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Perspective

Perspective on "Quantentheoretische Beiträge zum Benzolproblem. I. Die Elektronenkonfiguration des Benzols und verwandter Beziehungen"

Hückel E (1931) Z Phys 70: 204–286

Gernot Frenking

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35037 Marburg, Germany

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Abstract. Guided by an intuitive choice of approximations which shows remarkable chemical insight into the topic of aromaticity, Hückel mastered the difficult mathematical treatment of a complex molecule like benzene at a very early stage of quantum theory using method 1 (now valence bond theory) and method 2 (now molecular orbital theory). He concluded that method 2 is clearly superior to method 1 because the results of this method explain directly the peculiar behaviour of planar molecules with 6 π electrons.

Key words: Aromaticity – Molecular orbital theory – Valence bond theory

The year of the birth of quantum chemistry is 1927, when Heitler and London [1] showed for the first time that the chemical bonding between two neutral atoms can be understood in terms of fundamental laws of physics if the newly developed quantum theoretical principles are applied to the interactions between the two hydrogen atoms in H_2 [2]. It was only 4 years later that the epochal quantum theoretical study by Erich Hückel about the electronic structure of benzene, which has become the theoretical basis for our present understanding of aromaticity [3], was published.[1] It is remarkable that a much more complicated molecule than H_2 such as benzene could be treated in the infant days of quantum chemistry in a meaningful way.

Hückel's paper on benzene was his second quantum theoretical investigation of chemical bonding. His first topic was the nature of the double bond, which was published in two papers [7]. The study of ethylene was inspired by a molecular orbital (MO) analysis of O_2 by Lennard-Jones [8], which focussed on the question of why the ground state of dioxygen is a triplet. It was an early triumph of MO theory (the name was not used at that time though) that the $^3\sum_g^-$ ground state of O_2 could be easily explained when the symmetric and antisymmetric combinations of the atomic eigenfunctions are used as molecular eigenfunctions, which are then occupied according to the aufbau principle and Hund's rule. Hückel recognized in the work of Lennard-Jones that there are two different types of O—O bonds, which were at that time already labeled σ and π. By subsequent replacement of O with isoelectronic CH_2, he developed a qualitative model for the bonding situation, first in $CH_2{=}O$ and then in $H_2C{=}CH_2$. This work was important for his study of benzene because it led him to conclude that the two C—C bonds in ethylene are different and not equivalent as was generally believed and taught at that time. It was common to use van't Hoff's prequantum theoretical model of two tetrahedra sharing one edge for a discussion of the double bond [9]. Only 1 year after Hückel published his two papers on ethylene, Pauling [10] and Slater [11] independently developed a quantum theoretical description of ethylene with two equivalent C—C bonds, which are made up by overlapping two pairs of sp^3 orbitals. Pauling strongly opposed the idea that the C—C bonds in olefins are not equivalent.

Hückel began his quantum theoretical studies of chemical bonding following postdoctoral work at several locations, the most important one being Zürich, where he developed together with his Ph.D. advisor Peter Debye the well-known Debye–Hückel theory of electrolytic

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[1] The paper about benzene is part 1 of a series with the translated title "Quantum chemical contributions to the benzene problem. I. The electron configuration of benzene and related compounds." Three other papers followed. The second paper [4] has the same series title and the translated subtitle "II. Quantum theory of induced polarizabilities." The study is an attempt to correlate chemical behaviour of substituted benzenes with the charge distribution in the ring which becomes disturbed by the substituents. The third paper [5] has a slightly different series title with no further subtitle: "Quantum theoretical contributions to the problem of aromatic and unsaturated compounds. III." The final paper in the series [6] has the subtitle "Free radicals in organic chemistry"

solutions [12]. The work concerning the double bond was suggested to him by Nils Bohr, whom Hückel visited in Copenhagen in 1929 when he was in Leipzig as a stipendiary [13]. The benzene results were published in the famous landmark paper which has 83 printed pages. The publication was also his habilitation thesis to become a docent at the Technical High School (now University) Stuttgart, to where he moved in 1930.

The paper is divided into six parts, an abstract, and an appendix with mathematical details. Part 1 gives an introduction and outline of the problem, which shows that the physicist Erich Hückel had a pronounced knowledge about the chemical and physical properties of aromatic compounds. The chemical knowledge was certainly aquired from discussions with his brother Walter Hückel, who was a chemistry professor and textbook author [14]. Hückel discusses benzene, pyridine, pyrrol, furan, thiophene, isomeric forms of dihydrobenzene and chinone, cyclobutadiene, cyclooctatetraene, and cyclopentadiene. He points out that there is no satisfactory explanation for the observation why cyclobutadiene does not (at that time) exist, and why benzene and cyclooctatetraene are stable but chemically very different in their reactivity. Hückel emphasizes that the number 6 appears to play a particular role for aromatic compounds, which had been pointed out for the first time by Bamberger in 1890 [15].

The second part of the paper is entitled "General remarks about quantum theoretical methods for treatment of unsaturated ring systems." This part describes his fundamental approach of constructing the electronic structure of benzene in terms of the electronic state of the carbon atoms. Hückel argues that in a planar regular ring system, C_nH_n, each carbon atom interacts primarily with the three neighbouring atoms (two carbons, one hydrogen). The perturbation of the electronic states of the carbon atom by the nine valence electrons of the neighbouring atoms leads to energetically different atomic states with the order $(s) < (p) < (p)_{\mathrm{v}} < (p)_{\mathrm{h}}$, where v means vertical and h horizontal with regard to the ring plane.[2] Hückel uses symmetry arguments for deriving the energy order, which is determined by the number of neighbouring atoms that are found in the nodal planes. Thus, $(p)_{\mathrm{h}}$ is the energetically highest-lying atomic state because all three neighbouring atoms lie in the nodal plane of this state (orbital) [16]. The atomic electronic states lead to four different arrangements for benzene:

$$\begin{array}{llll} (s)^2, & (p)^2, & (p)_{\mathrm{v}}^2, & (p)_{\mathrm{h}} \\ (s)^2, & (p)^2, & (p)_{\mathrm{h}}^2, & (p)_{\mathrm{v}} \\ (s)^2, & (p)_{\mathrm{v}}^2, & (p)_{\mathrm{h}}^2, & (p) \\ (p)^2, & (p)_{\mathrm{v}}^2, & (p)_{\mathrm{h}}^2, & (s) \ . \end{array}$$

Hückel argues that the first of these terms, where the $(p)_{\mathrm{h}}$ state of carbon [$p(\pi)$ orbital in modern notation] is singly occupied, should be the energetically lowest-lying term for benzene; therefore, only this term is considered in the mathematical treatments of the electronic structure. In the final section of part 2 Hückel says that he is going to use two different mathematical treatments for the benzene problem. He calls them "first method" and "second method", which are now known as Valence bond (VB) and MO methods, respectively. Hückel cites papers by Heitler and London [1], Heisenberg [16], Slater [17], and Bloch [18] as fundamental for the first (VB) method and says that he is going to use Bloch's version for his work. For the second (MO) method he cites another paper by Bloch [19] and the famous publication of Hartree [20], but not Fock [21]. Hückel writes that Hartree's approximation neglects exchange interactions, but he notes that this can be accounted for later in the calculations. Before coming to the two central mathematical parts of the paper, Hückel notes that "...it will be seen that the second method is better suited for the real behaviour than the first method."

In the third part of the paper Hückel derives energy expressions for the different electronic terms of benzene using method 1. The wavefunction is given as a Slater determinant, and the solution of the Schrödinger equation is expressed in analogy to the Heitler–London paper [1] as

$$W = n \times w + \Delta W \tag{1}$$

$$\psi = \sum a_\mu \varphi\mu \ , \tag{2}$$

where ΔW is the interaction energy between the n π electrons which is determined by the coulomb integrals J_0 and the exchange integrals J.[3] The equations for determining ΔW and a are then given as

$$[\Delta W - nJ_0 + (n-t)\ J]a_\mu + J \sum a_\upsilon = 0 \tag{3}$$

Hückel uses symmetry and group theoretical arguments to finally derive (in chapter 5) the following energy expressions for n electrons in n-cyclic CH compounds given by method 1:

$$n = 3: \quad \Delta W_3 = 3J_0 \tag{4}$$

$$n = 4: \quad \Delta W_4 = 4J_0 + 2J \tag{5}$$

$$n = 5: \quad \Delta W_5 = 5J_0 + 1.24J \tag{6}$$

$$n = 6: \quad \Delta W_6 = 6J_0 + 2.6J \tag{7}$$

Chapter 4 describes the energy expressions for π electrons in cyclic conjugated systems using the familiar integrals α, for the energy of an unperturbed electron, and β, for the interaction between electrons at neighbouring atoms. Hückel notes that $\beta > 0$ if the wavefunction is nodeless, while $\beta < 0$ when the wavefunction has a node (Hückel defines α and β in such a way that positive values are stabilizing and negative values destabilizing).

The important part of this chapter concerns the wavefunction. Hückel cites Bloch [19] and notes that, for cyclic groups, each wavefunction, χ, may be expressed as

$$\chi^k(r, z, \varphi) = \exp(ik\varphi)\ u^k(r, z, \varphi) \ , \tag{8}$$

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[2] Hückel uses the words "state" (Zustand) and "term" in a different meaning than is used now

[3] This is the notation which is used by Hückel

where k is either a positive or negative integer or zero. The energy eigenvalues are then given by

$$W^k = W_0 - \alpha - 2\beta\cos(2\pi k/n) \quad (k = 0, 1, \ldots, n-1) \ . \tag{9}$$

Hückel notes that the eigenfunctions and eigenvalues are determined by the values for k

$$k = 0,\ \pm 1,\ \pm 2,\ \pm 0.5(n-1) \quad \text{if } n \text{ is odd} \tag{10}$$

$$k = 0,\ \pm 1,\ \pm 2,\ \pm(0.5n-1),\ +0.5n \quad \text{if } n \text{ is even} \ . \tag{11}$$

Another important result of this part of the paper is the number of different terms which arise when the lowest-lying eigenfunctions become occupied. The results are graphically shown in part 5, where the energy expressions which arise from method 1 (Eqs. 4–7) and method 2 (Eqs. 9–11) are compared. Hückel displays the qualitative ordering of the energies of the different terms which are given by the two methods for $n = 3$–6 in four figures. It becomes obvious that the energies given by method 1 (Eqs. 4–7) do not reveal the particular stability of the ring system with $n = 6$. Hückel notes that the only conclusion which can be drawn from Eqs. (4)–(7) is that cyclic compounds with an odd number of ring atoms should be higher in energy than those with an even number. He mentions that the underlying σ frame also influences the reactivity of the cyclic molecules, and that it is known from saturated compounds that small ring compounds with $n = 3, 4$ are higher in energy than compounds with larger rings. Similar behaviour should be expected for unsaturated compounds. He points out that the stability of a molecule is not only determined by the total energy of the compound. The chemical reactivity may also depend on the way the energy of the molecule changes when it is subject to external perturbation. Hückel says that there is substantial chemical evidence for a correlation between the constitution and the reactivity of organic molecules, and that only modest theoretical explanations are found in the literature. Here he cites the two-volume textbook of his brother Walter Hückel [14]. Then he switches to the discussion of the results of method 2 with the sentence: "We now believe that we can offer a new perspective for the ring systems considered."

The rest of chapter 5 is a far-sighted discussion of the conclusions which can be drawn from the results of method 2. Hückel points out that the occupation of the lowest-lying eigenfunctions leads to only one electronic state for $n = 6$, while there are four states for $n = 4$ and 8. This would indicate a closed-shell structure for benzene, while cyclobutadiene and cyclooctatetraene are not only high-energy molecules, but the open-shell structure should make them highly reactive. Hückel assumed planar structures for all the cyclic molecules considered (the nonplanar structure of C_8H_8 was not known at that time), but he was aware of possibly strong influences of nonplanar geometries on the stability and reactivity of the compounds. He says explicitly that this may be the case for $n = 8$ and 10. One formula which is frequently associated with the name Hückel is not found in the publication: $4n + 2$. This now familiar way to explain the aromaticity of cyclic conjugated compounds with the number of π electrons (Hückel's rule) was introduced much later by Doering [22].

Hückel discusses the experimental observation that cyclopentadiene reacts easily with potassium, while cycloheptatriene does not. He says that the formation of $C_5H_5^-$ could explain the results because it would have the same electron configuration as benzene. Further examples which are discussed in chapter 5 are pyridine, pyrrol, furan, and thiophene. The final chapter is devoted to hydrobenzenes. Hückel shows that the energy ordering of 1,2-dihydrobenzene and 1,4-dihydrobenzene predicted by method 2 is in agreement with experimental findings.

In retrospect, there are two aspects which make this paper a century-contribution. One aspect is the mathematical treatment of the immensely difficult problem at a very early stage of quantum chemistry, which was guided by an intuitive choice of approximations. The choice was made possible because of Hückel's chemical insight into the problem, which is the second remarkable aspect. It is surprising that the theoretical physicist Erich Hückel was able to build a bridge between the mathematical results and chemical observations. It is a pity that it took two decades before chemists started to become interested in Hückel's work.

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