The Kimball Free-Cloud Model
A Failed Innovation in Chemical Education?

William B. Jensen

Department of Chemistry, University of Cincinnati
Cincinnati, OH 45221-0172

The content of most introductory chemistry textbooks, at both the high school and college level, is largely determined by trickle-down from the graduate-school curriculum and the research literature. Though educational debates may ensue over which topics should be taught and when, or over how detailed and quantitative the coverage should be, teachers of introductory chemistry seldom have the hutzpah to introduce topics and theoretical models that are not viewed as directly relevant to the current practice of chemistry by their more esteemed research colleagues. As a consequence of this hierarchical system, most high-school chemistry texts are diluted clones of the introductory college text and these, in turn, of the undergraduate physical chemistry text.

There was, however, a brief period in the history of 20th-century chemical education when this was not the case. Beginning in the mid-1950s, both the space race and the ubiquitous cold war paranoia of the United States gradually morphed into a fear that we had somehow fallen behind the Russians in the fields of science and technology – a fear apparently confirmed by the Soviet Union's successful launch of Sputnik in 1957. In response, the second half of the decade saw the increasing availability of government funding for the development of programs designed to upgrade the teaching of science in our secondary schools.

Soon faculty in various colleges and universities were availing themselves of this opportunity by organizing various collaborative educational projects with high-school teachers for the purpose of revising the existing secondary curriculums in biology, physics and chemistry. The BSCS approach in biology, the PSSC and Harvard Project approaches in physics, and the CHEM Study and CBA projects in chemistry were all products of this movement, as well as numerous, more limited, attempts to reform the introductory college chemistry courses at various colleges and universities (1). By the end of the 1960s these reforms had resulted in the transformation of the introductory chemistry course, at both the high school and college levels, from a course in introductory descriptive inorganic chemistry into a watered down course in physical chemistry – a form which they have retained even to the present day.

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

One of the more controversial aspects of the curriculum reforms advocated during this period was the attempt by several chemical educators to introduce a highly approximate quantum mechanical bonding model – known variously as the charge-cloud model, the tangent-sphere model, or the hard-sphere model – into the introductory chemistry curriculum as a pedagogical bridge between the qualitative Lewis dot diagrams of the high-school textbook, on the one hand, and the more advanced valence-bond and molecular-orbital bonding models of the college textbook, on the other. Though this initial attempt ultimately foundered, it was thought that a detailed review of its assumptions and history might prove of value to present-day chemical educators with an interest in curriculum reform by allowing them to reassess both the model's pedagogical virtues and its shortcomings. In addition, since much of the resulting literature dealing with the model origi-

nally appeared in the *Journal of Chemical Education*, and aspects of it are still to be found in our textbooks, largely in connection with the teaching of VSEPR theory, it was thought that a detailed review of the model and its history would also be an appropriate way to celebrate the 90th anniversary of the Journal's founding.

Indeed, there is yet an additional justification for such a review, since many who have advocated this bonding model, in both the past and at present, have also, for some inexplicable reason, felt compelled to repeatedly rename it. This particular "marketing strategy" (for one scarcely knows what else to call it) has had two very unfortunate consequences. Firstly, it means that, unlike the cases of conventional MO theory and VB theory, there is no common "index entry," or acronym to guide those attempting to track down all of the pertinent literature using standard search engines. Secondly, as we will see, it has led to the creation of at least three – largely independent – lines of development for the model and to a situation in which the advocates of one or another of these three approaches are either unaware of the other two or have gone so far as to deny their relevance. As indicated by the title of this review, the original and historically correct name for this model is the "Kimball Free-Cloud Model," and this is the name which will be employed from this point on, save when explicitly commenting on the renaming issue that has marred so much of the literature on this subject.

George Elbert Kimball

As might be inferred from its name, the original free-cloud model was the brain-child of the renowned American quantum chemist, George Elbert Kimball (figure 1)**.** Born in Chicago in 1906 and raised in New Britain, Connecticut, Kimball received both his B.S. (1928) and Ph.D. (1932) degrees from Princeton University – the latter for work done under the supervision of Hugh Taylor. Following a two-year postdoctoral fellowship at MIT (1933-1935), where he worked with John Slater, Kimball returned to Princeton to continue a decade-long collaboration with Henry Eyring, first begun shortly after Eyring had joined the Princeton faculty in 1931 (2). In 1936 Kimball was appointed to the faculty of Columbia University in New York City, where in 1944 he coauthored, along with Eyring and John Walter, what is perhaps his best remembered contribution – the classic textbook, *Quantum Chemistry*, otherwise known during my graduate-school days as the "green diamond" in honor of both the color of its cloth binding and its concise and comprehensive coverage of the subject in question (3).

Origins of the Free-Cloud Model

However, even as he was putting the final touches on the manuscript of *Quantum Chemistry*, Kimball was beginning to experience severe doubts concerning the future of his chosen profession and was becoming increasingly convinced that rigorous quantum chemistry had reached an impasse of such a magnitude that further significant progress was unlikely. As he later described the situation in a popular lecture given in 1959 (4):

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 seemed to come to a stop. Most of the people who had been working in the field got into something different, and the situation today is not really very different from what it was in 1935.

The cause of this impasse, Kimball went on to explain, was quite simple (4):

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 (4):

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 impasse varied. As already noted by Kimball, many simply left the field for greener intellectual pastures. Thus Heisenberg moved 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 insights, would remain mathematically tractable – if of low quantitative accuracy. The Kimball free-cloud model was one such product of this movement, though by no means the only one. At least three additional radically simplified models – all proposed in the period 1948-1961 – also stand out as worthy of further consideration:

1. The particle in a box or free-electron model.

2. The valence-shell electron-pair repulsion model.

3. The Linnett double-quartet model.

Indeed, the historical development of the first of these three models has recently been discussed in some detail (5). And while our focus in this review will obviously be with the Kimball free-cloud model, it will soon become apparent that its history is in fact intimately entangled with those of both the valence-shell electron-pair repulsion or VSEPR model and the Linnett double-quartet or LDQ model. Though both of these models are worthy of detailed historical reviews of their own, they will be discussed in what follows only in so far as they are directly relevant to the development of the Kimball model.

In his popular lecture of 1959 Kimball also described his personal response to this computational crisis (4):

These [computational] 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 theses of five Ph.D. candidates, of the basic premises of the free-cloud model of the chemical bond in the period 1951-1956.

The Basic Assumptions of the Free-Cloud Model

Since Kimball published virtually nothing on his free-cloud model, it is worthwhile to briefly describe the contents of the five doctoral theses that served as its basis. The first of these, entitled *Free Cloud Approximation to Molecular Orbital Calculations,* by G. F. Neumark, dealt with the basic assumptions underlying Kimball's model and with its application to such simple systems as the H atom, the He^+ ion, the He atom, and the H_2 molecule (6).

As later summarized by Kimball in his lecture, the first step in any calculation is to decide on the basis set from which to construct the total wave function and here Kimball took the radical step of rejecting the use of the standard atomic orbitals used in both VB theory and in the conventional LCAO approach to MO calculations (4):

As far as I am concerned, the use of atomic orbitals has had such a long history of failure that I thought it was about time to throw it out, get rid of it, and start over again with a really fresh look, and see what could be done. As I said before, there are very few rules about having to make guesses at certain points. The fact that the use of atomic orbitals had led to poor results so consistently seemed to me to be plenty of evidence that atomic orbitals were in the category of bad guesses.

Instead Kimball proposed using orbitals that were not necessarily centered or anchored on the atomic nuclei but which could rather be located in any position that best served the task of ultimately minimizing the total potential energy of the system. Indeed, the use of orbitals was a mere formality, since he also proposed proceeding directly to the use of the corresponding probability functions for these orbitals, interpreted as time-averaged electron densities or charge clouds.
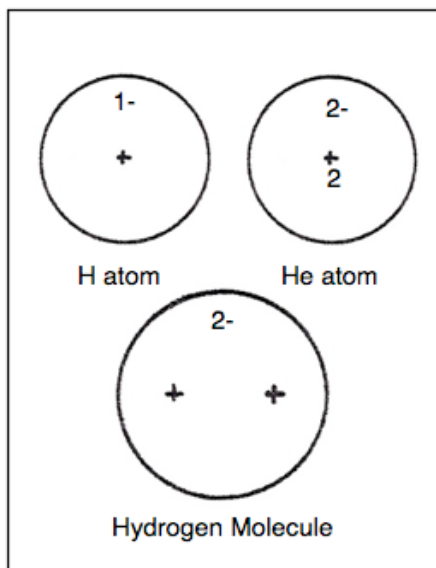
Figure 2. Free-cloud models of the H atom, the He atom, and the H₂ molecule as tested in Neumark's thesis of 1951.

Table I. Neumark's computational results (1951) for the electronic energy (in Hartree atomic units) of various species made using the constant charge density assumption.

Species	Calculated	Observed	Error
H	-0.50	-0.50	0%
He⁺	-2.00	-2.00	0%
He	-2.56	-2.90	12%
H₂	-1.21	-1.17	-3%

Since one was "free" to place these electron or charge clouds where needed, Kimball chose the name "free cloud" to describe his approach. Had he bothered to construct an acronym, like those used for either the LACO approximation to MO theory or the free electron or FEMO approximation, the result would have been the FCMO method.

The second step is to radically simplify the calculation of the various energy terms entering into the determination of the system's electronic energy (E_{el}):

$$E_{el} = T_e + V_{ee} + V_{nn} + V_{ne} - X \qquad [1]$$

where T_e is the total electronic kinetic energy, V_{ee} is the total electron-electron repulsion energy, V_{nn} is the total nucleus-nucleus repulsion energy, V_{ne} is the total nucleus-electron attraction energy, and X is the ex-

change energy due to orbital overlap. This simplification was accomplished in two stages.

The first stage was to assume that the electron clouds were spherical in shape. This simplified calculations by eliminating any dependence of the kinetic and potential energy terms on orbital or cloud shape and instead made both simple functions of the radius or size of the electron cloud (of course, the potential energy terms are also a function of the positions of the clouds relative to one another and the various nuclei). The second stage was to assume that electron clouds of like spin could not overlap with one another. In keeping with the Pauli exclusion principle, this approximated the consequences of having properly antisymmetrized the wave function, and resulted, in the case of diamagnetic ground-state species containing only doubly-occupied orbitals, in a further simplification of equation 1 through elimination of the term for exchange energy.

In keeping with these assumptions, Neumark, using the Heisenberg uncertainly principle, derived a simple expression (in Hartree atomic units) relating the kinetic energy (T_e) of an electron cloud to its radius (R):

$$T_e = 9/(8R^2) \qquad [2]$$

which predicted that the smaller the radius the greater the kinetic energy and vice versa. She also derived approximate expressions for the change in intra-cloud electron-electron repulsion energy as two singly-occupied clouds of opposite spin progressively overlapped, one based on assuming that the charge distribution within the clouds was Gaussian and the other on the assumption that it was uniform. Since the latter closely approximated the former but gave far simpler energy expressions, the assumption of a uniform charge distribution within the clouds became the fourth major assumption of the model. Because of the absence of overlap between doubly occupied clouds, the remaining inter-cloud electron-electron repulsion and electron-nucleus attraction terms could both be calculated using classical electrostatics.

Modeling both the H atom and the He⁺ ion as the appropriate nucleus placed in the center of a single singly-occupied electron cloud, and both the He atom and the H₂ molecule as the appropriate nuclei distributed within a single doubly-occupied electron cloud (figure 2), followed by writing down the appropriate kinetic and potential energy terms for each and minimization of E_{el} with respect to the cloud radius R, gave the results in Table I without use of any empirically adjustable parameters.

Though these results were well within the limits of the 10% accuracy range set by Kimball for his model,
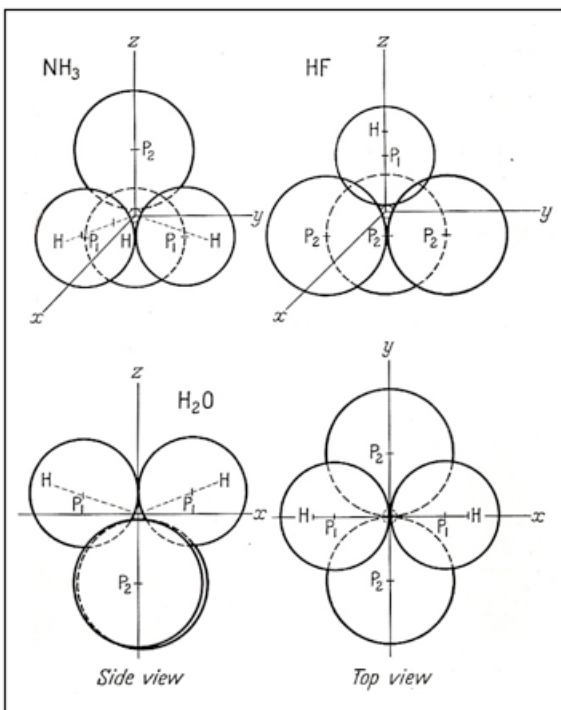
Figure 3. Free-cloud models of various second row hydrides tested by Kleiss in her thesis of 1952.

the same was not true when Neumark attempted to use the results to calculate the first ionization energy of He (E_{He+} - E_{He}) and the atomization energy of H_2, ($2E_H$ - E_{H2}), both of which represent the differences between two items in this table. Here the errors suddenly shot to 38% and -24% respectively. This was, of course, because such differences are much smaller than the separate terms from which they are derived and the errors in the latter propagate in the former. This is a common problem in quantum mechanical calculations and is similar, as pointed out by Coulson many years ago, to attempting to calculate the weight of the captain of an ocean liner by subtracting the weight of the empty liner from that of the liner with the captain aboard. Unfortunately, it is these differences, rather than the absolute values, that are of most interest to chemistry

Further Quantitative Testing of the Model

In the remaining four theses, Kimball's students attempted to apply this model to more complex situations and to also test several additional variations. Thus, the thesis entitled *Simplified Calculations of the Energies of the Second-Row Elements*, by H. R. Westerman, was an exploration of whether the free cloud approach could be used to approximate the behavior of conventional atomic orbitals and extended Neumark's results for the H and He atoms to the atoms

of Li, Be, B, C, N, O and F, as well as to their isoelectronic ions (e.g., Be, B^+, C^{2+}, N^{3+}, O^{4+} F^{5+}) (7). To do this, he tried modeling the 2s orbital as a hollow sphere of finite thickness and constant charge density surrounding, but not overlapping, the 1s orbital, and each 2p orbital as two spherical clouds set at 180° to one another, with each sphere occupied by either a half or a whole electron. The majority of the resulting calculated electronic energy values for the 39 neutral atoms and isoelectronic ions tested were within ± 3% of the observed values, but once again shot to ± 35% when used to calculate the corresponding ionization energies as differences between the individual electronic energy values.

The third thesis, by L. M. Kleiss, entitled *Calculations of Properties of Hydrides of Second-Row Elements*, once again returned to the themes contained in Neumark's original thesis (8). Here Kleiss proposed free-cloud models for the gas-phase forms of LiH, BeH_2, BH_3, CH_4, NH_3, H_2O and HF (figure 3) and calculated their corresponding electronic energies, bond lengths, bond angles, and dipole moments (Table II). She also tested the abilities of the last four species to form hydrogen bonded dimers and that of BH_3 to form the dimer B_2H_6 (figure 4).

Since there were several structurally nonequivalent electron clouds in these species (i.e. core versus valence, protonated versus nonprotonated, bridging versus terminal), E_{el} could no longer be analytically minimized with respect to a single unique R parameter and Kleiss had to instead empirically test several independent variations. Her final results are summarized in Table II, where the reported electronic energy values are again in Hartree units.

Unfortunately in 1952 insufficient experimental data were available to evaluate the accuracy of the calculated electronic energy values, whereas the calculated A-H bond distances were all less than the experimental values by as much as 23% and the bond
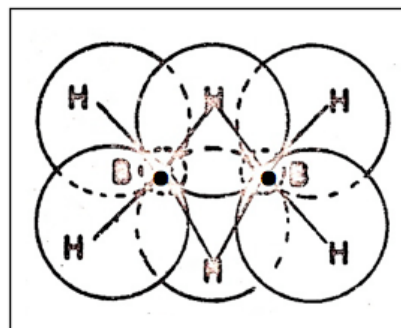

Figure 4. Model of B_2H_6 tested by Kleiss in her thesis of 1952 showing a free-cloud representation of a 3c-2e bond.

Table II. Example results from Kleiss' calculations (1952) on the hydrides of the second-row elements. Electronic energy values are in Hartrees.

Species	$-E_{el}/E_h$	$R_{AH}/Å$	AH_2 angle
LiH	7.527	1.53	——
BeH_2	15.409	1.30	180°
BH_3	25.439	1.11	120°
B_2H_6	53.334	——	120°
CH_4	40.910	0.98	109.5°
NH_3	56.461	0.85	109.2°
H_2O	75.360	0.74	110°
HF	98.975	0.70	——

angles greater by as much as 5%. The optimal energy values for NH_3, H_2O and HF were obtained by making the clouds corresponding to the lone pairs larger than those corresponding to the A-H bonds. The clouds for the atomic cores increased by a factor of 3.4 and those of the protonated valence clouds by a factor of 2.7 on passing from HF(g) to LiH(g).

The calculations of Kleiss were extended from discrete gas-phase molecular species to infinitely extended nonmolecular solids in the fourth thesis by J. L. Birman entitled *A Simplified Molecular Orbital Calculation of the Total Energy and Lattice Constant in Crystals of the Elements* (9). Using a cation/free-cloud lattice model of the solid-state structures of 23 main-block elements, both metallic and nonmetallic, all of which crystallized in either the bcc, ccp, hcp or diamond structures, Birman used the analogy with the standard cation-anion lattice model for binary ionic compounds to calculate their corresponding lattice energies, bond lengths and total energies to within 10-20% of the observed values. In addition, he explored several variations of the primary model, including inserting extra clouds in the vacancies of the more open bcc structure in order to more evenly disperse the electronic charge, and also compared his results with the standard Block model for metals.

Calculations of electronic energies using the free-cloud model often gave values lower than the observed values in direct contradiction to the variational principle, which assumes that the calculated energy will always be equal or higher than the observed value. Kimball suspected that this was because equation 2, which actually applies to a singly-occupied electron cloud, underestimates the kinetic energy of a doubly-occupied

cloud, and the fifth and last thesis, by J. D. Herniter, entitled *The Kinetic Energy of Localized Electrons*, was intended to explore better ways of estimating both the kinetic energy of doubly-occupied electron clouds and their intra-cloud repulsion energy (10). These improvements were tested using Kleiss' earlier model of methane (figure 3) and compared with those obtained using both the VB and MO methods (Table III). Herniter's evaluation of these results is well worth quoting (10):

The results obtained by the localized [free-cloud] electron method are as accurate as those obtained by either the simple valence bond or molecular orbital methods, and it is considerably simpler to employ than either of these methods. It completely eliminates the need to evaluate integrals and only requires minimizing with respect to various parameters. Although this method is not as good as the valence bond or molecular orbital methods when configuration interaction is included, we believe that the great simplification in the computations more than compensates for the small loss in accuracy of the results.

The CBA Project

During World War II Kimball became involved in war work for the U.S. Navy, including the development of a mathematical theory for optimizing the use of depth charges in antisubmarine tactics. This work eventually evolved into a generalized discipline known as "Operations Research," and in 1951 he coauthored, along with Philip M. Morse, one of the pioneering monographs on this subject – *Methods of Operations Research* (11). As his optimism over the future of quantum chemistry declined, his interest in the future possibilities of operations research increased, and in 1956, shortly after the completion of Herniter's thesis, Kimball resigned his professorship at Columbia and went to work as a technical expert for the industrial consulting firm of A. D. Little of Boston.

Table III. Herniter's comparative results (1956) for an improved free-cloud (FC) computation of the properties of methane. Electronic and atomization energy values are in Hartrees.

Method	$-E_{el}/E_h$	$\Delta E_a/E_h$	$R_{CH}/Å$
FC	35.56	0.44	1.51
VB	39.584	-0.408	1.06
MO	41.606	0.893	1.06
Observed	40.43	0.57	1.10

Figure 5. Laurence E. Strong (1914-2006).

As a result of this decision and his premature death in 1967, Kimball would personally publish virtually nothing on his free-cloud model. Though he prepared an internal report summarizing the model for A. D. Little in 1956, this document was generally unavailable to the chemical community at large (12), and a short paper published in the *Journal of Chemical Education* in 1959, though employing his technique of nonoverlapping electron clouds to approximate the results of antisymmetrization and to eliminate the fiction of exchange energies, actually dealt with justifying the use of dipole calculations in the description of complex ions and not with the free-cloud model *per se* (13). Indeed, it is fair to say that the free-cloud model may well have died of neglect, buried in the great detritus pile of unread and unconsulted doctoral theses, had it not been for a group of disgruntled chemistry teachers.

In response to the post-Sputnik calls for reform of the existing chemical curriculum a group of discontented high-school and college teachers (largely from small liberal arts schools) gathered at Reed College in Portland, Oregon, in June of 1957 for a conference sponsored by the ACS Division of Chemical Education and the Crown Zellerbach Foundation (14). Their purpose was to address both the lack of coordination between the typical high-school chemistry course and the

typical introductory college course and the lack of a central unifying theme for introductory chemistry courses in general, most of which had degenerated into a series of random topics. Among the final recommendations of the conference was that a reconstruction of the introductory curriculum be undertaken using the concept of the chemical bond as a unifying theme – an idea championed by Laurence Strong (figure 5) of Earlham College and partially inspired by the organizational approach used in the 1952 textbook, *Structural Chemistry of Inorganic Compounds*, by the German chemist, Walter Hückel (15, 16). Hückel had organized his text, not around the periodic table, but rather around the three limiting-cases of ionic, covalent and metallic bonding and the premise that, not only the properties, but also the methods of preparing, studying and characterizing compounds belonging to these three classes were sufficiently distinctive to merit separate consideration.

In June of 1958 a followup conference was held at Wesleyan College in Middleton, Connecticut, at which, among other things, the details of the chemical bond approach, based largely on conventional valence-bond theory, were further fleshed out (17). However, it was not until the following winter that an accidental encounter led Strong to the Kimball free-cloud model and to a reconsideration of the initial decision to employ a VB approach. As he later recalled (18):

It happened as a result of a trip I made to Boston in the winter of 1958-1959. I drove from Washington DC to Boston in a blinding snow storm to see Kent Wilson at Tufts University. He told me that there was a seminar the next afternoon given by this man Kimball that he wanted to attend, and I decided to go along – and Kimball talked about the free-cloud model. I was quite intrigued by his presentation and I guess I talked to him a little about it then. I promoted the idea of using it and we invited him to give a presentation during the writing conference at Reed the following summer.

The writing conference in question – the second to be held at Reed College – took place in the summer of 1959 and resulted in over 1000 pages of preliminary text material, as well as in a preliminary draft of a laboratory manual. It also resulted in the official adoption of the name "Chemical Bond Approach" or CBA for the overall project. Though Kimball's lecture was carefully transcribed and copies subsequently distributed to the attendees (4), no mention of it was made in the conference report published in the *Journal of Chemical Education* early the next year (19).

By 1963 the CBA project had published two volumes of reprints – one from the *Journal of Chemical*
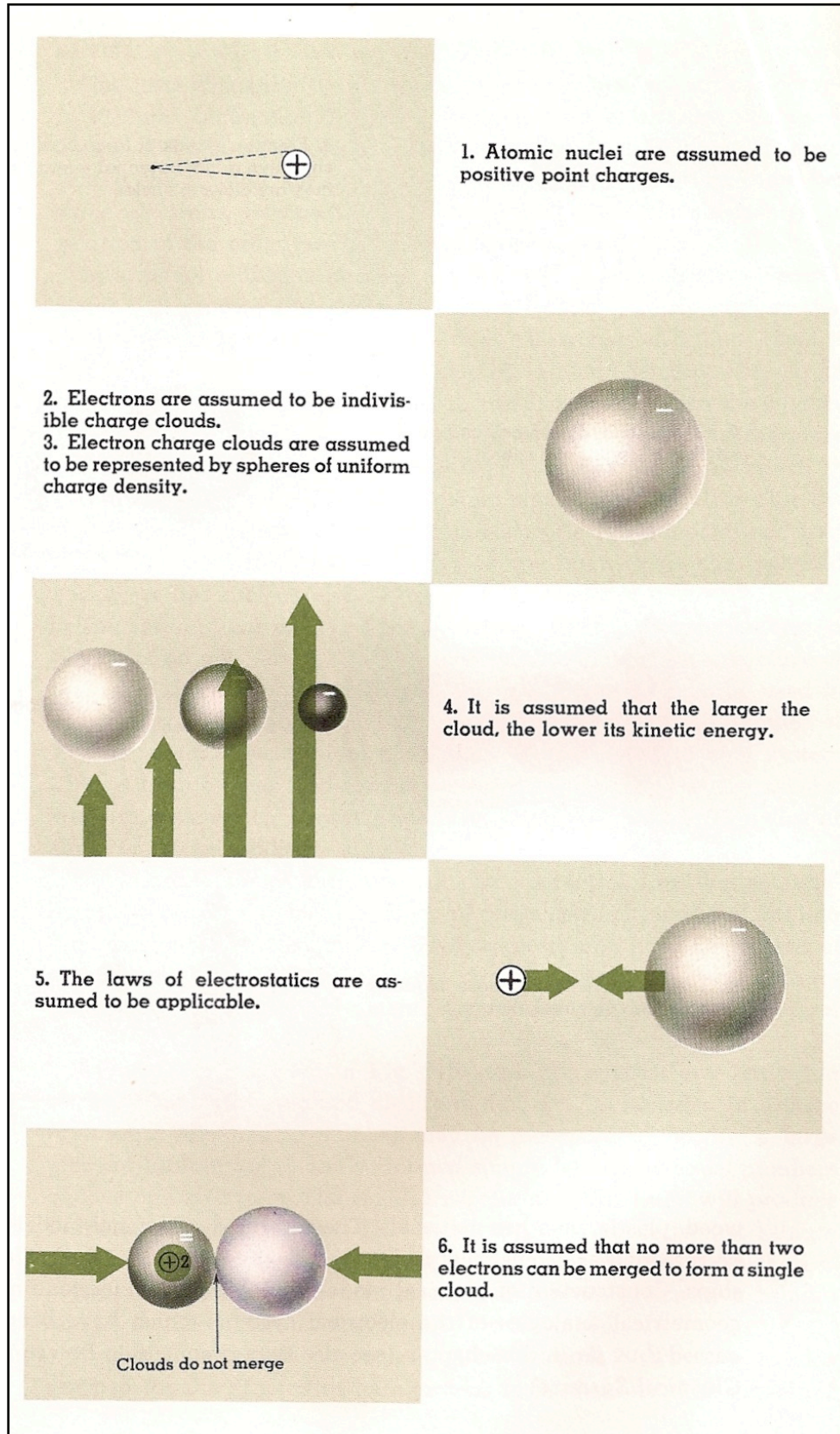
1. Atomic nuclei are assumed to be positive point charges.

2. Electrons are assumed to be indivisible charge clouds.
3. Electron charge clouds are assumed to be represented by spheres of uniform charge density.

4. It is assumed that the larger the cloud, the lower its kinetic energy.

5. The laws of electrostatics are assumed to be applicable.

6. It is assumed that no more than two electrons can be merged to form a single cloud.

Clouds do not merge

Figure 6. The CBA textbook's pictorial summary of the assumptions underlying the free- or charge-cloud model.
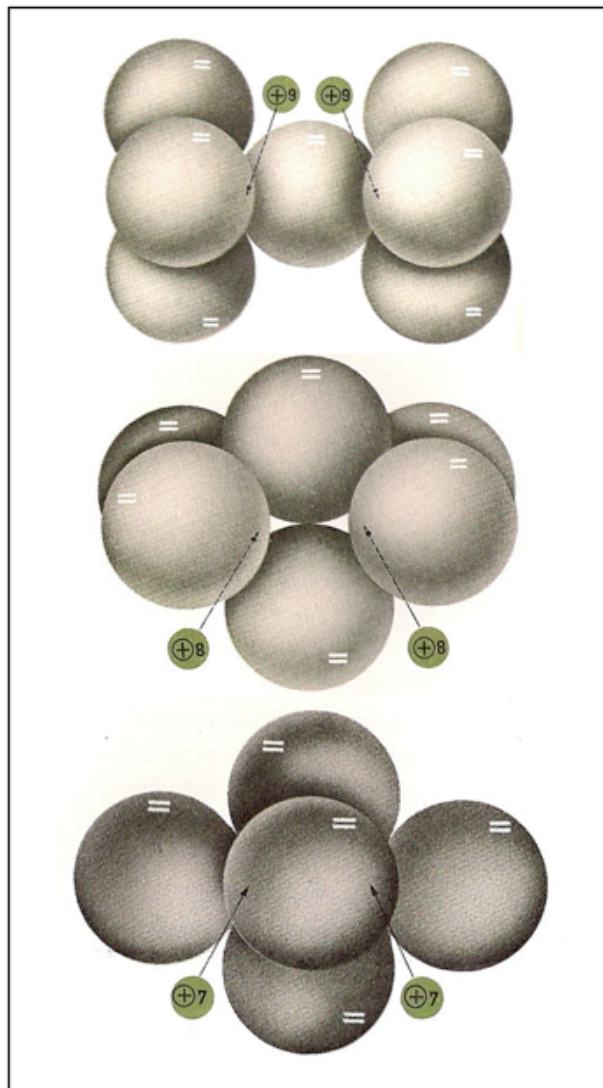
Figure 7. Some example illustrations of free-cloud models of simple diatomics from the CBA textbook: From top to bottom: F_2, O_2 ($^1\Sigma_g^+$ state), N_2. The diagrams incorrectly indicate nuclear rather than core charges.

Education (20) and one from *Scientific American* (21) – for use as background enrichment material for teachers adopting the CBA approach and a laboratory manual (22). The task of assembling the final version of the textbook had by then become headquartered at Earlham College, where Strong became heavily involved in adapting the free-cloud model for classroom use. To the best of his recollection, the five Ph.D. theses written by Kimball's graduate students were never consulted and the entire CBA presentation of the model was instead developed on the basis of Kimball's lecture at the 1959 Reed Conference (4). Surviving background documents from this period show that each of the equations and graphs given by Kimball in his lec-

ture was independently derived and tested by the teachers and the relationship of the model to conventional VB theory and the prediction of basic molecular geometries was explored (23-24). In addition, a fully mathematical presentation of the model was also developed and tested in the classroom by Strong as part of the Freshman chemistry course given for many years at Earlham (25).

Though Strong published a concise summary of the final curriculum and the free-cloud model in 1962 (26), it wasn't until 1964 that the long awaited textbook, *Chemical Systems*, and the accompanying teacher's guide were finally published (27-28). After three background chapters on basic electricity and chemical behavior, the free cloud-model was introduced in chapter 7 of the textbook. In his lecture at Reed Kimball had noted that, by stripping the model down to the bare quantum mechanical minimum, he had hoped (4):

... it would prove possible to get the calculations in a form which a reasonable number of people could handle with some facility. I won't go so far as to say a high-school student because I don't see how to proceed without some knowledge of calculus. On the other hand, in the system I want to talk about, the calculus required is calculus which is reached by about the first semester of a college calculus course. So far as I am concerned, while I am dubious about a high-school student being able to do it, I see no reason why a bright college freshman couldn't.

Strong had tested the latter conclusion in the Freshman course at Earlham and, in keeping with the former conclusion, he now developed a purely qualitative version for the CBA text. This was possible because, unlike the VB model, which rationalized chemical bonding and geometry using such mysterious, non-intuitive, effects as orbital overlap, exchange energies, and hybridization schemes, the basic underlying assumptions of the free-cloud model could be presented in simple straight-forward pictorial terms (figure 6). The optimization of structure as a function of total energy became in this pictorial representation a competition between expanding the size of the electron clouds in order to lower their kinetic energies and their unfavorable Coulombic electron-electron repulsions, on the one hand, and shrinking the size of the clouds in order to increase their favorable Coulombic core-electron attractions, on the other.

The art department of textbook's publisher, McGraw-Hill, further provided a series of attractive 3D drawings for the free-cloud models of several simple atoms and molecules (figure 7). But while the shading
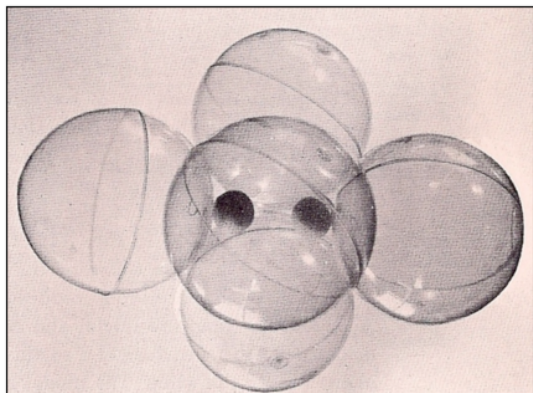
Figure 8. Photo of a clear plastic free-cloud model of N_2.

of the electron clouds provided a fairly good indication of their 3D arrangement, these drawing also called attention to a short-coming of the model – namely that the close-packing of the electron clouds completely obscured the placement of the atomic cores and hence which of the electron-cloud contacts corresponded to bonding versus nonbonding interactions. Lest we take this defect too seriously, however, we should remind ourselves that similar representations of the total electron density of a molecule or atom based on conventional quantum-mechanical calculations give us only a vague cloud that tell us little or nothing, without further dissection, about the underlying bonding topology and structure of the molecule.

On the other hand, any similar attempt to represent the total electron density as an explicit superposition of the component orbital densities (which is in effect what is done in a free-cloud representation) would, in the case of either the overlapping conventional s, p, d, f atomic orbitals or overlapping delocalized MOs, give us an entangled visual mess. Indeed, not only does the free-cloud model display the electron densities of all of filled valence orbitals simultaneously, rather than one at a time, as done with conventional orbital models, to the extent that the pockets in the cloud packing can be interpreted as incipient unoccupied orbitals, it also gives this information as well.

However, at least one photo in the CBA textbook (figure 8) indicates that some attempt was made to correct this problem of hidden atomic cores by using actual physical 3D models made by gluing together clear plastic spheres. As helpful as these models would have been in aiding the student to accurately visualize the proposed free-cloud structures, they were apparently expensive to make and no laboratory exercises or lecture demonstrations involving their use are to be found in either the CBA laboratory manual (22) or in the CBA teachers' guide (28).

Ironically, shortly after completion and publication of the CBA materials, a simple and effective solution to this problem was proposed by L. C. King of Northwestern University, who was an active participant in the CHEM Study rather than the CBA project (29-30). This involved the use of styrofoam balls held together with rubber bands (figures 9-10). The styrofoam balls represented the individual electron clouds while the intersection of the various rubber bands rep-
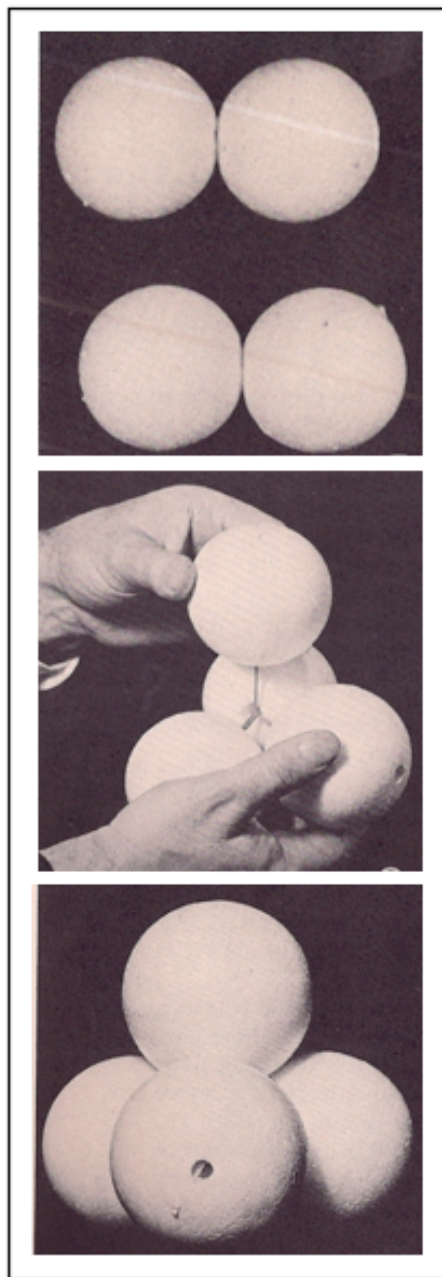

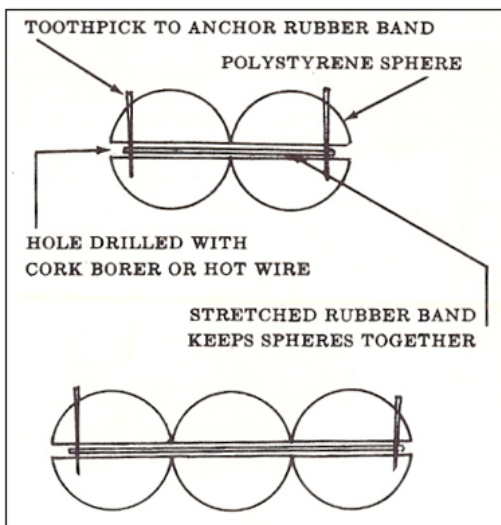Figure 9. Assembly of a free-cloud model of methane using King's styrofoam ball/rubber band analogs.

Figure 10. Instructions for the construction of King's styrofoam ball/rubber band analogs for free-cloud molecular models

resented the location of the atomic cores. Likewise, the elastic tension of the stretched rubber bands served to mimic the effects of the electron-core attractions, whereas the mechanical interference of one sphere by another was used to mimic both the effects of the Pauli exclusion principle and unfavorable inter-cloud electron-pair repulsions. In addition, the resulting models were dynamic. Any initial errors in the placement of the spheres were quickly corrected by simply shaking the model, which would then spontaneously snap into the proper equilibrium configuration. Though proposed too late to be included in the published CBA course materials, these models rapidly caught on among the high-school teachers. As Strong later recalled (18):

We took over King's model and introduced it in our summer institutes, making sets of the models that teachers could use in their classrooms. We also used them extensively at Earlham.

The Tangent-Sphere Approach

A second pathway for the development of the Kimball free-cloud model came about in 1963 when Henry Bent (figure 11), then at the University of Minnesota, published the first installment of a six-part series on the model in the *Journal of Chemical Education* (31-36). Over the next two decades Bent would also publish several additional popular articles on this subject (37-40), as well as applying the model in several advanced review articles dealing with a variety of other subjects

(41-44). More recently, Schultz has published a summary of various pedagogical applications of the model (45) and Bent has published a two-volume, book-length monograph (46).

Bent was not involved in the original CBA project and appears to have first encountered the free-cloud model via a review article on "The Chemical Bond and the Distribution of Electrons in Molecules," containing a brief summary of the work of Kimball and his students, that was published in 1961 by John Platt (47), one of the major developers of the free-electron approximation for conjugated π-electron systems (5). As we have seen, Kimball and his students originally used the descriptors "free cloud" or "electron cloud" when referring to their model (4, 6, 12). It was Strong (25) who first introduced the alternative descriptor of "charge-cloud" model. This he probably acquired from a reading of Charles Coulson's popular monograph of the period, *Valence* (48), and this was the descriptor subsequently used in all of the literature related to the CBA project. Though in his review proper Platt did not use Kimball's name for the model – preferring instead to describe it in detail as "a uniform electrostatic model with non-overlapping electron-pair spheres" – in a footnote he referred to it in passing as the "Kimball tangent-sphere approximation." This was the descriptor adopted by Bent and used in the majority of his papers during the 1960s. By 1968, however, Bent was also referring to it as the "electride ion" model (36) and by 1970 as the "electron domain" model (43). More re-
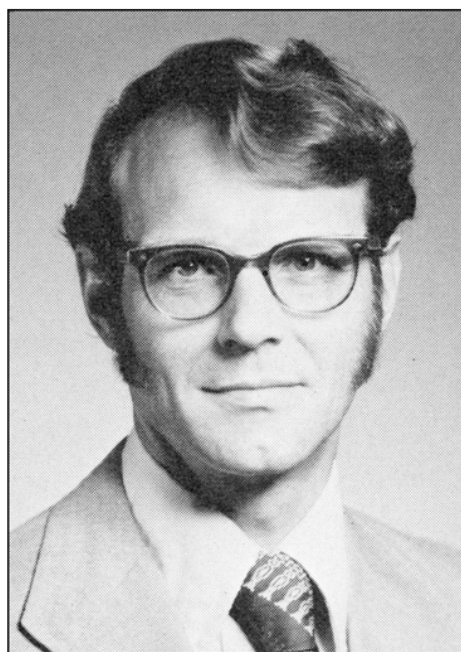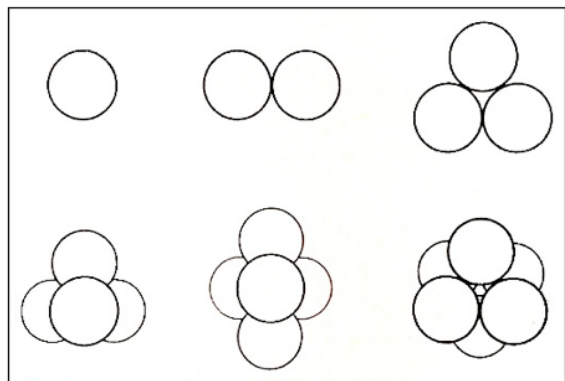

Figure 11. Henry A. Bent

Figure 12. Bent's depiction of the stereochemical implications of the free-cloud model for coordination numbers 1-6.

cently, he has used the descriptors "valence-sphere" (46) and "exclusive orbital" (49) model instead.

Bent first presented his ideas on the tangent-sphere model at a Gordon Conference in the summer of 1962. He was aware of the theses done by Kimball's students as a result of the Platt review and by the time he published his first article in 1963 was also aware of Kimball's Reed Lecture (4), his 1959 paper on complex ions (13), and both Strong's 1962 summary (26) and his class handout at Earlham (25). A footnote to his first paper also suggests that he had some direct contact with Kimball as well.

Though, as is apparent from the thesis titles of several of his students, Kimball viewed his model as a way of approximating localized MOs and as a method for radically simplifying approximate calculations – a view also emphasized by Platt in his 1961 review – these issues were largely obscured in the final CBA presentation, which, because of the nature of its target audience, had to adopt a purely qualitative approach and to rely instead upon the model's "picturability." Though Bent would mention the MO connection in passing (31, 43), his presentation of the model's underlying theoretical justification would also be purely
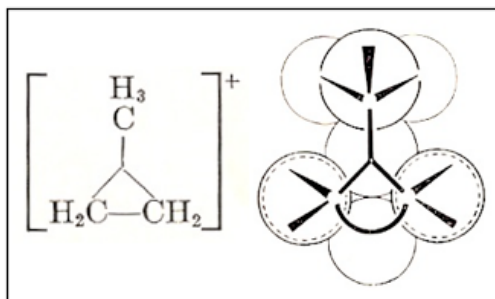

Figure 13. Bent's depiction of a free-cloud model of the $C_3H_7^+$ carbonium ion and its 3c-2e bond.

qualitative, with no mention of the computational aspects that were the central focus of the student theses. Rather than emphasizing the relationship to approximate MO calculations, this qualitative rationalization would instead emphasize the role of spin correlation and the concept of Fermi holes based largely upon several of the literature references cited in the Platt review in the sections immediately preceding its discussion of the Kimball model. Indeed, it was not until the work of Rioux in the 1970s and 1980s that examples of quantitative calculations based on the free-cloud model would finally appear in the published literature (50-53).

What Bent would instead seize upon was, not just the model's inherent picturability, but also its direct isomorphism with structural formulas based upon the Lewis electron-pair model – an insight for which his
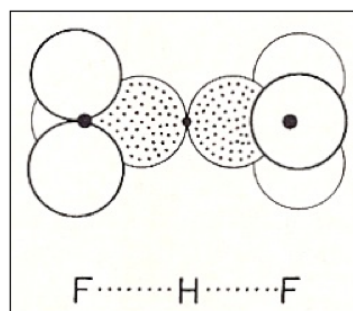

Figure 14. Bent's depiction of a free-cloud model of the symmetrical H-bonded HF_2^- anion. Note that it assumes duplet expansion.

previous work on the systematics of the VB approach had well prepared him (54-56). This meant that there was no necessity for the use of approximate calculations to predict optimal free-cloud structures, since these structures could be directly inferred from the existing VB structures. This isomorphism had, of course, also been appreciated by the CBA project, but they had introduced Lewis structures only after first introducing the free-cloud model itself and then only as a convenient two-dimensional method for summarizing the model's results. Bent reversed this emphasis and, more than anyone else, would explore the consequences of that reversal in detail by continuously testing the model through its application to both new molecules and new situations.

Already in Part II of his six-part series, he was the first to make explicit the model's stereochemical implications (figure 12) for coordination centers containing up to six electron pairs in their valence shells – a suggestion that would have important consequences, as we will see in the next section, for the future rationalization of the VSEPR model of molecular geometry.

Likewise, he seized upon the model's ability to represent the 3c-2e bonds found in the boron hydrides – an aspect already noted by both Kleiss and the CBA project – and applied it to the structures of certain metastable reaction intermediates, such as the $C_3H_7^+$ carbocation shown in figure 13, as well as proposing structures for such H-bonded species as the symmetrical HF_2^- anion (figure 14).

Even more innovative was his application of the model to the reaction mechanism for the well-known S_N2 displacement reaction (figure 15) and his recognition that the structure of the intermediate could also be used as a model for certain intermolecular donor-acceptor complexes (41, 44). Further applications of the model to reaction mechanisms were undertaken by Sunderwirth in 1970, who proposed free-cloud models for proton-transfer reactions, elimination reactions, addition reactions, and carbonium ion rearrangements (57), and yet once again by Bent the same year, who applied it to the mechanism for the Berry pseudorotation (43). Likewise, in 1980 Jensen discussed pos-
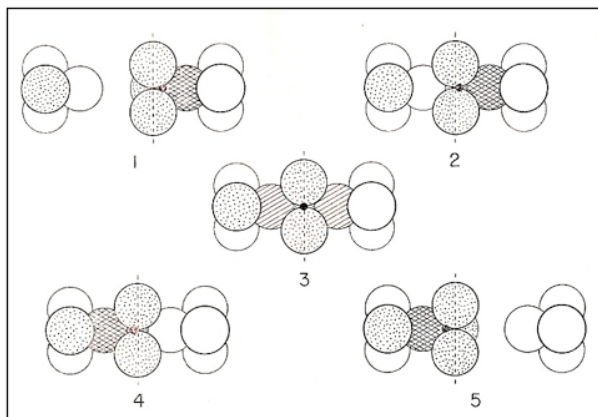

Figure 15. Bent's depiction of a free-cloud model of an S_N2 displacement reaction. Note the necessity of octet expansion.

sible free-cloud models for the n•n, n•σ*, σ•n and σ•σ* classes of donor-acceptor interactions (58).

The Geometry of Atomic Cores

The theses of both Neumark and Kleiss and the CBA project had applied the free-cloud model only to atoms and molecules of the first row (H-He) and second row (Li-Ne) elements. For the latter species the atomic cores consisted of a bare nucleus buried in the center of a single doubly-occupied electron cloud and hence were spherically symmetrical. However, the cores for the main-group elements in rows three and higher presumably consisted of an outer tetrahedral arrangement
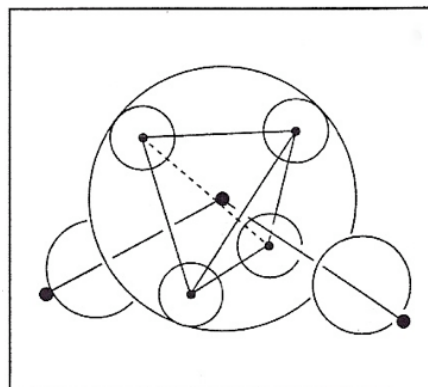

Figure 16. Possible effect of a tetrahedral core packing on the stereochemistry of the valence clouds of an AB₂(g) species sans lone pairs.

of four doubly-occupied clouds like that found in Ne. Consistent with the electrostatic assumptions of the model, this would require that the electron-clouds for the outer valence shells of these elements occupy the pockets in the faces of these tetrahedral cores, leading to the further prediction that triatomic, gas-phase AB_2 species, sans lone pairs on A, would necessarily have bond angles less than 180° (figure 16).

This has indeed been shown to be the case for some species, such as $CaF_2(g)$, $SrCl_2(g)$, $BaI_2(g)$. etc. However, many other species, such as $BeF_2(g)$, $MgCl_2(g)$ and $CaI_2(g)$, have proven to be linear. Rationalization of these linear structures required the assumption that the underlying atomic cores were not always tetrahedral but could, under certain conditions, also be cubic (figure 17) – an idea first introduced by Bent in Parts III and IV of his six-part series (33-34). This idea was acquired from Linnett double-quartet or LDQ theory, mentioned earlier, and was also partially anticipated by Platt in his 1961 review under the guise of "alternate orbital" theory.
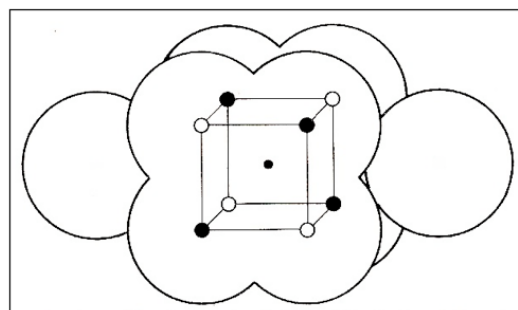
Linnett had proposed that spin correlation, due to

Figure 17. Possible effect of a cubic core packing on the stereochemistry of the valence clouds of an AB₂(g) species sans lone pairs.
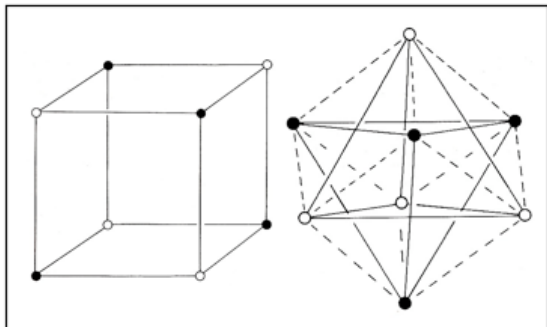
Figure 18. Left: The cubic arrangement of the two tetrahedral spins sets of an octet as envisioned by Linnett. Right: The same repositioned so as to explicitly show the two interpenetrating tetrahedral spins sets.

the Pauli principle, and charge correlation, due to electron-electron electrostatic repulsions, should be considered independently (59-60). In an atom like Ne, with a complete octet of valence electrons, the electrons were divided into two spin sets of four electrons each. Spin correlation meant that the electrons in each set arranged themselves in a tetrahedron, whereas charge correlation, in the absence of bond formation, meant that these two tetrahedra would be as anticoincident as possible, thus placing the eight electrons at the corners of a cube with alternating spins at each corner (figure 18). Bond formation with another atom (figure 19) would draw two electrons, one from each spin set, into coincidence in order to form a bonding pair concentrated in the region between the two bonded atomic cores. Coincidence of only one pair of electrons still
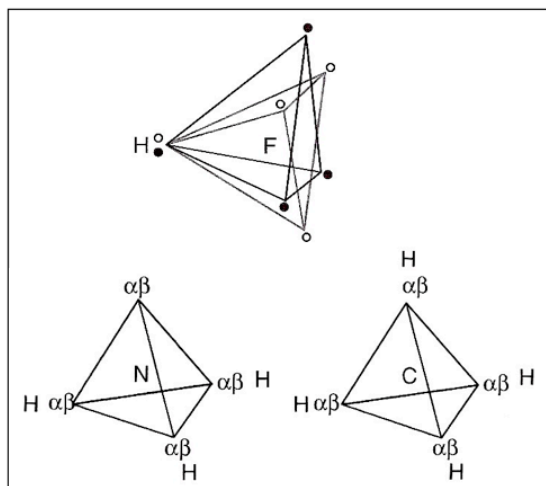

Figure 19. Top: Partial coincidence of the two spin sets resulting from bond formation in HF. Bottom: Complete coincidence of the two spin sets resulting from the formation of two or more bonds as in H_2O, NH_3 and CH_4.

left the remaining corners of the two spin tetrahedra anticoincident. Only when two or more pairs were forced into coincidence were all of the remaining corners also forced into coincidence. The resulting model allowed not only for the formation of conventional 2e-2c single bonds, 4e-2c double bonds, and 6e-2c triple bonds but also for 3e-2c and 5e-2c bonds and the resolution of many structural problems associated with free-radicals and the concept of resonance.

When translated into the terms of the free-cloud model, the cubic arrangement of two completely anticoincident spin sets corresponded to eight, nonoverlapping, singly-occupied electron clouds, whereas the tetrahedral arrangement, in which all of the corners of
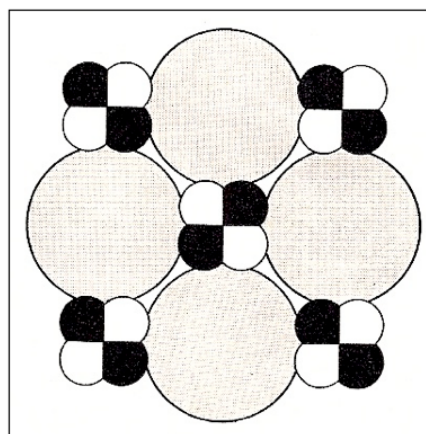

Figure 20. Bent's depiction of the cubic Ca^{2+} cores and spherical valence-electron clouds in a section of metallic calcium.

the spin sets were coincident, corresponded to the case of four, nonoverlapping, doubly-occupied electron clouds, as assumed by the original Kimball model. Intermediate cases of coincidence, on the other hand, corresponded to a partial pairwise overlap of the singly-occupied electron clouds.

Surprisingly Bent failed to apply this idea to the cores of linear triatomic AB_2 molecules, though he did show that it had consequences for many solid-state structures. Kimball and CBA had successfully rationalized the nonmolecular structures of such species as Li(s) and LiH(s) in terms of an infinitely extended cubic array of spherically symmetrical components and Birman had based his calculations of the lattice energies of the heavier main-block elements on the same assumption (9). However, the octahedral and cubic arrays found in such nonmolecular species as NaCl(s) and Ca(s) are incompatible with the presumed tetrahedral arrangement of the outermost electron-cloud layers of their components and it is for these cases that

Bent invoked a Linnett cubic array of non-closed paired electron-clouds in order to rationalize the observed structures (figure 20). Since then, both Stephens and Gamba have speculated on related electron-packing models for atomic cores, including those for the transition elements (61-62).

More recently Bent has also applied the free-cloud model to such topics as the optimal packing of discrete molecules in molecular solids and the evaluation of steric hindrance in certain molecules (46).

The VSEPR Approach

The suggestion that simple molecular geometries are determined largely by electron-electron repulsions among the valence electrons of the central core was proposed, in one form or another, at least a half-dozen times between 1903 and the 1950s (63). However, it was not until the publication of a definitive review on inorganic stereochemistry in 1957 by the British chemists, Ronald Nyholm (figure 21) and Ronald Gillespie (figure 22), that this idea began to attract widespread attention among chemists (64).

The developers of the CBA project were well aware of the Nyholm-Gillespie review. As Strong later recalled (18):

With Nyholm's blessing we made a large number of reprints of the Nyholm-Gillespie article and distributed

Figure 22. Ronald Gillespie.

them around to anyone who was willing to take one.

Indeed Nyholm's assistance was acknowledged in the preface to the CBA textbook (27). However, despite this interest and the fact that surviving working documents for the project show that the implications of the free-cloud model with respect to the prediction of molecular structures were fully appreciated (23), no simple summary set of rules for predicting the shapes of molecules having coordination numbers ranging from 2-6 appeared in the final textbook aside from the single case of four tetrahedrally arranged electron-clouds (65).

Beginning in the 1960s Gillespie undertook an active campaign to further refine and popularize the contents of the original review. This eventually led to the acronym VSEPR, for valence-shell electron-pair repulsion model, and to the publication of more than a dozen popular articles and reviews, as well as three full-length books (66-68). In both the original review and in Gillespie's early articles, the VSEPR approach was quantum mechanically justified largely in terms of the Pauli principle and the spin correlation studies done by Linnett and his students in the early 1950s (69). However, starting around 1972, Gillespie began to increasingly employ both Bent's tangent-sphere structures and King's styrofoam sphere/rubber band models when rationalizing the VSEPR approach (70). The only problem was that King was never given credit for his dynamic models and neither the terms free-cloud or charge-cloud nor the CBA text were ever mentioned. Though Kimball himself was briefly mentioned in

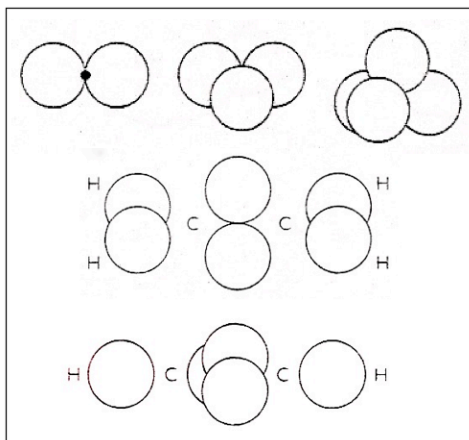Figure 21. Ronald Nyholm (1917-1971).

Figure 23. Examples of Gillespie's so-called valence-shell electron domain or VSED models which are obviously relabeled versions of Kimball's original free-cloud models.

passing in the full-length books, no direct literature references to his work were included, and he was almost never mentioned in the popular articles and reviews.

In addition, Gillespie, like Bent, began to almost immediately relabel everything. The tangent-sphere model soon became the "hard-sphere" model, and then the "electron-pair domain" model. By the 1990s Gillespie was making the further dubious claim that the so-called "valence-shell electron domain" or VSED model (figure 23) was in fact an *alternative* to orbital models, rather than a crude method for approximating localized MOs (71), and that the VSEPR approach itself did not require the use of any orbitals whatsoever for its theoretical justification (72):

... the VSEPR model is not an orbital model and does not rely on any particular orbital description of a molecule.

In the earlier articles, it was further claimed that the VSEPR model was not based on electrostatic repulsions between the various valence-electron pairs, but rather solely on the operation of spin correlation (73):

This mistaken idea [that VSEPR geometries are determined by electrostatic repulsions] is prevalent in a number of introductory textbooks ... The potential energy of any given system of nuclei and electrons arises from their mutual electrostatic repulsions and attractions, but the distribution of the electrons around the central nucleus is determined by the exclusion principle.

The first of these claims is no doubt based on the fact that, despite many studies by others showing that VSEPR can easily be rationalized in terms of localized

MO theory (74), Gillespie in his own research publications has instead chosen to use more generalized theoretical approaches based on various criteria for the dissection of total electron densities into significant regions of localized maxima and minima, initially employing the "atoms in molecules" approach of his associate Richard Bader (75) and, more recently, the ELF or electron-localization function of Savin and Nesper (76). Though the resulting electron density maxima generally conform to the locations of the various valence-electron pairs predicted by VSEPR, these localized regions, unlike orbitals, seldom have integral electron populations.

If the intent of the first quote was to claim that a correlation between the number valence-electron pairs on the central core and the resulting molecular geometries, as embodied in a set of VSEPR *rules,* is empirically true, irrespective of any particular theoretical rationalization, then there is no problem. However, if it specifically refers to use of the VSED model as an alternative to orbitals, then there is a problem, since the division of the valence-electron density of molecules into spherical, nonoverlapping domains with integral populations consisting of pairs of electrons of opposite spins, is identical – however you may choose to relabel it – to use of the Kimball free-cloud model and definitely corresponds, despite claims to the contrary, to the use of an orbital model.

The second of the above claims was no doubt based on the initial use of the spin correlations studies of Linnett *et al* to justify the model in the original review of 1957. However, these studies were based on explicitly ignoring the electrostatic repulsions between the electrons and focusing instead solely on the influence of the Pauli principle on the localization of electrons of like spin in singly-occupied orbitals. When electrostatic repulsion and electrons of opposite spin were added to the mix, the result was LDQ theory rather than VSEPR theory. In the Kimball free-cloud model the Pauli principle is taken into account through the use of nonoverlapping, doubly-occupied electron clouds. However, the optimal orientation of these clouds with respect to one another, and hence the resulting geometry of the molecule, is determined solely by their mutual electrostatic interactions with one another and with the positive atomic cores. Relabeling the electron-clouds as electron domains alters neither the underlying assumptions nor the underlying physics.

Unfortunately, a similar obfuscation of origins and underlying assumptions also appeared in Bent's later writings. Thus in a major 1970 review, no mention of Kimball was made, and rather than giving the correct historical origins of the model as originating in the early 1950s in an attempt to approximate and simplify
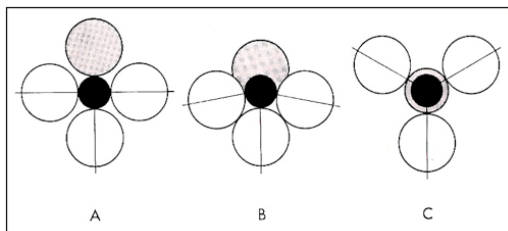
Figure 24. Bent's violation of the premises of the free-cloud model to rationalize stereochemical inactivity of lone-pairs by allowing overlap of doubly-occupied core and valence clouds in situations B and C.

calculations based on localized MOs, it was instead strongly implied that it originated in 1960 as an extension of sphere-packing models originally designed to represent van der Waals domains and close-packing models of ionic solids, and that, as such, it was merely *analogous* to a localized MO representation rather than being an actual simplified MO approximation (43).

Unintended Consequences

I should emphasize that I in no way believe that this progressive disenfranchisement of Kimball has done deliberately. Rather it was almost certainly an unintended result of adopting an ahistorical qualitative approach and of being preoccupied with conceptual issues other than historical accuracy – a not uncommon scenario in technical writing (77). Nevertheless, it has had two very unfortunate consequences.

The first of these is that, when the Kimball model is used in the current textbook literature, this usage often goes unrecognized since the model is usually either left unidentified (78) or is misidentified (79). In yet other cases, the model is used without the textbook authors even realizing it. This most frequently occurs when the textbooks use photos of balloon clusters to illustrate the VSEPR rules (80). These analogs were first introduced by Jones et al. in 1961 and were originally based on cylindrical modeling balloons like those used by clowns to make balloon animals (81-82). Though these looked nothing like standard hybrid orbitals or like spherical electron clouds, they did mechanically mimic the standard geometries for 2-6 electron-pairs. Later variants have used spherical balloons instead, so the results look like the usual free-cloud models, though they lack the dynamic character of King's styrofoam ball/rubber band analogs (83).

Nevertheless, the resulting photos are never identified as Kimball free-cloud analogs. If anything, the textbooks usually imply that they are analogs of hybrid orbitals. The problem with this misidentification is that the VB rationale of molecular geometries is not based

on the mutual repulsion of nonoverlapping orbitals like the Kimball model and the balloon analogy, but rather on the principle of creating whatever set of hybrid orbitals most effectively maximizes the overlap between the resulting hybrids and the ligand orbitals, leading, in turn, to maximization of the resulting exchange energy upon bond formation.

The second unintended consequence is that, by losing track of the underlying physical assumptions of the Kimball model, both Gillespie and Bent have been inconsistent in their use of the model and have even, on occasion, proposed extensions which violate these basic assumptions. As an example of the former, one might cite Gillespie's willingness to invoke a tetrahedral core packing (figure 16) when rationalizing bent $AB_2(g)$ species sans lone pairs, but to dispense with all references to core packings when discussing linear $AB_2(g)$ species, or the supposed overall ellipsoid cores of transition-block species (84). As an example of the latter, one might cite Bent's rationale (figure 24) of the nonstereoactivity of lone pairs in certain compounds of the heavier main-block elements, which directly violates the rule that the doubly-occupied clouds of the atomic cores cannot occupy the same region of space as the doubly-occupied clouds of the valence shell (43, 85).

Inherent Limitations

The chemical literature is filled with attempts to theoretically evaluate the VSEPR model using other alternative bonding models (86). To the extent that these studies conclude that the VSEPR model is incorrect because the explanation that it offers for molecular geometries is not the same as that offered by the competing model, such studies are worthless. Since both models are approximate and both are based on differing sets of initial assumptions, disagreement over the cause of a given phenomenon tells us nothing more than that the models are different from one another. If, on the other hand, both models can explain phenomenon A, however differently, but only one of the two can also explain phenomenon B, then we have a valid basis for claiming that the latter model is superior in some fashion to the former model. Even then, if this superior explanatory power is obtained only at the cost of much greater complexity and loss of intelligibility, there may still be valid reasons for continuing to prefer the first model – at least under certain circumstances.

Adopting the second of these methods of evaluation, just what are the inherent limitations of the free-cloud model? Given our previous emphasis on its direct isomorphism with the Lewis electron-pair model, the answer to this question is straightforward:

The free-cloud model has the same inherent limitations as the original Lewis electron-pair model and the use of Lewis dot diagrams.

Among the more serious of these are its inability to deal with species requiring the use of resonance within the context of the Lewis-VB model and the necessity of postulating both duplet expansion and octet expansion when dealing with species in which H has a coordination number greater than one and main-block elements have coordination numbers greater than four.

In his Reed lecture Kimball readily acknowledged that, using only spherical electron clouds, his model was unable to deal with species requiring the use of resonance (4):

Now there is one situation where the approach I have been talking about breaks down. That is the case which is usually labeled with the word resonance. I can most simply illustrate it with benzene.

Kimball then proceeded to construct a free-cloud model of the sigma bonding system in benzene and to point out that this system had twelve low potential-energy pockets, one above and one below each of the six carbon atoms, each of which could accommodate another electron cloud, though only enough valence electrons remained to create three. So as a compromise it becomes necessary to abandon the spherical-cloud approximation for these electrons and to instead adopt a more complex cloud shape that extends around the entire ring and avails itself of all 12 of the low potential-energy pockets.

Neither Gillespie nor Bent have ever faced up to this limitation and Bent, in particular, has on occasion advocated instead a time-dependent flip-flop between two or more limiting-case free-cloud models, even though this particular interpretation of resonance has long been known to be incorrect (87). Indeed the improbability of this interpretation can be easily demonstrated using King's styrofoam ball /rubber band models. These models readily show the ease of interconverting between a square-based pyramidal and a trigonal bipyramidal geometry or between a square planar and a tetrahedral geometry. All that is required is gentle shaking of the model. However, even violent shaking of a free-cloud model of one of the two limiting Kekulé structures for benzene fails to convert it into the other.

Likewise, both Bent and Gillespie are strong advocates of duplet and octet expansion (recall figure 12 and 14) as this is the only way in which one can retain the use of conventional 2c-2e bonds and spherical electron clouds when representing the structures of most hypervalent species, despite the fact that repeated quantum mechanical calculations for these species have long supported the validity of both the duplet and octet rules as upper-limit rules and the use of open 3c-4e bonding schemes (88).

Other attendant problems involve the model's apparent inability to provide satisfactory representations of excited states and of many free-radical species (e.g. the paramagnetic O_2 molecule), to account for metallic conductivity, or to represent the concept of bond polarity. Similarly, the model fails to provide satisfactory alternatives to such apparent triumphs of delocalized MO theory as the Hückel 4n+2 aromaticity rule, the Woodward-Hoffmann rules for pericyclic reactions, or the Wade-Williams electron-counting rules for cluster species.

Even Bent's own rules regarding the role of *s*-character in hybrid-bond formation cannot be represented using the spherical electron-cloud model (54-55). In essence these rules state that the angular volume occupied by an orbital and its radial separation from the central core of an atom are inversely related and correlate with the degree of *s*-character in the orbital. In other words, the greater the *s*-character of an orbital, the greater the angular spread of its electrons and closer their approach to the central nucleus. However, in the case of a spherical electron cloud, the angular spread and the radial separation are directly rather than inversely related. In other word, increasing the size of a spherical electron cloud in order to increase its angular spread also automatically increases the distance between its center and the central atomic core.

Bent has attempted to circumvent this problem by postulating that the atomic cores are not tangent to their valence electron-clouds but rather have room to rattle around in the potential pocket created by the surrounding valence spheres (34). Upon bond formation, core-core repulsions may displace the cores to one side of this pocket and even, on occasion, push them into the electron cloud of an adjacent lone-pair, thus diminishing the distance from the center of the lone pair cloud to the core. However, this latter scenario once again violates the basic premise of the model that doubly-occupied electron clouds, whether valence or core, are mutually impenetrable, whereas the former scenario almost certainly violates the virial theorem, which is vital to all quantitative applications of the model (89). The primary mechanism for lowering the potential energy of the system is through favorable core-valence electron attractions and the valence electron clouds will shrink as much as possible consistent with maximizing this attraction and thus lowering their separation from the core, even though this is done at the expense of increasing their electron-electron repul-

sions and their kinetic energies, a scenario which appears to have been verified by the few quantitative calculations done by Kimball's students (8). In short, core rattling is highly improbable.

As already mentioned, the Kimball-Lewis close-paired model is actually a special limiting case of the more general Linnett double-quartet model, and VSEPR, in turn, is merely a summary of the structural implications of the Kimball model. Many of the above limitations associated with resonance, duplet and octet expansion, and the representation of both excited states and free radical species are easily soluble using full LDQ theory, and a proper and consistent use of this model, rather than just occasionally cherry-picking bits and pieces, as has been done in the past by both Gillespie and Bent, would go a long way toward eliminating some of these defects. Likewise, Bent has generated a list of interesting parallels between the Kimball model for covalent species and packing models for ionic solids (36, 43). Not included in this list, however, is how the ionic model deals with so-called defect structures, though pursuit of this particular analogy may well provide a hint for how to incorporate the phenomenon of metallic conductivity into the model's current static electride ion picture of metals (90). Along similar lines, Hooydonk has suggested that bond polarity might also be incorporated into the model using an order-disorder analogy (91). Also of note is Gillespie's attempt, in his 1979 Nyholm Lecture, to extend the model to at least a few cluster species of the main-block elements by minimizing core-core repulsions instead of electron-pair repulsions (92).

Pedagogical Implications

The present-day successes of computational quantum chemistry have ensured that the Kimball free-cloud model has long ceased to be of interest to the practicing chemist concerned with accurate calculations of electronic energies and other molecular parameters. Rather its current value, as intuited by Strong more than a half century ago, lies in its potential use as a teaching model – as an introductory bridge between the qualitative bonding concepts embodied in Lewis dot diagrams, on the one hand, and more rigorous quantum mechanical calculations, on the other.

As such, the model allows for the introduction of several basic quantum mechanical concepts: the uncertainty principle through its representation of electrons as diffuse charge clouds rather than as point particles, the Pauli principle through the rule that electron clouds can overlap only in pairs of opposite spin, and the role of both kinetic energy and the virial theorem in atom and molecule formation via its simple correlation between electron-cloud size and kinetic energy content (93). Moreover, by further eliminating orbital overlap, such mysterious effects as exchange energy are also eliminated and all potential energy interactions reduced to simple electrostatics easily understandable by students with an elementary physics background.

As shown by its use in the introductory college course at Earlham (25) and by the publications of Rioux (50-52), the model also allows for actual quantitative calculations of ground-state energies for simple atoms and molecules which fall well within the abilities of a talented college freshman, and, as shown by the CBA textbook, the model can also be taught to more elementary students lacking such math skills by exploiting its inherent picturability, its isomorphism with Lewis dot diagrams, and the use of the dynamic King styrofoam ball/rubber band models. Lastly, by honestly confronting cases where the model fails (e.g. resonance, excited states) or where its use is problematic (e.g., duplet and octet expansion), one can provide a motivation for the introduction of alternative and/or more advanced quantum mechanical models at a later point in the curriculum.

Some of these points can be underscored by contrasting them with the more conventional quantum mechanical models which currently dominate the chemistry textbook and especially with regard to the issue of picturability. The importance of this characteristic, not only as an alternative to a formal mathematical approach, but also as an aid to mathematical thinking itself, has been stressed by the popular mathematical writer Ian Steward (94):

Some mathematicians, perhaps 10 percent, think in formulae. Their intuition deals in formulae. But the rest think in pictures. Their intuition is geometrical. Pictures carry so much more information than words. For many years schoolchildren were discouraged from drawing pictures because "they aren't rigorous." This was a bad mistake. Pictures are not rigorous, it is true, but they are an essential aid to thought and no one should reject anything that can help them to think better.

Precisely the same point was made by the British educational expert, M. B. Ormerod, when he attempted to develop a purely pictorial approach to the teaching of elementary MO theory in the late 1960s and early 1970s (95):

... human ability can be factored into three major group factors: verbal, numerical, and spatial. For centuries education has proceeded via the first two factors. The advent of modern visual aids and cheap carvable plastic materials has made education via the third fac-
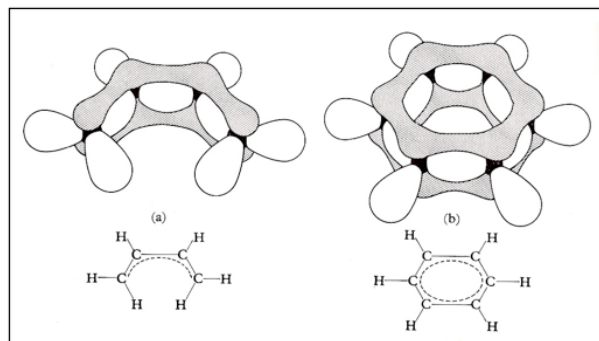
Figure 25. PEEL models for butadiene and benzene showing the use of delocalized π-lobes.

tor more feasible. There is some reason to believe that high spatial ability often compensates for low mathematical ability. Hence it is not unreasonable to expect that the presentation of the simpler branches of molecular orbital theory via models might succeed with many for whom the mathematical approach is impossible.

In pursuit of this goal Ormerod designed a set of commercially available styrofoam models known as PEEL models (an acronym for "probability envelope of electron location"), and a stencil for producing 2D drawings of the resulting 3D physical models (95-96). In addition to atomic cores, the model kits included repre-

sentations of electron-density lobes corresponding to three kinds of localized MO domains: terminal unprotonated 1c-2e orbitals, terminal protonated 2c-2e σ-orbitals, and shared unprotonated 2c-2e σ-orbitals, as well as a variety of delocalized π-electron-density lobes – all of these components being color coded and assembled using a standard peg and hole mechanism.

As may be seen from figures 25 and 26, PEEL models certainly possess picturability. Indeed, one could argue that they are superior in this regard to the free-cloud model. Like the free-cloud model, all of the electron-density clouds are displayed simultaneously. However, unlike the free-cloud model, the atomic cores are clearly visible in the PEEL models, there is no visual confusion as to which contacts are bonding versus nonbonding, and, via their π-components, they are able to deal with situations requiring resonance. In addition, they can easily be extended to large molecules, whereas free-cloud models become rapidly undecipherable in such cases (figure 27) without an accompanying framework structure to indicate the overall bonding topology. This is precisely the problem traditionally encountered with the use of conventional molecular models – framework models are good at showing connectivity but poor with respect to volume considerations, whereas space-filling models have the exact opposite characteristics, with ball and stick models functioning as a sort of compromise between these
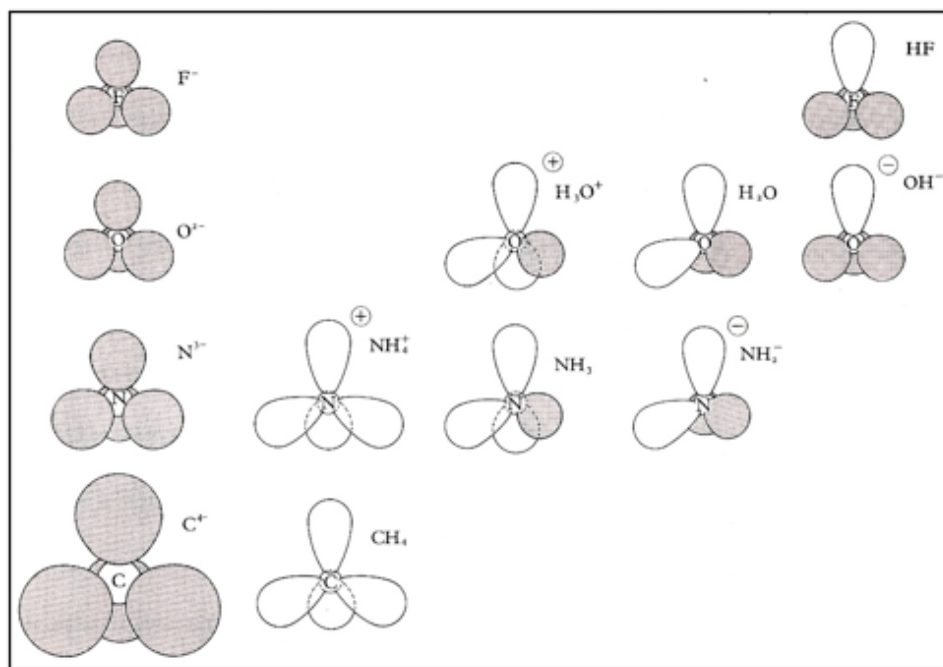

Figure 26. PEEL models for a series of simple isoelectronic ions and molecules. Shaded lobes are unprotonated, unshaded lobes are protonated.
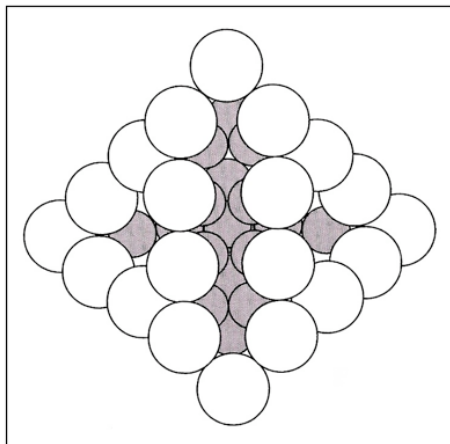
Figure 27. Bent's free-cloud depiction of tetra-t-butyl tetrahedrane. Note how, in the absence of an accompanying topological formula, it is impossible to tell what this is supposed to represent.

two extremes. Free-cloud models are the electron-density equivalents of space-filling molecular models, whereas PEEL models are the electron-density equivalents of ball and stick models.

That said, however, there are also some important disadvantages to the use of PEEL versus free-cloud models. Whereas students can easily understand the physics behind the free-cloud models and even mechanically mimic their formation via use of King's ball and rubber band analogs, they must simply accept the PEEL structures as "givens" generated via calculations and assumptions that are beyond their understanding. This is not a trivial problem. The function of models and theories in science is to provide a unifying reductive rationale for a diversity of otherwise apparently unrelated facts (97). However, if students are unable to either understand or apply the theory to new situations on their own but rather must be given the theoretical rationale for each individual case, where is the reductive simplification? In such cases the theory has just become another set of apparently unrelated results or labels to be memorized. Yet this is precisely the situation with regard to the random fragments of MO and VB theory currently taught in most textbooks.

In addition, the PEEL models are based on a mixture of two distinct MO approaches rather than representing a single self-consistent model. The σ-system is based on the use of a localized MO approach and the π-system on the use of a delocalized MO approach. A consistent use of a delocalized MO approach would give a set of σ-orbitals very different from those used in the PEEL models (98), whereas a consistent use of a localized MO approach would give a very different set of π-orbitals (99, 100). Of course this mixed picture is

universally used in all organic textbooks and, if anything, is elegant testimony as to how shoddy and problematic current textbook use of these quantum mechanical models really is.

But in fact this problem is actually more serious than just the mixing of two alternative MO representations. In the localized σ-system each bonding component is assumed to represent the electron density of a single localized orbital. In the case of the delocalized π-systems, however, each component must, with the exception of isolated double bonds, represent not the electron density of a single MO but rather the total integrated electron density of all of the filled delocalized MOs (two in the case of butadiene and three in the case of benzene), though the drawings given in figure 24 look suspiciously like those of only the lowest occupied π-orbitals (in which case the electron counts for such PEEL models are incorrect). The free-cloud model, though more limited in the kinds of molecules it can be applied to, is at least physically and theoretically self-consistent.

Conclusion

It is hoped that this review will not only serve to clarify the historical record but also function as a resource paper for chemical educators interested in reforming the chemical curriculum at both the high school and university levels. In his 1959 lecture at Reed College Kimball noted that many early (pre-1935) ideas in quantum chemistry had rapidly gotten into the elementary textbook and there they have remained as a sort of implacable textbook dogma impervious to virtually everything that has since happened in the research literature. This means that anything that deviates from this dogma is viewed with suspicion and as necessarily being either incorrect or inappropriate for the eyes of introductory students. Only time will tell whether the Kimball free-cloud model was truly a failed innovation in chemical education or whether it still has a role to play in correcting this deplorable situation.

Acknowledgements

References and Notes

1.   See the various papers published in the April and May 1958 issues of the *Journal of Chemical Education* dealing with the reforms at various individual colleges and universities based on a symposium held at the 132nd National ACS Meeting in New York City in September of 1957.

2.   P. M. Morse, "George Elbert Kimball, 1906-1967," *Biogr. Mem., Nat. Acad. Sci.* **1973**, *43*, 129-146.

3.   H. Erying, J. E. Walter, G. E. Kimball, *Quantum Chemistry*, Wiley: New York, NY, 1944.

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

5.   W. B. Jensen, "The Free-Electron Model: From Otto Schmidt to John Platt," in E. T. Strom, A. K. Wilson, Eds., *Pioneers of Quantum Chemistry*, ACS Books: Washington DC. 2013, pp. 117-137.

6.   G. F. Neumark, *Free-Cloud Approximation to Molecular Orbital Calculations*, Ph.D. Thesis: Columbia University: New York, NY, 1951.

7.   H. R. Westerman, *Simplified Calculations of the Energies of the Second-Row Elements*, Ph.D. Thesis: Columbia University: New York, NY, 1952.

8.   L. M. Kleiss, *Calculations of Properties of Hydrides of the Second-Row Elements*, Ph.D. Thesis: Columbia University: New York, NY, 1952.

9.   J. L. Birman, *A Simplified Molecular Orbital Calculation of the Total Energy and Lattice Constants in Crystals of the Elements*, Ph.D. Thesis: Columbia University: New York, NY, 1952.

10. J. D. Herniter, *Kinetic Energy of Localized Electrons*, Ph.D. Thesis: Columbia University: New York, NY, 1956.

11. P. M. Morse, G. E. Kimball, *Methods of Operations Research*, Wiley: New York, NY, 1951.

12. G. E. Kimball, *Note on Free-Cloud Method for Ground States of Molecules*, A. D. Little Company Report: Boston, MA, 1956. The author has never seen this document and is aware of its existence solely because it was listed in the bibliography for Kimball given in reference 2.

13. G. E. Kimball, E. M. Loebl, "A Quantum Mechanical Model of Complex Ion Formation: The Electrostatic Nature of Binding," *J. Chem. Educ.,* **1959,** *36*, 233-237. Reprinted in reference 20, pp. 113-117.

14. Anon., "The Reed College Conference on the Teaching of Chemistry," *J. Chem. Educ.*, **1958**, 35, 54-55. Reprinted in reference 20, pp. 1-2.

15. L. E. Strong, "Chemical Bonds: A Central Theme for High School Chemistry," *J. Chem. Educ.*, **1958**, 35, 56-58. Reprinted in reference 20, pp. 3-5.

16. W. Hückel, *Structural Chemistry of Inorganic Compounds*, Vol. 1, Elsevier, New York, NY, 1950, Chapter 2.

17. M. G. Burford, H. F. Lewis, "The Wesleyan Conference of 1958," *J. Chem. Educ.*, **1959**, 36, 90-91. Reprinted in reference 20, pp. 6-7.

18. W. B. Jensen, *Interview with Laurence E. Strong*, Conducted on 16 March 1995, Oesper Collections, University of Cincinnati.

19. A. H. Livermore, L. E. Strong, "A Writing Conference for CBA High School Chemistry Project," *J. Chem. Educ.*, **1960**, 35, 209-211. Reprinted in reference 20, pp. 8-10.

20. R. K. Fitzgerel, W. F. Kieffer, Eds. *Supplementary Readings for Chemical Bond Approach*, Journal of Chemical Education: Easton, PA, 1960

21. Anon, *Supplementary Readings for the Chemical Bond Approach*, W. H. Freeman: San Francisco, CA, 1961.

22. H. A. Neidig et al, *Investigating Chemical Systems: Chemical Bond Approach Projec*t, McGraw-Hill: New York, NY, 1963.

23. E. S. Scott, "Comparison of the Kimball and Orbital Models," Working Paper, CBA Project, c. 1960.

24. E. S. Scott, "Sample Solution of Potential Energy of a Proton and an Electron," Working Paper, CBA Project, c. 1960.

25. L. E. Strong, *A Charge-Cloud Model for Molecules*, Earlham College: Richmond, IN, 1963-1971.

26. L. E. Strong, "Facts, Students, Ideas," *J. Chem. Educ.*, **1962**, *39*, 126-129.

27. O. T. Benfey et al, *Chemical Systems: Chemical Bond Approach Project*, McGraw-Hill, New York, NY, 1964, Chapter 7, also pp. 324, 377, 687.

28. J. V. DeRose et al. *Chemical Systems: Teachers' Guide*, McGraw-Hill, New York, NY, 1964.

29. L. C. King, "Molecular Architecture," *Chemistry,* **1964**, *37(2)*, 12-17

30. L. C. King, "Molecular Architecture," *Amer. Sci. Teach.*, **1966**, *33(6)*, 27-34. This version replaced the toothpicks with brass paper fasteners inserted into the ends of the bore holes with their ends bent to form hooks for the rubber bands, thus allowing for easier replacement of broken rubber bands. Later variants used plastic easter eggs instead of styroform balls, though these were no longer spherical and instead resembled typical hybridized orbitals. See J. P. Birk, S. Abbassian, "Teaching VESPR: The Plastic Egg Model," *J. Chem. Educ.*, **1996**, *73*, 636-637.

31. H. A. Bent, "Tangent-Sphere Models of Molecules: I. Theory and Construction," *J. Chem. Educ.*, **1963**, 40, 446-452.

32. H. A. Bent, "Tangent-Sphere Models of Molecules: II. Uses in Teaching," *J. Chem. Educ.*, **1963**, 40, 523-530.

33. H. A. Bent, "Tangent-Sphere Models of Molecules: III. Chemical Implications of Inner-Shell Electrons," *J. Chem. Educ.*, **1965**, 42, 302-308.

34. H. A. Bent, "Tangent-Sphere Models of Molecules: IV. Estimation of Internuclear Distances; The Electronic Structure of Metals**,**" *J. Chem. Educ.*, **1965**, 42, 348-355.

35. H. A. Bent, "Tangent-Sphere Models of Mole-

cules: V. Alfred Werner and the Doctrine of Coordination," *J. Chem. Educ.*, **1967**, *44*, 512.

36. H. A. Bent, "Tangent-Sphere Models of Molecules: VI. Ion Packing Models of Covalent Compounds," *J. Chem. Educ.*, **1968**, *45*, 768-778.

37. H. A. Bent, "The Tetrahedral Atom. I. Enter the Third Dimension," *Chemistry*, **1966**, *39(12)*, 8-13.

38. H. A. Bent, "The Tetrahedral Atom. II. Valence in Three Dimensions," *Chemistry*, **1967**, *40(1)*, 9-15.

39. H. A. Bent, "Where is Education in Chemistry Headed?," *J. Coll. Sci. Teaching*, **1971**, *1(2)*, 20-25.

40. H. A. Bent, "Chemistry" in R. Harré, Ed., *Scientific Thought, 1900-1960*, Oxford University Press: Oxford, 1969, Chapter 5.

41. H. A. Bent, "Structural Chemistry of Donor-Acceptor Interactions," *Chem. Rev.*, **1968**, *68*, 587-648.

42. H. A. Bent, "Electron Correlation and Bond Properties in Some Selected Sulfur Compounds," in N. Kharasch, Ed., *Organic Sulfur Compounds*, Vol. 2, Pergamon: New York, NY, 1963, Chapter 1.

43. H. A. Bent, "Localized Molecular Orbitals and Bonding in Inorganic Compounds," *Fortschr. Chem. Forsch.*, **1970**, *14(1)*, 1-48.

44. H. A. Bent, "The Nature of Intermolecular Donor-Acceptor Bonds," *Tech. Chem. (NY)*, **1976**, *8*, 65-93.

45. E. L. Schultz, "Tangent Sphere Model: An Analog to Chemical Structure," *J. Chem. Educ.*, **1986**, *63*, 961-965.

46. H. A. Bent, *Molecules and the Chemical Bond, An Introduction to Understanding Conceptual Valence-Bond Theory and the Stereochemical Implications of Valence Sphere Models of Molecules*, Vol. 1, Trofford: Pittsburgh, PA, 2011; *Molecules and the Chemical Bond, An Introduction to Conceptual Valence-Bond Theory: The Shortest Route to Electron Density Profiles*, Vol. 2, Trofford: Pittsburgh, PA, 2013.

47. 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.

48. C. Coulson, *Valence*, 2nd ed., Oxford University Press: Oxford, 1961, pp. 18-19.

49. H. A. Bent, *Commentary on Hunting Dimers of C(BH)₂ and C(AlH)₂, With a Concluding Essay on Lines of Converging Evidence Regarding Exclusive Orbital Models of Molecules*, Privately Printed: Pittsburgh, PA, 2012.

50. F. Rioux, "The Stability of the Hydrogen Atom," *J. Chem. Educ.*, **1973**, *50*, 550-552.

51. F. Rioux, P. Kroger, "Charge-Cloud Study of Atomic and Molecular Structure," *Am. J. Phys.*, **1976**, *44*, 56-59.

52. F. Rioux, "An Ionic Model for Metallic Bonding," *J. Chem. Educ.*, **1987**, *64*, 789-790.

53. Electrostatic calculations of molecular energies closely related to those of Kimball have since been reported by Sachs. See L. J. Sacks, "Coulombic Models in Chemical Bonding: I. Description and Some Applications of a Coulombic Model," *J. Chem. Educ.*, **1986**, *63*, 288-296; "Coulombic Models in Chemical Bonding: II. Dipole Moments of Binary Hydrides," *Ibid.*, **1986**, *63*, 373-376; "Coulombic Models in Chemical Bonding: III. Barriers to Internal Rotation in Ethane," *Ibid.*, **1986**, *63*, 487-489.

54. H. A. Bent, "Distribution of Atomic s-Character in Molecules and Its Chemical Implications," *J. Chem. Educ.*, **1960**, *37*, 616-624.

55. H. A. Bent, "An Appraisal of Valence-Bond Structures and Hybridization in Compounds of the First-Row Elements," *Chem. Rev.,* **1961**, *61*, 275-311.

56. W. B. Jensen, "Electron-Counting Rules and Bonding Topology," *De educacion quimica*, **1978**, *3*, 210-222. A generalization of Bent's earlier work on bonding topology. An English translation is available upon request from the author.

57. S. G. Sunderwirth, "Donor-Acceptor Interactions in Organic Chemistry," *J. Chem. Educ.*, **1970**, *47*, 728-732.

58. W. B. Jensen, *The Lewis Acid-Base Concepts: An Overview*, Wiley-Interscience: New York, NY, 1980, Chapters 3-4.

59. J. W. Linnett, "A Modification of the Lewis-Langmuir Octet Rule," *J. Am. Chem. Soc.*, **1961**, *83*, 2643-2653.

60. J. W. Linnett, *The Electronic Structure of Molecules: A New Approach*, Methuen: London, 1964.

61. P. S. Stevens, "A Geometric Analog of the Electron Cloud," *Proc. Nat. Acad. Sci.*, **1966**, *56*, 789-793.

62. A. Gamba, "Atomic and Nuclear Models," *Physics Lett.*, **1967**, *24A*, 64-65.

63. W. B. Jensen, "Repulsion Models of Molecular Geometry," Unpublished manuscript.

64. R. J. Gillespie, R. S. Nyholm, "Inorganic Stereochemistry," *Quart. Rev. Chem. Soc.*, **1957**, *11*, 339-380. Also R. J. Gillespie, R. S. Nyholm, "The Stereochemistry of Inorganic Molecules and Complex Ions," in W. Klyne, P. B. D. de la Mare, Eds., *Progress in Stereochemistry*, Vol. 2, Academic Press: New York, NY, 1958, Chapter 8.

65. Reference 27, pp. 269-275. This was in part because CBA, in keeping with Kimball's original work, applied the model only to compounds of the elements in rows 1 and 2 of the periodic table.

66. R. J. Gillespie, *Molecular Geometry,* Van Nostrand: New York, NY, 1972.

67. R. J. Gillespie, I. Hargittai, *The VSEPR Model of Molecular Geometry*, Allyn and Bacon: Boston, 1991.

68. R. J. Gillespie, P. L. A. Popelier, *Chemical Bonding and Molecular Geometry: From Lewis to Electron Densities*, Oxford University Press: New York, NY, 2001.

69. J. W. Linnett, A. J. Poe, "Directed Valency in Elements of the First Short Period," *Trans. Faraday Soc.*, **1951**, *47*, 1033-1041 and C. E. Mellish, J. W. Linnett, "Directed Valency in Elements of the First and Second Short Period," *Trans. Faraday Soc.*, **1954**, *50*, 657-664. These two papers basically contained the substance of the VSEPR approach several years before the publication of the Nyholm-Gillespie review, including recognition of the greater stereo-

chemical requirements of lone pairs and the perturbing effects of ligand electronegativities on bond angles.

70. See reference 66, Chapter 2, also reference 73.

71. R. J. Gillespie, "Bonding without Orbitals," *Educ. Chem.*, **1995**, *33*, 107-106.

72. R. J. Gillespie, "Bent Alkaline-Earth Dihalides," *Educ. Chem.*, **1996**, *33*, 9.

73. R. J. Gillespie, "A Defense of the Valence-Shell Electron-Pair Repulsion (VSEPR) Model," *J. Chem. Educ.*, **1974**, *51*, 367-370

74. See, for example, P. Linder, S. Lunell, "The VSEPR Model and Molecular Orbital Theory," *Chem. Scrip.*, **1984**, *24*, 105-106.

75. R. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press: New York, NY, 1990.

76. A. Savin, R. Nesper, "ELF: The Electron Localization Function," *Angew. Chem. Int. Ed.*, **1997**, *36*, 1809-1832.

77. For a discussion of how the sociology of citation distorts the historical record, see W. B. Jensen, "Sociology and the History of Chemistry: Some Footnotes to Merton and Stigler," in press. Preprints available upon request. In fairness to Gillespie and Bent, the CBA textbook also failed to mention Kimball by name in connection with its discussion of the charge-cloud model. The argument that such a mention would have been inappropriate in an elementary textbook is countered by the fact that Linus Pauling is mentioned by name several times in the text in connection with his own work.

78. See, for example, L. B. Clapp, *The Chemistry of the OH Group*, Prentice-Hall: Englewood Cliff, NJ, 1967, pp. 7, 16-17. Though Clapp was one of the developers of the CBA course, he used the free-cloud model in this text without any explicit identification or comment and later switched to the VB model, again without comment.

79. See, for example, J. N. Spencer, G. M. Bodner, L. H. Richard, *Chemistry: Structure and Dynamics*, 3rd ed.,Wiley: New York, NY, 2006, pp. 143-146. Here diagrams identical to those in Kimball and the CBA text are used, but, following Gillespie, are misidentified as being based on the so-called "electron domain model" and this, in turn, is described as a new alternative to the older VSEPR model.

80. See, for example, M. S. Silverberg, *Principles of General Chemistry*, 2nd, ed., McGraw-Hill: New York, NY, 2010, p. 316

81. H. R. Jones, R. B. Bentley, "Electron-Pair Repulsions: A Mechanical Analogy," *Proc. Chem. Soc.*, **1961**, 436-440.

82. H. R. Jones, "Molecular Shapes and the Balloon Analogy," *Educ. Chem.*, 1**965**, *2*, 25-31.

83. R. M. Roberts, J. G. Traynham, "Molecular Geometry: As Easy as Blowing Up Balloons," *J. Chem. Educ.*, **1976**, *53*, 233-234.

84. Reference 67, pp. 100-101, 162-163. Also reference 72.

85. In fairness, it is difficult to decide from Bent's wording whether he is claiming that the lone pair merely changes location or whether he is claiming that it simultaneously changes shape as well. If the latter, it would have the shape of a truncated crescent moon in B and that of a hollow sphere (ignoring either tetrahedral or cubic core packings) in C. Though this would mitigate the overlap problem, it would also lead to a large increase in the kinetic energy of these electrons, since, as Kimball pointed out in his original formulation, kinetic energy depends not only on the size of the electron cloud, it also depends on how complex or "wavy" its shape is. It also raises the question of why, if one is willing to abandon the use of spherical clouds in this case, one is unwilling to do so in the case of benzene and other species requiring the use of resonance?

86. See, for example, M. B. Hall, "Stereochemical Activity of *s*-Orbitals," *Inorg. Chem.*, **197**8, *17*, 2261-2269; R. Ahlrichs, "Gillespie und Pauling Modell – ein Vergleich," *Chem. unserer Zeit*, **1980**, *14*, 18-24.

87. H. A. Bent, private correspondence. G. Wheland, *The Theory of Resonance and Its Application to Organic Chemistry*, Wiley: New York, NY, 1944, pp. 2-3.

88. For a summary, see W. B. Jensen, "The Origin of the Term 'Hypervalent'," *J. Chem. Educ.*, **2006**, *83*, 1751-1752.

89. It not apparent whether the few calculations done by Kimball's students properly obey the virial theorem. Given the model's apparent underestimation of the kinetic energy of doubly-occupied electron clouds, this would seem unlikely.

90. F. A. Kröger, *The Chemistry of Imperfect Crystals*, North Holland: Amsterdam, 1964.

91. G. van Hooydonk, "Bond Polarity: An Order-Disorder Phenomenon?," *J. Mol. Struct.*, **1975**, *24*, 389-392.

92. R. J. Gillespie, "Ring, Cage, and Cluster Compounds of the Main-Group Elements," *Rev. Chem. Soc.*, **1979**, *8*, 315-352.

93. The tendency of most elementary textbooks to ignore the role of electronic kinetic energy in molecule, atom, and ion formation and to rely instead on potential energy-only arguments when rationalizing such topics as Hund's rule, VSEPR, and ionization energy profiles has recently been the subject of debate in the *Journal of Chemical Education*, see F. Rioux, R. L. DeKock, "The Crucial Role of Kinetic Energy in Interpreting Ionization Energies," *J. Chem. Educ.*, **1998**, *75*, 537-539; R. J. Gillespie, R. S. Moog, J. N. Spencer, "Deducing the Shell Model from Ionization Energies and the Use of Models in Introductory Chemistry," *Ibid.*, **1998**, *75*, 539-540; J. P. Lowe, "Comments on Kinetic, Potential, and Ionization Energies," *Ibid.*, **2000**, *77*, 155-156; numerous "Letters to the Editor," *Ibid.*, **2002**, *79*, 29-31; 429-431; 605-607; and F. Rioux, "Hund's Multiplicity Rule Revised,*" Ibid.*, **2007**, *84*, 358-360.

94. I. Steward, *Concepts of Modern Mathematics*, Dover Books: New York, NY, 1995, p. 5.

95. M. B. Ormerod, *The Architecture and Properties of Matter: An Approach Through Models*, Arnold: London, 1979, p. 1.

96. A. Walton, *Molecular and Crystal Structure Models*, Horwood: Chitcheser, 1978, pp. 150-151.

97. For a classic study of role of models and analogy in theory formation, see M. Hesse, *Models and Analogies in Science*, University of Notre Dame: Notre Dame, IN, 1966.

98. For examples of delocalized σ-MOs, see W. L. Jorgensen, L. Salem, *The Organic Chemist's Book of Orbital*s, Academic Books: New York, NY, 1973; and R. F. Hout, W. J. Pietro, W. J. Hehre, *A Pictorial Approach to Molecular Structure and Reactivity*, Wiley-Interscience: New York, NY, 1984.

99. For examples of localized π-MOs, see W. England, K. Ruedenberg, "Localized π-Orbitals, Pauling Bond Orders, and the Origin of Aromatic Stability," *Theoret. chim. Acta*, **1971**, *22*, 196-213. See also W. England, "The LMO Description of Multiple Bonding and Multiple Lone Pairs," *J. Chem. Educ.*, **1975**, *52*, 427-428.

100. For a discussion of the question of whether resonance necessarily implies delocalization, see W. B. Jensen, "More on the Nature of Resonance," *J. Chem. Educ.*, **2006**, *83*, 1290.

Publication History

Addendum

Since writing the original draft of this paper it has come to my attention that Ernst Schumacher of the University of Bern has posted the studies made by himself and his students over the past several decades of the quantified free-cloud model described in the five theses of Kimball's students. See the link:

http://www.kimball-model.org/Kimball/kmain.htm

There is also a downloadable computer program for performing such calculations embedded in the above link. See S. Perego, E. Schumacher, "KIMBALL.EXE – Ein Programm zu Berechnung von Molekülen: Weiterwicklung eines Model von George E. Kimball" at:

http://www.kimball-model.org/Kimball/KimballP.pdf

as well as many additional links to specific topics.

More curious, if not disturbing, is the final comment of Schumacher in his introductory English summary:

I did not publish any of this in the scientific literature for lack of time and courage. I do not mention more names because one gymnasium chemistry teacher (not associated with me) has recently been fired by his university for presenting Kimball's model to didactics students. Myself, being beyond 20 years after retirement, am no longer afraid of getting fired ...