-ray studies, Bohr's early rings became known as electron shells.

The shell model was able to qualitatively explain many of the previously mysterious atomic properties that had become codified in the late 19th century. From the perspective of the Seaborg periodic table formulation of the mid-1940s (the most common modern form of the periodic table):

- Across a period, atomic radii get smaller toward the right (Li to Ne) and become much larger at the start of the next period (Li, Na, K...).
- Every element on the last column of the table is a chemically inert noble gas, He, Ne, Ar, etc., with a full or complete Bohr shell.
- Atoms to the left of the periodic table are electropositive metals that tend to lose electrons ( $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$ ), while atoms to the right are electronegative non-metals that tend to gain electrons ( $\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$ ). Both cases give ions with ‘a complete shell’ or ‘octet of electrons’ that are isoelectronic with the corresponding noble gas.

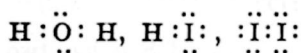
## Lewis theory

To the modern eye, G.N. Lewis’s 1916 paper (Lewis 1916) (Lewis 2024a, b) looks very strange with its diagrams of cubic atoms; some odd ideas about an atom’s ‘kernel’; the notion that in non-polar molecules the electrons ‘do not move very far from their normal positions’ but that in polar molecules the electrons are ‘more mobile’; and the redundant suggestion that electrons should be included in molecular formulae, i.e. that ammonia,  $\text{NH}_3$ , should be written as:  $\text{NH}_3\text{E}_8$ . Then, on page 770 we read:

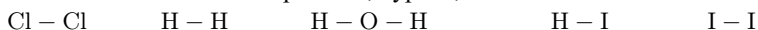
Thus we may write  $\text{Cl}_2$  as  $\text{Cl} : \text{Cl}$ .

The three main types of hydrogen compounds may be represented therefore by  $\text{H} : \text{Cl}$ ,  $\text{H} : \text{H}$ , and  $\text{Na} : \text{H}$ .

We may go further and give a complete formula for each compound by using the ordinary atomic symbol and by adjoining to each symbol a number of dots corresponding to the number of electrons in the atomic shell. Thus we may write  $\text{H} : \text{H}$ ,



Lewis had just introduced the shared pair two-electron covalent bond<sup>1</sup> known to every beginning student of chemistry. Indeed, so universal has the idea become that its representation has been reduced to a simple dash, hyphen, or line rather than a colon:



The idea that a line between two atoms equates with a shared electron pair covalent bond idea is now so robust that *whenever* a dash or line is used between atoms, it is deemed to represent a two-electron covalent bond. This is nicely illustrated with a counterexample by way of a common high school exam question:

<sup>1</sup> Sodium hydride,  $\text{NaH}$ , mentioned in the Lewis text in solid form is ionic,  $\text{NaH(s)}$ , and so should not be written “ $\text{Na} : \text{H}$ ” but more correctly as  $\text{Na}^+$  and  $\text{H}^-$ . Gas phase sodium hydride,  $\text{NaH(g)}$ , exists as the polar diatomic molecule.

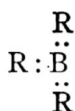
Question: ‘*What is wrong with writing Na–Cl?*’

Answer: ‘*The bonding in [solid] sodium chloride is ionic, not covalent, so it is incorrect to use a line to show the bonding between the sodium and chlorine as a line implies covalent bonding.*’

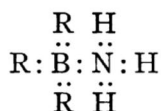
In his 1923 book (Lewis, 1923), these ideas were developed to include the double covalent bonds of ethylene (ethene), represented as both  $\text{H}_2\text{C}::\text{CH}_2$  and  $\text{H}_2\text{C}=\text{CH}_2$ , and triple covalent bonds acetylene (ethyne),  $\text{HC}:::\text{CH}$ . (Lewis *mainly* used the colon construction, but he occasionally used the – (line/dash) to represent the covalent bond.)

In the chapter *Exceptions to The Rule of Eight*, on page 98 Lewis writes (Lewis 2024a, b):

The alkyl compounds of  
boron have vapor densities corresponding to the simple formula  $\text{BR}_3$ .  
Thus we may write for boron trimethyl or triethyl the formula



There seems to be no way in which boron can have more than three electron pairs in its valence shell. And the properties correspond to the above formula, for boron trialkyl is highly reactive toward any substance which is capable of furnishing the electron pair to complete its octet. Thus with ammonia it forms a compound which remains undissociated when dissolved in benzene. This compound may be represented by the formula



where a free electron pair (or, as Huggins calls it, a lone electron pair) of the nitrogen completes the boron octet. In the older valence theory the formation of such a compound would be unintelligible.

Lewis is identifying that the trialkyl boron compound,  $\text{BR}_3$ , acts as an electron pair acceptor species, and the ammonia,  $:\text{NH}_3$ , behaves as an electron pair donor species. These interact to give – in modern parlance – an adduct or complex using what we would now call a ‘*dative*’ or ‘*coordinate*’ covalent bond. On page 142, Lewis writes (Lewis 2024a, b):

It seems to me that with complete generality we may say that *a basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom*, and that *an acid substance is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms*. In other words, the basic substance furnishes a pair of electrons for a chemical bond, the acid substance accepts such a pair.

Due to this paragraph, subsequent authors have designated those substances that fit Lewis's definition of a base as '*Lewis bases*' and those substances that fit Lewis's definition of an acid as '*Lewis acids*'. Succinctly, Lewis bases are electron pair *donor* species, and Lewis acids are electron pair *acceptor* species. A Lewis base interacts or reacts with a Lewis acid to form a *complex* or *adduct*, where the species are joined with a shared pair of electrons, i.e., a two-electron covalent bond.

However, this definition of a Lewis acid has caused (and causes) no end of confusion because a Lewis acid is *NOT* an acid in the usual sense that '*an acid turns litmus paper red*' or '*an acid is an  $H^+$  (proton) donor*'. A Lewis acid is *not* a Brønsted acid. Actually, Brønsted acid is a Lewis base:  $H^+$  complex, as Lewis himself stated. Indeed, it has been incorrectly suggested (Chang 2012) that the term '*Lewis acid*' is so misunderstood by chemistry practitioners that it has led to a rather general confusion about the concept of acidity. While we dispute this analysis, we do feel that the terminology '*Lewis electron pair donor*' or '*Lewis donor*' and '*Lewis electron pair acceptor*' or '*Lewis acceptor*' would have been better expressions than the potentially ambiguous terms '*Lewis acid*' and '*Lewis base*'.

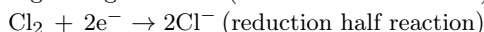
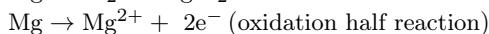
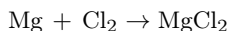
## Modern Lewis theory

Lewis' ideas have dominated chemical structure, bonding, and reactivity thinking since the 1920s, and have been extensively developed. Two examples of modern Lewis theory: the use of curly arrows, representing the movement of electron pairs, in organic reaction mechanisms and the use of valence shell electron pair repulsion (VSEPR) to predict the shapes of atomic centres in molecules and molecular ions (Sidgwick and Powell 1940), (Gillespie and Nyholm 1957). VSEPR has been codified into molecular mechanics and molecular dynamics software.

The Lewis idea of counting electrons (electron accountancy) can be extended to include five rather general reaction chemistries (Leach 1999) (Leach 2005):

**Lewis acid/base chemistry** Electron pair acceptor/electron pair donor chemistry. This includes all discussion of complexation, Brønsted acidity, nucleophiles, electrophiles, leaving groups,  $S_N1$ ,  $S_N2$ ,  $E_1$ ,  $E_2$   $SE_{Ar}$  reaction pathways, Michael addition, transition metal complexes, ligands, etc. The movement of the Lewis electron pair is indicated with a curly arrow.

**Redox** (reduction and oxidation) electron transfer chemistry. During redox processes, an electron or electrons are transferred from one entity to another. The entity that '*gives up*' electrons – the reducing agent – is deemed to be oxidised, and the entity '*receiving*' the electrons – the oxidising agent – is deemed to be reduced. Many redox processes proceed via single electron transfer.

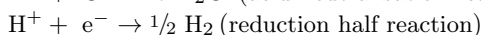
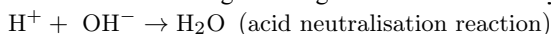


**Radical chemistry** involves species with single electrons rather than electron pairs. A classic example of radical chemistry is the conversion of methane to chloromethane, initiated by UV light. Many polymerisation reactions – for example, ethene to polyethene – proceed by radical mechanisms. Radical mechanisms commonly proceed via chain reactions and are prone to producing a multitude of products, although this can be controlled. In reaction mechanism diagrams, the movement of a single electron is shown with a ‘fishhook’ or ‘half’ curly arrow.

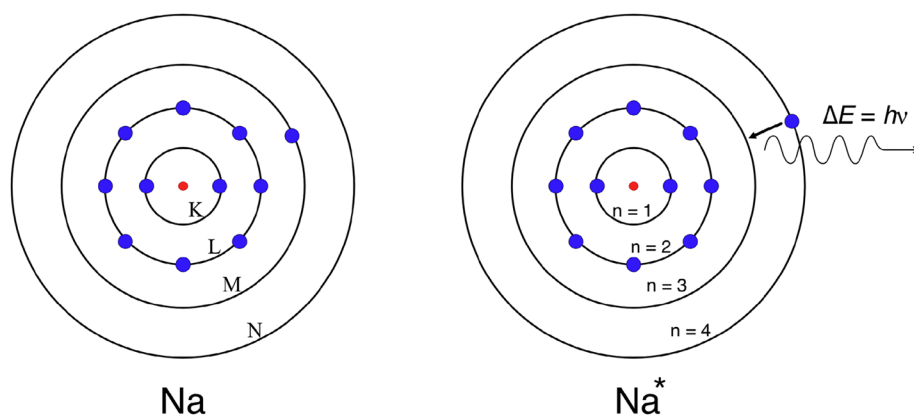
**Diradical chemistry** The reactive intermediate methylene,  $\text{CH}_2$ , can exist in singlet or triplet forms, where the triplet form shows Lewis acid/base reactivity characteristics, and the singlet form behaves more like two radicals. Oxygen,  $\text{O}_2$ , is a diradical.

**Photochemistry** The Bohr atom has particle-like electrons moving between energy levels, emitting or absorbing electrons of specific wavelengths. For many metals, these can be the visible part of the spectrum and are employed in flame tests, Fig. 1.

There are many ‘Venn diagram’ type overlaps between the five reaction chemistries. A couple of examples: When a Brønsted acid reacts with a Brønsted base such as sodium hydroxide ion water is formed; however, when a Brønsted acid reacts with a metal of sufficient reactivity, hydrogen gas,  $\text{H}_2$ , is produced. In this latter instance, the Brønsted acid is acting as an oxidising agent: the  $\text{H}^+$  ion is reduced to  $\text{H}_2$ . The corresponding ionic equations show the  $\text{H}^+$  ion is acting as the agent of Brønsted acidity and/or as an oxidising agent:



Likewise: the hydride ion,  $\text{H}^-$ , is both a Lewis base (nucleophile and  $\text{H}^+$  acceptor) and a reducing agent; many radical reactions are initiated by a photochemical initiation step; some redox reactions proceed in Brønsted acidic environments, others in alkaline environments; transition metal/ligand complexes can change oxidation state,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \rightarrow [\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{e}^-$ ; etc.



**Fig. 1** The sodium atom displayed using the Bohr model. On the left is the ground state atom with the X-ray shell designation. On the right is an excited state sodium atom,  $\text{Na}^*$ , in the process of moving to the ground state by emitting a photon. The energy of the photon,  $h\nu$ , is equal to the difference in energy between the  $n=4$  shell and the  $n=3$  shell

To conclude this section:

Most of the structure and reaction chemistry – both organic and inorganic – taught to high school and university students is described and explained in terms of Lewis theory, with its easily understandable, countable, particle-like electrons.

## Quantum mechanics (QM)

QM differs from classical mechanics:

- Energy, momentum, angular momentum, etc., are restricted to discrete or *quantised* values.
- Objects have characteristics of both particles and waves: they exhibit ‘*wave–particle duality*’.
- There are limits to how accurately the value of a physical quantity can be predicted prior to its measurement, the Heisenberg uncertainty principle.

The modern formulation of QM emerged in the second half of the 1920s after work by Niels Bohr, Louis de Broglie, Erwin Schrödinger, Werner Heisenberg, Max Born, Paul Dirac, Albert Einstein, and others. Very, very briefly:

In 1924, the French physicist Louis de Broglie suggested that the electron could be considered as a wave. In 1926, Schrödinger published his famous equation that described the behaviour of a wave-like electron. In 1928, Dirac developed a wave-equation for the electron that was consistent with special relativity that contained a four-dimensional component, the Dirac spinor. In turn, this led to the equation having four solutions: the spin-up electron, the spin-down electron, the spin-up positron and the spin-down positron; furthermore, quantum spin had a value of  $\frac{1}{2}$ . The Dirac approach introduced the idea that even in a perfect vacuum, there are oscillating quantum fields with zero-point energy. Quantum electrodynamics (QED) is the quantum field theory that deals with the electromagnetic force. After developments in the nineteen thirties, forties and fifties, Richard Feynman is said to have called QED ‘*the jewel of physics*’.

QM – as currently formulated – requires the understanding and manipulation of complex numbers, matrices, linear algebra, differential and partial differential equations, group theory, perturbation theory, unitary gauge transformations, renormalisation, Hamiltonian operators, Hilbert space, Feynman diagrams, wave-functions, and many other techniques and concepts. Once mastered, QM gives profound insights into the physical world of protons, electrons and photons:

- The uncertainty principle says that no matter how a quantum particle is prepared or how carefully experiments upon it are arranged, it is impossible to have a precise prediction for a measurement of its position and at the same time for a measurement of its momentum.

- Quantum objects have properties of mass, charge, and *spin*, where spin has no classical counterpart. The electrons and protons exist in two spin states:  $+\frac{1}{2}$  and  $-\frac{1}{2}$ . Particles with non-integer spins are classed as fermions. Those with integer spins are bosons.
- Quantum interference can be illustrated with the *very strange* double-slit experiment.
- Quantum tunnelling: a particle that goes up against a potential barrier can cross it, even if its kinetic energy is smaller than the maximum of the potential.
- When quantum systems interact, the result can be the creation of quantum entanglement: the properties become so intertwined that a description of the whole solely in terms of the individual parts is no longer possible.

Quantum mechanics in the form of modern QED can give astonishingly accurate agreement between theory and experiment, with up to 11 significant figures of precision, but only for the *very* simplest physical systems such as: measurements of the electromagnetic fine-structure constant,  $\alpha$ , (approximately  $1/137$ ); the process of a high energy  $\gamma$ -ray photon becoming an electron-positron pair (and vice versa); the Lamb shift of the isolated hydrogen atom (which consists of just one proton and one electron), the anomalous magnetic moment of the electron, etc.

But – and this is possibly the biggest ‘but’ in all science – the QM phenomena can only be fully explained and truly understood in terms of mathematics. QM is the math. Anything else is a simplification. An example:

An electron’s wave-function is a complex<sup>2</sup> mathematical formulation commonly used to describe the behaviour of the electron is determined from the Schrödinger wave equation and it provides information, in the form of *probability* amplitudes, about a particle’s energy, momentum, time evolution, and other physical properties.

There are some good visualisations of the electron wavefunction on YouTube (Khutoryansky 2016a, b), (Khutoryansky 2016a, b). The printed page simply does not do the dynamic wave-function justice... except when represented as the mathematics.

## Spectroscopy

Spectroscopy is the study of the interaction between light and matter as a function of the wavelength (or frequency) of the radiation. A quantum mechanical analysis is always required to understand and explain spectroscopy and interpret spectra. Indeed, spectroscopy is where the chemistry student first becomes properly exposed to quantum mechanics, and it can come as something of a shock having been immersed in high school science and Lewis theory for several years. There are many, many spectroscopies involving the absorption, emission, elastic scattering, reflection, resonance, etc. of electromagnetic radiation. These can occur across the electromagnetic spectrum: radio, microwave, infrared, visible, ultra-violet, X-ray and  $\gamma$ -ray. Three examples:

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<sup>2</sup> The term ‘*complex*’ is being used in the mathematical sense that the imaginary number  $i$ , which has the value of  $i = \sqrt{-1}$ , is being employed.

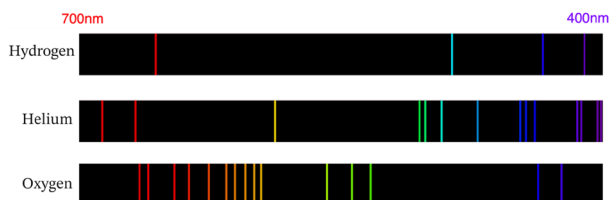
**Atomic spectroscopy** Every element has a set of energy levels, leading to a unique spectral fingerprint, Fig. 2, allowing the identification and quantification of elements in a sample (Moore 1965). The spectrum of the hydrogen atom, consisting of one proton and one electron, can be solved analytically – i.e., it is understood with complete mathematical precision – in that theory and experiment agree perfectly. As atoms gain additional electrons, approximations must be made in the mathematical analysis; atomic spectra can be understood well, but not perfectly. Atomic emission spectral lines are an experimental reality that QM models strive to explain.

**Microwave spectroscopy** When a gas phase diatomic molecule with a dipole moment: CO, NO, HCl, DBr, etc., is exposed to microwave or far infrared radiation, the molecule will adsorb the electromagnetic energy and start rotating. The rotational spectrum is not classical, as only certain, discrete modes of quantized rotation are allowed. Energy difference between a rotational state,  $E_J$ , and the next excited state,  $E_{J+1}$ , is given by  $E_{J+1} - E_J = 2B(J+1)$ , where  $J$  has the quantised integer values of  $J=1, 2, 3\ldots$  and  $B$  is the molecule-specific rotational constant.

**NMR spectroscopy** In proton nuclear magnetic resonance spectroscopy, the  $\frac{1}{2}$  nuclear spin of a  $^1\text{H}$  hydrogen atomic nucleus can, while in a strong magnetic field, adsorb radio waves of a very precise frequency, causing the proton's spin to resonate between its up and down spin states. The presence of adjacent  $^1\text{H}$  atom(s) causes the proton's signal to be split into various splitting patterns: singlet, doublet, triplet, quartet, etc. NMR uses quantum phenomena to give a direct view of molecular structure and is routinely used by organic research chemists.

## Spectrometry

The associated field of analytical spectrometry does not require a deep understanding of QM, even though spectrometry relies on quantum phenomena for its operation. Briefly, quantum systems can be used for *quantitative* measurement purposes, often at a fixed wavelength. An example: Benzene adsorbs UV radiation at 254 nm ( $\lambda_{\text{max}}$ ), but ethanol does not. This makes it possible to measure the concentration of benzene in ethanol in a UV spectrometer set to 254nm where the absorbance,  $A$ , at 254nm is directly proportional to the amount (concentration) of benzene present.



**Fig. 2** The spectral lines of atomic hydrogen, helium, and oxygen that occur in the visible part of the spectrum, 700–400 nm. The red lines, to the left, are low energy and long wavelength. The blue and violet lines to the right are short wavelength and high energy

## Quantum chemistry

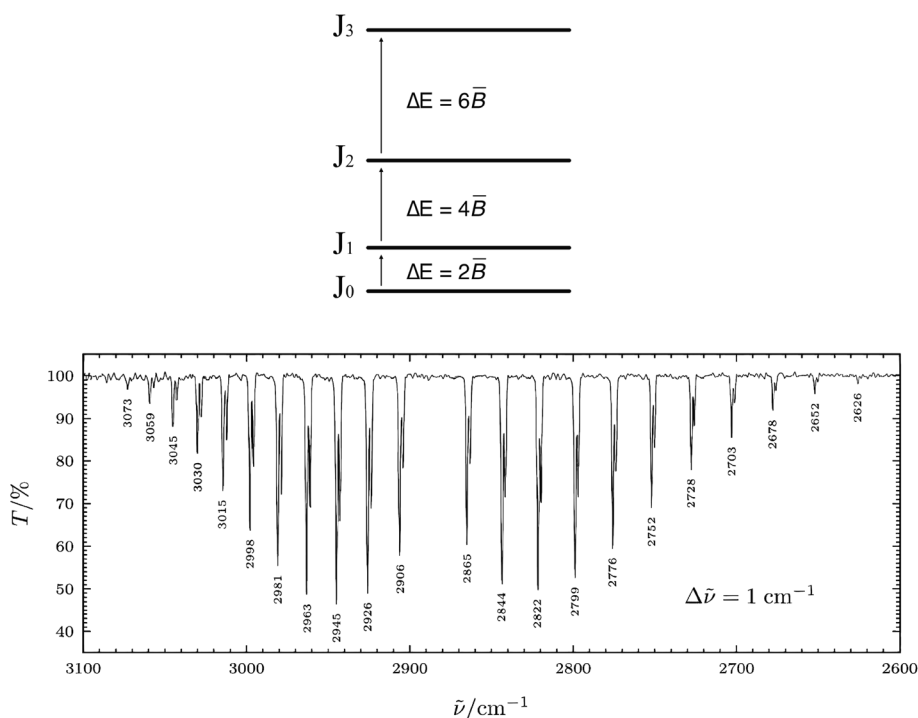
The section on quantum mechanics, above, may have seemed a little devoid of discussion of chemical systems, apart from the hydrogen atom... *because it was!* Multi-electron atoms and atomic ions, molecules, bonding, and molecular structure are simply too complicated – too many particles, too many interactions, not enough computer time – to be studied at the level of QED. (Intriguingly, it is hoped that developments in quantum computing will make high-level quantum chemical calculations easier/faster.)

As the old quantum theory developed into QED and quantum field theories during the middle years of the twentieth century, two things happened: the mathematics of QM became ever more byzantine while the physical systems being studied became simpler. With multi-electron atoms and molecules, a different approach was required: hence the development of *quantum chemistry*.

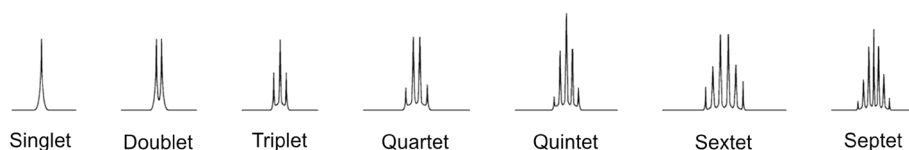
In this paper, we are using the term *quantum chemistry* in a general way to describe techniques that model chemical systems wave-mechanically, in contrast to the Lewis classical analysis. However, a section reviewing quantum chemistry methods would simply be a re-telling of the ideas and concepts fully covered in most modern inorganic and organic chemistry textbooks: quantum numbers and atomic orbitals; Madelung's rule; molecular orbitals: hydrogen H<sub>2</sub>, methane CH<sub>4</sub>, etc.; hybridization and valence bond theory; the  $\pi$  bond; aromaticity; frontier molecular orbital (FMO) theory; pericyclic reactivity; computational quantum chemistry, etc. For that reason, we will not be covering these topics in any detail here. That said, it should be noted that one of the striking features of quantum chemistry is the extraordinary *patterns* that emerge:

- The four quantum numbers and how they interact to give: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p... atomic orbitals, Fig. 9.
- Shapes and phases of atomic orbitals, Fig. 9.
- $sp^3$ ,  $sp^2$ , and  $sp$  hybrid orbitals.
- Madelung's Rule.
- The Periodic Table: Janet (Left-Step) and Seaborg formulations; periodicity.
- $J$ ,  $J_{+1}$ ,  $J_{+2}$ ,  $J_{+3}$ ... rotational spectra, Fig. 3.
- The singlet, doublet, triplet, quartet, quintet, sextet, and septet splitting patterns in NMR spectroscopy, Fig. 4, and how the splitting and peak heights can be mapped to Pascal's triangle.
- $\pi$ -LUMO and  $\pi$ -HOMO FMO geometries of  $\pi$ -systems, Fig. 7.
- The Woodward-Hoffmann rules and FMO cycloaddition, Fig. 7.
- Hückel's  $4n+2$  rule for aromatic systems.
- etc.

Yes, these *beautiful* quantum patterns do distort and even break as systems become larger: Madelung's rule breaks with the  $d$ -block and heavier elements due to electron energy exchange interactions; not all NMR spectra are first order; the Hückel rule stops working reliably when  $n>4$ ; FMO controlled pericyclic reactions are subject to steric effects; rotational spectra of triatomic and larger species are far more involved than those of diatomics; etc (Fig. 5).



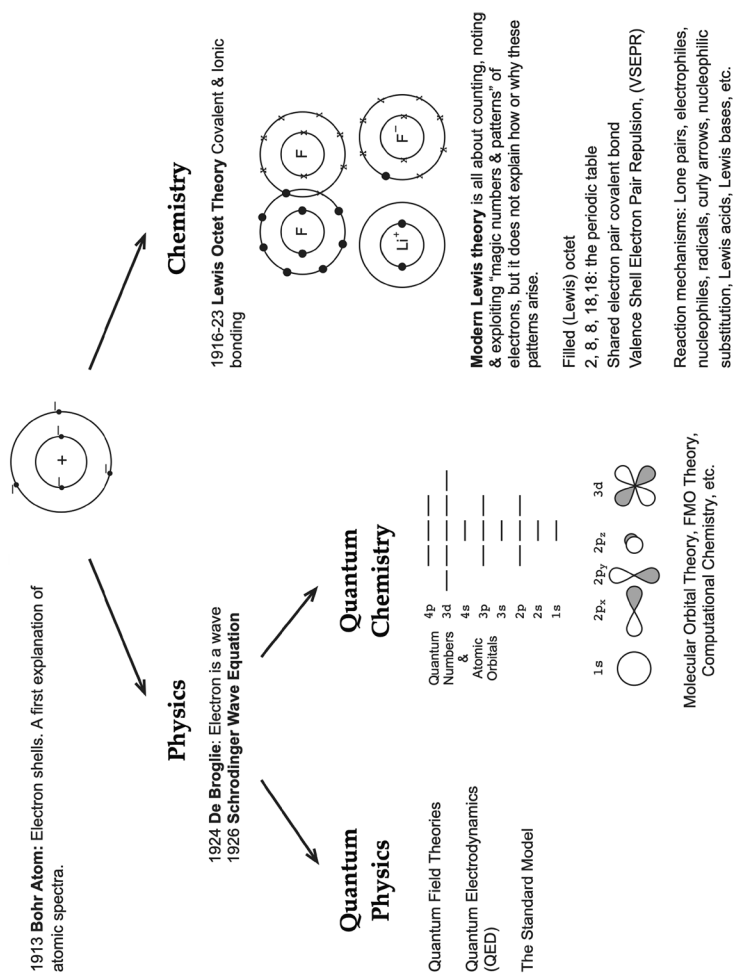
**Fig. 3** The upper image shows the  $J$  values. The lower image is the rotational spectrum of gaseous hydrogen chloride. The P- and R-branches correspond, respectively, to  $v=0$  and  $v=1$ . The absorption intensities depend on the isotopes present in the sample, e.g.,  $^1\text{H}-^{35}\text{Cl}$  vs.  $^1\text{H}-^{37}\text{Cl}$ . ([https://commons.wikimedia.org/wiki/File:Ir\\_hcl\\_rot-vib\\_mrtz.svg](https://commons.wikimedia.org/wiki/File:Ir_hcl_rot-vib_mrtz.svg))



**Fig. 4** Examples of signal splitting in  $^1\text{H}$ -NMR spectra

## A map of chemical theory

Science underwent a transformation in the first half of the twentieth century, from the Bohr model of the atom to molecular orbital theory. There are now three broad areas: (1) quantum physics, which is too fundamental for chemistry systems, (2) quantum chemistry, which is used in teaching and software to model and explain structure and bonding, and (3) classical Lewis theory, which is used to explain molecular shape and reaction mechanisms, Fig 5.



**Fig. 5** A map showing how science split into physics, chemistry and quantum chemistry from the Bohr atom.

## Combining Lewis theory and quantum chemistry

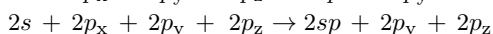
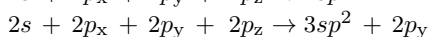
Linus Pauling wrote about the new and emerging quantum mechanics (Pauling 1928) (Pauling 2020) saying:

It may be pointed out that this theory is in simple cases entirely equivalent to G. N. Lewis's successful theory of the shared electron pair, advanced in 1916 on the basis of purely chemical evidence. Lewis's electron pair consists now of two electrons which are in identical states except that their spins are opposed.

The shared electron structures assigned by Lewis to molecules such as  $\text{H}_2$ ,  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{CH}_4$ , etc., are also found for them by London. The quantum mechanics explanation of valence is, moreover, more detailed and correspondingly more powerful than the old picture.

Using this thinking, Pauling developed *hybridization* and  $\sigma$ - $\pi$  *separability*, two ideas that rationalise quantum chemistry ideas of bonding with respect to Lewis theory (Pauling 1931). Hybridization involves mathematically combining *s*, *p*, and *d* atomic orbitals to give 'hybrid' or 'mixed' orbitals. For the Period 2 element carbon, its one *2s* orbital and three *2p* orbitals can mix in three ways to give  $sp^3$ ,  $sp^2$ , or *sp* hybrid orbitals:

Atomic Orbitals Hybrid Orbitals.



The *huge* advantage<sup>3</sup> of hybridization is that Pauling's hybrid orbitals are lobe-shaped and clearly directional, while this is not so immediately obvious when using the un-hybridized AOs. Moreover, hybrid orbitals give the same geometry about an atomic centre as predicted by the classical Lewis/VSEPR method.

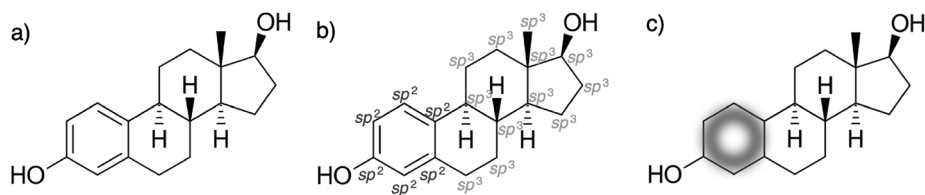
- Using *hybridization* the carbon in methane,  $\text{CH}_4$ , has four  $sp^3$  orbitals that give methane a tetrahedral geometry with a  $109^\circ 28'$  bond angle.
- Using *VSEPR* carbon in methane,  $\text{CH}_4$ , has four electron pairs in its valence shell that repel each other to give a tetrahedral geometry with a  $109^\circ 28'$  bond angle.

Using Pauling's idea of  $\sigma$ - $\pi$  separability, organic chemists construct the  $\sigma$ -skeleton of a molecule using hybrid orbitals (which correspond to the VSEPR picture) and then *superimpose*  $\pi$ -systems, as and when required, Fig. 6.

## Frontier molecular orbital (FMO) theory

Fukui, working on aromatic hydrocarbons, suggested that a good approximation for reactivity could be found by looking at a molecule's highest occupied molecular orbital or HOMO and the corresponding lowest unoccupied molecular orbital or LUMO, which he designated

<sup>3</sup> Atkins points out that strictly, hybridization is quite unnecessary (Atkins, 1986).



**Fig. 6** Organic chemists visualise an organic molecule (a) in terms of the hybridisation state of the carbon atoms in the structure (b). They then view the molecule's  $\sigma$ -skeleton with  $\pi$ -systems superimposed (c)

the frontier molecular orbitals, or FMOs (Fukui 1952). These ideas were further developed in the Klopman-Salem equation (Klopman 1968) (Salem 1968) and employed in the Woodward-Hoffmann rules (Hoffmann and Woodward 1965) for explaining/predicting the stereochemical outcome of electrocyclic/pericyclic reactions such as Diels-Alder cycloaddition. Briefly, when two molecules approach each other:

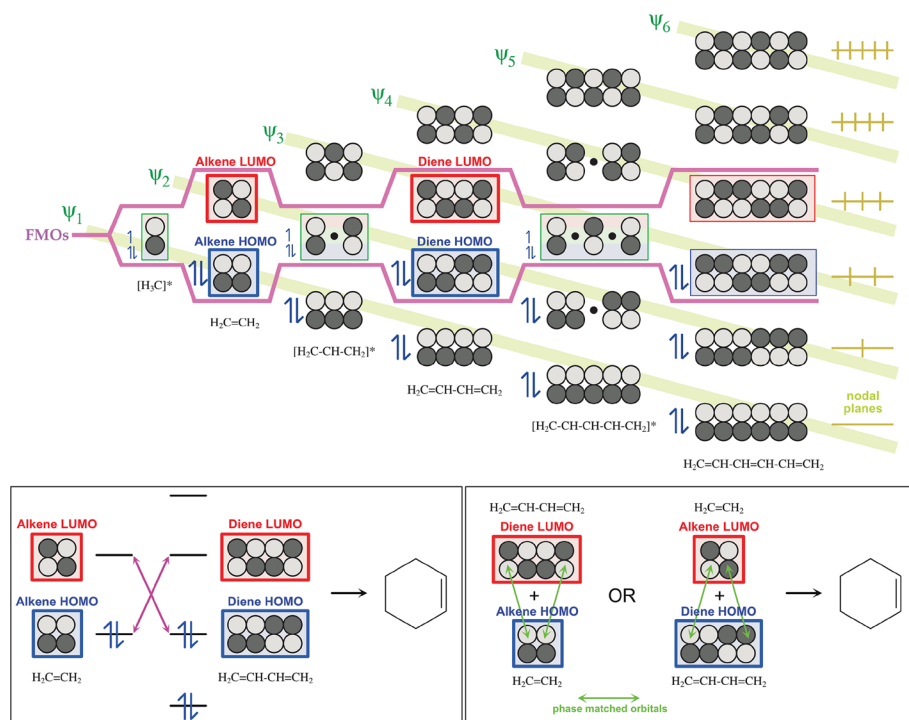
- The occupied orbitals of the two molecules repel each other. Two  $H_2$  molecules repel/'bounce off' each other at 25 °C.
- Positive charges of one molecule attract the negative charges of the other. This is Coulombic or electrostatic attraction.
- The occupied orbitals of one molecule interact with the unoccupied orbitals of the other (especially the HOMO and LUMO), causing attraction, leading to bonding if the mutual geometries are correct. The relative orbital phases of participating  $\pi$ -systems are crucial when considering  $\pi + \pi$  interactions: Diels-Alder cycloaddition (Fig. 7).

Building on Fukui's ideas, Fleming (Fleming 1976) and Pearson (Pearson 1997) pointed out that electron pair donating Lewis bases react via their HOMO and electron pair accepting Lewis acids react via their LUMO. Thus, Lewis acid/base reaction chemistry can be considered in terms of quantum chemical FMO interactions.

## The Lewis acid/base interaction matrix

Pearson's HSAB analysis classifies Lewis acids and Lewis bases as 'hard', 'borderline', or 'soft' and observes that hard Lewis acids prefer to bond (complex) with hard Lewis bases and vice versa (Pearson 1997). Unfortunately, the HASB analysis fails to consider the mutual geometry of the FMOs and so misses much of the richness of Lewis acid/base interaction chemistry. As discussed in detail (Leach 1999) (Leach 2005), various types of electron pair donating Lewis bases and electron pair accepting Lewis acids can be classified when their frontier molecular orbital (FMO) geometries are sorted into distinct and rather general types. There are four distinct types of Lewis base that interact (with Lewis acids) via their highest occupied molecular orbital (HOMO):

- The  $s$ -HOMO Lewis bases: the hydride ion,  $H^-$ , and molecular  $H_2$ .
- Complex Anion Lewis bases:  $[BF_4]^-$ ,  $[SbF_6]^-$ , etc.
- Lobe-HOMO Lewis bases: hydroxide ion,  $[OH]^-$ , cyanide ion,  $CN^-$ , etc.
- $\pi$ -HOMO Lewis bases (electron-rich  $\pi$ -systems): ethene, allyl anion, benzene, etc.



**Fig. 7** A diagram showing the  $p$  and  $\pi$  molecular orbitals for: 1, 2, 3, 4, 5, and 6 conjugated carbon systems. The 2, 4, and 6 carbon systems correspond to ethene, buta-1,3-diene and hexa-1,3,6-triene. Consider ethene: the lower molecular orbital contains two electrons and is the highest occupied MO or HOMO, and the empty MO above is the lowest unoccupied MO and is the LUMO. The  $\psi_1$  MO has one nodal plane, where there is a phase change; the  $\psi_2$  MO has two nodal planes, and there are two phase changes; etc. The \* on the odd numbered carbon systems indicates that these can be anions, radicals, or cations. Thus, \* represents  $-$ ,  $\cdot$  or  $+$ . The HOMO of ethene,  $\text{H}_2\text{C}=\text{CH}_2$ , is 'phase matched' to the LUMO of buta-1,3-diene,  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ , and vice versa. As a result, these two compounds can electrocyclically Diels-Alder 'cyclo-add' to form cyclohexene via a concerted six-membered ring transition state

Likewise, there are six distinct types of electron pair acceptor that interact (with Lewis bases) via their lowest unoccupied molecular orbital (LUMO):

- The Proton Lewis acid:  $\text{H}^+$ .
- s-LUMO Lewis acids:  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , etc.
- Onium ion Lewis acids:  $[\text{NH}_4]^+$ ,  $[(\text{CH}_3)_3\text{O}]^+$ , etc.
- Lobe-LUMO Lewis acids: carbenium ions,  $[\text{CH}_3]^+$ , electrophiles.
- $\pi$ -LUMO Lewis acids: allyl cation, electron-poor  $\pi$ -systems.
- Heavy Metal Lewis acids:  $\text{Ni}$ ,  $\text{Pd}^{2+}$ ,  $\text{Cr}^{3+}$ , etc.

In this approach, the Lewis technique of an electron pair donor interacting with an electron pair acceptor is being extended to consider various common frontier molecular orbital (HOMO+LUMO) geometries. The four types of electron pair donating, HOMO reacting, Lewis bases interact with the six types of electron pair accepting, LUMO reacting Lewis acids to give 24 Types of Lewis acid/base interaction complexes (Fig. 8).

**Fig. 8** A schema showing the interaction of four types of Lewis base interacting with six types of Lewis acid to give 24 types of Lewis acid/base complex

| Lewis<br>Bases                                                                    | Complexation Chemistries                                                          |                                                                                   |                                                                                   |                                                                                    |                                                                                    |
|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
|                                                                                   | s-HOMO<br>$0\sigma^-$                                                             | Complex Anion<br>$^-$                                                             | Lobe-HOMO<br>$0\sigma^-$                                                          | $\pi$ -HOMO<br>$0\sigma^-$                                                         |                                                                                    |
|                                                                                   |  |  |  |  |                                                                                    |
|                                                                                   | Lewis Acids                                                                       |                                                                                   |                                                                                   |                                                                                    |                                                                                    |
|                                                                                   | The Proton<br>$+$                                                                 | Type 1                                                                            | Type 2                                                                            | Type 3                                                                             | Type 4                                                                             |
|                                                                                   |  |  |  |   |  |
|                                                                                   | s-LUMO<br>$+$                                                                     | Type 5                                                                            | Type 6                                                                            | Type 7                                                                             | Type 8                                                                             |
|  |  |  |  |  |                                                                                    |
| Onium Ion<br>$+$                                                                  | Type 9                                                                            | Type 10                                                                           | Type 11                                                                           | Type 12                                                                            |                                                                                    |
|  |  |  |  |  |                                                                                    |
| Lobe-LUMO<br>$0\sigma^+$                                                          | Type 13                                                                           | Type 14                                                                           | Type 15                                                                           | Type 16                                                                            |                                                                                    |
|  |  |  |  |  |                                                                                    |
| $\pi$ -LUMO<br>$0\sigma^+$                                                        | Type 17                                                                           | Type 18                                                                           | Type 19                                                                           | Type 20                                                                            |                                                                                    |
|  |  |  |  |  |                                                                                    |
| Heavy Metal<br>$0\sigma^+$                                                        | Type 21                                                                           | Type 22                                                                           | Type 23                                                                           | Type 24                                                                            |                                                                                    |
|  |  |  |  |  |                                                                                    |

- The s-LUMO Lewis acid  $\text{Na}^+$  interacts with the Lobe HOMO Lewis base  $[\text{OH}]^-$  to give sodium hydroxide,  $\text{NaOH}$ , a Type 7 Lewis Acid/Base Complex.
- Classical transition metal complex chemistry generally involves Type 23 Complexes.
- Diels-Alder Cycloaddition chemistry is Type 20 Lewis acid/base chemistry.
- Electrophilic aromatic substitution,  $\text{S}_{\text{Ar}}\text{E}$ , involves Type 16 interactions.
- Brønsted acids are all Proton/Lewis base complexes.
- Etc.

## How does Lewis theory works at all?

In chemistry, the Lewis and quantum approaches are so *foundationally* different that we may reasonably ask how it is that such simple ‘*back of an envelope*’ techniques like Lewis theory and VSEPR can possibly work as well as they do? Little math is involved: the ability to count to 18, the skill to add and subtract small positive and negative integers, a little middle school geometry, and knowing how to navigate the periodic table will get a student a long way in describing and predicting chemical structure and reactivity.

Quantum mechanics tells us that electrons are fermions with  $\frac{1}{2}$  spin that occupy orbitals subject to the Pauli exclusion principle. Usually, the most stable configurations are when orbitals are either doubly occupied with two electrons of opposite spin or are empty. The quantum *two-electrons per orbital* constraint maps to the Lewis picture of *electron pairs*, as Pauling pointed out (Pauling 1928). The Lewis model is not derived from wave mechanics, but it reflects the consequences of orbital filling.

VSEPR considers electron bonding pairs and lone pairs about a central atom as repelling each other, allowing the structure to settle into a geometry that has minimal repulsion. QM supports this. During MO calculations, the geometry of molecules is constrained by

| Is Good At:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | Is Bad At:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p><b>Lewis Theory</b></p> <p>Being easy to teach and understand. It gives a ‘<i>good enough</i>’ explanation of most of the chemical structure and reactivity required by most students most of the time. The Lewis approach works surprisingly well with compounds containing only <i>s</i> and <i>p</i> block elements, and as that includes most organic and main group chemistry, it covers most biochemistry, medicinal chemistry, pharmacy and pharmacology.</p> <p>The VSEPR method of predicting molecular geometry is an outstanding example of the success of modern Lewis theory. Likewise, reaction mechanisms.</p> <p>Due to the notion of <math>\sigma/\pi</math> separability, <math>\pi</math>-systems, such as aromatic rings, can either be considered as (Lewis/Kekulé) alternating double bond systems or as a <math>\pi</math>-system ‘added to’ or ‘<i>superimposed</i>’ onto a Lewis hydrocarbon <math>\sigma</math>/VSEPR structure.</p> <p><b>Quantum Theory, QED</b></p> <p>Studying the interaction of electromagnetic radiation with the simplest physical systems, such as photons interacting with the two-particle hydrogen atom.</p> <p>QED is required to explain why chiral molecules rotate plane-polarised light.</p> <p>QED predicts and explains quantum tunnelling: many reaction transition states proceed via quantum tunnelling.</p> | <p>Lewis theory does not explain spectroscopy or <math>\pi</math>-systems.</p> <p>The triplet diradical structure of the <math>O_2</math> molecule – liquid oxygen is diamagnetic – shows that Lewis theory is, at heart, an oversimplification.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| <p><b>Quantum Chemistry</b></p> <p>Being adaptable and generating atomic and molecular structure and reactivity patterns.</p> <p>Using the LCAO approach: MOs can be constructed from AOs, and MOs can be deconstructed back into the participating AOs, which can be hybridized to <math>sp^3</math> and <math>sp^2</math> orbitals.</p> <p>Quantum Chemistry allows the concept of <math>\sigma/\pi</math> separability and focusing on the HOMO and LUMO FMOs during reactions.</p> <p>All but the most subtle spectroscopies can be explained in terms of quantum chemistry.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | <p>QM/QED is not intuitive. Analysis is only possible in terms of advanced mathematical techniques.</p> <p>Modelling multi-electron systems of chemical interest: molecules, liquids, solids, reaction mechanisms, hydrogen bonding in water, etc., due to the difficulty of the calculations and the large amount of computer time required to get meaningful results.</p> <p>Quantum Chemistry consists of an assortment of overlapping ideas rather than being a single theory.</p> <p>Inorganic chemists tend to discuss molecular structure in terms of molecular orbitals, while organic chemists prefer <math>sp^3</math> and <math>sp^2</math> hybrid orbitals. While hybridization and <math>\sigma/\pi</math> separability are conceptually useful, they are also [strictly] unnecessary.</p> <p>Quantum chemistry is good at describing molecules <i>in silico</i> (in the computer), and this approximates to isolated gas phase molecules, but quantum chemistry is not so good with bulk materials such as liquid water.</p> <p>[This becomes the science of solid-state physics, which is outside this author’s area of expertise.]</p> <p>Users should be aware that implementations of molecular orbital theory in commercial computer code hide the mathematical ideas, approximations and simplifications inside a black-box, behind the software user interface.</p> |

electron–electron repulsion and nuclear repulsion. Thus, VSEPR translates a semi-quantitative approach of electron density energy minimisation into a geometric rule. Indeed, while molecular wavefunctions are mathematically complex, many molecules can be approximated as networks of localized two-electron bonds and lone pairs using the linear combina-

Philosophical  
Differences (Harré  
1986) (Brakel  
2000)

|                | Lewis Theory                                                                                     | Quantum Theory                                                                                         |
|----------------|--------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|
| Ontology       | Classical objects: electrons, atoms, bonds. These are deemed to be real spatial entities.        | Wavefunctions are delocalised, probabilistic mathematical constructs that are not directly observable. |
| Epistemology   | Deterministic knowledge is possible in principle. Lewis structures are deemed to mirror reality. | Quantum analysis only gives probabilistic knowledge. Uncertainty is intrinsic, not due to ignorance.   |
| Representation | Diagrams and models <i>picture</i> the real structure.                                           | The mathematical formalism can predict observables, but it does not pictorially represent structure.   |
| Causality      | Classical cause and effect: electrons move and form bonding pairs.                               | Nonlocal and indeterministic processes. Measurement affects reality.                                   |
| Realism        | Strong representational realism. Theory is deemed to correspond directly to reality.             | Structural or instrumental realism: only the formal, mathematical relationships exist.                 |
| Metaphysics    | Mechanistic, corpuscular, Aristotelian substance ontology.                                       | Relational, probabilistic ontology.                                                                    |

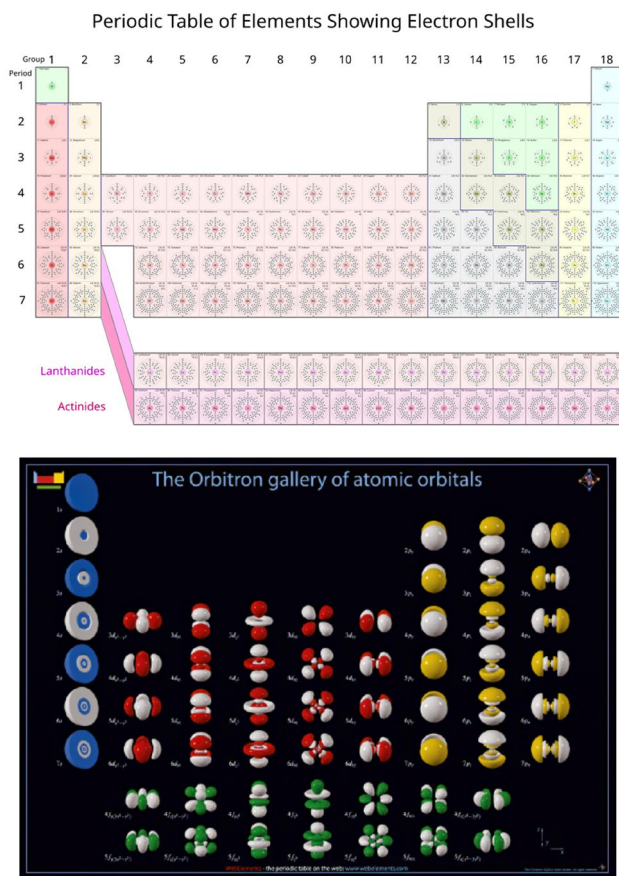
tion of atomic orbitals (LCAO) approach, essentially, this gives the valence bond view of molecular structure, as shown in Fig. 6.

VSEPR correctly predicts that boron trifluoride,  $\text{BF}_3$ , is trigonal planar; methane,  $\text{CH}_4$ , is tetrahedral; and sulfur hexafluoride,  $\text{SF}_6$ , is octahedral. These are symmetrical molecules with geometric bond angles:  $120^\circ$ ,  $109^\circ 28'$ , and  $90^\circ$ , respectively. Water,  $\text{H}_2\text{O}$ , and hydrogen sulfide,  $\text{H}_2\text{S}$ , are correctly predicted to be bent or angular by VSEPR, but the technique does not consistently predict the bond angles. For example:  $\text{H}_2\text{O } \angle = 104.5^\circ$  and  $\text{H}_2\text{S } \angle = 92.1^\circ$ .

Organic chemistry, biochemistry, medicinal chemistry, and pharmacology are dominated by hydrogen, carbon, nitrogen, oxygen, fluorine, sodium, phosphorus, sulfur, chlorine, potassium, bromine, and iodine. For small molecules, molecular ions, and macromolecules made of these main group elements, Lewis theory, VSEPR, molecular mechanics, and molecular dynamics work astonishingly well for much of the time. While classical theory is not good at accounting for *d*-orbital participation, hyperconjugation, delocalization, or hydrogen bonding, these sub-structures can be *added on*, as shown in Fig. 6.

## Summary

1. Modern theoretical chemistry starts with the Bohr atom of 1913, and its immediate developments, to give the shell model of the atom, Figs. 1 and 9. The shell model can be used to explain much empirical chemistry.
2. Ideas and theory rapidly progressed over the decade or so from the Bohr atom to give, on one hand, Lewis theory with its classical particle-like electrons and, on the other, a very mathematical quantum theory that was interested in light, quantum fields, and very simple physical systems like the hydrogen atom.



**Fig. 9** The chemical elements showing electron shells and/or atomic orbitals.

Source: Periodic\_Table\_of\_Elements\_showing\_Electron\_Shells.svg, Graphemecluster, CC BY-SA 4.0.  
Orbitron Gallery © Mark Winter.

3. In the late 1920s, Pauling strongly and successfully advocated that the new quantum theory was both compatible with and was more advanced than Lewis theory.
4. In the 1930s, the emerging field of quantum chemistry took ideas from the new physics – regarding the electron as a wave rather than as a particle – and applied these to chemical problems like bonding and aromaticity.
5. Pauling introduced hybridization and  $\sigma/\pi$  separability, which enabled chemists to visualise structure and bonding in terms of wave-like electrons.
6. Lewis theory continued to borrow ideas from quantum chemistry, for example, by regarding Lewis bases as reacting via a species' highest occupied molecular orbital (HOMO) and Lewis acids as reacting via a species' lowest unoccupied molecular orbital (LUMO).
7. Lewis theory has continued to develop, with ideas like valence shell electron pair repulsion (VSEPR), molecular mechanics, molecular dynamics, the Lewis Acid/Base Interaction Matrix, etc.

8. Molecular orbital theory has many pragmatic simplifications compared with quantum electrodynamics (QED, a true quantum theory). Chemical systems with their many nuclei and electrons are currently just too complicated for QED calculations.
9. Quantum chemistry has developed into computer code using methods such as Hartree-Fock (HF), post-HF, density functional theory, etc. However, the intricate details of the underlying mathematical assumptions and simplifications are hidden behind the user interface with mouse-driven drop-down menus. These menus may include: molecular mechanics, semi-empirical, and *ab initio* methods like Hartree-Fock etc.
10. The electromagnetic radiation used in spectroscopy always looks *through* the classical Lewis structure, bonding and reactivity veneer, and *sees* the underlying quantum configuration. Thus, spectral interpretation always requires a quantum mechanical level of analysis.
11. The periodic table is agnostic to theory type and can be shown with either Bohr-Lewis electron shells or with wave mechanical orbitals, Fig. 9.

The Lewis theoretical world is made of *things with properties*: electrons, atoms, and molecules. The quantum world is made of *relations and probabilities*: wavefunctions, operators, entanglements, observables. The quantum mechanical electron does not have a classical position; it is in a superposition of *relations* with other electrons and its environment.

## Conclusions

There are two successful but fundamentally unrelated ways to consider chemical structural theory: classical Lewis theory with particles and quantum theory with wavefunctions. Superficially, there is a *similar* situation in physics with regard to gravity, which can be modelled in terms of Newton's theories or Einstein's general relativity (GR). In Newton's analysis, gravity is a force, whereas the Einstein approach describes gravity as the curvature of space-time. Sending a rocket to Mars requires only Newtonian analysis [apparently], whereas understanding the perihelion precession of Mercury's orbit or black hole dynamics requires GR. School students are taught Newton; Physics majors are taught general relativity. But this is *not* the same situation as in chemistry because Newtonian gravity is, strictly, a *limiting case* of GR.

In chemistry, when we move from the Lewis world view to quantum mechanics, there is a profound shift from explanation to calculation. Lewis theory proposes understanding in pictorial, mechanical terms, whereas quantum mechanics offers mathematics and *prediction*. The quantum approach can be extraordinarily accurate, but it is not, *and it makes no attempt to be* intuitively understandable. Thus, there is an epistemic shift from visualisable realism to mathematical formalism. Inevitably, this leads to a deep semantic shift as well. Lewis diagrams are deemed to *mean* something because they are intended to *look like* what they represent. Quantum wavefunctions also *mean* something, but only through the formal rules of probability and measurement. Lewis theory is all about the diagrams, whereas quantum mechanics is all about mathematics. A philosophical consequence is the realisation that theories do not need to be representational to be explanatory.

Lewis structures are easy to draw, easy to teach, and easy to generalise. They are like Feynman diagrams in physics: not literally the thing itself, but a convenient symbolic system that encodes the science. The Lewis/VSEPR analysis provides *qualitative*, not quantitative, accuracy. Yet for many “*what shape is the molecule?*” questions, Lewis/VSEPR analysis will suffice. The classical methods succeed because the two-electron bond and electron-pair repulsions are not just cartoons; they offer simple expressions of deeper quantum principles: the Pauli principle, electron density minimization, and orbital localization, etc.

Finally, the thesis of this paper has pedagogical implications, because chemistry educators have different student cohorts.

- Student doctors require the mechanistic cause-and-effect logic of chemistry, which underpins modern evidence-based medicine.
- Student engineers require some atomic-level understanding of the materials they work with.
- Student analytical scientists need knowledge of sample preparation and handling as well as how to operate the instrumentation at their disposal, and how to interpret the results.
- Student biological scientists need to understand the molecular and cellular structure and biochemistry of the organisms they work with.

For these cohorts, Lewis theory and spectrometry will probably suffice. However, for students *majoring* in chemistry, the Lewis approach is simply not enough; they must have an appreciation of quantum theory/mechanics to have any meaningful understanding of spectroscopy, chemical bonding, and reactivity. Furthermore, chemists should fully understand when they are switching modes between classical Lewis models and quantum wave-mechanical treatments.

**Author contributions** ML wrote the main text and prepared the illustrations.

**Data availability** No datasets were generated or analysed during the current study.

## Declarations

**Competing interests** The authors declare no competing interests.

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