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The career and scientific work of Ronald J. Gillespie: an appreciation and overview☆

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Abstract

An account is given of Ronald Gillespie's career and his scientific contributions to research and to chemical education from the perspective of the author, an accomplice who for more than 40 years has profited enormously from countless long hours of scientific discussion and beneficial comradeship. His career is charted from his early fascination with chemistry, through his university experience at University College, London, where he benefited greatly from the influence of Sir Christopher Ingold, to his long association with McMaster University, and his continuing unremitting activity in retirement. A personal account is given of some of his major contributions, including his pioneering work on superacids, his seminal work in furthering our understanding of the factors that influence molecular structure and bonding through his valence shell electron repulsion (VSEPR) and ligand close-packing

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☆ Dedicated to Professor Gillespie on the occasion of his 75th birthday.

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(LCP), models, and his contributions to chemical education.

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1. Introduction

As a friend, former student, and scientific colleague of many years standing, of Professor Ronald James Gillespie, it is a special pleasure and privilege to have this opportunity as we approach the millennium and celebrate his 75th birthday to highlight some of the milestones in his career and to describe some of his outstanding contributions to chemical research and education. Of course many will be curious about what has been the secret of his success in making such a long and uninterrupted contribution in expanding the frontiers of chemistry and relentlessly reconsidering some of its basic concepts? Fortunately, while a life-long infatuation with chemistry has undeniably been his constant driving force, this tenacity has not been confined to chemistry alone but he has also been blessed with the ability to constantly regenerate his mental energy by pursuing his main leisure activities of sailing and skiing with equal energy and enthusiasm, providing a model of how to distribute one's talent and energies from which we could all could profit.

For more than 5 decades, at first in England and for the past 40 years in Canada, Ronald J. Gillespie and his many students have been making many important and original contributions to chemistry. Although Ronald Gillespie is best known as a distinguished inorganic chemist, he truly belongs in a world of increasingly narrow specialization among the handful of modern chemists that have had the ability and courage to maintain a broad perspective in their approach and to constantly achieve inspiration from the interplay of teaching and research. A common characteristic at the core of his many contributions has been his ability to question conventional wisdom and look for new creative ideas and fresh explanations. And then to accept the responsibility to try to explain these new ideas to as wide an audience as possible.

Thus, it is no accident that Ron Gillespie has long been recognised among internationally renowned chemists not only for being at the leading edge of research but also for his leadership as an innovative and inspiring teacher. Uncommonly, he has always been prepared to find the time in a busy research schedule to invest a considerable amount of his time and effort to think about ways in which the quality and effectiveness of teaching can be improved and put this into practice in large introductory courses. Indeed, through his textbook writing he has made a considerable effort to demonstrate how fact and theory might be interwoven and larded with demonstrations, so that today's beginning college and university students, with little early exposure to the kind of hands-on experimental work that sparked for many of our generation their interest in chemistry, can gain more intrinsic value from their introductory college experience — through learning about science and the basic models of chemistry in ways that stress the primacy of experimental observations in courses that are structured to be less mysterious and daunting than has so often been the case historically — while at the same time maintaining interest and intellectual challenge for the most able, and designed to have a lasting benefit whatever the student's ultimate choice of career.

Ron Gillespie was born in London, England, on August 21, 1924, and at the age of 11 he was awarded a scholarship to the local grammar school where, despite difficulties imposed by less than affluent family circumstances, he prospered and while admitting to spending considerable time playing sports he always did well in the final examinations, particularly in science subjects. During the final 2 years at school he specialized in chemistry, physics, and pure and applied mathematics and did particularly well in chemistry because he had the good fortune to be inspired by a chemistry teacher, George Cast, who had the gift to make chemistry lessons much more exciting than the text book and to expose his students to a great deal of laboratory work that Ron found interesting and fascinating. Among his fellow students was William Moffit who although brilliant in Mathematics was also inspired to become a chemist, went on to Oxford where he worked with C.A. Coulson, and eventually became a professor of theoretical chemistry at Harvard but died tragically at an early age.

Well into the Second World War years, Gillespie left school in 1942 and was awarded a bursary to do a special 2-year war-time degree at University College, London, which at the time was evacuated to the University of Wales in Aberystwyth. Towards the end of his second year in Wales, the head of department, C.K. Ingold (later Sir Christopher), the distinguished pioneer of modern physical organic chemistry, assumed without question that Ron Gillespie would stay and do research, and so by the time that University College moved back to London in the summer of 1944 Gillespie had become part of the team working on the mechanism of aromatic nitration. Ingold was more than a kineticist and attacked problems from a broad perspective. He was an organic chemist, a physical chemist, and not unfamiliar with inorganic chemistry, so Gillespie's initial role was to look at solutions of nitric acid in sulfuric acid to see if evidence for the presence of the nitronium ion, NO_2^+, could be found using the method of freezing point depressions (cryoscopy). Concurrently fellow students were taking other approaches: D.J. Millen using Raman spectroscopy, D. Goddard attempting to prepare stable nitronium salts such as $NO_2^+BF_4^-$, and others working on the kinetics of aromatic nitration [1,2].

Fortunately, although Ingold's approach to students was very formal and his reserve left the impression with many that he was rather forbidding and autocratic, his approach to graduate student supervision was beneficially quite relaxed. While he always had a good knowledge of what his students were doing or should be doing, he interacted with them quite infrequently and left them with considerable freedom to follow up on their own ideas, from which Gillespie profited, because when the nitration problem had been resolved he was allowed to continue to pursue his studies in sulfuric acid in new directions of his own invention and he began to look at the ionization of other solutes in anhydrous sulfuric acid. As was his custom, Ingold alone wrote up the work and published a group of nine papers based upon Gillespie's work in the Journal of the Chemical Society in 1950, with several of them carrying Gillespie's name only [3–11]. Thus began a detailed study of sulfuric acid and its solutions which led later to the quest to discover other superacid systems of even greater acidity and the study of their unique ability to stabilize many novel, otherwise elusive, important chemical species, many with unusual structures.

Gillespie was awarded his Ph.D. by the University of London in 1949, but even before this milestone Ingold suggested to him one day in casual conversation that he should prepare a few lectures of his own choosing on molecular properties, and Gillespie was surprised a few weeks later to receive a letter from the University of London informing him that he had been appointed an Assistant Lecturer. Thus, his university career began at University College, London, even before he was awarded the Ph.D. He was now quite independent of Ingold and continued with his research on sulfuric acid and its solutions and began to extend his studies to electrical conductivity and other measurements with the help of a few graduate students assigned to him from time to time by Ingold, as was his privilege as department head. This was how I myself fortuitously became a member of the Gillespie team in 1955 when Sir Christopher suggested that I should do my research with Ron, with whom I was previously only barely acquainted, and I was assigned the task of looking at the sulfuric acid chemistry of a great variety of inorganic solutes.

The continuing studies on sulfuric acid solutions had showed that they seem to behave almost ideally, which gave Ron the idea that sulfuric acid must have a very high dielectric constant, so that in 1953 when he was awarded a Commonwealth Fund Fellowship to work in the United States, he elected to work at Brown University with Robert Cole, an expert in dielectric constants. The measurements were very difficult because pure 100% sulfuric acid is very highly conducting on account of its extensive self-ionization, but a high value of 120 was successfully established [12]. The Fellowship also afforded him the opportunity to travel extensively in the USA and to write up his impressions and Madge Gillespie joined Ron in this enjoyable experience for the summer. At this time in Britain, money for research was difficult to obtain and Ron had found that everything that he needed had to be obtained through Ingold, which made his quest for the expansion of support for his research rather onerous and daunting. It was then that he began to think that it might be advantageous to move to North America.

Back at University College he soon became fully engaged once more in teaching and research in inorganic chemistry where a newly appointed inorganic colleague was another very innovative researcher and memorable teacher, Professor Ronald (later Sir Ronald) Nyholm from Australia. By this time Ron Gillespie was teaching quantum mechanics and in presenting bonding theory he had become dissatisfied with textbook explanations of molecular geometry in terms of hybrid orbitals, which seemed to him to be a circular argument. But when he came across a paper by Sidgwick and Powell [13], which showed that geometry could be related to the number of valence shell electron pairs, and another by Lennard–Jones [14] on the importance of the Pauli Principle in determining geometry, he discussed these with Nyholm extensively and they agreed to write their now classic, regularly and often quoted, joint review of inorganic stereochemistry, with Gillespie tackling the main groups and Nyholm the transition metals. Thus, the influential rules of the valence shell electron pair repulsion (VSEPR) model of molecular geometry were first advanced [15]. As it later became clear, the name chosen for this now well-known and highly useful model was not the most appropriate and surely hampered its ready acceptance by many chemists, especially almost all physical chemists, although it was adopted by most inorganic chemists and was soon featured as a useful teaching tool in most new introductory and inorganic textbooks. Unfortunately, VSEPR conveyed the erroneous impression that the model is a purely electrostatic one, even though the initial paper took pains to make it clear that the model is in truth soundly based upon the primacy of the Pauli exclusion principle in determining molecular structure.

Frustrations with the difficulty in obtaining research equipment continued. However, Ron was successful in building University College's first tiny, but not greatly useful, NMR spectrometer and he and Nyholm were trying to raise the money to purchase a better one. Then, while on a visit to California to visit Varian, Ron Gillespie made the propitious decision to make a side trip to McMaster University in Hamilton, Ontario, where fellow chemist Arthur Bourns, who had previously spent some time at UCL, was Dean of Graduate Studies. At the time McMaster University was still a small Baptist college but was rapidly expanding under the leadership of Harry Thode who envisioned it becoming the major research university it is today. Tempted by an offer of twice his British salary, the promise of both a new NMR machine and a Raman spectrometer, and the chance of good research support from the National Research Council of Canada, Gillespie decided that it was time to cross the Atlantic and settle in Canada., which he did in the summer of 1958.

I had completed my Ph.D. at UCL with Ron in the spring of 1958 and he invited me to join him in Canada as a postdoctoral fellow to help to get his new laboratory established and to continue my work on sulfuric acid chemistry, turning now mainly to the field of vibrational spectroscopy and using the then rarely utilized technique of Raman spectroscopy, because infrared measurements were largely technically inaccessible due to the very corrosive nature of our strong acid systems. In those pre-laser days, Raman spectroscopy was not a central tool because of the need for long exposure times of many hours to capture the spectra on very sensitive photographic plates, but this work turned out to be much more successful than we had anticipated after we had secured a very intense mercury arc lamp courtesy of its inventor Harry Welsh of the Physics Department of the University of Toronto. This meant that we were able to obtain excellent photographically recorded spectra using a prism instrument and with exposure times of just a few minutes.

After 3 more years, I moved on in 1961 to an appointment as Assistant Professor at the University of Toronto where I joined two other émigrés from Britain, Maurice Lister (from Oxford) and the late A.D. (Bert) Allen (also from University

College, London) and thereby expanded the size of its inorganic group by 50%. Fostering inorganic chemistry in Canada was at the time clearly an important British invisible export. Fortunately for me, despite other responsibilities from 1965 on, due to my foray into university administration in connection with the foundation of Erindale College, University of Toronto's new campus in Mississauga, my collaboration with Ron Gillespie in both text book writing and research has continued intermittently over the years, because fortuitously the Mississauga campus is situated geographically midway between Toronto and McMaster University in Hamilton. Thus, I have been able continuously to have a foot in both camps. Now we are both 'retired' and free of other routine commitments, we have again joined forces to develop our new ligand close-packing (LCP) model, which enhances the VSEPR model in furthering the understanding of the factors that influence molecular geometry.

Prior to the late 1950s the pursuit of modern inorganic chemistry, particularly main group chemistry, had a very shallow base in North America, and particularly in Canada, which meant that Ron has had a unique and important role in the establishment and development of this branch of chemistry in Canada. Thus, his very important contributions to Canadian inorganic chemistry began and now he has been associated with McMaster University for more than 40 years and has many former students and postdoctorals working across Canada. He retired in 1989 and decided to give up further laboratory work to concentrate on research dedicated to furthering our greater understanding of molecular structure and geometry and this has been essentially his full-time occupation for the last decade. In 1993 his long-time service and contributions to McMaster University were recognized by the award of an honorary D.Sc. degree.

To list all of Ron Gillespie's research accomplishments is well-nigh impossible but among the most exciting and probably of the greatest impact are the following:

1. The investigation of nonaqueous acidic solvents and the discovery and study of the media of the highest known acidity, now known as the superacids.
2. The exploitation of superacid media for the preparation of many novel inorganic and organic species, including new carbocations and particularly a wealth of new nonmetal polyatomic cations.
3. Studies of noble gas cations in hydrogen fluoride and other acidic media.
4. The development of the VSEPR, model of molecular geometry and its popularization.
5. Further work on the VSEPR model to establish its fundamental basis in quantum mechanics and its extension to include the ligand close-packing model.

Each has been recognized as a significant body of original research; each has led to new insights and applications, and each has provided the inspiration to others for new research. For his work Gillespie has been internationally recognized through his election to the Royal Societies of London and Canada and by many other national and international awards.

2. Superacid chemistry

For a long time the best known strong acids were sulfuric acid and aqueous perchloric acid; indeed, it was long thought that perchloric acid was the strongest known acid. However, nonaqueous systems such as anhydrous sulfuric acid are now known to be very much more acidic than any aqueous system and their study has extended our knowledge of acid–base chemistry into many previously uncharted regions. That sulfuric acid is now one of the best studied nonaqueous solvents is almost entirely due to the work of Gillespie and his co-workers [16–19]. Although some studies of anhydrous sulfuric acid and the slightly aqueous acid were made as early as the turn of the 20th century, notably by Hanztsch [20], and the acidities of sulfuric acid–water mixtures were determined by Hammett in the 1930s [21], it is largely through the work of Gillespie and his students, beginning in the 1950s, that the physical and solution chemistry of anhydrous sulfuric acid and the new superacid media have been developed. These are the strongest acidic systems known and have acidities that are many orders of magnitude greater than can be obtained in aqueous solution. The work has been characterized by exact and careful experimental studies on systems not easily handled experimentally, utilizing a wide range of preparative and classical, and modern physicochemical methods as each has become available and often before their use was routine. For example, Gillespie has always made routine use of Raman spectroscopy [22–30] and NMR spectroscopy [31–33], including a paper on Se NMR [34] quite early in his research career.

As noted above, Gillespie's interest in superacids originated in his Ph.D. work. Later the use of electrical conductivity measurements in sulfuric acid was developed and, subsequently, this and the early work led to an comprehensive and detailed study of pure 100% sulfuric acid and its solutions. This work clearly demonstrated that the properties of the pure acid are different from those of the slightly aqueous H_2SO_4 that had been the solvent of choice in most previous investigations and how important it was to fully understand the complex self-dissociation equilibria of the pure acid before its solution chemistry could be reliably interpreted. Electrical conductivity measurements revealed that although 100% sulfuric acid is some 27 times as viscous as water, so that most ions have very small mobilities, nevertheless, the pure acid is highly conducting, and it was shown that this is almost entirely due to the $H_3SO_4^+$ and HSO_4^- ions that result from the extensive autoprotolysis equilibrium, $2H_2SO_4 \rightleftarrows H_3SO_4^+ + HSO_4^-$. Like the H_3O^+ and OH^- ions in water, $H_3SO_4^+$ and HSO_4^- in sulfuric acid conduct both by normal transport and by a Grotthus chain mechanism of proton transfer, but in sulfuric acid the latter mechanism dominates. This enabled electrical conductivity measurements on solutions of, for example, all solutes that behave as bases in sulfuric acid to be easily interpreted because solutions of the same specific conductivity contain essentially the same concentrations of HSO_4^- ions. It soon became apparent that the combination of electrical conductivity measurements (which give the number of HSO_4^- ions formed in solution from a single solute molecule) and cryoscopic measurements (which give the number of ions and/or molecules formed in solution from one solute molecule) make it possible to unambiguously establish the modes of reaction of nearly all solutes in sulfuric acid.

In the same way that Gillespie's use of sulfuric acid to protonate very weak bases greatly extended our knowledge of acid–base chemistry, so did the discovery of new acids of the sulfuric acid system, such as $HB(HSO_4)_4$ which is a strong acid of the H_2SO_4 system. Another important use of electrical conductivity was to follow the progress of acid–base titrations in sulfuric acid.

On the basis of his rather complete understanding of the H_2SO_4 solvent system, Gillespie was then able to develop the chemistry of nonaqueous media with even greater acidities; notably fluorosulfuric acid and hydrogen fluoride. The work was characterized by the experimental ingenuity with which the difficulties in working with such hygroscopic and highly corrosive systems have been mastered. While sulfuric acid had proved invaluable for preparing stable solutions of important species such as the nitronium ion, NO_2^+, and some aromatic acylium and carbocations, these more acidic, more weakly basic, systems proved even more valuable in stabilizing unusual species. Of particular importance was a study of solutions of the strong Lewis acid SbF_5 in HSO_3F, and in HF, which were shown to be unique media with the highest known acidities [35,36]. It was to describe their remarkable properties that the term superacid was coined. To quote from the comprehensive inorganic chemistry textbook 'Chemistry of the Elements' by Greenwood and Earnshaw [37]: "Such solutions $SbF_5/HSO_3F/SO_3$ have been termed 'superacid media' and they are, indeed, the strongest known proton donors at the present time. They have been extensively studied because they are able to protonate virtually all organic compounds".

As Gillespie first demonstrated, one of the important practical advantages of using fluorosulfuric acid and its solutions is that they remain liquid at very low temperatures. This, for example, allows the sites of protonation of molecules to be established using NMR spectroscopy [38–42].

The use of superacid media, especially HSO_3F–SbF_5, 'magic acid', continued to be extensively exploited, notably in organic chemistry by G.A. Olah [43]. As a result of Gillespie's work, sulfuric acid, fluorosulfuric acid, and hydrogen fluoride, are among the limited group of non-aqueous solvents whose physical and solution chemistry has been thoroughly investigated in detail. One notable achievement was the completion of the difficult task of extending the acidity function measurements of Hammett into these very acidic media [44–46].

3. Polyatomic cations of the nonmetals

In inorganic chemistry, Gillespie and his co-workers used their superacid media for the discovery and preparation of many new and unexpected species of the main group elements. which has extended their chemistry far beyond what is possible in aqueous solution. For example, although some previous evidence existed for cationic iodine species, the recognition that these are polyatomic ions was conclusively demonstrated by Gillespie and led to the characterization of a large variety of cations of iodine, bromine, chlorine, sulfur, selenium, tellurium, and even mixed atom species. Using superacid media, Gillespie has prepared many exotic ions such as I_2^+, I_4^{2+}, Br_2^+, Br_3^+, S_4^{2+}, S_8^{2+}, S_{19}^{2+}, Se_4^{2+}, Se_{10}^{2+}, Te_4^{2+}, Te_6^{2+}, and $Te_4Se_2^{2+}$, both in solutions and as crystalline salts. He has determined the structures of many of these species by X-ray crystallography and shown many of them to have novel and unexpected structures, the study of which has extended our understanding of structure and chemical bonding in the realm of the heavier main group elements [47–51]. This line of research was extended to a study of reactions of these nonmetal cations with transition metal carbonyls and cyclopentadienyl complexes and the discovery of transition metal–nonmetal cluster cations [52].

In organic chemistry, as has been noted above, superacids have been used not only to protonate extremely weak bases but also for the preparation of stable solutions of unusual carbocations, notably by Olah and co-workers [43] which has made possible their characterization by spectroscopic measurements, especially NMR spectroscopy, the earliest measurements of which took place in Gillespie's laboratory at McMaster University. This has led to the use of Gillespie's superacid media to investigate acid-catalyzed alkylations; indeed, Gillespie's approach to the identification of reaction intermediates in superacid media has become a relatively common tool in physical organic chemistry research.

Work on the HSO_3F–SbF_5 and HF–SbF_5 systems has also led to the recognition that SbF_5 has unique properties not only as a strong Lewis acid but also as an oxidizing agent. Thus, the use of SbF_5 in solution in sulfur dioxide or SO_2ClF, as well as HSO_3F or HF, has become a widely used and widely applicable method for the preparation of yet other novel cations. Noteworthy among these applications by Gillespie is the discovery of new sulfur–nitrogen cations such as S_2N^+, $S_3N_2^+$, $S_4N_4^{2+}$ and $S_6N_4^{2+}$ using SbF_5 [53–57].

In another remarkable application using SbF_5 or AsF_5 in SO_2, Gillespie has prepared the ions Hg_3^{2+} and Hg_4^{2+} and several unique mercury compounds with infinite chains of mercury atoms and compositions such as $Hg_{2.91}SbF_6$ and $Hg_{2.85}AsF_6$. He has shown these to be essentially ionic substances that conduct electricity along their mercury chains but not in other directions. This large anisotropy in their electrical conductivities has greatly interested solid state physicists; their structures and electric and magnetic properties has received considerable attention [58–66].

4. Noble gas fluorocations

Another important application of the HF–SbF_5 superacid system was for the preparation and study of several novel cations of the noble gas fluorides, such as XeO_2F^+, $XeOF_3^+$, XeF_3^+, KrF^+ and $Kr_2F_3^+$. This led to other important studies of the noble gas fluorides which included extensive pioneering studies of the NMR and Raman spectra and structures of noble gas fluorocations [67–71].

Today, the HSO_3F–SbF_5 and HF–SbF_5 media developed by Gillespie remain (in the Brønsted–Lowry sense) the most highly acidic media known. The combination of the strongest Lewis acid SbF_5 with the strong proton acids HSO_3F and HF has opened up fertile and entirely new fields of inorganic and organic chemistry that continue to be actively investigated. Gillespie's extensive contributions to superacid chemistry was acknowledged in the book by Olah, Prakash, and Sommer in which they state: "Professor R.J. Gillespie's pioneering work on the inorganic chemistry was of immense value and inspiration to the whole field" [43].

5. The VSEPR model of molecular geometry

Particularly in the last 30 years, modern methods of structure determination, such as X-ray crystallography, electron diffraction, and microwave spectroscopy have provided a wealth of increasingly reliable and detailed information on the structures of molecules. However, we have been far from a complete understanding of the factors that account for the large variety of the structures that have been obtained experimentally. In contrast to the structures of organic substances that can be largely understood on the basis of the tetrahedral carbon atom, the structures of inorganic molecules are far more varied and correspondingly more difficult to rationalize.

While the first important step towards the understanding of these structures was the use of the hybrid orbital theory developed particularly by Linus Pauling for this purpose, subsequently it has been appreciated that this approach is most useful for describing the bonding in molecules of known geometry, but is more limited in its ability to predict geometries and to describe and rationalize trends in bond lengths and bond angles in series of related molecules. In contrast the VSEPR model developed by Gillespie is a simple yet extremely useful approach for predicting and understanding the basic geometries of most of the molecules formed by the main group elements and for accounting qualitatively for the variations in bond lengths and bond angles in series of related molecular species. Indeed, soon after its formulation [15] the VSEPR model began to be accepted as the simplest and most widely applicable approach for predicting and understanding in surprising detail the structures of most simple molecules. It has the enormous advantage of being equally accessible to beginning students and to established researchers alike. Gillespie has continued for more than forty years to explain and extend the applicability of this model. His latest review giving an account of the more recent developments was published in 1996 [72].

G.N. Lewis provided the first explanation for valence and for molecular formulas in terms of the primacy of the electron pair bond and the VSEPR model represents essentially an extension of the Lewis postulate to account for molecular geometry. Subsequent to the paper by Gillespie and Nyholm [15], Gillespie alone further developed and refined these ideas and has demonstrated their wide applicability in a large number of papers of which he is sole author. The total concept and its applications were treated in detail in his book 'Molecular Geometry' [73], and in a more recent book entitled 'The VSEPR Model of Molecular Geometry' [74]. The latter has proved to be particularly valuable to chemists concerned with the teaching of general chemistry and inorganic chemistry courses.

Moeller in his textbook 'Inorganic Chemistry' published in 1982 says: "It was not until 1957, however, that these ideas were developed and extended to a large number of covalently bonded species by R.J. Gillespie and R.S. Nyholm, in what must be considered a classic publication" — and to quote A.F. Williams in his 'A Theoretical Approach to Inorganic Chemistry', published in 1979: "The VSEPR model is extremely successful for elements of the p-block of the periodic table and has found extensive application in non-metal chemistry. An excellent survey is given in the book by Gillespie".

Gillespie's VSEPR model, which more precisely is better described as the valence shell electron pair domain model [72], gives a simple, readily understood, qualitative description of the electron density distribution in many molecules and is the only simple model by which the shapes of most ground state molecules can be confidently predicted and understood, and which simply and satisfactorily accounts, for example, for variations in bond angles in series of molecules such as CH_4, NH_3, and H_2O, or PF_3, PBr_3, and PI_3, and the bond length differences between the equatorial and apical bonds in molecules such as PCl_5 or BrF_5. Although the model was first developed to account for the structures of molecules and ions of the main group elements, Gillespie has also extended it to structures involving weak intermolecular and interionic interactions in the solid state, such as are found, e.g. in halogen bridge formation. No other simple model gives such a satisfactory account of such a wide variety and number of molecular structures.

Although molecular orbital and other theories can in principle be used as a basis for understanding molecular geometries, they are generally less useful for this purpose than is the VSEPR model and less easily understood or rationalized. Detailed ab-initio calculations can give accurate predictions of molecular shape and quantitative bond lengths and bond angles. However, they provide little insight into the factors that control molecular shape. Among the many successes of the VSEPR model was the correct prediction of the shapes and bond lengths in the molecules formed by the noble gases, before they had been determined experimentally. Notably, the structure of XeF_6 was correctly predicted as nonoctahedral, while initial predictions from molecular orbital theory concluded that the structure would be regular octahedral [75].

Although the VSEPR model was regarded for many years by perhaps the majority of chemists as based empirically on a set of rules that happen to work, albeit remarkably well, the recent determination by X-ray diffraction of the electron density difference maps of a number of molecules has provided direct experimental confirmation of the validity of the description of their molecular geometry in terms of bonding and nonbonding electron pairs, as the VSEPR model assumes [76,77], but this approach is as yet somewhat uncertain and time consuming and has some disadvantages and limitations.

Fortunately, however, the theoretician Richard Bader and Ron Gillespie have been long-time colleagues at McMaster University and the atoms in molecules (AIM) approach of Bader and his coworkers [78], which is soundly based upon quantum mechanics provides ways of calculating exact wave functions which can then be analyzed either in terms of the orbital model or to give the electron density distributions in molecules. And it is the latter that can be analyzed via the Laplacian to demonstrate the existence of localized concentrations of electronic charge in both the bonding and nonbonding regions of many molecules that have the same properties as those ascribed to electron pairs in the VSEPR model. Thus, long after its success had been established empirically, direct experimental and theoretical support for the basic postulates of the VSEPR model has emerged from the work at McMaster University. In several publications, Bader and Gillespie have shown that Bader's work on localized charge concentrations provides a firm theoretical basis for the VSEPR model, and they have begun to investigate how the VSEPR model could possibly be useful for describing molecules formed by the transition metals, [72,79–83].

During the years since the publication of the much cited 1957 paper, the VSEPR model has become firmly established as one of the essential models for the discussion of molecular shapes — in research papers, in textbooks of inorganic chemistry, and in introductory textbooks. A chapter or section on the VSEPR model now forms part of every new general chemistry or inorganic chemistry textbook; the model has had a profound effect on chemistry teaching, and the insight that it provides gives even the beginning student of chemistry a comprehensive and easily understood entry into the complex subject of molecular geometry.

The fact that the VSEPR model was first developed as a teaching aid exemplifies Professor Gillespie's long standing interest in communicating research results in a simple way to students, for which he has been recognized through a number of prestigious awards in Chemical Education. At a conference on the teaching of introductory university chemistry which brought together a large number of North America's leading chemical educators at McMaster University in 1979, there was unanimity that new approaches to teaching and learning in chemistry were long overdue [84], and it was anticipated that many would take up the challenge to produce improved textbooks. However, it soon became clear that few were prepared to accept the challenge and it finally fell to a team led and inspired by Gillespie to do something tangible about the 'McMaster Recommendations'. This led to the publication of the innovative textbook, 'Chemistry' in 1985, and a second edition in 1989 [85], which was followed in 1994 by another effort, 'Atoms, Molecules and Reactions' [86], which set out to demonstrate how facts and theory can be successfully interwoven to introduce students not only to the fundamental ideas of chemistry but also to important questions of current political, economic, and environmental concern, the basic science of which should be understood by all educated citizens.

6. The ligand close-packed (LCP) model of molecular geometry

Although the VSEPR model works well, some molecular structures that are puzzling exceptions have emerged over the years to challenge its validity. These are mainly molecules with highly polar bonds. Examples include: $SeCl_6^{2-}$ and $SeBr_6^{2-}$ with a regular octahedral geometry rather than the expected distorted octahedral structure for molecules of the AX_6E type; AX_3E molecules such as those of the $N(SiR_3)_3$ type that are planar rather than trigonal pyramidal, and molecules with unexpectedly large bond angles greater than 120°, such as is found, e.g. at the bridging oxygen atom in molecules of the $[X_3Si]_2O$ type and many others.

To better understand the nature of polar bonds and the properties of their shared and unshared electron pairs, the validity of the empirical Schomaker-Stevenson equation [87] which has been used for more than 50 years to predict the lengths of polar covalent bonds from single covalent radii, was recently re-evaluated, with the conclusion that there is no valid basis for the continued use of this equation either in fact or theory [88]. Consequently, because back-bonding has been customarily used to explain bond lengths in molecules such as BF_3 and SiF_4 that are even shorter than this equation predicts, it also became clear that this idea required re-examination.

Gillespie then turned to the use of the powerful AIM method to calculate the charges on the atoms in some molecules with highly electronegative ligands, because this method stands alone in providing a sound way to partition electron densities between the individual atoms in molecules and hence to obtain reliable atomic charges. The results for the Period 2 and 3 molecular fluorides, [88] were very revealing because they showed that not only are the bonds in molecular LiF and BeF_2 in Period 2, and NaF and MgF_2 in Period 3, more than 50% ionic but that this is also true for BF_3, CF_4, AlF_3, SiF_4, PF_3, and SF_2. Because, chemists have assumed that most fluorides other than those of the alkali and alkaline earth metals are best described by the Lewis covalent model [89], rather than by Kossel's ionic model [90], this result opened up the way to some interesting new considerations, the most important of which is ligand close-packing.

Because the structures of many ionic crystals are largely determined by the close packing of large anions around small cations, the possibility that the structures of many of the molecular fluorides (and other molecules with highly polar bonds) might also be similarly largely determined by the close packing of anion-like ligands around their cation-like central atoms was postulated and found to be true for many molecules. Thus, what Gillespie has called the LCP model has been developed and found to have a wide applicability throughout chemistry [88,91–93].

Previously, in work starting in the late 1950s that has not since received much attention, L.S. Bartell had drawn attention to the importance of interligand contacts in determining the geometry of molecules in which the central atom is carbon and had assigned a radius for each ligand [94–101]. But, because the charge on a ligand, and hence its radius, depends primarily on the electronegativity of the atom to which it is bonded, Gillespie's work due attention to the fact that the Bartell radii are only appropriate for ligands bonded to carbon but not to other central atoms. For example, while a F ligand radius of 108 pm is valid for CF bonds, this radius is 113 pm for BF bonds. This is no doubt the reason why Bartell's bold proposals have been largely overlooked. Thus, Gillespie has rediscovered this model by an alternative and more convincing route and made it more general and convincing, but it is interesting to note that he did not recognise the connection with Bartell's earlier work until after his own discovery.

How then does the LCP model affect the validity of the VSEPR model? For very many molecules the LCP model predicts the same geometry as the VSEPR model but, in addition, it allows interligand distances to be predicted. In fact, the models are essentially equivalent if the bond–bond repulsions of the VSEPR model are replaced by the ligand–ligand repulsions of the LCP model and any repulsions between ligands and lone pairs of electrons on the central atom are taken into account. It is also now clear that exceptions to the VSEPR model seem to occur only when any nonbonding electrons are not localized, or only weakly localized, into pairs and are therefore stereochemically inactive or only weakly so.

7. Conclusions

Although this brief attempt to give an account of Ron Gillespie's unique contributions and influence on the development of very important and broad areas of modern chemistry of central significance, and to the improvement of teaching and learning, cannot possibly do full justice to all that he has achieved, I trust that I have been able to put many of the highlights into balanced perspective.

My own career has been closely linked to his and he has been my mentor and friend for nearly 45 years. The only serious way in which we have ever departed in our priorities is in the area of university administration, where I have dallied and which he has wisely largely avoided in favor of the more serious, enduring, contribution to science of which only he is capable. His long career has been marked by the high priority he has always given to his science and his adherence to sound principles, both scientific and personal. He has quietly pursued his goals with great energy and intensity, but without generating individual animosity or envy as attested to by the many professional and personal friendships he has developed. All I can wish him in his 75th year is a continuation for many years to come of the satisfaction and great pleasure he derives from his work. As a postscript I can add that Ron Gillespie's efforts to improve our insights into bonding and molecular geometry continue intensively and he is currently bringing all these ideas together in a new book that is now almost ready for publication.

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