

# The Free-Electron Model

## From Otto Schmidt to John Platt

William B. Jensen

Department of Chemistry, University of Cincinnati  
Cincinnati, OH 452201-0172

### 1. The Lull in Quantum Chemistry

Beginning about 1935, and extending through the mid-1960s, quantum chemistry hit a lull. The reasons for this were vividly outlined in a lecture given at Reed College in July of 1959 by the quantum chemist, George Kimball (figure 1), of Columbia University (1, 2):

*Quantum mechanics was first invented or discovered in about 1925, and from there until about 1935 the field seemed to open right up. Progress was extremely rapid, all kinds of ideas came tumbling out, many of which very rapidly got into quite elementary books. Then, all of a sudden, about 1935 the whole thing seem to come to a stop. Most of the people who had been working in the field got into something different, and the situation today [i.e., in 1959] is not really very different from what it was in 1935.*

The reason for this lull, Kimball went on to explain, was quite simple (2):

*Now the reason why progress seemed to stop is the fact that all the easy things were done. In trying to tackle further problems the mathematical difficulties were so great they simply overwhelmed everybody who tried them.*

Noting that even the advent of the early electronic computer had so far failed to solve this problem, Kimball pessimistically concluded that (2):

*When you take a cold-blooded look at the situation it is really discouraging. In the face of all of the problems in atomic and molecular structure, the only ones which have been solved with real precision are: the problem of the hydrogen atom, the problem of the helium atom, the problem of the hydrogen molecule,  $H_2$ , and that's all. That has been the absolute limit to which really complete calculations have been carried.*

Responses to this situation varied. As already noted by Kimball, many simply left the field for greener intellectual pastures. Thus Heisenberg moved



Figure 1. George Elbert Kimball (1906-1967).

into the field of nuclear physics, whereas Schrödinger and a host of younger physicists and quantum chemists, such as Walter Elsasser, Max Delbrück, and Leslie Orgel would be attracted to the rising field of molecular biology. Others, such as John Platt, H. Christopher Lonquet-Higgins, and ultimately Kimball himself, would leave physical science altogether, whereas yet others would stick it out by resigning themselves to the laborious working out of ever better approximations for apparently intractable integrals and ever more complex computational algorithms as the computer gradually increased in power and efficiency.

Though we owe the current successes of quantum chemistry to the persistence of this latter group, there was yet a third group, who, hoping for a quicker return, would opt instead for the pursuit of radically simplified approximate bonding models which, while retaining the qualitative essences of quantum mechanical in-

sights, would remain mathematically tractable – if of low quantitative accuracy. Indeed, this third approach was taken by Kimball himself before ultimately deserting the field altogether. As he explained in his lecture (2):

*The other problems have produced an almost ridiculous flow of approximate calculations. It struck me, some time ago, that there was a remarkable feature that all these approximate calculations had in common, and that was that, starting from almost any old assumption, including some that were definitely known to be wrong, one ground a mathematical crank and came out with answers that were within 10% or so of the truth. Almost any assumption would give that degree of accuracy; but even the most sophisticated work, trying to improve that degree of accuracy, got nowhere.*

*Well I beat my head against this business about trying to get better accuracy for a long time, and finally I got tired of it and said, "Let's try a different angle. Instead of trying to make a better calculation, let's try reversing the situation and see how bad a calculation we can make and still come out with the same first approximation." There seemed to be abundant evidence that you could make perfectly terrible first approximations and come out with this 10% sort of accuracy.*

The result of Kimball's discontent was his development, via the Ph.D theses of five graduate students spanning the period 1952-1957, of an approximate localized MO model known as the "charge-cloud model" which became the basis of the 1964 CBA high school chemistry textbook and was further refined, under the rubric of the "tangent-sphere model," in a series of more than a dozen papers and reviews published by Henry Bent during the 1960s (3).

Likewise the early work of Linnett and Mellish was amplified by Nyholm and Gillespie in 1957 and further refined by Gillespie throughout the 1960s into what is now known as the "Valence-Shell Electron Pair Repulsion" or "VSEPR" model of molecular geometry (4), and Linnett, again during the 1960s, eventually elaborated his earlier work into a refinement of the original Lewis model known as "double-quartet theory" (5).

Though the present author feels that both the charge-cloud and the double-quartet models still have much to recommend them – certainly far more than the circa 1916 Lewis dot structures and memorized random fragments of VB and MO theory which currently dominate the Freshman textbook – of these approximate models, only VSEPR theory has survived as an inherent part of both the introductory and inorganic textbook. However, yet a fourth approximate bonding

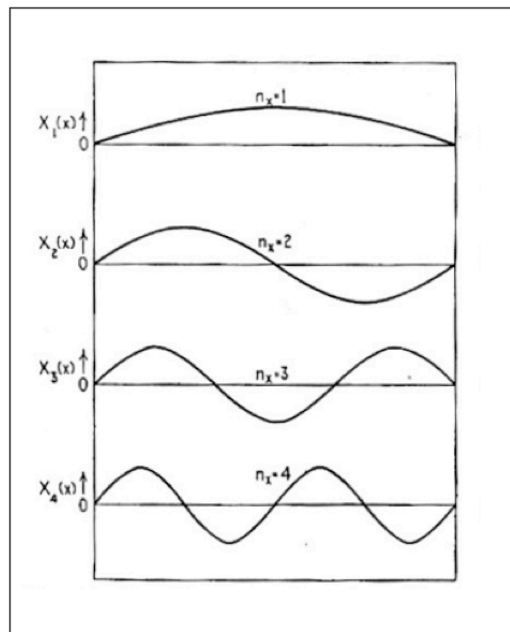


Figure 2. The graphical representation of the results for the simple one-dimensional particle in a box problem as given in the 1935 text by Pauling and Wilson.

model developed during this period in response to these pressures has also survived in the textbook literature, albeit not in the Freshman text. This is the free-electron model for  $\pi$ -conjugated electron systems and is the central focus of this paper.

## 2. Otto Schmidt and the Double-Bond Rule

By the mid 1930s the classical problem of a particle in a one-dimensional box with infinite walls had made it into textbooks on quantum mechanics, as illustrated by figure 2, which is taken from the classic 1935 text by Pauling and Wilson (6). Here it was used to illustrate one of the simplest quantitative applications of the Schrödinger equation – a pedagogical role which it continues to play in textbooks on quantum mechanics even to this day.

The first attempt to apply this model, not just as a simple exercise in mathematical computation, but as an actual physical approximation for the  $\pi$ -electron systems of conjugated molecules, was made by the German organic chemist, Otto Schmidt (figure 3), in a series of papers published between 1938 and 1942 (7-10). Born in Cologne in 1874, Schmidt studied chemistry at Bonn and Zürich, receiving a doctorate in chemistry from Bonn in 1900 for work done under Eugen Bamberger. After a stint in academia, Schmidt became an industrial chemist in the employ of the Badische Anilin und Soda Fabrik (BASF), where he remained



Figure 3. Franz Otto Schmidt (1874-1943).

until his retirement in 1931, after which he maintained an affiliation with the University of Darmstadt until his death in 1943 (11).

Schmidt is best remembered today for his development of the so-called “double-bond” or “Schmidt rule,” which states that the presence of a double bond or of a conjugated system, such as a phenyl group, in an organic molecule tends to stabilize the sigma bonds immediately adjacent to it (i.e. in the  $\alpha$ -positions) but weaken and thus activate those once removed (i.e. in the  $\beta$ -positions) (12).

Schmidt’s exploration of the free-electron model was ultimately driven by his attempts to find a theoretical rationale for his double-bond rule. Though he spent the period 1931-1932 as a visiting Professor at Caltech and interacted with Linus Pauling, he would reject the standard VB rationale of the rule involving differing degrees of resonance stabilization for the various alternative products formed after sigma bond cleavage. Likewise, though he would distinguish between tightly bound “A-electrons” and the loosely bound “B-electrons” unique to multiple bond and conjugated systems, he would never adopt the more conventional MO designations of sigma ( $\sigma$ ) and pi ( $\pi$ ) for these two types of electrons. Rather he assumed that the loosely bound B-electrons (i.e.  $\pi$ -electrons) of the multiple bond system could interact with the adjacent sigma bonds in the parent molecule to cause an alternation in bond strengths, making the immediately adjacent sigma bond stronger, the sigma bond once re-

moved weaker, the sigma bond twice removed stronger, etc., with the effect gradually dying out as one moved further from the multiple bond system.

It was this concept of loosely bound B-electrons coupled to alternating bond strengths – and hence alternating electron densities – which no doubt attracted Schmidt to the problem of the particle in the box, with its alternating nodal properties, in the hope that it would support his theory of the double-bond rule. In his papers, he applied the free-electron model almost exclusively to benzene and related aromatic systems, modeling their  $\pi$ -electrons (i.e., B-electrons) as freely moving particles in a cylindrical box of constant potential (figure 4). In recognition of this assumption he eventually came to refer to the theory as the *Kastenmodell* or “box model” of the chemical bond.

The disruptions of the Second World War and the fact that Schmidt chose to publish in journals not widely read by quantum chemists meant that his initial application of the free-electron model to conjugated systems went largely unnoticed. It was not until 1948 that interest in this approach was rekindled when three independent papers dealing with the model appeared in rapid succession – the first by the Australian spectroscopist, Noel Bayliss (13), the second by the Swiss chemist, Hans Kuhn (14), and the third by the American chemist, William Simpson (15). The next year this trio was joined by yet a fourth author – John R. Platt, of the Department of Physics at the University of Chicago (16).

None of these four authors seems to have initially been aware of Schmidt’s pioneering work, though Kuhn and Platt would eventually come to acknowledge it. Indeed, both Bayliss and Kuhn suggested that they had been inspired instead by Sommerfeld’s original 1928 free-electron model of the metallic

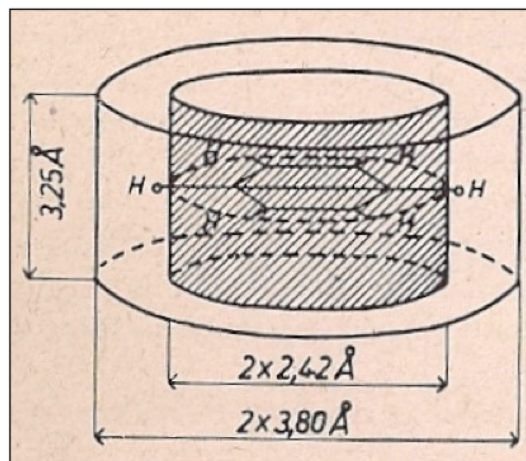


Figure 4. Schmidt’s cylindrical box model for the  $\pi$ -electrons of benzene.

bond and even Schmidt had made passing comparisons between his so-called *B*-electrons and the conduction electrons in metals (17).

Though Bayliss would go on to write the first definitive review article on the free-electron model in 1952 for the British journal *Quarterly Reviews* (18), it is Kuhn and Platt who would eventually emerge over the next decade as the major advocates of the model and whose contributions thus require closer scrutiny.

### 3. Hans Kuhn and Dye Chemistry

Born in 1919 in Berne, Switzerland, Hans Kuhn (figure 5) studied chemistry at both the ETH in Zürich and the University of Basel, receiving his doctorate in chemistry from the latter institution for work done under the guidance of Werner Kuhn (no relation). From 1946-1947 he was a postdoctoral fellow with Linus Pauling at Caltech. In 1951 he was appointed Professor of Chemistry at the University of Basel, followed in 1953 by his move to the University of Marburg, where he served as Director of the Institute of Physical Chemistry. In 1970 he joined the Max Planck Institute for Biophysical Chemistry in Göttingen, where he served as Director of the Department of Molecular Systems Assembly until his retirement in 1985.

As is well known by those attending this symposium, the standard solution for a particle in a one-dimensional box with infinite walls gives a series of energy levels defined by the equation:

$$E = (h^2/8m)(n^2/L^2) \quad [1]$$

where  $h$  is Planck's constant,  $m$  is the mass of the par-

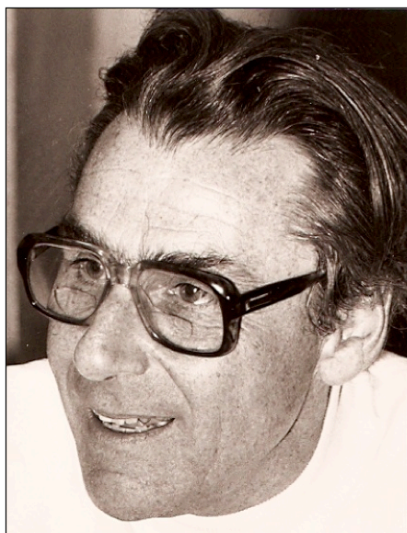


Figure 5. Hans Kuhn (b. 1919)

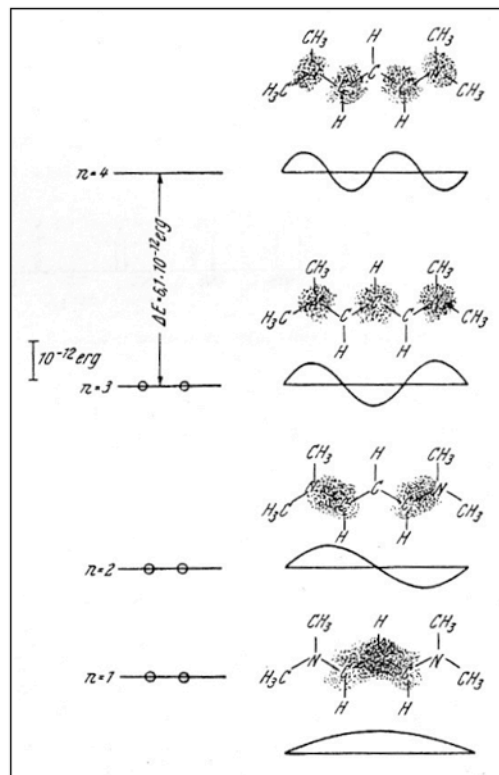


Figure 6. Application of the free-electron model to the linear  $\pi$ -system of the  $(\text{CH}_3)_2\text{N}-\text{CH}=\text{CH}-\text{CH}-\text{N}(\text{CH}_3)_2^+$  ion.

ticle and  $L$  is the length of the box. For a box containing  $N$  electrons, the energy of transition,  $\Delta E$ , between the highest occupied energy level and the lowest unoccupied energy level will correspond to a transition between the quantum levels  $n_{HO} = N/2$  and  $n_{LU} = N/2 + 1$  and will give the final result:

$$\Delta E = E_{LU} - E_{HO} = (h^2/8m)(N + 1)/L^2 \quad [2]$$

or, alternatively, in terms of the corresponding wavelength for the transition:

$$\lambda = hc/\Delta E = (8mc/h)L^2/(N + 1) \quad [3]$$

By expressing both  $N$  and  $L$  as reasonable functions of the number of carbon atoms ( $Z$ ) in a conjugated hydrocarbon chain and the average bond length ( $l$ ) between each atom, this result becomes a simple model for the excitation of the molecule's  $\pi$ -electrons (figure 6):

$$\lambda = (8ml^2c/h)[Z^2/(Z + 1)] \quad [4]$$

and allows one to establish a correlation between  $\lambda$  and  $Z$  for a series of related compounds.

In his initial paper, Bayliss had applied these results to the spectra for a series of simple linear poly-

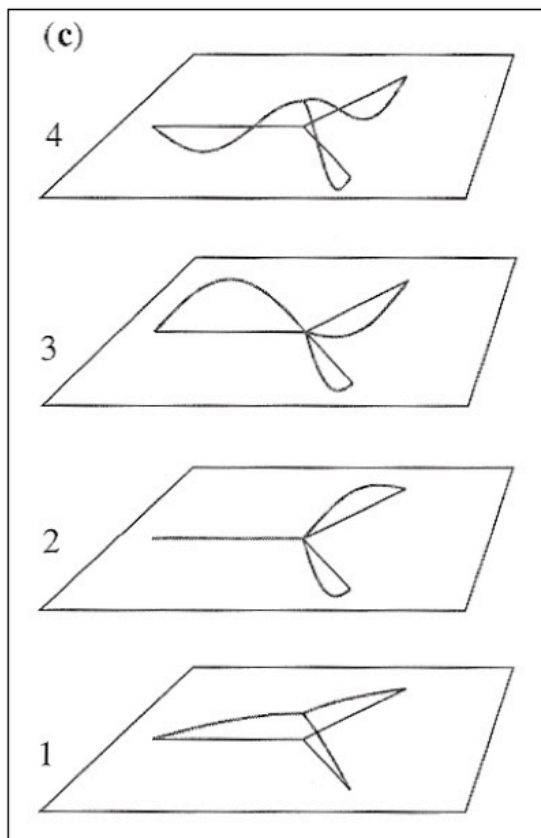


Figure 7. Application of the FE model to the branched  $\pi$ -system of the guanidinium cation  $C(NH_2)_3^+$ .

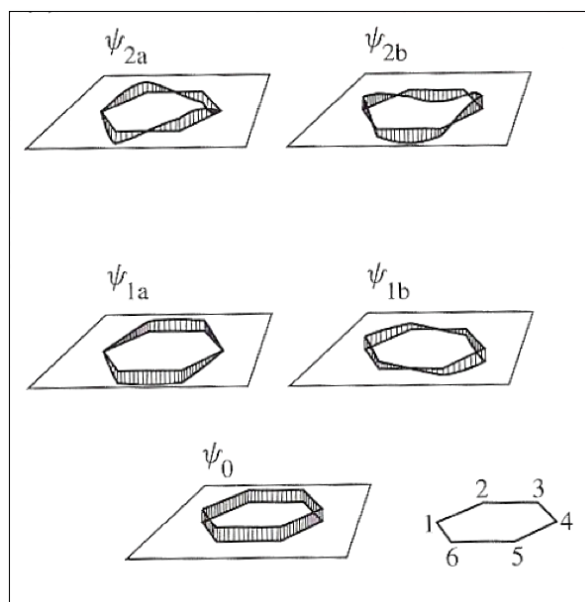


Figure 8. Application of the FE model to the cyclic  $\pi$ -system of benzene.

enes but had obtained only moderate agreement between the calculated and measured values of  $\lambda$  (13). In contrast, Kuhn, after a preliminary study of the spectra of various conjugated chain systems, concluded that the symmetrical cyanine dyes, which consisted of conjugated polyene chains with resonance-equivalent auxochrome groups attached at each end, displayed the most regular spectra and was able to obtain excellent agreement between the calculated and measured values of  $\lambda$  for the maximum absorption peak for these systems (14).

Between 1948 and 1963 Kuhn and his coworkers would publish more than two dozen papers, reviews and notes dealing with various aspects of the free-electron model (19). Though they would also explore the application of the model to branched (figure 7) and cyclic (figure 8) conjugated systems, as well as free-electron (FE) analogs of both the H atom (figure 9), and the  $H_2^+$  molecule, the central focus would always remain the linear conjugated dye systems which had prompted the initial work. While some of the papers done in conjunction with his graduate students at Marburg were quite mathematical, Kuhn would repeatedly publish general interest articles in both German and English in a wide variety of chemical journals di-

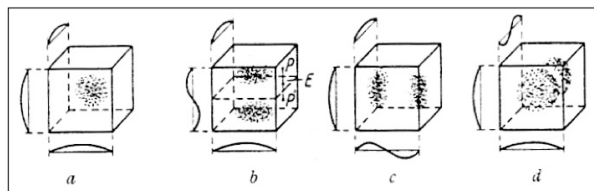


Figure 9. A FE analog of the s- and p-orbitals of a H atom based on an electron in a 3D box.

rected primarily at practicing organic chemists in which results of interest were presented with a minimum of mathematical detail and with striking diagrams and figures designed to effectively summarize the results. As a consequence, by the 1960s and early 1970s brief treatments of the free-electron model of conjugated systems had begun to appear in both books on dye chemistry and in textbooks dealing with physical organic chemistry (20, 21).

The culmination of Kuhn's work came with the publication of a small monograph (figure 10) in German entitled (in translation), *The Electron-Gas Method*, which was Kuhn's preferred name for the free-electron model. This was based on a series of lectures given in September of 1963 at a conference on the Theory of  $\pi$ -Electron Systems held in Constance Germany and contains a fairly comprehensive bibliography of his publications on this subject (22).

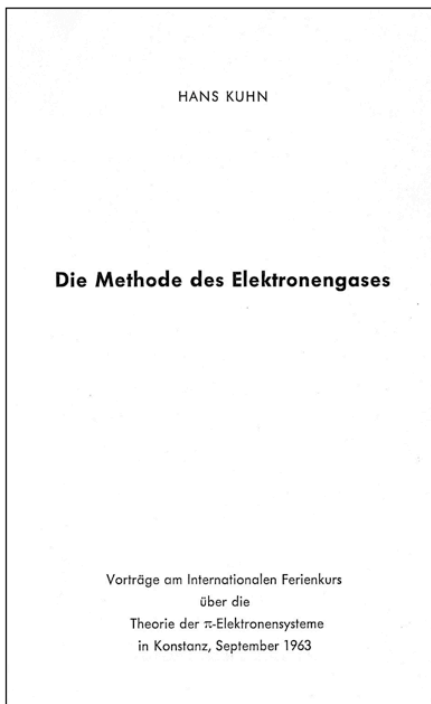


Figure 10. The title page of Kuhn's 1963 lectures on *The Electron-Gas Method*.

#### 4. John Platt and the Chicago Group

The work of Platt, on the other hand, shows some significant contrasts with that of Kuhn, many of which are



Figure 11. John Rader Platt (1918-1992).

traceable to the simple fact that he was trained as a physicist rather than as a chemist. John Rader Platt (figure 11) was born in 1918 in Jacksonville, Florida, and was educated at Northwestern University and the University of Michigan, from which he received his doctorate in physics in 1941. From 1945-1965 he taught physics at the University of Chicago and was also a member of Robert S. Mulliken's Laboratory for Molecular Structure and Spectra (figure 12).

Between 1949 and 1964 Platt and his students and associates at Chicago would publish roughly 21 papers dealing with the free-electron or FE-model, as they preferred to call it, and another 35 papers dealing with the measurement and systemization of the spectra for conjugated systems. In 1964 these papers were reissued as collected volumes by the laboratory at Chicago, the first set (figure 13), dealing with FE theory, under the title *Free-Electron Theory of Conjugated*



Figure 12. Members of the Laboratory for Molecular Structure and Spectra, circa 1949. *Back row (left to right):* Charlene Scott, Robert Parr, Robert Mulliken, John Platt (with pipe), Harrison Shull. *Front row (left to right):* Clemens Roothaan, Putcha Venkateswarlu, H. Christopher Longuet-Higgins.

*Molecules: A Sourcebook* (23), and the second set, dealing with spectra, under the title *Systematics of the Electronic Spectra of Conjugated Molecules: A Source Book* (24).

Whereas Kuhn's work had centered primarily on linear conjugated chain systems, that of Platt and his associates was centered primarily on condensed or polynuclear conjugated ring systems. Likewise, whereas Kuhn made an effort to communicate his results to practicing organic and industrial chemists, the work of the Chicago group was directed almost solely at other theoreticians and was far more mathe-

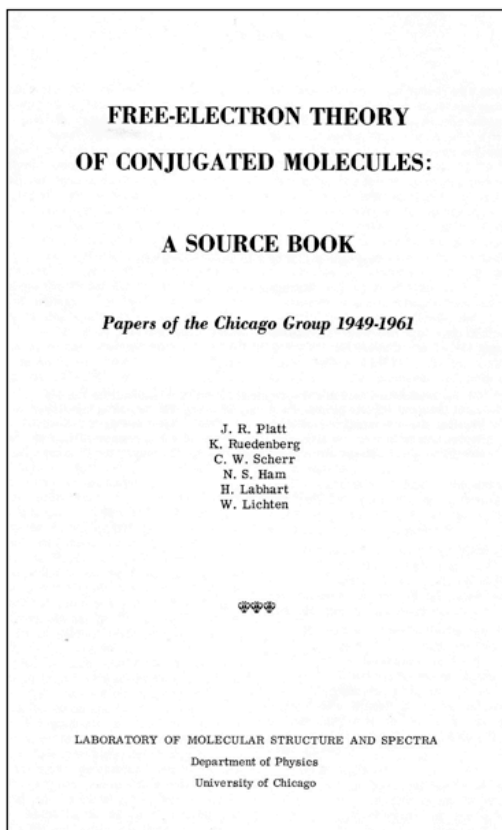


Figure 13. Title page to the Chicago group's collected papers on FE Theory.

mathematical and formal in nature. This is also reflected in the fact that virtually all of it was published in the *Journal of Chemical Physics*, whereas Kuhn, though occasionally publishing in this journal, placed his work in a much broader range of journals and also published in both German and English. Though Platt did publish several papers dealing with the construction of visual models to represent the electron densities predicted by the FE model – one involving wire and wooden pegs and the other plaster casts (figure 14), for the most part the publications of the Chicago group lacked the abundance of visual aids characteristic of many of Kuhn's more popular reviews (25).

While many of these differences, as already suggested, simply reflect a difference in the research styles typical of physicists versus chemists, they are also a partial reflection of a unique emphasis within the Chicago group itself. Though the major attraction of the free-electron model lies in its physical and computational simplicity, Mulliken was fully convinced that what was needed in quantum chemistry was a more rigorous *ab initio* approach to computation. As a result, much of the work at Chicago also involved an effort to both elucidate the nature of the assumptions under-

lying the FE model and its formal relationship to the more conventional LCAO approach to MO theory. Many years later Mulliken would rather tersely summarize his final take on the entire enterprise in his autobiography (26):

*The free-electron model, a favorite with Platt, is rather artificial and not rigorous, but gives interesting and suggestive results similar to those of MO theory.*

Though Platt was undoubtedly the guiding spirit behind the work of the Chicago group on FE theory and published several papers on the theory himself, the most significant contribution of the group – a sophisticated mathematical version of the theory specifically designed to deal with branching and polycyclic systems known as the “Free-Electron Network Model” – was actually the work of his colleagues, Charles Scherr, Norman Ham, and especially that of a young German-born postdoctoral fellow named Klaus Ruedenberg (figure 15). In a recent assessment of this work, Ruedenberg has noted that (27):

*The distinctive difference between our work and that of Kuhn and Bayliss was that we were interested in demonstrating and did demonstrate the rigorous equivalence between the free-electron-network model and the Hückel-type LCAO model. This equivalence provided a conceptually instructive visualization of Hückel-type LCAO coefficients as amplitudes of harmonic network waves and entailed for the LCAO resonance integral the order of magnitude. These equivalences were important to John Platt. On the other hand, they also exhibited the limitations of the free-electron model by showing that it gives reasonable results because it abstracts essential features of the LCAO coefficient variations and not because it correctly describes the local shapes of the electron cloud in detail.*

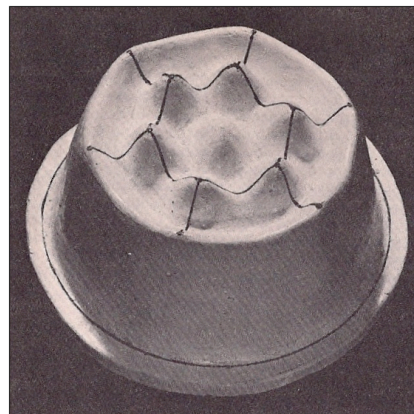


Figure 14. One of Platt's plaster models for electron density distributions. This one is for the sigma densities on benzene.



Figure 15. Klaus Ruedenberg (b. 1920). Taken about the time he was working on the FE Network Model.

As many in the audience are aware, Ruedenberg would go on to have a highly distinguished career in theoretical chemistry at Iowa State University (28). Among his many accomplishments are his definitive analysis of the roles of the kinetic versus the potential energy terms in covalent bond formation and his extensive studies of localized MO distributions, both of which strongly influenced the present author while still a graduate student at the University of Wisconsin.

In 1965 Platt, like Kimball before him, left the field of quantum mechanics to pursue research in the fields of sociology, political science, and biophysics, eventually becoming Associate Director of the Mental Health Research Institute at the University of Michigan, from which he retired in 1977. He died in Boston in 1992 at age 74 (29).

### 5. Other Contributors

In focusing on the work of Schmidt, Kuhn, Platt, and Ruedenberg I do not mean to imply that there were no other contributors to the development of the free-electron model. In a bibliography of papers and books dealing with the model, and spanning the years 1938-2010, I have identified no less than 131 contributions and 220 individual contributors (19). Thus, the French physicist, Segré Nikitine, for example, contributed nearly a dozen papers in the early 1950s, as did a number of Japanese investigators, including Gentaro Arkai,

Takeshi Nakajima, Kenichi Fukui, Yuzuru Oshika, and Shigeru Huzinaga.

Just as Schmidt preferred the term “box model,” Kuhn the term “electron-gas model,” and Platt the term “free-electron model,” so Nikitine – following the lead of Bayliss – always referred to it as the “modèle métallique” or “metallic model” of the chemical bond (30). In addition to the calculation of spectroscopic transition energies, electron densities, bond orders, and bond lengths pioneered by Kuhn and Platt, these other workers also suggested further applications to account for such diverse phenomena as electronegativity effects (31), aromatic substituent effects (32), and even color changes for acid-base indicators (33).

### 6. Pedagogical Consequences

In the preface to the 1964 edition of the collected papers of the Chicago group on the FE model, Platt also commented on the potential pedagogical advantages of the model (23):

*These equivalencies have established the free-electron network model as the most fruitful and, in fact, the only natural way of conceptually grasping LCAO wave functions in conjugated systems. It is therefore a useful teaching device and a valuable subject for the beginner and the advanced chemist alike. Moreover, it permits a number of interesting problems to be solved quantitatively even by first-year chemistry students without the help of matrix algebra, which is indispensable for the LCAO approach.*

Just about the time that Platt penned these words, the nature of the literature dealing with the free-electron model began to change in such a fashion as to partially justify these claims. More and more papers began to appear in the chemical education literature rather than in the primary research literature and the focus began to shift from refinements and extensions of the initial model to potential pedagogical applications. Between 1963 and 2010 at least two dozen papers dealing with either the free-electron model or with other applications of the particle-in-a-box model have appeared in the *Journal of Chemical Education*. By creatively invoking a variety of differently shaped potential wells (figure 16), it has been successfully applied as a useful approximate rationalization for the Bohr atom, the spacing of molecular rotational and vibrational levels, the Jahn-Teller effect, and bond polarity effects, to name but a few (19).

Some of these simple applications were actually incorporated into the short, introductory, undergraduate supplements on bonding theory and quan-



## THE FREE-ELECTRON MODEL

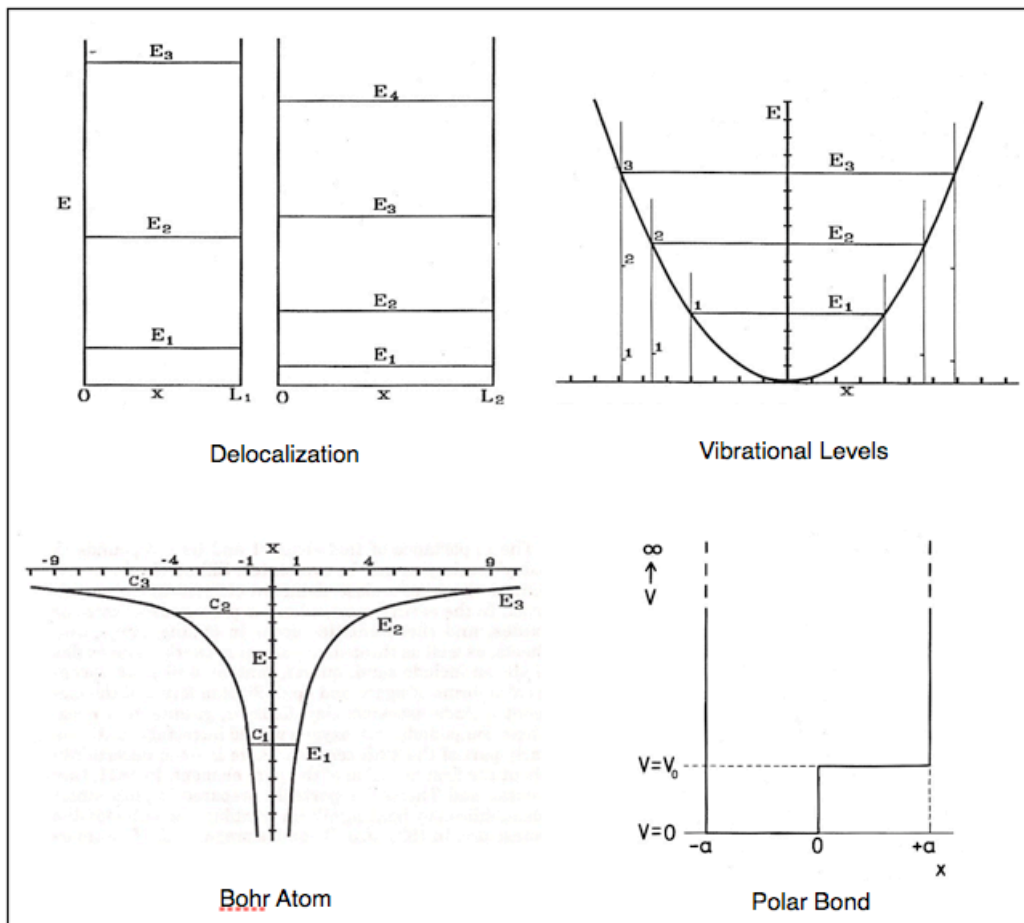


Figure 16. Some of the potential wells that have been used to develop particle-in-a-box analogs for a variety of fundamental chemical concepts.

tum mechanics that were popular throughout the late 1960s and the 1970s (34). Though this particular publishing genre seems to have now largely disappeared, many of these simple applications have more recently been included in the superb textbook of physical chemistry coauthored by Hans Kuhn after his retirement and which is now in its second edition (35).

The only part of Platt's assessment that has not been fulfilled is the application of the FE model to first-year chemistry courses. Given the well-known lack of mathematical competency among American college students, such an application would be possible only by "physically" fitting the wave function to the allowed path length of the postulated potential well:

$$L = n\lambda/2 \quad [5]$$

and invoking the de Broglie relation:

$$\lambda = h/mv = h/(2mE)^{0.5} \quad [6]$$

rather than by solving a simplified Schrödinger equation. Such an application would also require a radical reformation of the current "memorized fragment" approach to both MO and VB theory currently found in the Freshman textbook. Indeed, it would require a recognition of the point made by Mulliken in his 1966 Nobel Prize lecture (36) – namely that, while both the total energy and the total electron density of a ground-state atom or molecule are invariant, the dissection of these two parameters into contributions from various component orbitals is to some extent arbitrary. Of these various alternatives, Mulliken singled out two choices for analyzing a given molecule – either in terms of a set of fully delocalized, symmetry-adapted MOs, which he called *spectroscopic orbitals* because of their use in rationalizing spectra, ionization energies and other one-electron properties, or in terms of a set of relatively nonoverlapping localized MOs, which he called *chemical orbitals* because of their use in rationalizing the ground-state structures of molecules. Obvi-

ously the free-electron model would be a simple way of illustrating the use of a typical set of spectroscopic orbitals, whereas the Kimball charge-cloud model would be a simple way of illustrating, *a la* the VSEPR rules, the use of a typical set of chemical orbitals (37).

Though these quantum mechanical concepts are now well over a half century old, I am not particularly optimistic that such a reformation is still possible. As the American university becomes increasingly dominated by the corporate business mentality, which demands interchangeable educational credits and standardized exams with standardized and memorizable black and white answers and vocabulary, chemistry departments have increasingly lost creative control of their introductory chemistry courses, whose contents are now largely determined by the marketing departments of the book publishers rather than by the actual instructors.

The adoption of the spectroscopic/chemical orbital dichotomy would be profoundly at odds with this trend as it would require recognition that theoretical models are not God-given truths to be memorized for exams but rather pragmatic solutions to certain problems and that, as the nature of the problem changes, so must the theoretical model. Part of the skill of a good scientist is knowing how to select the proper model for a given problem and even more so how to select the proper level of sophistication for the model through the creative application of Einstein's famous dictum:

*Make it as simple as possible, but no simpler.*

## 7. Acknowledgements

I would like to thank Bernard Hoogenboom of the Department of Chemistry of Gustavus Adolphus College for sharing his knowledge of the life and work of Otto Schmidt and for donating a high-quality photo of Schmidt to the Oesper Collections many years ago. I would also like to thank the late Hans Jaffe of the Department of Chemistry of the University of Cincinnati for his extensive files of reprints dealing with the free-electron model, which provided much of the material for the preparation of this paper, and Dr. Klaus Ruedenberg of the Department of Chemistry of Iowa State University for sharing his memories of the Chicago group and for providing figures 11 and 15, as well as several pertinent references.

## 8. References and Notes

1. An invited lecture given as part of the symposium

"Pioneers of Quantum Chemistry" held at the 241st National ACS Meeting, Anaheim, CA, on 28 March 2011.

2. G. Kimball, "The Application of Wave Mechanics to Chemistry," Lecture given at Reed College Writing Conference for CBA, 20 July, 1959. Typewritten transcript, Oesper Collections, University of Cincinnati.

3. See W. B. Jensen, "Bibliography of the Kimball Charge-Cloud Model," University of Wisconsin, June 1977, Copies available on request.

4. R. J. Gillespie, R. S. Nyholm, "Inorganic Stereochemistry," *Quart. Rev. Chem. Soc.*, **1957**, *11*, 339-380. Summarized in R. J. Gillespie, *Molecular Geometry*, Van Nostrand: New York, NY, 1972.

5. J. W. Linnett, "A Modification of the Lewis-Langmuir Octet Rule," *J. Am. Chem. Soc.*, **1961**, *83*, 2643-2653. Summarized in J. W. Linnett, *The Electronic Structure of Molecules: A New Approach*, Methuen: London, 1964.

6. L. Pauling, E. B. Wilson, *Introduction to Quantum Mechanics with Applications to Chemistry*, McGraw-Hill: New York, NY, 1935, pp. 33-34, 95-100.

7. O. Schmidt, "Die Beziehungen zwischen Dichteverteilung bestimmter Valenzelektronen (*B*-Elektronen) und Reaktivitat bei aromatischen Kohlenwasserstoff," *Z. physik. Chem.*, **1938**, *39B*, 59-82.

8. O. Schmidt, "Die Charakterisierung der einfachen und Krebs erzeugenden aromatischen Kohlenwasserstoffe durch die Dichteverteilung bestimmter Valenzelektronen (*B*-Elektronen)," *Z. physik. Chem.*, **1939**, *42B*, 83-110.

9. O. Schmidt, H. Schmidt, "Weiter Untersuchen zum Kastenmodell (Zylinderring Kompression der *B*-Elektronen)," *Z. physik. Chem.*, **1939**, *44B*, 185-193.

10. O. Schmidt, "Verschiebungen in den Absorptionsspektren einkerniger Aromaten," *Berichte*, **1941**, *74*, 987-1001.

11. O. Hecht, "Otto Schmidt, 1874-1943," *Berichte*, **1943**, *76A*, 121-125.

12. B. E. Hoogenboom, "A History of the Double-Bond Rule," *J. Chem. Educ.*, **1998**, *75*, 596-603. Though this otherwise excellent article discusses Schmidt's earlier rationale of the rule based on spin interactions, it does not mention his later use of the free-electron model. However, after completing the initial draft of this paper, Dr. Klaus Ruedenberg brought an interesting article to my attention by Werner Kutzelnigg which contains a tribute to Schmidt and his work on free-electron theory as well as fascinating information on Hückel's opposition to Schmidt's work. See W. Kutzelnigg, "What I Like About Hückel Theory," *J. Comput. Chem.*, **2006**, *28*, 25-34.

13. N. S. Bayliss, "A 'Metallic' Model for the Spectra of Conjugated Polyenes," *J. Chem. Phys.*, **1948**, *16*, 287-292.

14. H. Kuhn, "Free-Electron Model for Absorption Spectra of Organic Dyes," *J. Chem. Phys.*, **1948**, *16*, 840-841; and "Elektronengasmodell zur quantitativen Deutung der Lichtabsorption von organischen Farbstoffen," *Helv.*

*Chim. Acta*, **1948**, 31, 1441-1455.

15. W. T. Simpson, "Electronic States of Organic Molecules," *J. Chem. Phys.*, **1948**, 16, 1124-1136.

16. J. R. Platt, "Classification of Spectra of Cata-Condensed Hydrocarbons," *J. Chem. Phys.*, **1949**, 17, 484-495.

17. Bayliss and other early writers on the free-electron model generally reference the treatment of the Sommerfeld free-electron model of metals given in N. F. Mott, H. Jones, *The Theory of the Properties of Metals and Alloys*, Clarendon: Oxford, 1935, pp. 51-56.

18. N. S. Bayliss, "The Free-Electron Approximation for Conjugated Compounds," *Quart. Rev. Chem. Soc.*, **1952**, 6, 319-339.

19. See W. B. Jensen, "Bibliography of the Free-Electron Model," University of Cincinnati, January, 2011. Copies available upon request.

20. See for example, P. Rys, *Fundamentals of the Chemistry and Application of Dyes*, Wiley-Interscience, New York, NY, 1972 and J. Griffiths, *Colour and Constitution of Organic Compounds*, Academic Press: New York, NY, 1976, pp. 24-27.

21. See for example, G. Karagounis, *Introductory Organic Quantum Chemistry*, Academic Press: New York, NY, 1962, pp. 155-164; and C. Sandorfy, *Electronic Spectra and Quantum Chemistry*: Prentice Hall: Englewood Cliffs: NJ, 1964, Chapter 14.

22. H. Kuhn, *Die Methode des Elektronengases: Vorträge am Internationalen Ferienkurs über die Theorie der  $\pi$ -Elektronensysteme*: Konstanz, 1963.

23. J. R. Platt et al, *Free-Electron Theory of Conjugated Molecules: A Source Book*, Laboratory of Molecular Structure and Spectra: University of Chicago: Chicago, IL, 1964.

24. J. Platt et al, *Systematics of the Electronic Spectra of Conjugated Molecules: A Source Book*, Laboratory of Molecular Structure and Spectra: University of Chicago: Chicago, IL, 1964.

25. See papers 4, 10, and 11 of reference 23.

26. R. S. Mulliken, *Life of a Scientist*, Springer-Verlag: Berlin, 1989, p. 123.

27. Correspondence with K. Ruedenberg, 22 February 2010.

28. K. Ruedenberg, "Autobiography," *J. Phys. Chem.* **2010**, 114A, 8490-8495.

29. E. Page, "John R. Platt, 74, Scientific Scholar in Many Disciplines," *The New York Times*, 23 June, 1992.

30. Both Kuhn and Platt would also eventually come to use Schmidt's term "Box Model" for certain applications of the FE approach.

31. S. Basu, "Nitrogen Electronegativity Correction in Free-Electron Network Theory," *J. Chem. Phys.*, **1954**, 22, 162.

32. S. Basu, "Free-Electron Treatment of the Orientation of Substituents in Aromatic Molecules," *J. Chem. Phys.*, **1954**, 22, 1952.

33. S. Nikitine. "Sur le modèle métallique de la thionine et du bleu de méthylène. Essai d'une théorie quantique d'indicateurs colorés," *J. chim. phys.*, **1951**, 48, 175-184.

34. See, for example, J. N. Murrell, S. F. A. Kettle, J. M. Tedder, *Valence Theory*, Wiley: New York, NY, 1965, pp. 10-13, 291-292; J. Barrett, *Introduction to Atomic and Molecular Structure*, Wiley: London, 1970, pp. 52-56, 185-186, 224-228, M. Orchin, H. Jaffe, *Symmetry, Orbitals and Spectra*, Wiley-Interscience: New York, NY, 1970, Chapter 4; A. R. Denaro, *A Foundation for Quantum Chemistry*, Butterworths: London, 1975, Chapters 3, 5, 7.

35. H. Kuhn, H-D. Försterling, D. H. Waldeck, *Principles of Physical Chemistry*, 2nd, ed, Wiley: Hoboken, NJ, 2009.

36. R. Mulliken, "Spectroscopy, Molecular Orbitals, and Chemical Bonding," *Science*, **1967**, 157, 13-24.

37. Interestingly, Platt summarized both the free-electron and Kimball charge-cloud models in his last major review on chemical bonding: J. R. Platt, "The Chemical Bond and the Distribution of Electrons in Molecules" in S. Flügge, Ed., *Handbuch der Physik*, Vol. 37 (II), Springer: Berlin, 1961, pp. 173-281.

## Publication History

E. T. Strom, A. K. Wilson, Eds., *Pioneers of Quantum Chemistry*, ACS Books: Washington, DC, 2013, pp. 117-137.

## Update

Since completing the original lecture and article it has come to my attention that Professor László von Szentpály, now at the University of Stuttgart, and a former student of Kuhn, has in fact continued to further refine and develop the free-electron model in a series of more recent research publications. See:

\* L. von Szentpály, "Molecular Model Potentials: Combination of Atomic Boxes," *Theoret. Chim. Acta*, **1979**, 52, 277-301.

\* L. von Szentpály, "Correlation of Free-Electron Molecular Orbital Energies with  $\pi$ -Ionization Energies of Aromatic Hydrocarbons," *Chem. Phys. Lett.*, **1979**, 67, 63-68.

\* L. von Szentpály, "Inorganic and Biological  $\pi$ -Systems Computed with a Pocket Calculator," *J. Molecul. Struct.*, **1980**, 60, 391-394.

\* L. von Szentpály, "Electrophilic Aromatic Substitution: A Free-Electron Approach," *Chem. Phys. Lett.*, **1981**, 77, 352-358.

\* L. von Szentpály, "Free Electron PMO:  $F$ -Omega Model with Variable Electronegativity and Self-Interaction Correction: Application to Ionic Reaction Intermediates," *J. Molecul. Struct. (Theochem)*, **1989**, 187, 139-160.