

Photo: Tita Binz, Mannheim

Fritz Hückel

A scientist caught between two stools: physicists found his work too nonphysical, and chemists didn't listen to him because he was a physicist.

Erich Hückel, Pioneer of Organic Quantum Chemistry: Reflections on Theory and Experiment

Jerome A. Berson*

In the period between 1930 and 1937, Erich Hückel, a theoretical physicist, made profound contributions to organic chemistry in his quantum mechanical descriptions of unsaturated and conjugated compounds. A brief account of his academic career is followed by simplified expositions, from the point of view of an organic chemist, of the highly approximate theoretical methods he used. Of special significance in the case of cyclic molecules of the class C_nH_n is the concept of filled shells when the number of π electrons is $(4N+2)$ ($N =$

$0, 1, 2, \dots$). Examinations of key applications of Hückel's ideas reveal how they eventually motivated the exploration of new fields in organic synthesis and organic reaction mechanism. Another significant (but until recently, virtually ignored) contribution by Hückel was the recognition that atomic connectivity is a strong determinant of spin multiplicity in non-Kekulé molecules. This idea provides, in principle, a basis for predicting violations of Hund's rule, as recent computational and experimental developments confirm. The interac-

tion of experiment with different styles of quantum theory, and the impact of this relationship on the development of chemistry, are briefly considered. Speculations are given on why Hückel's work exerted so little influence on organic chemistry for decades before its importance finally began to be recognized.

Keywords: aromaticity · history of chemistry · Hückel, Erich · pericyclic reactions

1. Introduction

Erich Hückel's position as one of the early leaders in the development of quantum chemistry now is secure. Every modern chemist uses ideas that sprang from his work. Yet certain causes, undoubtedly connected but still not entirely clear, marked his career with bitter frustration, delayed the recognition that he deserved, and not incidentally, retarded the development of organic chemistry by muffling the impact of his contributions.

To trace the intellectual origins of his work is a challenge to the historian of science. How did a man trained as a theoretical physicist have the insight to choose problems of such significance to organic chemistry? Where did he find the daring self-confidence to make the gross (but ultimately successful) approximations of Hückel molecular orbital theory? What circumstances delayed the incorporation of his ideas into the everyday working knowledge of organic chemists?

2. Biographical Sketch^[1-3]

This is the centennial year of Erich Hückel, who was born on August 9, 1896, the second of three sons of Marie and Armand Hückel. The intellectual development of the three boys was strongly influenced by their father, a physician with an interest in pure science. In the family line were several scientific notables, including the distinguished botanist Josef Gärtner (1732–1791). Erich Hückel enriched this heritage in 1921, when he married Anne Zsigmondy, the daughter of Professor Richard Zsigmondy of Göttingen, a renowned colloid chemist (Nobel Prize in Chemistry, 1925). The marriage endured until Hückel's death in 1980. Erich Hückel's brothers, Rudi (1899–1949) and Walter (1895–1973), followed in the family tradition. Rudi became a physician, but died prematurely. Walter achieved prominence as a professor of organic chemistry and a prolific author of significant research contributions and influential textbooks.^[4]

Erich Hückel was trained as a physicist. His thesis for the D. Phil. at Göttingen (1921) under the supervision of Peter Debye was an experimental study of the scattering of X-rays. Afterward, he served briefly as an assistant to the mathematician David Hilbert at Göttingen but then rejoined Debye, who had moved to the Eidgenössische Technische Hochschule in Zürich. Hückel stayed in Zürich until 1927. Two years on a Rockefeller

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Foundation scholarship, which he spent with Donnan in London and with Bohr in Copenhagen, were followed by two more years on a Deutsche Notgemeinschaft scholarship in Leipzig with Heisenberg and Hund. It was in Leipzig in 1930 that Hückel finished the first of his landmark papers on organic quantum chemistry.

Note that nine years after the D. Phil, Hückel still had no permanent job. In effect, his situation was like that of all too many of today's postdoctoral researchers, who float in semi-employed limbo. Through Debye's intervention, a *dozentur* of sorts was arranged for him at the Technische Hochschule in Stuttgart during the period 1930–1937. However, this was not a regularly budgeted position, and even Hückel's salary was insecure. In his book published in 1975,^[1] Hückel relates that his wife often referred to this time as "seven years of disgrace".

Finally, in 1937 came a call to Marburg as Extraordinary Professor (Associate Professor) of Theoretical Physics. Except for a brief period immediately following the war, Hückel held this position until it was upgraded to that of Ordinary (Full) Professor in 1961, a year before his formal retirement. It was a mean career, blighted by marginalization and outright humiliation, and in some ways incommensurate with the magnitude of his contributions to science. As we shall see, some of his difficulties in gaining recognition arguably were self-inflicted, but others were not. More research would be needed to unravel all the causes, but there is little doubt that the personal frustrations of Hückel's career mirrored the decades-long delay in general acceptance of the significance of his work.

3. Hückel's Early Contributions to Fundamental Physical Chemistry: The Debye–Hückel Theory of Electrolytic Solutions

As an assistant in Zürich, Hückel collaborated on the famous Debye–Hückel theory of strong electrolytes (1923),^[5] which is described authoritatively elsewhere.^[2, 6, 7] The details of the theory need not detain us here, but even an amateur comes away after reading these accounts with an appreciation of two major characteristics of Hückel's later independent work, particularly in the field of organic quantum chemistry: first the identification of the significant questions for which no satisfactory answers were yet available, and second the design of a theory based upon bold simplifying assumptions, which although perhaps not rigorously justifiable at the time, nevertheless showed the way to plausible explanations of known facts and to testable predic-

tions. What is really operating here in this early phase of Hückel's career is a particular style of theory in which the goal is not a perfect, unshakable construct that will last for eternity, but rather a more pragmatic procedure, which might be described with the motto: *let's see if this works, and if it does, let's keep using it until it shows deficiencies*. Of course, this is the way many theoreticians often operate, whether or not they admit as much.

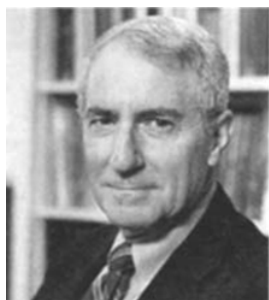
It is true, as has been said,^[2] that we don't know for sure whether Debye or Hückel was the dominant partner in designing the approach to their joint problem, but this issue is almost beside the point here. One way or another, Hückel learned (or invented, or re-invented) this style in the work on the theory of electrolytes. It was to be a hallmark of his later independent research.

4. The Nature of the Double Bond

4.1. Origins of Hückel's Interest in Organic Chemistry

In searching for a pattern of influence on Hückel's famous 1930 papers^[8] "Zur Quantentheorie der Doppelbindung," we note that he acknowledges the stimulus given by Bohr, in whose institute in Copenhagen he began the work in the summer of 1929. The first paper was finished in Leipzig at the end of the year. Hückel's autobiography^[1] implies that Bohr's role consisted largely of identifying chemistry as a field to which the new quantum ideas might be fruitfully applied. There is no indication that Bohr made specific suggestions as to the areas of chemistry that might be interesting to examine.

Where then did Hückel get the idea to work on unsaturated and aromatic compounds? One might imagine that this much insight into the details of so foreign a discipline would have been unusual for a theoretical physicist of the time. It is conceivable that as a student or subsequently in preparation for his theoretical work, he may have acquired enough knowledge of chemistry, especially of organic chemistry, to generate the required motivation, but he makes no mention of special study. One can hardly avoid the conjecture that Walter Hückel's encyclopedic knowledge of the subject offered a far more accessible source. According to Erich Hückel's acknowledgment in the 1930 paper, Edward Teller was especially helpful on quantum mechanical questions and Walter Hückel on chemical matters. Our understanding of the human factors that condition the interaction of theory and experiment would be greatly enhanced if we knew



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more about Walter's role. Although Erich's autobiography and other writings so far available to me are quite nonspecific about just what Walter provided, it is my (as yet undocumented) working hypothesis that Walter served as more than a mere source of factual information. It seems likely that his professional immersion in the culture of organic chemistry made it natural for him to point out to Erich several profound unsolved problems of the structure and reactions of organic compounds which one could hope to illuminate with the new quantum theory. In other words, Walter was in a position to perform a crucial service to Erich: he could ask the right questions. Whether he did so remains to be established.

4.2. Restricted Rotation of Double Bonds

In his first paper on organic quantum chemistry, Erich Hückel undertook to solve an intimidatingly deep problem, which is concisely stated in his own words:^[8]

"The chemist, especially the organic chemist, tends to link more to the concept of valence than merely the valence of the atoms. He would like to ascribe to the valence lines between bonded atoms a definite real existence, in which, especially in the chemistry of carbon, not only the number of valence bonds, but also their direction in space should have significance. . . In this work the generality of this question will not be treated; rather only a special case will be examined, which makes a contribution to this question. This case concerns what chemists call the 'restricted rotation of double bonds'".

The persistence of stereochemical configuration about C=C and C=N bonds had long been known and had been rationalized by the postulate of restricted rotation in such compounds. J. H. van't Hoff^[9] had provided a classical (that is a prequantum theoretical) "explanation." The carbon-carbon double bond was imagined to be made up by contact of two tetrahedrally disposed valences of each atom (Fig. 1). This would result in the

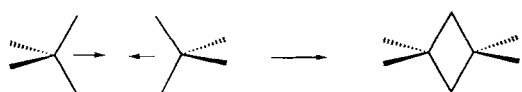


Fig. 1. Junction of two sets of tetrahedral carbon valences to produce a double bond, in the manner of van't Hoff [9]. The bonds lie outside the C-C direction; the remaining four valences lie pairwise above and below the plane of the paper.

stereochemistry shown, with the four remaining valences lying in the same plane as the carbon atoms. The structure would be resistant to rotation of the carbon atoms with respect to each other about the line joining them, because such twisting would diminish the contact of the valences. Of course, this proposal begged the question that Hückel was concerned with: what is the physical nature of these valences?

Soon after the first^[8] of Hückel's papers on the double bond appeared, Pauling^[10a] and Slater^[11] independently were to develop a quantum mechanical description of ethylene which was very close in spirit to van't Hoff's representation. They visualized the two carbon-carbon bonds as *equivalent entities* made

up by overlap of sp^3 hybrid orbitals whose axes lay on either side of the actual C-C internuclear line. As part of a general theory of directed valence, these same sp^3 hybrid orbitals had been postulated to account for the tetrahedral orientation of the bonds of tetravalent carbon atom.

Several textbook authors have wrongly ascribed to Pauling the concept of trigonal (sp^2) hybridization of the doubly bonded carbon atoms in ethylene (see below). Pauling's example of this hybridization was graphite, not ethylene. In fact, he remained strongly opposed to the concept that the two ethylene C-C bonds were different, an unavoidable consequence of trigonal hybridization. The H-C=C angle in a trigonally hybridized alkene is predicted to be 120° , but Pauling's *The Nature of the Chemical Bond* (1961 edition^[10a]), which cites a number of experimental determinations near $125^\circ 17'$, stoutly defends the tetrahedral model, which predicts the latter value (half the difference between 360° and the tetrahedral angle H-C-H angle $109^\circ 26'$). It is probably fair to say that in the current era of ab initio theory, a decision between these two approaches, which are after all only models, has become moot.^[10b]

Curiously, one often sees, in implied or direct form, similar misattributions of the trigonal hybridization concept to Hückel. It is true that the essence of Hückel's model is that the two C-C bonds are *nonequivalent*, one σ and one π bond, a basic distinction from the tetrahedral model favored by Pauling. However, Hückel's ethylene model in the first instance did not arise from hybridization considerations and did not require trigonal hybridization. In fact, the σ - π ethylene model originated in the quantum theoretical treatment of a seemingly very different molecule, molecular oxygen, O_2 . How Hückel's new plant sprang from such unlikely soil makes a long story, but the lessons to be learned about the genesis of ideas justify an abbreviated version. The hybridization question is discussed in more detail in Section 4.4.

4.3. From Dioxygen to Formaldehyde to Ethylene

In 1929 the year just preceding the appearance of Hückel's paper, Lennard-Jones^[12] had made a molecular orbital analysis of the electronic structure of dioxygen in its ground state, which he represented as having the following occupation pattern: $(1s)^2(1s)^2(2s)^2(2s)^2(2p_+)^2(2p_-)^2(2p\sigma)^2\{2p\pi_+, 2p\pi_-\}$. As Hückel points out,^[8] this notation differs from the "united atom" MO formalism of Hund and Mulliken, which is more familiar now, and which had been developed for diatomic molecules. Lennard-Jones's notation is more suitable for showing the electronic states that are being generated during dissociation of the "united atom."

The results are shown in Figure 2.^[13] Note that the interaction of the two filled 2s atomic orbitals gives rise to no net bonding in this approximation, which (with apologies) limits the discussion to the molecular orbitals (MOs) derived from the atomic 2p orbitals and alters Lennard-Jones's presentation to a "united atom" form. An oxygen atom in its ground state has four electrons in the three mutually perpendicular p atomic orbitals (AOs). When two such atoms are brought into bonding distance, the six AOs give rise to six MOs. Two of the MOs, a strongly bonding ($\sigma 2p$) and a strongly antibonding ($\sigma^* 2p$) pair,

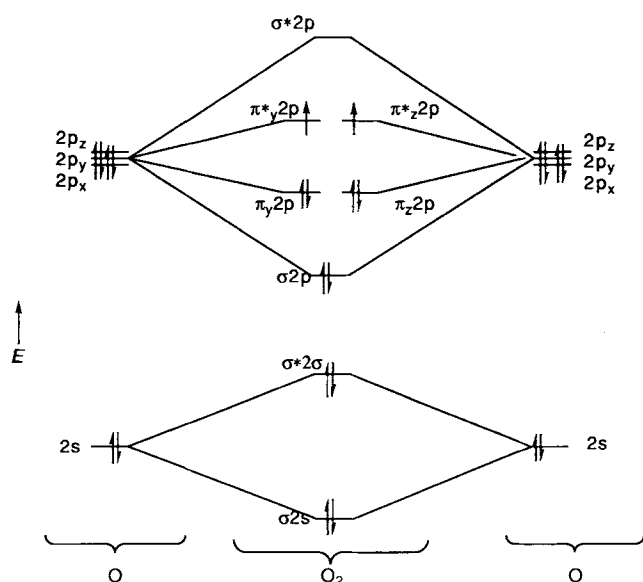


Fig. 2. Formation of O_2 molecular orbitals from oxygen atomic orbitals. The occupation pattern and spin state are derived by application of Hund's highest multiplicity rule. The energies are shown schematically (adapted ref. [13] with permission of Oxford University Press).

result from mixing of the two original p orbitals that lie along the internuclear line. The remaining four atomic p orbitals mix to form two degenerate π MOs and two degenerate π^* MOs. The nodal planes of the π MOs are a mutually perpendicular (arbitrarily chosen) pair containing the two atomic nuclei, and the π^* MOs each have the same pair of nodal planes in addition to a perpendicular nodal plane bisecting the internuclear O–O line. The total of eight electrons (originally from p orbitals) now must be fed into this set of MOs. Two each, with opposed spins, go into the bonding σ and the two bonding π MOs. Although formally the remaining two electrons can go into the pair of π^* orbitals in any of several occupancy and spin configurations, Lennard-Jones assumed that, in energy, "that state is held to be lowest which has the greatest multiplicity, as is the case in atoms". Here, this would be a triplet state, in which the last two electrons each occupy one of the degenerate π^* and π^* orbitals and their spin vectors are parallel. The nominal overall bond order is two, since although there are three bonds, one of them can be considered to be formally cancelled by an antibond.

By this explanation of the experimentally known fact that dioxygen is paramagnetic in its ground state, Lennard-Jones's analysis provided a brilliant early triumph for the quantum theory. Apparently, Hund's first rule,^[14, 15] which originally had been promulgated for atoms, also applies to certain molecules. Dioxygen is a case in which the rule might be expected to apply strictly, because of the symmetry-enforced degeneracy of the π^* orbitals (see below).

Nevertheless, this insight was not the major focus of Hückel's interest in Lennard-Jones's paper. In fact, the triplet nature of dioxygen might well have bemused a lesser intellect, and a connection between the intriguing special case of dioxygen and the less spectacular but far more general problem of ethylene might never have become clear. What attracted Hückel was the idea that there can be *two kinds* of oxygen–oxygen bonds, σ and π .

The next step toward the description of doubly bonded carbon was an ingenious *gedanken* experiment. Hückel imagined the conversion of one of the oxygen nuclei of dioxygen to carbon by the extraction of two protons, which then were bound to the resulting carbon nucleus to give formaldehyde. If we today were following this protocol, we probably would make formaldehyde analogously to the construction of dioxygen shown in Figure 2, with the exception that one of the oxygen atoms would be replaced by an sp^2 -hybridized fragment CH_2 , and the units would be brought together so that all four atoms were in a common plane. Again, one of the carbon 2p orbitals could form a σ bond by overlapping a 2p orbital of the oxygen, and the other carbon 2p orbital would form a π bond with the oxygen p orbital. However, Hückel declined to make the assumption of coplanarity at the start, and argued his way through alternative geometries before rejecting them in favor of the planar one. Also, in 1930, it was not obvious what should be the ordering of the energies of the MOs resulting from the procedure. Hückel again presented arguments that favored the ordering we accept today.

The details, though interesting, are too lengthy to give here, but one major point is worth emphasizing. In both arguments, Hückel resorted to experimental data to make his decisions. With regard to the multiplicity question, it was clear that because of the need to bind the substituent hydrogens to the carbon atom in formaldehyde, the π^* MOs would not be each singly occupied, and the degeneracy that causes a triplet ground state in dioxygen would not exist in formaldehyde. Nevertheless, it was (then) a difficult computational problem to decide whether the multiplicity of the ground state of formaldehyde should be a singlet π or a triplet $\pi-\pi^*$. Hückel's basis for rejecting the triplet was analogical: although no experimental information on the magnetic properties of formaldehyde was available, it was known that acetaldehyde was diamagnetic and hence a singlet.

Similarly, with regard to the molecular geometry, Hückel pointed out that a nonplanar monosubstituted formaldehyde, for example, acetaldehyde, would be pyramidal, with three nonequivalent substituents, and hence one would predict the existence of optical isomers. No such isomers were known. It is heartening to realize that Hückel, a pioneer of theory, was in the latter case not too proud to use the organic chemist's traditional (but nonrigorous) argument of isomer numbers! We have no evidence that Walter Hückel provided this insight to his brother, but it is easy to imagine his doing so.

Formaldehyde-to-ethylene then required only a repetition of the oxygen-to- CH_2 *gedanken* step. Again, the presence of the substituent hydrogens is the key structural feature that favors a singlet ground state. Hückel had now achieved his first objective, a quantum mechanical description of the double bond that would explain restricted rotation. In his model, the C=C double bond is made up of a σ and a π bond. The σ bond is axially symmetric about the internuclear C–C line, but the π bond is not. Rotation of one of the CH_2 groups out of the plane of the other is resisted because to continue this process to 90° would require breaking a π bond. Hückel did not provide a quantitative estimate of the strength of this bond, but it must be substantial to account for the thermal stability of olefinic *cis-trans* isomers. He emphasized the deep structural difference between this model and that of van't Hoff, in which both of the C–C bonds are equivalent.

4.4. Hybridization in Double Bonds

It will be clear that a bit of mystery still lingers over Hückel's picture of ethylene at this point: What is the nature of the C–H bonds? Hückel never clarified this but left it to others. In 1931 and 1932, the years immediately following Hückel's first paper on ethylene, the concept of quantum mechanical hybridization was introduced as the basis of a theory of directed bonding. As we have seen, this idea played an important role in the development of the Pauling–Slater equivalent-bond model of ethylene. In 1933 Mulliken^[16] suggested trigonal hybridization of the carbon valences in ethylene, and in 1934 Penney^[17] made a more extensive comparison of this model with two alternatives, the so-called “right angle” model and the van't Hoff-like Pauling–Slater tetrahedral model.

In the right angle model (Fig. 3), Penney imagined the C–H bonds to be pure $2p\sigma$ bonds, and the double bond joining the two carbons to be made up of one (s,s) and one (σ,σ) bond.

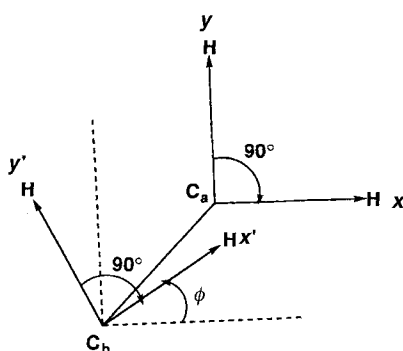


Fig. 3. Penney's right angle model (ultimately rejected in favor of the σ – π model) for ethylene.

The vicinal hydrogen interactions are neglected, and the C–C bonds, although not equivalent, are both axially symmetrical about the C–C direction, so that the energy of the configuration does not depend on the angle ϕ through which one carbon is rotated with respect to the other. As Penney recognized, this model predicts free rotation about the C=C bond, and therefore cannot account for one of the characteristic properties of alkenes.

Penney compared the tetrahedral model and the trigonal model by means of a valence bond calculation and concluded that the trigonal model was energetically preferred. Although the sp^3 hybrid orbitals of the tetrahedral model have more extension along the orbital axis than the sp^2 orbitals of the trigonal model, the sp^3 orbitals are necessarily canted outward from the internuclear C–C line and hence overlap poorly. He subsequently proposed trigonally hybridized carbon as the building block of the σ framework of the benzene ring.

Eventually these suggestions became widely adopted for discussions of doubly bonded carbon. In part, this acceptance must have been furthered by later group theoretical arguments by Kimball,^[18] but one may speculate that it also was based on the simple conceptual continuity of the hybridization picture (sp^3 for methane, sp^2 for ethylene, sp for acetylene), which made the idea pedagogically attractive. Actually a more hard-eyed evaluation of the quantitative merits of Penney's calculations might

have been appropriate. One certainly should have been concerned about Penney's conclusion that the energy needed to rotate one CH_2 plane in sp^2 hybridized ethylene by 90° with respect to the other was “quite small, probably about $1/2$ volt,” (about $11.5 \text{ kcal mol}^{-1}$). If a similar value were required in substituted ethylenes, stable *cis*–*trans* isomerism could not have been observed at room temperature. In other words, were one to take the calculation at face value, the same argument used to reject the right angle model logically would have required rejection of the trigonal model.

5. The Benzene Problem

It might be surmised that Hückel proceeded from ethylene to conjugated chain compounds such as allyl, butadiene, pentadienyl, hexatriene, etc., and then to benzene, and other cyclopolynes, in the systematic manner that we teach Hückel molecular orbital (HMO) theory to students today. Actually, this is not the sequence that occurred. Hückel eventually considered unsaturated chains as a class,^[19] but in the breakthrough paper in 1931,^[20] his target was benzene itself.

The paper was Hückel's *Habilitationsschrift* for attaining the *venia legendi* (right to teach) in theoretical physics at the Technische Hochschule Stuttgart. A massive document of 84 printed pages, it gave two descriptions of benzene and other conjugated cyclopolynes: the “first method,” which eventually came to be the valence bond (VB) theory, and the “second method,” now called the molecular orbital (MO) theory. Hückel gave reasons for preferring the MO procedure, and although some of these might not be very convincing today, he persisted in this choice thereafter. Both the first method and the second method assumed that the unique properties of cyclic conjugated systems could be attributed approximately to the π electrons without explicit consideration of their interaction with the σ electrons.

5.1. Hückel's First Method and Classical Valence Bond Theory

The valence bond method, which Hückel had rejected, was taken up soon after by Pauling and others,^[10, 21–25] who simplified the mathematical procedures and gave reasons for preferring the VB to the MO method. Again, with regard to the problem of cyclic conjugated molecules, their reasons seem insufficient today, but these workers held unwaveringly to their choice in later years. This “classical” VB method, and Pauling's pedagogical packaging of its major results in the form of the “theory of resonance,” dominated theoretical chemistry for 25 years after 1930. The reasons for this, further examined below, were not necessarily that the theory was “correct” in any absolute sense, but rather that Pauling, with consummate knowledge of the whole field of chemistry, convincingly showed how a broad range of chemical phenomena, especially in small molecules, could be explained by some kind of quantum ideas^[10a] and thereby established a faithful and largely uncritical following. As it happened, however, the classical VB method, in the truncated form of it he used, was to prove theoretically inadequate when applied to the problem of aromaticity.

It is true that with the emergence of high-speed digital computers, as is described elsewhere,^[14, 26, 27] the MO method, in increasingly sophisticated manifestations, gradually became the major basis for the explosive computational development of electronic structure theory. However, one should not conclude that VB theory is without adherents today. On the contrary, many investigators have contributed developments of advanced VB methods and successful applications to significant problems, including as we shall see, the reconciliation of the VB and MO theories of aromaticity.^[28, 29]

The most characteristic feature of the valence bond method is that it considers the combining atoms as a whole.^[30] The formation of a molecule is thought of as arising from the bringing together of complete atoms, which are then allowed to interact. In this it differs from the MO method, in which only the nuclei (or nuclei + electron inner shells) are first brought into position, and afterwards the valence electrons are allotted to polycentric molecular orbitals. Clearly the VB method corresponds more closely with the conventional chemical picture, which probably accounts for its widespread acceptance in the form presented by Pauling.

Hückel's first method, the early form of VB theory, was derived from Heitler–London^[31] theory for the formation of molecular hydrogen from two hydrogen atoms. It starts with each atom in a specified quantum state and then introduces exchange. The exchange procedure, which takes into account the indistinguishability of the two electrons 1 and 2 in the form of the exchange integral $\langle \Psi_A(1)\Psi_B(2) | \mathcal{H} | \Psi_B(1)\Psi_A(2) \rangle$, has major significance in the VB method. For example, the binding energy of hydrogen calculated without exchange is only 5.5 kcal mol⁻¹ but when exchange is included in the wave function, the binding energy rises to 69 kcal mol⁻¹, a substantial fraction of the experimental value of 104 kcal mol⁻¹.^[30]

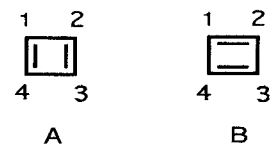
By application of group theoretical procedures, Heisenberg^[32] used this exchange method to explain ferromagnetism. Slater^[32] then developed a useful determinantal method which made possible the treatment of interaction among a large number of atoms without group theory and applied it to electrons in metallic lattices. This method was further applied by Bloch^[33] in place of the Heisenberg group theoretical method for the theory of ferromagnetism. Hückel used the Bloch formalism directly in his first method.

As described by Hückel,^[34] the treatment of a conjugated molecule (such as benzene) by the classical VB method begins by assigning to each carbon atom a π electron which is in a given state with the positional eigenfunction $\phi_a(r_{ia})$, where the suffixes indicate the i th electron in the atom a . The total positional eigenfunction, taking coupling of the π electrons into account, is written as a linear combination of the products $\phi_1(r_{i1}) \dots \phi_6(r_{i6})$. Starting from this, the Heitler–London perturbation method is worked out to the first approximation. Spin is taken into account, and only the linear combinations that conform to the Pauli principle are considered.

In the Pauling modification of VB theory,^[21] one selects from these linear combinations those which correspond to the smallest value of the total spin (in this case $S = 0$), and chooses from these the ones that are linearly independent. These functions which belong to the value $S = 0$ can be associated with models of the valency pattern of the π electrons in which the

atoms are joined in pairs by single bonds, one and only one bond radiating from each atom in such a way that the bonds do not cross one another. Pauling called the schemes of valencies corresponding to the functions "canonical structures." One then formulates and solves the secular perturbations corresponding to these functions, restricting the coupling to that between adjacent atoms.

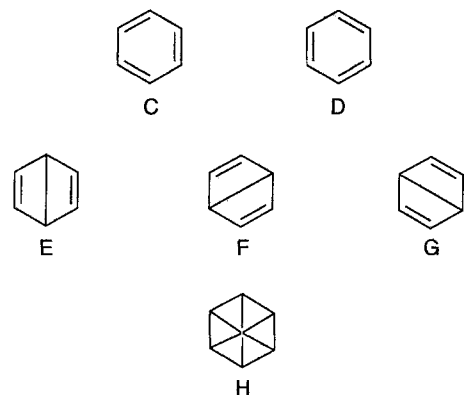
Wheland^[22] gives a simple example of the application of this method to the case of cyclobutadiene. The canonical structures are **A** and **B**. One designates the eigenvalue of the energy as W , the 2p function on the i th carbon atom as Ψ_i , the coulomb integral $\langle \Psi_1\Psi_2\Psi_3\Psi_4 | \mathcal{H} | \Psi_1\Psi_2\Psi_3\Psi_4 \rangle$ as Q , and the single exchange integral between adjacent carbons, for example, $\langle \Psi_1\Psi_2\Psi_3\Psi_4 | \mathcal{H} | \Psi_2\Psi_1\Psi_3\Psi_4 \rangle$ as α' . All single interchange integrals of the energy between nonadjacent atoms, all multiple interchange integrals, and all interchange integrals of unity are neglected. The Slater valence-bond eigenfunction may be expressed as secular equation (a).



$$\begin{vmatrix} Q + \alpha' - W & (1/2)Q + 2\alpha' - (1/2)W \\ (1/2)Q + 2\alpha' - (1/2)W & Q + \alpha' - W \end{vmatrix} = 0 \quad (\text{a})$$

This has the solutions $W = Q + 2\alpha'$ and $W = Q - 2\alpha'$, of which the former represents the ground state since the exchange integral α' is presumably negative. The resonance energy is obtained by subtracting from this a quantity $Q + \alpha'$, the energy of one of the two canonical structures: $Q + 2\alpha' - (Q + \alpha') = \alpha'$.

In the case of benzene, there are five canonical structures with corresponding canonical functions: **C** and **D** correspond to the Kekulé forms, **E**, **F**, and **G** to the Dewar forms. Other structures,



such as for example **H**, that of Claus, can be expressed as linear combinations of the canonical functions [Eq. (b)].

$$\phi_{\text{H}} = \phi_{\text{C}} + \phi_{\text{D}} - [\phi_{\text{E}} + \phi_{\text{F}} + \phi_{\text{G}}] \quad (\text{b})$$

Following a procedure similar to that used for cyclobutadiene, the coupling energy for benzene is $6Q + 2.6055\alpha'$, and the molecular eigenfunction is given by Equation (c).

$$\phi_{\text{benzene}} = 0.62435 (\phi_{\text{C}} + \phi_{\text{D}}) + 0.27101 (\phi_{\text{E}} + \phi_{\text{F}} + \phi_{\text{G}}) \quad (\text{c})$$

In the sense of the approximation, the ground state thus may be considered to result from the superposition of the two Kekulé and the three Dewar forms.

One might be concerned about the approximation which limits the exchanges to pairwise nearest neighbors. Clearly there are many more permutations that could be included. Wheland^[22] himself states:

“This assumption is an extremely drastic one and no rigorous justification for it can be given. The integrals we ignore are probably, to be sure, rather smaller in magnitude than the other ones which we retain. There are, however, an enormous number of the former integrals, and, even though some of them are positive and some are negative, we can have no assurance that their net effect is negligible. We shall, nevertheless, make the assumption because, without it, our calculation would become impracticably complicated, and because, with it, surprisingly satisfactory results can be obtained.”

As we shall see, the neglect of some of these other permutations has serious consequences for the description of cyclic conjugated systems.

Although the classical VB procedure came to be called^[22] the Heitler–London–Slater–Pauling (HLSP) method, Slater in fact preferred to put some distance between himself and Pauling in applications of the method. Thus, in a discussion^[35] at the International Conference of Physics in 1934, Slater remarked that he was in “entire agreement” with Hückel and Hund that the MO method is superior to the Heitler–London method for computing interatomic forces, and that “the calculations of Pauling, for instance, seem to make quite unwarranted use of the theory.” Slater gave no further details, but it seems a reasonable conjecture that he was expressing misgivings over the truncation.

5.2. Hückel's Second Method and Molecular Orbital Theory

This procedure, subsequently called^[22] the Hund–Mulliken–Hückel (HMH) method, had as an immediate intellectual precursor another study^[36] by Bloch on the quantum mechanics of electrons in crystal lattices. Bloch, at that time in Leipzig, was actively developing the theory of metals in order to understand such phenomena as conduction and magnetism. Subsequently, of course, he became famous for providing some of the theoretical foundations for the field of nuclear magnetic resonance.

Bloch approached the problem of the electronic interactions in a many-electron system by considering the properties of a single electron in a spatial force field perturbed by the atomic nuclei and the statistical charge distribution of the remaining electrons. The idea is very similar to the Hartree–Fock method for treating many-electron atoms. In Bloch's sinewy words, “the force field has the same periodicity as the crystal lattice itself,” and “we are thus dealing with plain de Broglie waves which are modulated in rhythm with the lattice.”

The procedure Hückel used^[20] was to set up such a lattice for benzene, calculate the MOs (wave functions) and energy levels in terms of the parameters α and β (defined below) by solving the Schrödinger equation, and construct the electronic configuration by *aufbau*, in accord with the Pauli principle and in analogy

to the practice of Hund, Mulliken, and Lennard-Jones for diatomic molecules. Hückel's benzene lattice was a regular hexagonal array of carbon $2p_z$ orbitals. As every chemistry student now knows, the results can be expressed as shown in Figure 4,

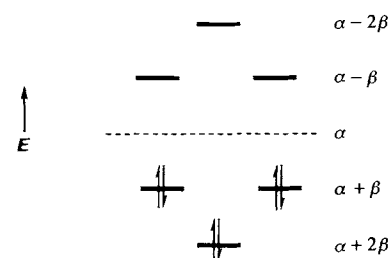


Fig. 4. Energy levels of benzene and occupation pattern in the ground state as calculated by Hückel's second method. The parameters α and β are defined in the text.

where α is the energy of an electron in an unperturbed carbon $2p$ orbital, and β is the stabilization energy (relative to α) experienced by an electron when two such units interact at a defined distance.

Hückel generalized this result to other conjugated systems with n centers, both to rings of other sizes and to chains.^[19, 20, 34, 37] The energy levels can be expressed in the famous Hückel Equations (d), $j = 1, 2, 3, \dots, n$, and (e), $k = 0, \pm 1, \pm 2, \dots, m$, where $m = (n - 1)/2$ for n odd and $m = n/2$ for n even.

$$\text{Chains } C_n H_{n+2}: E = \alpha + 2\beta \cos[j\pi/(n+1)] \quad (\text{d})$$

$$\text{Rings } C_n H_n: E = \alpha + 2\beta \cos[2k\pi/n] \quad (\text{e})$$

Among the messages that these equations convey are that the energy levels for the chains are unique, whereas some of those for the rings are doubly degenerate, that is, the eigenvalues sometimes occur in pairs of equivalent energy. As Hückel pointed out,^[37] these degeneracies are a direct consequence of the cyclic nature of the electron circulation in the ring compounds. The physical reason is that in the energy states that have a finite angular momentum associated with the electronic motion, the circulation is *directional* in either a clockwise or a counterclockwise sense. The eigenfunctions corresponding to these states are not identical, even though the energies are, so *two* MOs must exist at that energy. An equally important point is that for n even or odd the lowest eigenvalues of the ring compounds are unique, and for n even, the highest also are unique. These are nonintuitive results that come out of the solution of the Schrödinger equation and that mark this approach as fundamentally different from the old (Bohr) quantum theory. Whereas in the old theory, for example, the lowest atomic s states still had angular momentum $h/2\pi$, in the new theory the s states now have zero angular momentum. Similarly, in the unique states of benzene, the angular momentum is zero, and consequently, the “sense” of the electronic circulation becomes meaningless.

This difference between rings and chains will be familiar to students of elementary quantum mechanics,^[38–41] where a favorite pedagogical exercise is the calculation of the eigenvalues of the “one-dimensional” Schrödinger equation. An electron is

imagined to be constrained to move along a line or in a circle under zero potential. The solutions for the linear case are unique; those for the circular case have the lowest energy level unique but all the rest pairwise degenerate.

Hückel^[19, 20, 34, 37] emphasized that the MO method, in producing such energy level patterns, led to the idea of closed electron shells analogous to those of the noble gas closed shells in atoms. Particularly significant for the n even conjugated rings was the case of six electrons in benzene, which had been recognized for some time as a feature leading to aromatic properties. Since the Pauli principle allows each orbital to accommodate two electrons of opposite spin, filling the first three orbitals (first two energy levels) of the benzene set 1, 2, 2, 1 in this way would give a stable configuration. On the other hand, four electrons in cyclobutadiene would not give a closed shell, since only the lowest level of the 1, 2, 1 set could be filled. The next higher level could accommodate four electrons but only would have two available. Moreover, in the case of ions derived from odd-membered rings, where all levels above the lowest are degenerate, a closed shell configuration again is reached with six electrons, as in the cyclopentadienide ion, but not with eight, as in the cycloheptatrienide ion or with four as in the cyclopentadienylum ion.

This rule, subsequently stated by others in the abbreviated form $(4N + 2)$ ($N = 0, 1, 2, \dots$), namely that aromaticity should be associated with monocyclic π electron systems containing 2, 6, 10, ... electrons, was in accord with the known facts of organic chemistry at the time. In addition, predictions now could be made about the existence and properties of unknown but easily imaginable new structures. Although the rule does not apply strictly to polycyclic compounds such as naphthalene or biphenyl, Hückel showed by explicit MO calculations^[37] that these systems too should be considered aromatic, as might have been expected. There are limitations to the rule, but much computational research in recent years confirms the essential fact that Hückel's broad classification of aromatic and antiaromatic character survives at higher levels of MO theory and is not just an artifact of the approximations used in the early treatment.^[42]

Significantly, the classical VB method did not produce these results. For example, it predicted that cyclobutadiene should have the highest resonance energy per electron of any of the even cyclic polyenes, and it gave no reason to expect that cyclopentadiene should be a much stronger acid than cycloheptatriene. These failures of classical VB theory were among the reasons that Hückel in 1931 turned away from it as a basis for understanding aromaticity. More than half a century later, the opinion persists^[43] that classical VB theory is "decisively unsuccessful"^[44] for this purpose.

Nevertheless, one feels intuitively that a higher level of VB theory should be capable of reproducing the Hückel rule. After all, both the MO and the VB approaches are approximations of the complete solution of the Schrödinger equation. At successively higher degrees of approximation, the two methods should converge to give equivalent results. In fact, such convergence can be shown analytically for a simple molecule such as H_2 and is expected generally, however complicated the molecule may be.^[45] It comes as no real surprise, therefore, that eventually methods for deriving the Hückel rule by VB theory should emerge.^[44, 46, 47] The key insight in solving this problem is the

crucial necessity to include *cyclic* permutations of the π electrons in the exchange procedure. Just such exchange integrals were among those omitted in the classical VB method. An experimentalist senses a gratifying propriety in this result.

6. A Chilly Reception from the Experimentalists

Hückel's pioneering papers on the molecular orbital theory of unsaturated and aromatic compounds appeared in the period 1930–1931, but they seemed to make little impact on the community of chemists for many years after. In their biographical memoir on Hückel, Hartmann and Longuet-Higgins^[3] ascribe the general neglect of his results to the national culture of German science:

"... physicists in that country in any case were not ready to accept investigations about more complicated chemical bond phenomena as a typical contribution of a physicist. Still more difficult was his (Hückel's) relationship to the chemists. Before World War II, especially in the Anglo-Saxon countries, chemical physics and within that field quantum chemistry also was accepted by both physicists and chemists as an interesting new field of science. Chemists in Germany, on the other hand maintained that chemistry is what chemists do. They did not do quantum chemistry and therefore this kind of science did not belong to chemistry."

It may well be true that German chemists of that period or even later resisted quantum ideas. Although Rolf Huisgen reports^[48] that he was teaching Hückel's results (but not the details of how the calculations were done) as early as 1949, this undoubtedly was exceptional. Even Walter Hückel makes only cursory reference in his textbook^[49] to the contribution his brother had made to the problem of the aromatic sextet.

However, I regret to say that crediting a more receptive attitude to "Anglo-Saxon" chemists, especially the experimental organic chemists, pays them a higher compliment than most of them deserve. Again, there were scattered exceptions. For example, Ingold^[50] in Britain and Hammett^[51] in the United States clearly were aware of the importance of Hückel's work. Elsewhere in these countries, however, even though the problem of aromaticity was prominent in the minds of chemists, and much experimental effort was devoted to it, whatever theoretical reasoning experimentalists brought to bear on such issues in their research or teaching depended almost entirely on resonance theory.^[52] Noller's review of 1950,^[53] ostensibly an exposition of molecular orbital theory prepared for the edification of organic chemistry teachers, does not cite a single reference to Hückel. Most elementary and even advanced textbooks of those years make no mention whatever of Hückel's ideas. One of the most influential books in the field, the second edition (1943) of the multi-authored *Organic Chemistry – An Advanced Treatise*, edited by Gilman, contains a substantial chapter by Fieser on aromatic compounds.^[54] The question of aromaticity is presented only from a historical perspective, and for a theoretical rationale, Fieser defers entirely to Pauling, who contributes a chapter on theory in the same work,^[23] using the already well-known resonance method. Although Pauling mentions the Hückel theory there, he declines to discuss it further on the grounds that the

resonance approach "is the more closely related to the usual concepts of chemistry". Not surprisingly, Pauling's omissions of scholarly exposition and comparison here and elsewhere infuriated Hückel.^[1]

It is true that there was a flurry of theoretical activity, especially in Britain, following up further implications of some of Hückel's ideas. This included work^[55] by, among others, Coulson on mobile bond orders, Coulson and Rushbrooke on alternant π -conjugated systems, Longuet-Higgins on non-Kekulé-molecules, and Dewar on a range of chemical properties deducible from perturbational MO considerations. These papers, written in the elegant lapidary style familiar to mathematicians, and often published outside the conventional chemical journals, were important, but they were either unknown or largely unintelligible to many organic chemists.

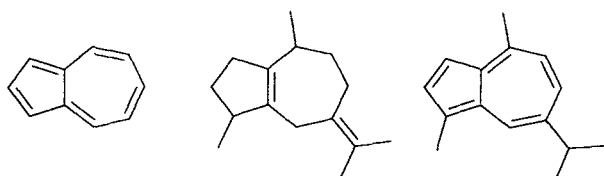
Similarly, a key two-part paper^[56a] by Mulliken and an important early textbook by the Pullmans,^[56b] both in French, influenced a few young theoretically able workers such as Simonetta, and through him, Heilbronner,^[57] but their immediate impact on the thinking of most organic chemists was not great.

Having lived through that period, I can attest that the attitude of many American organic chemists toward MO theory was uninformed and indifferent, if not hostile. Few of them would have taken the trouble to slog through Hückel's highly technical papers, which bristled with equations and matrices, and which, with one obscurely placed exception,^[34] were not available in English. The charismatic Pauling had provided them with a theory which at some level required no mathematics and could be applied by using familiar bond structures. Most of them were content with that.

7. Experimental Tests of the MO Description of Conjugated Cyclic Compounds

If organic chemists were to a large extent unaware of the Hückel rule, how could there have been deliberate tests to explore its scope? In fact, a number of molecules synthesized or discovered in nature after Hückel's papers in the early 1930s eventually turned out to be relevant test species, even though the authors originally had some other motivation for studying them. In this inadvertent process, we see again the familiar paradoxical sequence encountered so frequently in science: "Here's the answer, what's the question?"

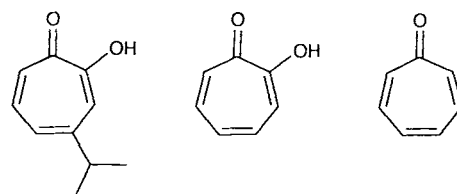
Early examples of this come from the chemistry of the azulenes (Scheme 1), a fascinating group of blue or violet substances, several of which, including the parent compound, are found in nature as such or are formed by chemical transformation of hydroazulenenic sesquiterpenoid precursors.^[58-60]



Scheme 1. Structural formulae of azulene (left) and its derivatives guaiene (center) and guaiazulene (right).

The substantial variety of natural and synthetic azulenes available from the work of Plattner^[58] and others^[59] was augmented by the powerful new Ziegler-Hafner synthesis,^[61] which made azulenes accessible in a small number of steps without the difficult final dehydrogenation previously employed. A rich store of facts embodying the chemical and physical properties of these substances now called for theoretical rationalization, which, as has been instructively summarized by Heilbronner,^[60] Hückel MO theory ultimately provided.

This theme of answers anticipating questions lies at the heart of one of the inspiring stories of organic chemistry, the discovery of the troponeoids.^[62] Space does not permit a full recounting here, but a brief outline may suffice to make the relevant point. In 1926 the Japanese chemist Tetsuo Nozoe settled in Formosa (now Taiwan), where he was to live and work for the next 22 years. During the period between 1944 and 1947, he and his co-workers had deduced the structure of hinokitiol (Scheme 2),



Scheme 2. Structural formulae of hinokitiol (β -thujaplicin, left), tropolone (center), tropone (right).

an isopropyltropolone, but because of disruptions caused by the war and the remoteness of his location, he was not aware of related activity elsewhere,^[62] nor did others know of his work on this subject, most of which was not published in readily accessible journals until 1950.

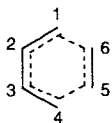
Nozoe^[62] recounts his attempts to explain by the theory of resonance the peculiar aromatic properties of hinokitiol and of tropolone itself, which he subsequently synthesized. His first exposure to this form of quantum theory came in 1942/43, when copies of the 1940 edition of Pauling's *Nature of the Chemical Bond* became available in Formosa. However, although one could write resonance structures, this gave no real enlightenment on the aromaticity of tropolone, and the matter remained somewhat mysterious to him until 1951. In that year, simultaneously published papers by Dauben and Ringold^[63a] and by Doering and Detert^[63b] described the first syntheses of tropone. Both papers called attention to the electronic structure of this ketone and emphasized the presence of a potential aromatic sextet. The Doering paper, giving an explicit reference to Hückel's 1937 summary^[37] of π electron theory, pointed out that the sextet was but one of a general class of stable configurations characterized by having $(4N + 2)$ π electrons. (To my knowledge, this was the first time that Hückel's rule was stated in this succinct form). Nozoe reports^[62] that at that time, he had not heard of such a rule, but it was immediately obvious to him that tropolone's aromaticity must be derived from the same source.

Forerunners of numerous contributions by many authors that followed,^[64] the two tropone papers^[63] clearly were examples of directed rather than serendipitous tests of π electron

theory. Nevertheless, the most persuasive pieces of evidence leading to the acceptance of Hückel's ideas seem to have been the subsequent syntheses of tropylium^[65] and cyclopropenylium^[66] ions, which were specifically mentioned in the citation to Hückel's Otto Hahn Prize in 1965 (see below).

8. Orbital Symmetry—The Extension of Cyclic π -Electron MO Theory to Transition States of Pericyclic Reactions^[67–69]

Pericyclic reactions, as the name implies, are those “in which all first-order changes in bonding relationships take place in concert on a closed curve”.^[69] It would be natural to conjecture that Hückel MO methods, which had been successful in rationalizing the behavior of *ground state* conjugated cyclic molecules, also might give a fruitful account of the *transition states* of pericyclic reactions. The idea of applying π -electron theory to reactions with cyclic transition states probably was first put forth by M. G. Evans in 1939.^[70] He treated the six-electron transition state of the Diels–Alder reaction as an analog of benzene (Scheme 3) and actually wrote down a secular determi-



Scheme 3. The transition state of the Diels–Alder reaction between butadiene (centers 1–4) and ethylene (centers 5 and 6) as benzene analogs.

nant for it differing from that of benzene only in the 1,6 and 4,5 bond integrals. In his words:

“very qualitatively we may say that whereas in the initial state the mobile electrons are those characteristic of an ethylene and a butadiene structure in the transition state they simulate the behaviour in a benzene structure.”

This is a definite insight, quite remarkable for its time. However, it is questionable to maintain, as some have, that Evans was thus formulating a “rule” of aromatic transition states. Such a rule requires not only that one assert that aromatic transition states are more favorable, but also that one have a procedure for recognizing which transition states are aromatic. Without such a procedure, a “rule” of aromatic transition states verges on a tautology. Evans undoubtedly recognized this, and in fact, he attempted to provide a procedure. Unfortunately, his suggestions did not solve the problem. Apparently as a result of an improper conflation of MO and classical VB resonance ideas, Evans had only an uncertain grasp of the concept of aromaticity and especially of antiaromaticity. In this way, he was led to a formulation that stressed the *total number* of reactive electrons:

“... there are qualitative rules which follow. The energy levels of the mobile electrons lie lower in cyclical structures than in straight chain compounds with the same number of centres available. The energy levels of the mobile electrons are lower the greater the number of available centres. These rules imply that the lowering of the activation energy due to the reso-

nance effect will be greater in cyclisation reactions than in chain formation and that the resonance energy in the transition state will increase with the increasing degree of conjugation of the reacting molecules.”

These rules must be carefully distinguished from the orbital symmetry rules. The overarching lesson taught by orbital symmetry and related theories is that favorable (“allowed”) pericyclic transition states *in a given geometry* can be recognized according to whether the number of reactive electrons is $4N$ or $4N + 2$. In disrotatory electrocyclic reactions and *supra–supra* cycloadditions, for example, this number is $4N + 2$, whereas in conrotatory electrocyclic reactions and *supra–antara* cycloadditions it is $4N$. The predictions thus alternate accordingly. Violation of these requirements results in a “forbidden” reaction.

A literal application of the Evans rule favoring more highly conjugated reactants would predict, for example, that resonance stabilization in the cyclooctatetraene-like transition state of the hypothetical *supra–supra* [4+4] dimerization of butadiene should be greater than that in the benzene-like transition state of the *supra–supra* [4+2] association of butadiene and ethylene. But we now recognize the *supra–supra* [4+4] transition state as *antiaromatic* and therefore orbital symmetry forbidden.

Moreover, stereochemistry and electron count are inseparably entwined in orbital symmetry theory. Because Evans had no experimental examples of reactions whose stereochemistry would be favorable with $4N$ electrons, he could not have incorporated them into his thinking except by imagining them, which he did not do. Nothing in his paper gives any indication that he anticipated the idea that is central to orbital symmetry, that of allowed versus forbidden (aromatic vs. antiaromatic) transition states dependent on orbital phasing. To the contrary, continuation along the direction he started would have ended in a theoretical cul-de-sac. Therefore, Evans's contribution was at most a collateral, rather than a lineal, antecedent in the development of orbital symmetry theory.

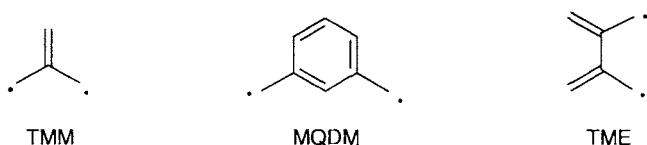
On the other hand, the intimate relationship of orbital symmetry and the Hückel “magic numbers” is obvious. Quite analogously to our previous discussion of ground state molecules, it is precisely because of the *cyclic* nature of pericyclic reactions that one expects them to be more properly described by Hückel MO methods than by classical VB theory. The major extension needed for the application of Hückel theory to transition states was the expansion of the original Hückel ($4N + 2$) magic numbers, derived for conventional cyclic conjugated π -electron systems with no forced orbital phase inversions, to another arrangement with a forced phase inversion, for which the magic number is $4N$.

9. Violations of Hund's Rule in Biradicals

As we have seen, Lennard-Jones^[1,2] applied to molecules (for example, O_2 , B_2) the generalization that later came to be known as Hund's first rule. This governs the prediction of the spin multiplicity in cases where two electrons occupy degenerate orbitals: “that state is held to be lowest which has the greatest

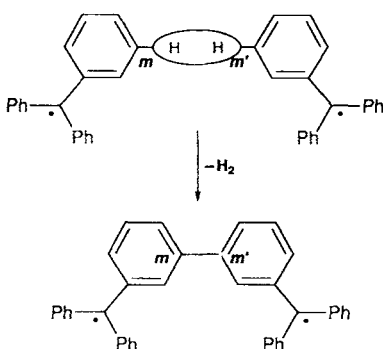
multiplicity."^[12–15] Some theoreticians choose to interpret Hund's rule as applicable only when the orbitals in question are exactly degenerate, which except for rare accidental cases, would limit the rule to molecules like O₂, in which the degeneracy is symmetry-enforced. Other theoreticians apply the rule even when the degeneracy is only approximate.

Longuet-Higgins^[15] invoked the approximate form (without so identifying it) in a seminal 1950 paper, which is perhaps the most influential theoretical writing on π -conjugated biradicals in the period between 1930 and 1970. He showed that, at the Hückel MO theoretical level, non-Kekulé molecules such as trimethylenemethane (TMM), *meta*-quinodimethane (MQDM), and tetramethylenethane (TME), each have a de-



generate pair of nonbonding (NB) MOs occupied by only two electrons, and predicted for each of these molecules a triplet ground state. The symmetry point group of TMM (D_{3h}) contains E representations, but those of MQDM (C_{2v}) and TME (D_{2h}) do not. Thus, in the latter two cases, the NBMO degeneracies are not symmetry-enforced, and the energies are expected to split apart at higher levels of theory.

Longuet-Higgins cited no precedent for his predictions of spin multiplicities in organic biradicals, and apparently there had been only one prior such case in the literature: In 1936, Hund himself^[7] had predicted a triplet ground state for one of the Schlenk–Brauns hydrocarbons studied by Müller et al. (Scheme 4).^[72] This molecule too has degenerate NBMOs at the Hückel level of theory and would have fit easily into the Longuet-Higgins scheme.



Scheme 4. Formal synthesis of the m,m' -Schlenk–Brauns hydrocarbon.

However, Hund's prediction was immediately challenged by Hückel,^[73] who pointed out reasons why the rule of highest multiplicity was of dubious validity in the case of the Schlenk–Brauns compound. Hückel's argument developed from his recognition that the Schlenk–Brauns structure could be derived

(conceptually) by a union of two triphenylmethyl radicals at the m and m' positions. In the NBMO of triphenylmethyl, the m positions of the phenyl rings are *nodes*, that is, they have π -electron coefficients of zero at this level of approximation. In these circumstances, the exchange energy between the two halves of the Schlenk–Brauns molecule is close to zero. Since it is essentially just the exchange energy that accounts for the separation between the triplet and the lowest singlet,^[14, 15] these two states will be almost degenerate. Note that the argument has nothing directly to do with the fact that the NBMO degeneracy in the Schlenk–Brauns hydrocarbon is accidental and will be lifted at higher levels of theory. Instead, in MO terminology, it really is a recognition of the spatial separability of the NBMOs, a property later to be called “disjoint” by Borden and Davidson^[74a] (see below). Hückel's main conclusion was that the ground state is not predictable at this level of theory, contrary to the previous assumption of Hund's rule.

The Schlenk–Brauns hydrocarbon, one of the few biradicals known in 1936, after all was an esoteric species. One might then think of Hückel's argument as pertaining to a highly specialized compound of little interest to those outside the small field of biradicals. Indeed the paper stimulated little or no interest. In my view, however, it had significance far beyond the specific compound, because it showed that the magnetic properties of molecules cannot be treated by imagining that the exchange interaction of two electrons in the field of the nuclei and the remaining electrons will always favor the triplet. On the contrary, such a problem must take into account the *connectivity* of the atoms. This is a profoundly *chemical* point of view, which emphasizes something familiar to every chemist: molecular structure determines molecular properties.

A simple extension of Hückel's argument reveals that of the three biradicals TMM, MQDM, and TME, the latter has the same connectivity feature as the Schlenk–Brauns compound: it can be made by a union of two radicals (allyl in this case) at NBMO nodal positions. Applying Hückel's argument, we can see that TME should not have been classified by Hund's rule.

Because of Longuet–Higgins' (deservedly) high reputation in the field of theory, his unqualified use of Hund's rule in this case had the effect of steering experimentalists along the same oversimplified line of thinking. Also, the absence of a citation to Hückel's 1936 work contributed to decades of obscurity for that paper. One does not disparage the seminal significance of the work of Borden and Davidson^[74a] and of Ovchinnikov^[74b] by noting that they rediscovered the essence of Hückel's connectivity argument after a lapse of forty years. As might be expected after such a passage of time, these papers went far beyond Hückel's original rather qualitative discussion.^[73] They brought to bear the full power of modern electronic structure theory to derive, by both MO (Borden and Davidson) and VB (Ovchinnikov) methods, the idea that when the π -electron system of a biradical has the Hückel type of NBMO node-to-node connectivity, only a small energy gap separates the multiplet states.^[75] Ironically, at the time of their publications, these workers also were unaware of Hückel's paper!

Recent experimental and computational confirmations that Hund's rule is violated in properly constituted disjoint π -conjugated biradicals are reviewed elsewhere.^[76]

10. Honors

Formal recognitions of Hückel's work were sparse until late in his career. Three notable distinctions were: in 1965, the Otto Hahn Prize, jointly awarded by the German Chemical Society and the German Physical Society; in 1966, nearly 30 years after his departure, an honorary degree from the Technische Hochschule in Stuttgart; and in 1977, election as a Foreign Member of the Royal Society.

11. Reflections on Hückel's Career

Hückel's entire contribution to organic quantum chemistry amounted to 17 papers, a list that includes several summaries and reviews. After 1937, when he was only 41 years old, his original contributions to this field virtually stopped. (If Hückel were working now, subject to our dubious emphasis on "productivity", that publication record would put his grant applications in grave jeopardy). As a member of the Marburg physics department, he unsuccessfully tried to initiate work on the theory of the nucleus, but apparently did not bestir himself to seek professional contact with chemists such as, for example, the talented and creative Hans Meerwein, then professor of organic chemistry at Marburg. One cannot put all the blame for the missed collaborative opportunities on Hückel, however. For example, in the period around 1950, Meerwein tried to persuade one of his graduate students to undertake the preparation of the cycloheptatrienide ion,^[77] apparently unaware that a few yards away in the physics department lived a man who twenty years before had predicted the properties of this very species.

The history of the field of organic quantum chemistry after 1937 shows that there was much more to be done. What can explain Hückel's withdrawal? Some have the opinion that he became discouraged when he failed to develop any further ideas in the field comparable in significance to his early work. This may be true, but, of course, it merely pushes the problem one step deeper: Why did he run out of ideas?

Although there are shadowed aspects of Hückel's life that may hide some clues, I think we already know enough to make a few plausible speculations. Hückel^[1] blamed the experiences of the war, the political atmosphere of the Third Reich, and a succession of illnesses for the exhaustion of his energies. The recollection of several colleagues who knew him tend to confirm this diagnosis, but there is also agreement that his was a difficult and even paradoxical personality—shy yet sardonically witty, hypochondriacal, petulant, pessimistic, depressed, ultimately lethargic and withdrawn from academic contact with colleagues and students. Reasons why these characteristics came to dominate Hückel's psyche remain to be elucidated.

A glimpse of Hückel's quirky character comes through in the story of his absence from the Hahn Prize ceremony, which was held in Bonn in September 1965, simultaneously with a symposium celebrating the 100th anniversary of Kekulé's benzene formula. In his letter^[78] to Richard Kuhn, president of the German Chemical Society, Hückel pleads that, "the state of my health does not permit me to receive this honor in person", but from his autobiography^[1] we get a significantly different ex-

cuse: "I was on vacation and dreaded first the trip and then the pompous style in which the Kekulé symposium was planned. In November the medal was presented to me in a small ceremony, which went very harmoniously and was more to my taste than a big display."

Hückel's personality traits surely contributed to his inability to persuade others of the significance of his scientific work.^[1, 77, 79] This would have required a level of showmanship above his capacities. The dull, pedagogically ineffective lectures for which Hückel was known,^[79] for example, did little to enhance his impact.

Particularly damaging was his confrontation with Pauling. As we have seen, Pauling's classical VB theory, although successful in other applications, really did not provide a good account of conjugation and aromaticity, yet his ideas dominated the field for decades. Here was a clear case of the power of persuasion. Pauling's personal magnetism, expository skill, and intellectual breadth were dazzling. Few organic chemists really knew the theoretical basis of Pauling's ideas on aromatic molecules, but he made it easy for them to apply his theory, such as it was. One can only guess what the history of this field might have been had Hückel just made an effort to reach his potential constituency in chemistry, for example by casting his equations in the form of the simple mnemonic diagram put forward twenty years later by Frost and Musulin,^[80] or even by making use of the catchy $(4N + 2)$ slogan. These steps would have gone far to popularize his results and make them more intelligible.

12. Summary and Outlook

In the introduction to his landmark paper on partial valence, Johannes Thiele^[81] gives his view of the role of theory in nurturing a fruitful relationship with experiment:

"The opinions about unsaturated compounds that I shall develop in the following may appear quite rash to many. However, if one holds fast to the idea that a theory actually is nothing other than a point of view which permits known facts to be surveyed in a unified way and new facts to be predicted, a point of view whose value and significance naturally can change with the progress of scientific knowledge, then it seems to me that my opinions satisfy both of these requirements."

Certainly, the development of modern electronic structure theory, from the early approaches by Hückel and his followers to the powerful methods of today, illustrates this view. Because the original Hückel MO method was a very approximate form of a theory that others later took to a much higher level, one senses now a certain amused condescension from some adepts, who view it as a quaint relic. One must ask, however, whether any other theoretical advance ultimately has done more to enlighten the thinking of organic chemists than Hückel's brief, bright flare of cognition, regrettably quenched too soon. Words suitable to his legacy are found in Eliot's terse homage to pioneers:^[82]

"Someone said: 'The dead writers are remote from us because we *know* so much more than they did.' Precisely, and they are that which we know."

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