Trends in Physical Chemistry

Mini-Review

Pauling, chemistry and orbitals

J. F. Ogilvie[1,2,3]

[1]Centre for Experimental and Constructive Mathematics, Department of Mathematics, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia, V5A 1S6, Canada. [2]Escuela de Quimica, Universidad de Costa Rica, Ciudad Universitaria Rodrigo Facio, San Pedro de Montes de Oca, San Jose, 11501-2050, Costa Rica. [3]Institute of Quantum Physics, Irkutsk National Research Technical University, 83 Lemontov Street, Irkutsk 664074, Russian Federation.

ABSTRACT

In introducing atomic orbitals into a qualitative treatment of molecular structure in 1931, Pauling failed to recognise the cognitive dissonance between logical categories of molecules, as physical things, and of orbitals, as algebraic formulae from the solution of the Schroedinger equation for the hydrogen atom in coordinate variables. The failure to disclose systems of coordinates for the hydrogen atom other than spherical polar and the extrapolation of hydrogen functions for application to atoms with multiple electrons enabled Pauling to construct a web of deceit about hybrid atomic orbitals to explain molecular structure in circular arguments. Being precisely algebraic formulae, orbitals have a legitimate role only within mathematical calculations, never in qualitative descriptions of molecular structure.

KEYWORDS: orbitals, molecular structure, hydrogen atom, coordinate systems.

INTRODUCTION

Linus Carl Pauling (1901-1994) has been considered, in the context of USA at least, to be one of the two greatest scientists of the twentieth century. Pauling certainly made significant contributions to scientific knowledge; for instance, in 1928 he published [1] an anti-symmetrised product of spin-orbital functions, developed from the work of Heisenberg and of Dirac independently in 1926, which is universally known as the Slater determinant. Pauling also made notable mistakes; for instance, despite his thorough grounding in X-ray crystallography that was the basis of his doctoral research, he proposed [2] a triple helix for the structure of DNA on the basis of various X-ray photographs, rather than the correct double helix that Watson and Crick identified from an X-ray photograph of R. Franklin.

Orbitals in qualitative description of molecular structure

In 1931 Pauling published in *Journal of the American Chemical Society* an article [3] of length 34 journal pages in which he laid the foundations for introducing orbitals into *qualitative* descriptions of molecular structure. By definition, an orbital is, fundamentally, a solution of the Schroedinger equation for the hydrogen atom, and is hence precisely an *algebraic formula*. Any atom, such as a hydrogen atom, as a massive particle (even if composite), clearly belongs to a logical category distinct from the category of algebraic formula [4]. The use of an orbital, as an algebraic formula, is perfectly legitimate in appropriate calculations, such as of observable atomic and molecular properties, for instance the energies of states of the hydrogen atom of which the differences imply the frequencies of spectral lines. In contrast, an implication that an electron is *in* some orbital or other or that an orbital is somehow involved in a chemical bond simply lacks logical sense. That distinction is really the crux of the matter: if one fails to accept the logical consequence of the undeniable disparity between the category of chemical and physical matter and the category of algebraic formula, or the corresponding separate domains of knowledge, one perpetuates the logical fallacy that Pauling inflicted upon his uncomprehending audiences and readers since 1931.

That paper of Pauling (1931) [3] is replete with many further objectionable aspects. For instance he proffered four algebraic formulae that totally lacked scientific substantiation, despite their resemblance to the angular parts of orbitals in spherical polar coordinates, i.e. for a *hydrogen* atom; he brazenly utilised these formulae to generate tetrahedral hybrid combinations for a *carbon* atom with six electrons, entirely neglecting the repulsion between the electrons of that atom that has no role for the hydrogen atom with its single electron. Associated with the angular parts of those functions are radial parts that differ between '2*s*' and '2*p*' functions, but that difference was never taken into account. Pauling confused orbital and basis function: "there are four orbitals in the valence shell of the carbon atom" [3].

The most invidious artifice applied in Pauling's account was his abject failure to disclose the fact that orbitals are derivable in coordinates other than spherical polar, although he cited elsewhere [5] Schroedinger's paper of 1926 [6] in which the latter author derived amplitude functions for a hydrogen atom in paraboloidal coordinates. Disparate orbitals in four systems of coordinates are characterized with both sets of quantum numbers and the corresponding shapes of surfaces of constant amplitude (at a selected value of that amplitude) [7]. Energy quantum number n is the result of experiment, arising in the formulae of Balmer and Rydberg, and must be common to all sets of orbitals. The amplitude functions or orbitals in spherical polar coordinates are specified with quantum numbers k ($= n - l - 1$), l and m; for instance, those integers k, l, $|m|$ indicate the number of radial and angular nodal surfaces associated with coordinates r, θ, ϕ respectively. In a symbol such as $2p_0$, the components imply $n = 2$, $l = 1$ for p, $m = 0$, so $k = 0$. For comparison, for the amplitude functions in paraboloidal coordinates, which Schroedinger himself derived in the third part of his renowned sequence *Quantisation as a Problem of Proper Values* [6], the quantum numbers are (now) designated n_1, n_2, m, with $n = n_1 + n_2 + |m| + 1$, and with analogous relations to the numbers of nodal surfaces. As two of the latter algebraic formulae, specified explicitly with quantum numbers $n_1 = 1$, $n_2 = 0$, $m = 0$, and $n_1 = 0$, $n_2 = 1$, $m = 0$, have exactly the same geometric properties as Pauling's digonal or '*sp*' hybrid formulae from spherical polar coordinates, the latter hybrid orbitals are entirely superfluous for his disingenuous purpose. The shapes of surfaces of constant amplitude ψ depend not only on their quantum numbers but also on their coordinate system, even though we view all such surfaces in Cartesian coordinates [7]. In 1930 Teller had announced [8] that a solution of the hydrogen atom in ellipsoidal, also known as prolate spheroidal, coordinates with the proton at one centre or focus of the ellipsoid enabled another atomic nucleus to be located at the second centre, so that the atomic orbital became a molecular orbital; this condition is obviously more amenable to describe a chemical bond than orbitals in spherical polar coordinates derived in spherical symmetry. It was crucial for Pauling to conceal the fact of alternative sets of orbitals, because their existence completely undermined the credibility of his arbitrary selection of spherical polar functions to form those hybrids. The quantum numbers for these ellipsoidal atomic orbitals are designated n_ξ, n_η, m, with $n = n_\xi + n_\eta + |m| + 1$ [7], which differ again from the symbols and significance of both spherical polar and paraboloidal quantum numbers. It is almost certain that Pauling was aware of Teller's discovery, but he chose to ignore the possible use of ellipsoidal coordinates. The significance of these remarks about coordinate systems is that both the shapes of orbitals, as indicated by surfaces of constant amplitude at a particular chosen value, and their designating quantum numbers, apart from n, are artefacts of a particular system of coordinates, and thus have no logical meaning outside that particular system, but these shapes or orientations are crucial to their application in Pauling's hybrid functions.

In a recent essay Truhlar *et al.* [9] demythologized several aspects of the application of orbitals in various chemical and spectrometric contexts, but they likewise overlooked entirely the existence of multiple sets of orbitals for the hydrogen atom, each set in its respective system of coordinates; such neglect is almost to be expected, because no known textbook of chemistry has ever mentioned this multiplicity, whereas many textbooks of quantum mechanics for physics include the topic of paraboloidal functions because of Schroedinger's own derivation. Truhlar *et al.* emphasized that there is no unique electron configuration for systems of two or more electrons, but what the recognition of multiple systems of coordinates for the hydrogen atom signifies is that there is, likewise, no unique electron configuration even for the hydrogen atom with one electron. For instance, an orbital might be specified unambiguously with quantum numbers k, l, m for spherical polar coordinates, n_1, n_2, m for paraboloidal coordinates, n_ξ, n_η, m for ellipsoidal coordinates and so forth. As a particular and atypical example, values of quantum numbers $k = 0$, $l = 1$, $m = 1$ specify an orbital in spherical polar coordinates of exactly the same size and shape (of surfaces of its real and imaginary parts at a common constant value of ψ) and properties as $n_1 = 0$, $n_2 = 0$, $m = 1$ [7] for an orbital in paraboloidal coordinates.

Pauling's hybrid atomic orbitals are obviously algebraic artefacts of one particular system of coordinates – spherical polar, and have hence no legitimate meaning outside *calculations* in that context. Pauling's four formulae, mentioned above, are purely real, whereas the direct solutions of the hydrogen atom are in general complex: at least one formula of the four direct combinations of orbitals for energy quantum number $n = 2$ (of hydrogen) must be purely imaginary. Boeyens wrote "hybridization [is] an artificial simulation without scientific foundation", and, for tetrahedral hybrid orbitals, "the idea of sp^3 hybridisation is therefore as ludicrous as perpetual motion" [10]. As a result of his systematic investigations of the structure of many hydrocarbon molecules, Bartell declared [11] "Hybridisation is a fraud", which implies that Pauling was a fraudster. To obtain the solution of the Schroedinger equation in spherical polar coordinates so as to generate the orbitals that Pauling mimicked, spherical symmetry is required, such that the vicinity contains no other atom and no external electric field, whereas Pauling used these orbitals to describe a bond between two adjacent atoms in contravention of that spherical symmetry. A fourth system of coordinates in which solution of Schroedinger's equation is practicable involves spheroconical coordinates [12]; this system has a further advantage that all amplitude functions have purely real formulae, i.e. no imaginary parts, but that solution was unknown in 1930. Although Pauling's particular orbitals were derived for a hydrogen atom, he applied them to chemical bonds around a carbon atom. He invoked solutions of Schroedinger's equation that belong to wave mechanics, which is only one method, among at least nine [13], applicable to calculations on systems on an atomic scale and that collectively constitute quantum mechanics [14]. Quantum mechanics, which is distinct from quantum physics and quantum chemistry, is hence not a chemical theory, nor even a physical theory, but a collection of such methods or algorithms, so that orbitals as artefacts of wave mechanics have no meaning outside that one particular method, and hence outside calculations undertaken with that method. Any attribution of orbitals outside the context of calculations according to wave mechanics in one particular coordinate system is thus yet another logical fallacy.

Dirac wrote that "science is concerned only with observable things" [14]. Being an algebraic formula, an orbital is not an observable thing – tangible things and algebraic formulae belong to disparate and separate logical categories. A direct association of observable molecular properties with such artefacts as orbitals, or their combinations as hybrid atomic orbitals, is hence logically unsound. Pauling failed to recognise that, because molecular structure is incompatible with quantum mechanics – both in principle [15] and in practice [16], to seek a quantum-mechanical explanation (rationalisation) of molecular structure is illogical. It should have been unremittingly obvious, even in 1931, that, if one undertakes a rigorous calculation according to wave mechanics in which basis functions are hence applied equitably to both atomic nuclei and electrons and with integrations performed over all coordinates, at the end of the calculation there remains no recognizable classical molecular structure [16]; trivial cases such as diatomic molecules are exceptions – because one can invariably distinguish between electrons and atomic nuclei. Alternatively, Primas [4] stated that, "most chemists refuse to see that the Einstein-Podolsky-Rosen correlations predicted by pioneer quantum mechanics compellingly exclude any classical concept of molecular structure". Although the latter correlations reported in 1935 antedate Pauling's seminal article [3], in subsequent publications such as his book [17] Pauling ignored that fact: because molecular structure is incompatible with quantum mechanics, we must recognize that to seek quantum-mechanical explanations of molecular structure, such as involving orbitals, is absolutely illogical and unjustifiable.

Discussion

Pauling was involved in questionable scientific activities over many years; the first such notable case, perpetrated on physicists in 1929, has been recently exposed [18]. In a joint paper Podolsky (separately of Einstein-Podolsky-Rosen fame) and Pauling [19] purported to derive a momentum distribution for the hydrogen atom based on a transformation from amplitude functions in the space of spherical polar coordinates, but that derivation failed to conform to the correct conjugacy relations that Podolsky had stipulated only a year previously [20]. Although the *radial* part of their momentum distribution is plausible and approximately correct, the transformation of the angular coordinates yielded functions of exactly the same form as in the spatial functions. It is difficult to believe that this result is not a deliberate hoax because of the dissonance between these two articles of which Podolsky was author or coauthor.

A much more blatant instance was Pauling's fantastic claim that ascorbic acid in massive doses helps to prevent or to cure cancer, the common cold and other adverse medical conditions. This claim that was devoid of substantiating scientific or medical evidence was made popular in a book, of title *Vitamin C and Cancer*, that Pauling published without scientific or medical review by peers, which eminently qualifies its description as a hoax. Paul Offit, paediatrician and coinventor of a rotavirus vaccine -- hence a significant scientist, declared that Pauling's assertions about the benefits of dietary supplements "were so spectacularly wrong that he was arguably the world's greatest quack" [21]. Pauling's flagrant influence in promoting the sale in USA of ascorbic acid without medical prescription resulted from his fame, being an *American* who had received *two* Nobel prizes, one for chemistry and one for peace, arising from his demonstrated opposition to weapons of mass destruction. His prominence in the latter cause also benefited from his fame as Nobel laureate in chemistry, which relied on the success of his second hoax.

The fourth egregious hoax was Pauling's denial of the existence of quasi-periodic materials, which are ordered but not periodic; in a lecture he is reported to have stated "There is no such thing as quasicrystal, only quasi-scientists" [22]. He contrived to publish nine papers incorrectly attributing the properties of various quasi-crystalline substances to multiple twinning. Pauling's opposition likely caused some delay to the recognition of the innovative work of D. Shechtman on these materials, for which a Nobel prize was awarded in 2011, based on his discovery in 1982 and subsequent profound explanation.

Pauling's second hoax, as delineated in the preceding section, was about orbitals that as algebraic formulae belong to a logical category distinct from that of structures of molecules as tangible things, compounded with his dishonesty in failing to report orbitals in other sets; this hoax was his greatest and most enduring. How was Pauling so successful, until the present day, in perpetrating this hoax upon chemists? Mulliken [23] described Pauling as "a master salesman and showman"; since antiquity such traits have been associated with the promotion of goods of questionable quality. Valiunis characterised Pauling as "a showman who dazzled the credulous masses – that sad benighted chemistry professoriate – with beguiling simplifications" [24]. Any chemist who refers to an orbital outside the context of a calculation, in which it is an artefact of particular conditions such as a method and a system of coordinates, commits a logical error and is an unwitting dupe of Pauling. Even in calculations according to wave mechanics, orbitals, or functions mimicking them, are superfluous because the application of density-functional theory free from orbitals [25] yields values of observable properties of accuracy sufficient for practical chemical purposes; orbitals are hence dispensable even for calculations according to wave mechanics. Moreover, molecular mechanics that lacks quantum-mechanical provenance is also applicable to evaluate such properties in many cases of chemical interest [25]. For an interpretation of atomic and molecular spectra, the quantum laws [26], or laws of discreteness, suffice for all purposes in which orbitals might be invoked without actual calculations.

CONCLUSION

For qualitative explanations or rationalizations of molecular structure, orbitals were introduced into chemistry in the form of unsubstantiated assertions and invalid mathematical and physical arguments. In the intervening decades since that introduction much pertinent physical and mathematical information has become available, which shows the fallacy and fraudulence of Pauling's original claims and ideas. For chemistry to advance as a logical science, chemists must completely abandon orbitals except for their use in actual calculations.

CONFLICT OF INTEREST STATEMENT

The author states no conflict of interest.

REFERENCES

1. Pauling, L. C. 1928, Chem. Rev., 5(2), 173-213.
2. Pauling, L. C. and Corey, R. B. 1953, Nature, 171, 346.
3. Pauling, L. C. 1931, J. Am. Chem. Soc., 53(4), 1367-1400.
4. Primas, H. 1981, Chemistry, Quantum Mechanics and Reductionism, Springer-Verlag, Berlin Germany, 53 and 250.
5. Pauling, L. C. and Wilson, E. B. 1935, Introduction to Quantum Mechanics, McGraw-Hill, New York USA, 49.
6. Schroedinger, E. 1928, Collected Papers on Wave Mechanics, authorized translation into English, (papers originally published in Z. Phys. 1926), AMS Chelsea, Providence, RI USA, 2014.
7. Ogilvie, J. F. 2016, Ciencia y Tecnologia, 32(1), 1-24, https://arxiv.org, arXiv:1603.00899; 2016, Ciencia y Tecnologia 32(2), 25-39, https://arxiv.org, arXiv:1612.05098
8. Teller, E. 1930, Z. Phys., 61(7), 458-480.
9. Truhlar, D. G., Hiberty, P. C., Shaik, S., Gordon, M. S. and Danovich, D. 2019, Angew. Chem. Int. Ed., 58, 12332-12338.
10. Boeyens, J. C. A. Chemistry From First Principles, 62; Springer, Dordrecht, Netherlands, 2008; The holisttic molecule, chapter 20 in Models, Mysteries and the Magic of Molecules, 458; Boeyens, J. C. A., Ogilvie, J. F. ed. Springer, Dordrecht, Netherlands, 2008.
11. Bartell, L. S. 2000, Coord. Chem. Rev., 197, 37-49.
12. Ball, P. Will we ever understand quantum theory?, https://www.bbc.com/future/article/20130124-will-we-ever-get-quantum-theory
13. Dirac, P. A. M. 1958, Principles of Quantum Mechanics, fourth edition, Oxford University Press, Oxford UK.
14. Styer, D. F., Balkin, M. S., Becker, K. M., Burns, M. R., Dudley, C. E., Forth, S. T., Gaumer, J. S., Kramer, M. A., Oertel, D. C., Park, L. H., Rinkoski, M. T., Smith, C. T. and Wotherspoon, T. D. 2002, Am. J. Phys., 70(3), 288- 297.
15. Woolley, R. G. 1976, Adv. Phys., 25(1), 27-52.
16. Cafiero, M. and Adamowicz, L. 2004, Chem. Phys. Lett., 387(1), 136-141.
17. Pauling, L. C. 1960, The Nature of the Chemical Bond and the Structure of Molecules and Crystals: an Introduction to Modern Structural Chemistry; Cornell University Press, Ithaca, NY USA, third edition.
18. Lombardi, J. R. and Ogilvie, J. F. 2020, Chem. Phys., 538, 110886.
19. Podolski, B. and Pauling, L. C. 1929, Phys. Rev., 34(1), 109-116.
20. Podolski, B. 1928, Phys. Rev., 32(3), 812-816.
21. Offit, P. 2013, The vitamin myth – why we think we need supplements, The Atlantic, 7, 19.
22. Shechtman, D. 2013, Rambam Maimonides Med. J., 4(1), e0002, https://www.rmmj.org.il
23. Mulliken, R. S. 1989, Life of a Scientist, Springer-Verlag, New York USA, 60
24. Valiunis, A. 2015, The man who thought of everything, The New Atlantis, 60-97. https://www.thenewatlantis.com/publications/the-man-who-thought-of-everything
25. Lewars, E. G. 2016, Computational Chemistry: Introduction to the Theory and Applications of Molecular and Quantum Mechanics, Springer, Berlin Germany.
26. Ogilvie, J. F. 1990, J. Chem. Educ., 67(4), 280-289.