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A structural chemist's entanglement with Gillespie's theories of molecular geometry

Lawrence S. Bartell *

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, USA

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Contents

Abstract

An account of Ronald Gillespie's 40-year-old approach to the understanding of molecular structure is presented from the point of view of its influence on the research of the author, a structural chemist. In addition, a review is given of some of the background of structural chemistry that led to Gillespie's recent reformulation of ideas about molecular geometry. His well-known valence shell electron-pair repulsion (VSEPR) theory has changed the way structural chemistry is taught. His current research program on ligand close-packing and atomic charges promises to revise the way chemists think about the nature of the chemical bond. © 2000 Elsevier Science S.A. All rights reserved.

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* Tel.: + 1-313-767-7375; fax: + 1-313-764-8776.
E-mail address: lbart@umich.edu (L.S. Bartell)

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1. Introduction

It may very well be that Ronald Gillespie's most important contributions to chemistry are concerned with the understanding of inorganic reactions that the author, a physical chemist, knows little about. But what the world knows him best for is his popular valence shell electron-pair repulsion (VSEPR) model of molecular structure [1–7]. His ways of looking at molecular architecture have played a major role in the research programs of many structural chemists, including my own. Even though my first encounter with Ronald Gillespie a third of a century ago was hardly an auspicious one, the longer I have known him the more I have come to appreciate his insight. For a number of years, beginning in the late 1950s, my research concentrated on determining the structures of organic molecules, particularly hydrocarbons. Hydrocarbons are simple, available to one with few resources, and they made it possible to get American Petroleum Institute grants to support the research of my first structural student, Russell Bonham. Moreover, these subjects turned out to be an excellent choice for reasons I never anticipated. Our results ultimately forced me into a new, unorthodox way of interpreting structural theory, although it took me a long time to recognize the clues provided by our experiments. Initially, nothing in either of our research programs remotely suggested that Gillespie and I would ever cross scientific paths. And the following review of my early work provides few hints that there are any significant connections with Gillespie's research. But there are. The story begins with an account of the aforementioned early work on organic structures encountering ligand-close packing. It then sketches how our research corroborated and extended Gillespie's VSEPR theory. Finally, the story concludes with a recapitulation of the initial theme, ligand close-packing, only in an enormously expanded version formulated by Gillespie and co-workers.

2. Intramolecular nonbonded interactions

Among other examples, my students studied structures of *n*-alkane chains by electron diffraction techniques, both in surface films where the molecules extended themselves parallel to each other (to minimize the potential energy), and in the gas-phase where they crumpled up (to increase their entropy). Although this was good bread and butter stuff, it wasn't nearly as provocative as our findings for 1,1-dimethylethylene (isobutylene) [8]. What seemed strange about this alkene was that the CH_3–C–CH_3 angle differed from 120°, the angle 'predicted' by the hybridization theory of directed valence that was popular at the time. Not only did it differ, it was distinctly smaller, a deviation opposite in direction to that guessed by every chemist I asked. Everyone supposed that steric interactions between the methyls would open up the angle from that expected for sp^2 hybridization. But whatever the reason, this result was most unfortunate as far as I was concerned. My goal at the time was to refine the gas-phase electron diffraction technique to a new standard of accuracy. Note that the derivation of structures from diffraction patterns of randomly-oriented gas molecules corresponds, essentially, to the inference of a three-dimensional structure from a one-dimensional spectrum of internuclear distances. And this spectrum is appreciably blurred by molecular vibrations. An accurate determination of the C–C–C angle in isobutylene, then, would require the C···C nonbonded distances to be clearly resolved from each other. But they are not. Unfortunately, it looked as if nature had been very unkind by severely overlapping the peak for the $H_2C\cdots CH_3$ distances with that for the $H_3C\cdots CH_3$ distance, greatly interfering with our precision. As it turned out, the outer carbon atoms were roughly in an equilateral triangle. While fretting about this one day in 1959 it struck me that perhaps nature was trying to tell us something, after all! Why is it ingrained into the psyche of chemists that they look only at the steric interactions between methyl groups in the substituted ethylene without even seeming to notice that the CH_2 group may matter, too? Perhaps it isn't hybridization (whatever that really means) which governs bond angles, but rather the avoidance of nonbonded atoms. Certain ways to visualize molecules have proven to be helpful over the years but the teaching of these ways can, and still does, leave great gaps in one's conception of structure. This is shown in Fig. 1 which illustrates how steric interactions not only squeeze down the C–C–C angle in isobutylene but also rationalize the shortness of the C–C bond length in comparison with that in alkanes. This figure is reprinted from a paper [9] I presented at a 1967 Division of Chemical Education symposium 'Models for Discussion of Molecular Geometry' in which Gillespie [5] was also a participant. But Gillespie's participation is not the reason for the present discussion.

If avoidance of nonbonded atoms is supposed to be a major influence in structure, it seemed from my approach that the H–C–H angle in ethylene itself should also be less than 120°, just as in isobutylene. But the spectroscopic result [10]

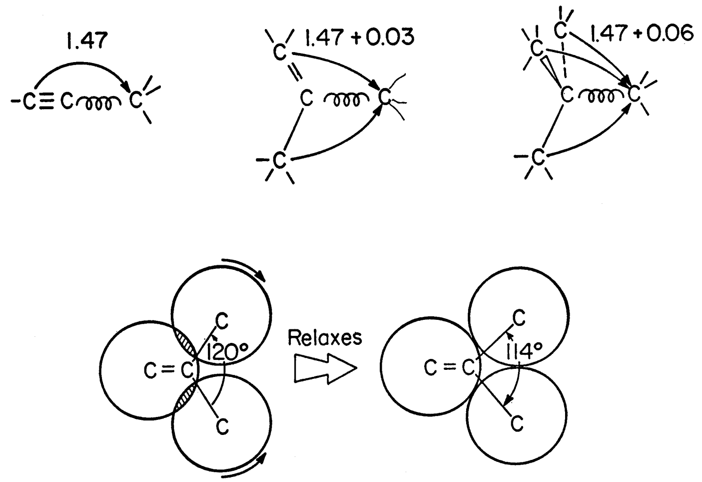

Fig. 1. Some structural features of hydrocarbons which suggested the nonbonded interaction model. Reprinted from [9] by permission. Copyright 1968, American Chemical Society.

reported for the angle was almost exactly 120°, the 'sp^2' value. This result surely colored the thinking of the hybridization proponents in the first place. Since I no longer believed in hybridization as a structural principle I was skeptical of the spectroscopic result. Fortunately for the nonbonded interaction hypothesis it turned out that the spectroscopic structure was wrong. When Bonham redetermined ethylene's structure [11], he found that the H–C–H angle of 116° accorded with the steric picture rather than the hybridization 'theory.'

Building on the idea of intramolecular steric interactions, I discovered that, to a surprisingly good approximation, the bond angles X–C–X, X–C–H, and X–O–X in a number of substituted methanes, ethers, ethylenes, and ketones were given by a model of close-packed geminal atoms where nonbonded radii were assigned to X atoms, including X = H, C, O, F, S, and Cl [12]. Later Glidewell added radii of several other atoms [13]. It was curious how little chemists believed that effects of geminal steric interactions (now characterized by Gillespie as 'ligand close-packing') could be important. Prominent theorists told me throughout the 1960s and even later that such 'trivial interactions' would surely have little influence on structure and other properties. But much evidence was uncovered by the time of the 1967 Chemical Education Symposium (referred to above) corroborating the idea that ligand interactions are, indeed, of the magnitude required for the steric model to work [9]. When represented by more realistic potential functions than those of hard-spheres and incorporated into the force field formulation of molecular mechanics, nonbonded interactions accounted quite well for trends in bond angles and bond lengths in a large assortment of hydrocarbons [14,15]. They even accounted for kinetic isotope effects of deuterium substitution on rates of reaction which the physical–organic chemists were turning out in large numbers. These chemists attributed their results to hyperconjugation or hybridization. But the steric model worked quite well, positing that deuterium, which possesses smaller zero-point amplitudes of vibration than hydrogen, behaves as if it is less bulky in its interactions [16,17].

As will be seen subsequently, evidence that intramolecular nonbonded interactions play a major role in determining structures of molecules has become compelling. Perhaps if I had been as active in publicizing the importance of nonbonded interactions as Gillespie was in promoting his VSEPR theory, chemists would have accepted the message far sooner. Part of the reason for chemists' neglect of the consequences of intramolecular nonbonded interactions was the lack of any tradition that such interactions mattered. Part was the inconvenience of including them explicitly in formulations of computer codes for molecular mechanics routines. But part of the reason was my dalliance with Gillespie's VSEPR theory at a time when it would have been propitious to have written more about nonbonded themes.

3. Valence shell electron-pair repulsions

Our specialization in organic structures came to a sudden end in 1963 when Earl Muetterties of the du Pont research laboratories sent us a very attractive series of fluorophosphoranes, $P(CH_3)_nF_{5-n}$, with n ranging from 0 on up to 3 by the time we were finished [18–20]. Their structures, determined beautifully by Katy Wirth Hansen and Shirley Yow, are compared in Fig. 2 with their analogs containing valence shell lone-pairs instead of methyl groups. Structures of the latter compounds were determined by microwave spectroscopy [21,22]. It would be hard to find a prettier set of molecules to illustrate the impressive predictive power of the Gillespie–Nyholm VSEPR theory. The series demonstrates not only the stereochemistry implied but also the variations in bond angles and bond lengths to be expected. Those as unfamiliar with VSEPR rules as I was when we published the structures should be aware that the rules make electron pairs in bonds to methyl groups 'larger' than those in bonds to fluorines but 'smaller' than lone pairs. Consequently, methyl groups and lone pairs tend to go to equatorial sites in trigonal bipyramids, which sites suffer only two repulsions from close (90°) electron pairs compared with three for the axial sites. Once there, electron pairs repel neighboring pairs in accordance with their respective sizes and distort bonds as illustrated.

However well our structures supported the VSEPR theory, our paper visited the wrath of Ronald Gillespie upon us [23] in no uncertain terms! Actually, Ron is far too much of a gentleman to display his spleen in public. But he did protest that his theory, "in fact gives a better explanation of all the structural features of these molecules than does Rundle's theory" (the simplified extended Hückel MO theory Hansen and I adopted to rationalize our results). Moreover, he alleged that several of the structural results that were handled well by VSEPR considerations could not be accounted for by our MO treatment. This point of view was echoed by other reviewers until our rebuttal [24] spelled out the explicit framework of our MO treatment and its implications. It turns out that this simple MO model correlates surprisingly well with trends associated with the VSEPR rules. What led to all this trouble with Gillespie was the fact that I had been so ignorant of freshman chemistry that I knew nothing about his structural theory until the galley proof stage of our paper, and I appeared to give VSEPR short shrift. Once I became familiar with VSEPR rules and recognized how well they accounted for our

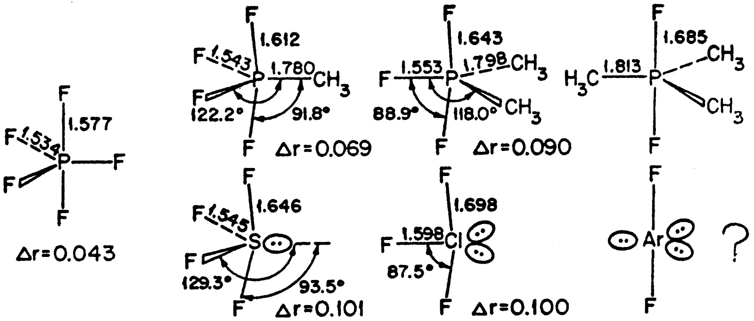

Fig. 2. Examples of stereochemistry and structural deformations well accounted for by the VSEPR theory.

structures, I became an ardent Gillespie disciple and spread the VSEPR gospel at every opportunity. I still do, but also continue to point out the importance of geminal nonbonded interactions, at least around first-row central atoms.

Soon after our study of fluorophosphoranes, our attention to VSEPR aspects of structure was reinforced when the Argonne National Laboratory invited us to study the strange substance XeF_6 they had recently synthesized. Some theorists had predicted it would be a regular octahedron. Then again, theorists had also predicted that XeF_4 would be tetrahedral instead of square–planar and that XeF_2 and XeF_6 couldn't be made. Those are engaging stories better left untold during the lifetimes of the misguided theorists. Experimentalists studying xenon hexafluoride by different physical techniques also had severe problems. They were a little like the blind men in the famous story about the blind men and the elephant. When each felt a different part of the beast's body he drew a different conclusion about the what the creature must look like. Spectroscopic, calorimetric, and molecular beam studies did not lead to a consensus. So it was necessary to determine the structure directly to remove doubt about its character. Since the material formed an oligomer in the solid state, X-ray and neutron diffraction studies were powerless to determine the structure of the monomeric substance. Therefore, gas-phase electron diffraction became the method of choice. Cedrick Chernick from Argonne came to Iowa State (where I was at the time) with special fittings and the expertise that made it possible for my student Bob Gavin to study the wickedly reactive material without decomposition in our apparatus [25–27]. Shortly after we determined the structure, but before we published I challenged Ron Gillespie to predict it in front of an audience at a meeting in 1965. Despite the predictions of the theorists, Ron stubbornly stuck to his guns, maintaining that XeF_6 must be distorted from a perfectly octahedral shape by its valence-shell lone pair. And, although the deformation from O_h symmetry was less than suggested by VSEPR rules, he was quite right!

Some perceptive comments by Brian Nicholson [27] added a certain amount of insight into the stereochemistry implied by VSEPR interactions. Nicholson pointed out that the deformation of XeF_6 from a regular octahedron could be understood as a consequence of the second-order Jahn–Teller theorem. A little reflection showed that second-order Jahn–Teller interactions could provide a symmetry rule applying to a variety of VSEPR cases and, in principle, to all of them. I illustrated the connection at the 1967 Chemical Education Symposium [9]. While the treatment worked transparently enough in many simple VSEPR examples, I soon found that a qualitative analysis failed in other cases, such as IF_7, where VSEPR guidelines had proven very useful. It isn't that the second-order Jahn–Teller idea is wrong, it just cannot always be applied qualitatively and intuitively without ambiguities arising. To get the right answer may require a quantum calculation that would already reveal the desired answer without needing the second-order formalism. Therefore, the VSEPR approach proved to be superior to it as a qualitative tool.

After our experience with XeF_6 it was natural to investigate other VSEPR candidates including a number of hypervalent fluorides, especially those containing fairly heavy atoms. In doing so we found two interesting facts. First, electron scattering theory needed to be extended to a new level of accuracy to account

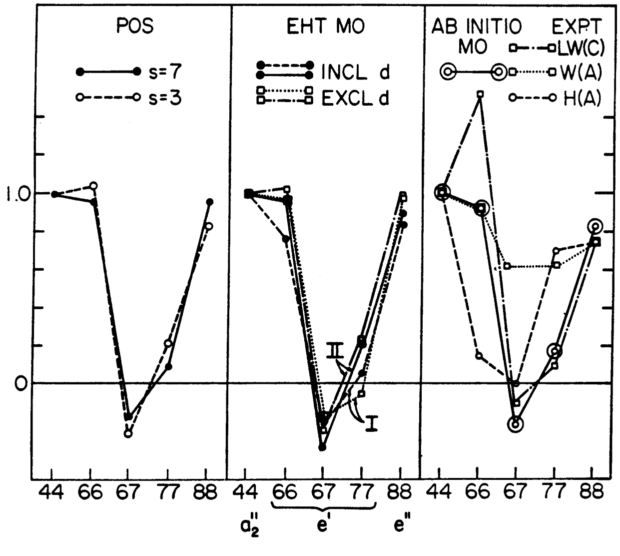

Fig. 3. Profile of quadratic force constants of bending deformations of PF_5 according to POS, ab initio and semiempirical molecular orbital computations, and various experimental force fields. Modes 6 and 7 correspond, respectively, to the axial bend and equatorial in-plane bend. Reprinted from [28] by permission. Copyright 1973, American Chemical Society.

adequately for the intensities of the diffracted electrons. Second, and more important for chemistry, was the discovery that the VSEPR theory could be cast into an elementary 'Points-on-a-Sphere' (POS) formulation yielding numerical values instead of just trends [28–31]. We were able to predict with uncanny accuracy the spectrum of bending force constants in a series of molecules, not only quadratic force constants but also those of higher-order. Two typical examples are illustrated in Figs. 3 and 4. In examining these figures it should be borne in mind that the

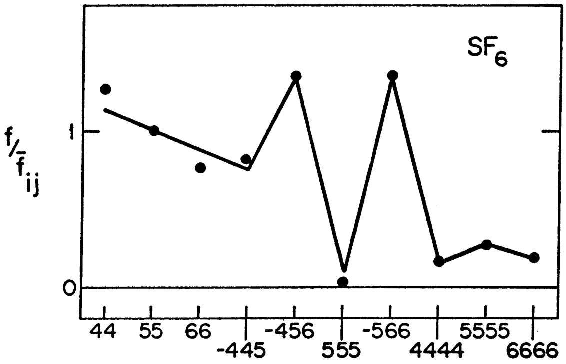

Fig. 4. Quadratic, cubic, and diagonal quartic bending force constants for SF_6. Lines, extended Hückel molecular orbital theory. Points, POS force field with $s = 4$.

repulsive force law between electron pairs was taken to be $-\partial V_{ij}(r)/\partial r \propto r^{-(s+1)}$ so that a Coulomb interaction would correspond to $s=1$. A value of s closer to 4 is required to represent real molecules. Experimental force constants were very unreliable as a rule, because of frequent errors in assigning frequencies, and higher-order force constants were very seldom derived from (or derivable from) conventional experiments. Therefore, the force constants adopted for comparison with the POS results were mainly deduced from quantum calculations. One of the virtues of the POS model is that computations are so simple that any undergraduate can calculate them. Consequently, as will be illustrated next by a true story, when assigning frequencies in molecules that are obvious VSEPR candidates, it would be a good idea to apply the POS model (or at least the qualitative VSEPR rules). After all, if the original theory has a valid basis, it should be quite as applicable to force fields as to structure.

In 1970 I met Ronald Nyholm for the first time. It was in a lovely Colorado mountain setting at the American Chemical Society Golden Anniversary Symposium on Chemical Education. After some general sessions participants were split up into small committees. By chance, I had the very good fortune to be assigned to a two-man committee with none other than Sir Ronald, himself, a scientist of legendary wisdom and creativity. This presented a wonderful opportunity to find just how much Nyholm believed in the model [1] which owed so much to his insight and experience. During a moment when we were relaxing from our duties, I asked him for his opinion about the VSEPR theory and had him guess the relative frequencies of the e′ axial and in-plane equatorial bending modes in trigonal bipyramids such as PF_5. Because vibrational spectra gave no clues about how to match modes of a given symmetry with the corresponding frequencies, assignments had been a problem for spectroscopists. Nyholm replied that he regarded the VSEPR theory primarily as a pedagogical device to which one shouldn't attach too much physical significance Then he guessed, as vibrational spectroscopists almost unanimously did, that the axial bend would be softer than the equatorial in-plane bend. A properly indoctrinated student of VSEPR theory would have come to an opposite (and correct) conclusion. Axial bonds, constrained by three close (90°) electron-pair repulsions resist e′ bending deformations much more strongly than equatorial bonds which experience only two in-plane repulsions from remote (120°) electron-pairs! This is borne out immediately by the POS model [28] (cf. Fig. 3). It was a strangely illuminating experience to find the master attributing so little importance to his own invention. In contrast, it is my impression that Ron Gillespie has regarded the theory as having a much more concrete physical basis. He has certainly written far more extensively in support of it over the years, even if he never applied it to bending force constants.

One thing is made very clear by the POS model: repulsions between valence-shell-electron-pairs are not simple coulomb forces between sites located where a chemist would imagine the electron pairs to be. The forces are much ‘harder’. A little reflection should convince one that a simple picture of coulomb forces can't work, anyway. Such a picture ignores the other comparable coulomb interactions besides those between electron pairs — namely those between nuclei and electrons and nuclei with other nuclei. Yet naive manuscripts appear with dismaying frequency claiming to have discovered that the VSEPR theory can be accounted for by simple electrostatic repulsions between electron pairs. Gillespie and Nyholm interpreted the repulsions differently, and essentially correctly, as a consequence of Pauli's exclusion principle. It is quite remarkable how the best compromise a molecule can make to maximize its binding energy consistent with the Pauli principle also optimizes the mutual avoidance of localized electron pairs.

It is curious, then, that Richard Bader, Gillespie's close colleague at McMaster, should have written a paper purporting to show that the Pauli basis of the VSEPR theory was untenable [32]. Bader is surely one of the most brilliant and original theorists I know, and has a much broader grasp of chemistry as a whole than most professional theorists. I suspect this has something to do with his beginnings as an experimental organic chemist. If it had not been for certain seemingly innocuous constraints he introduced into his treatment, his argument would have been correct. I mention this only to add emphasis to the fact that his later contributions were of major importance to the VSEPR formulation. His imaginative quantum treatments [7,33–35] supported Gillespie's qualitative picture and have led to profound new insights into the nature of the chemical bond.

Actually, it has not been uncommon for professional theorists to announce that they will show the rest of us why the VSEPR theory works once they have had some of the virtues of the theory pointed out to them (for the more esoteric of them rarely get introduced to VSEPR by teaching freshman chemistry), for example, once three outsiders, Ron Gillespie, myself, and a theorist of daunting reputation whose name I'll not mention, were invited to speak at an organic stereochemical conference at Bürgenstock, Switzerland, a place of breath-taking beauty high over Lake Lucerne. Gillespie presented a great deal of empirical evidence for his theory and discussed its basis and then I showed how it gave a good account of force fields and related it to the second-order Jahn–Teller theorem. The theorist, who up to that time seemed to have been unaware of the power of the VSEPR theory, stood up and told us all that he was going to work out its quantum basis as soon as he returned home. I thought it not quite right for the large group of organic chemists present to get the impression that our earlier suggestions had been ill-founded. So I replied that I suspected he was going to perform Edmiston–Ruedenberg transformations on molecular wavefunctions to localize the electron pair orbitals. That would surely place the electron pairs where we already knew they are, but since the transformation would leave the overall wavefunction absolutely unchanged, it would reveal nothing about intramolecular forces that wasn't already known before the transformation. He admitted that that transformation was what he had had in mind.

The VSEPR theory once got me into serious trouble with another group of organic chemists. When I asserted during a seminar at the ETH in Zürich that "Hybridization is a fraud!" the organic chemists became so furious at me I thought I was going to be assaulted. These chemists taught their students the importance of hybridization, sp vs. sp^2 vs. sp^3, etc., as if hybridization had an explanatory content, and they did not want their authority undermined in such a cavalier manner. My point had been that the VSEPR theory is so transparently a simplified model that students are not misled into believing otherwise. And it has true predictive power. On the other hand, 'hybridization effects' as presented to students masquerade as if they are based on firm quantum mechanical principles. Beginning students have no way of perceiving that, as generally taught, hybridization implies little more than the already known structure of the molecule under consideration. A large fraction of 'effects' attributed to hybridization ($sp^3 \rightarrow sp^2 \rightarrow sp$) can be accounted for simply by the changing environment of geminal nonbonded repulsions accompanying the change in coordination geometry from tetrahedral to trigonal to digonal (cf. Fig. 1). This argument is currently being vigorously pursued by Gillespie, as discussed next.

4. Ligand close-packing

A curious twist of fate has brought the above stories full circle. Initially concentrating on my theory of the role of intramolecular nonbonded repulsions (ligand close-packing), I later became an outspoken advocate of the VSEPR approach and significantly extended the theory's applicability (as sketched above). On the other hand, Ron, who promoted his VSEPR theory for many years until it became standard material in introductory courses in chemistry, has recently turned his attention to a ligand-packing theory, essentially a continuation of my 40-year-old idea. However, he and his colleague Edward Robinson have shown how it applies to a much wider class of molecules than I ever suggested [36–40]. Moreover, taking advantage of Bader's seminal work on quantum electron distributions, Gillespie and Robinson have not only enormously extended the range of applicability of the approach, they have uncovered some of its quantum underpinnings. In observed molecular structures they have found that ligand–ligand distances of a given kind are almost constant from one molecule to another, at least for fluorides, chlorides, oxides and hydroxides bonded to a given central atom, independent of the presence of other ligands, lone pairs, or of the coordination number. This constancy, then, governs both bond angles and bond lengths in a molecule. However, the interligand radii do depend upon the central atom, a property not recognized in my original investigations of atoms bonded to carbon. Central atoms investigated by Gillespie and Robinson include Be, B, C, P, and S. The dependence of ligand radii on the central atom is suggestive of a charge dependence. Indeed, quantum computations apportioning charges according to Bader's convention show that the charges on the ligands depend significantly on the central atom and are larger than has commonly been believed. To quote Gillespie and Robinson [39], it appears that a "model of ions close packed around a central atom is a better first approximation than the covalent model for these molecules. However, the ligand charges are not as large as the full ionic charges and so the ligands are not as large as the corresponding ions". Charges of ligands bonded to central atoms of low electronegativity are largest and the corresponding ligand radii are only slightly smaller than conventionally tabulated ionic radii. For example, Gillespie has concluded that molecules such as BF_3 and SiF_4 "are much more ionic than has hitherto generally been supposed" and that "the fully ionic model is a much better description of the bonding [in those molecules] than the fully covalent model" [38].

Here it can hardly escape notice that the VSEPR and ligand-repulsion models of structure imply very similar structural consequences. Just as electron pair bonds to highly electronegative atoms are supposed to be 'smaller' in VSEPR interactions than others, highly electronegative atoms are those with the largest nuclear charge in their row in the periodic table and, hence, have the smallest packing radii. In molecules with small, first-row central atoms, effects of ligand close-packing clearly dominate. With large central atoms, especially when ligands are not too crowded, the VSEPR model works well. Gillespie [39] has recently even implied that the ligand packing model is more or less the VSEPR model in a more quantitative form, since the sizes of ligands are known. Among other things, ligand packing is useful in determining whether valence shell lone pairs are stereochemically active or not. If there is room left in the coordination sphere after the ligands pack together, then lone pairs fill the gaps. For example, in XeF_6 [26] the fluorines are squeezed together as if by the lone pair until their internuclear distances reach the Shannon [41] packing distance. At this point the 'apparent size' of the lone pair, or space left to the lone pair, is substantially smaller than the VSEPR rules would predict. Even though there is a close resemblance between the structural implications of the two models, there does seem to be a VSEPR component over and above that of pure ligand packing. Evidence for this is the qualitative success of the second-order Jahn–Teller theorem and the following not unrelated argument. As pointed out during the first conflict of opinions between Gillespie and myself, the simplified extended Hückel MO model we pursued [24] qualitatively accounts for the same stereochemistry and deformations of bonds as the qualitative VSEPR model. This cannot be due to ligand packing considerations because the MO model formulated totally neglects ligand-ligand repulsions and electron repulsions. Its optimized geometry is that which gives the maximum binding energy of the ligands to the central atom allowable by the Pauli principle.

Roald Hoffmann [42] recently eloquently pointed out that the chemist's understanding implies more than solving the Schrödinger equation accurately. To quote a few lines from his article: "The experimentalist asks: 'What is the bond angle in water?' You the theorist, plug it into the best programs available and you get it right to three significant figures... The experimentalist asks the same question of TeH_2. You say 'wait a minute, I have to calculate it...', and you get it right; and you get it right for Li_2O and F_2O as well. But if that's all you do, no matter how well you do it, the experimentalist will grow increasingly unhappy. Because you haven't provided him/her with a simple portable explanation, one based on electronegativity, of relative energies of s and p orbitals, or donor or acceptor character or whatever set of factors he or she feels comfortable with... In many interesting areas of chemistry we are approaching predictability, but... I would claim, not understanding".

Not mentioned in the previous paragraph were VSEPR or ligand packing considerations. But surely these concepts would qualify for consideration in a framework of 'portable explanations' and they would surely be among the most useful in interpreting molecular structure. Much remains to be done before the optimal ‘portable explanation’ of structure is achieved. But Gillespie’s new attack outlined in the foregoing is uncovering systematic trends not recognized before. The new insights of Gillespie and his co-workers are likely to revise the way structure and bonding will be described in text books in the not too distant future.

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