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Professor Gillespie—a symbiotic relationship

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Abstract

This is an account of how the scientific interests of Professor Gillespie and myself eventually came to a common focus, resulting in a physical understanding of the VSEPR (Valence Shell Electron Pair Repulsion) model of molecular geometry and of how, from that point on, we have enjoyed a continuing exchange of ideas. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: VSEPR model; Fermi hole; Electron localization

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1. Our first meeting

I first met Ron Gillespie when he presented a seminar on his VSEPR (Valence Shell Electron Pair Repulsion) model [1,2] of molecular geometry at the National Research Council on Sussex Drive in Ottawa in 1960, 2 years after his joining the Department of Chemistry at McMaster University. I had begun my own academic career at the University of Ottawa about a year before and had already decided that the electron density was the vehicle for explaining and understanding chemistry. Thus, I understandably questioned him at the end of his talk on his use of a model of the neon atom that likened its physical form to that of four localized groupings of electron pairs, a model that was based on the electron localization studies of Lennard-Jones [3,4]. Using this model one could, by extracting protons one at a time from the neon nucleus, account for the bent geometry of water and the pyramidal geometry of ammonia and do so without invoking the model of orbital hybridization on the central atom. Lennard-Jones and Pople also presented their arguments using equivalent molecular orbitals to describe the density [5]. I questioned this model as well, because the density of a neon atom is spherical, decaying exponentially from the nucleus, without any indication of an angular localization of the electrons and from what I then knew about the total electron density in molecules, I doubted that one would find the 'rabbit ears' representing lone pairs of electrons, as pictured in terms of equivalent (localized) molecular orbitals, in the water or ammonia molecules.

My difficulty was the lack of any evidence of electron pairing in the electron density $\rho(\boldsymbol{r})$, the function, that for a stationary state, describes the static distribution of electronic charge throughout three-dimensional space. For an N-electron molecule, it is defined as

$$\rho(\boldsymbol{r}) = N\int \mathrm{d}\tau' \psi^* \psi \tag{1}$$

where the symbol $\int\mathrm{d}\tau'$ denotes a summation over all spins and an integration over the spatial coordinates of all the electrons save those associated with the coordinate $\boldsymbol{r}$. Thus, $\rho(\boldsymbol{r})$ is N times the probability of finding a given electron at $\boldsymbol{r}$ and for a stationary state $\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$ determines the amount of electronic charge in the volume element $\mathrm{d}\boldsymbol{r}$. When the wave function is expressed as a single determinant, the density is given by a sum of orbital density contributions each multiplied by its occupation number, $\Sigma_i n_i|\phi_i|^2$. Eventhough the molecular orbitals can be transformed into a set of equivalent orbitals whose spatial properties corresponded to bonded and non-bonded electrons, these characteristic forms do not survive when summed to give the relatively simple topology displayed by the total electron density, whose only maxima are those found at the positions of the nuclei. In retrospect, while my arguments against the orbital interpretations, which were used to justify the spatial pairing of electrons were correct, I failed to appreciate the underlying work of Lennard-Jones on the electron pair density that ultimately formed the basis for Professor Gillespie's spatial arguments [4]. It seems difficult now to understand why, after the initial work by Lennard-Jones on the importance of the pair density to chemistry, its further investigation along other than purely formal lines [6] was to languish for so long a period of time.

2. Initial studies of electron localization

I joined the Department of Chemistry at McMaster University in 1963, a time when Ron Gillespie was its chairman. I have his letter welcoming me to the Department and "hoping that we can have some further discussions on electron-pair repulsions etc., when you are next here." I was by then totally immersed in my studies of the electron density but I and many others were fascinated by the ability of the VSEPR model to account for molecular geometries of the main group elements and many attempts were being made by theoreticians to account for its success. It was always in the back of my mind as something I wanted very much to explain, being unconvinced (as was Ron Gillespie) with the attempts to do so using orbital based arguments. In 1966, I made an abortive attempt to account for the VSEPR model by attempting to incorporate the effect of the Pauli principle in a model of the electron density and the forces it exerts on the nuclei in an equilibrium geometry through the requirement of orthogonality on the set of orbitals used to describe the density [7]. The work served only to show that Gillespie's model based "on the idea that the arrangement of all the electron pairs (bonding pairs and lone pairs) in the valence shell of the central atom is determined by the operation of the Pauli exclusion principle" [1] was still very much on my mind. Further progress had to await the realisation that if one wanted to know what the electron pairs were doing in a molecule, then one should study the pair density, picking up where Lennard-Jones had left off.

2.1. Daudel's loge model

An early approach to the study of electron pairing in molecules, was the theory of loges developed by Daudel and his co-workers [8]. The real space of a molecule was divided into loges and the 'best' loges were to represent the most probable division of the space of a system into localized groups of electrons. Initially, the loges were modelled on the principal forms exhibited by localized molecular orbitals, without direct recourse to the wave function or the pair density. The idea of localized molecular orbitals evolved from the equivalent molecular orbitals that were introduced into chemistry by Lennard-Jones [9] to transform the delocalized canonical molecular orbitals into forms a chemist could associate with the presence of bonded and non-bonded pairs of electrons. The identification of localized orbitals, obtained from a one-electron theory by an arbitrary unitary transformation of the canonical orbitals to describe the spatial pairing of electrons, dominated chemical thinking in the 1950s and 1960s and unfortunately, for some, still does. As well as being arbitrary, such a unitary transformation of the orbitals leaves the density and all properties of the system, including the pair density, unchanged and one is left with the question as to why one set can be used to explain a property of a molecule while another set cannot.

In its beginning, loge theory was used to justify localized molecular orbitals, which were in turn used to justify the loges. This changed in 1971 when the loge model was restated in terms Shannon's information theory. The best loges were defined as being those which minimized the missing information function $I(P_n, \Omega)$ [10], akin to the entropy, as expressed in Eq. (2),

$$I(P_n, \Omega) = -\sum_n P_n(\Omega)\ln P_n(\Omega) \tag{2}$$

where $P_n(\Omega)$ is the probability, as determined from the wave function, that n electrons occupy the bounded region of space (loge) Ω and the remaining electrons are confined to the remainder of the system. Clearly, the missing information function is minimized—a situation corresponding to maximum knowledge of the system—when one event dominates and the corresponding $P_n(\Omega) = 1$. In this situation one is certain that n electrons occupy the loge Ω. For example, finding a region for which $P_2(\Omega)$ approached unity would imply a pair of electrons localized to that region. However, no applications of this idea were made by Daudel's group because they lacked the means of calculating the $P_n(\Omega)$, which requires specialised numerical techniques.

I met Professor Daudel at the Canadian Theoretical Chemistry Conference in Vancouver in 1972 where I presented our initial findings underlying the theory of atoms in molecules [11]: the observation of the paralleling transferable behaviour of the electron and the kinetic energy densities for spatial regions bounded by surfaces of zero-flux in the gradient vector field of the electron density, a condition expressed in Eq. (3),

$$\nabla\rho(\boldsymbol{r})\cdot\boldsymbol{n}(\boldsymbol{r}) = 0 \quad \text{for all points on the surface } S(\boldsymbol{r}) \tag{3}$$

where $\boldsymbol{n}(\boldsymbol{r})$ is a unit vector normal to the surface at $\boldsymbol{r}$. It was these observations that led us to pose the question as to whether the virial theorem would apply to such regions, an affirmative answer enabling us to define the energy and hence all properties of an atom in a molecule. Professor Daudel presented a talk on his loge theory at the same meeting and we discussed the question as to whether atoms satisfying the zero-flux boundary condition would at the same time correspond to the 'best' loges, those that minimized the missing information function. Because of our work on the partitioning of the density, my research group possessed numerical integration programs that could be used for the calculation of the $P_n(\Omega)$.

The results of our joint investigation were reported in 1974 [12]. As the calculation of the $P_n(\Omega)$ requires the full many-electron density matrix (i.e. one uses all of the information in the wave function), the systems studied were necessarily small and consisted of the hydrides LiH, BeH, BH and BeH_2. The density distributions in these molecules approach the ionic limit with a core on the A nucleus and with valence density localized on the protons. Using a variable radius centred on the A nucleus, it was found possible to define a core loge which simultaneously maximized $P_2(A)$ and minimized the missing information function.

The six electron BH system typifies the results obtained: one could add a variable planar surface within the valence region in BH to yield a three loge partitioning of core, non-bonded on boron and bonded pair localized primarily on the proton. The missing information function was minimized when the probability of the event of finding two electrons in each of the three loges was maximized. Since the zero-flux surface only yields atomic regions, a comparison with the loge results was possible only in some of the cases. In LiH, the zero-flux surface was found to yield a slightly greater value for $P_2(\Omega)$ and a lower one for the missing information function than obtained from the best spherical core loge. That a partitioning into loges could be found that minimized the missing information function for doubly occupied loges was indeed a promising result. However, this result was to prove to be the exception rather than the rule, as made clear when loge theory was applied to larger, non-ionic systems.

2.2. Minimization of the fluctuation in an electron population

The application to larger systems was made possible by the demonstration of an important point: the behaviour of the missing information function was faithfully mimicked by the fluctuation in the average population of the region in question [12]. The fluctuation $\Lambda(\Omega)$ is defined as,

$$\Lambda(\Omega) = \sum_n n^2 P_n(\Omega) - \left\{\sum_n n P_n(\Omega)\right\}^2 = N^2(\Omega) - N(\Omega)^2 \tag{4}$$

where $N(\Omega)$ is the average population of region Ω and $N^2(\Omega)$ the average of the square of the number of particles. Clearly, $\Lambda(\Omega)$ approaches zero when a single event dominates the distribution for then $N^2(\Omega)$ approaches $N(\Omega)^2$. It was next demonstrated that, unlike $I(P_n, \Omega)$ whose evaluation requires the full many-particle density matrix, $\Lambda(\Omega)$ is determined by just the pair density [13], making it possible to study the localization of electrons in any system whose wave function could be calculated. Such a study was made by myself and Michael Stephens, wherein we attempted to find bounded spatial regions exhibiting populations with a minimum in their fluctuation [14]. We found that this criterion for electron localization could be met for core regions and the previously studied ionic systems that was extended to include BH_4^-, but not for polar or covalently bound molecules, such as methane, ammonia, water, hydrogen fluoride, dinitrogen and difluorine. The valence electron pairs in these latter molecules are so strongly intercorrelated that the localized pair model ceases to afford a suitable description. That is, on the average many pairs contribute to each region. We could not, for example, find boundaries partitioning the valence region of the water molecule into four doubly occupied domains which exhibited minima in their fluctuations, to yield the VSEPR model of two bonded and two non-bonded isolated electron pairs for the water molecule.

The conclusion reached in this paper regarding the general lack of spatially localized electron pairs was overly pessimistic in its judgement of the presence and hence, ultimate importance of the spatial pairing of electrons. To approach the idealised limit of a physically localized electron pair requires that the region Ω be bounded by a surface such that the fluctuation in its average population could be minimized, a situation requiring $P_2(\Omega)$ to approach unity. However, as we were later to discover, this requirement is too restrictive in the sense that it excludes from consideration a region possessing a fluctuation which, while in excess of that required for the near localization of a single pair, is small enough to indicate a physically significant reduction in its average pair population. Certainly our initial conclusions regarding the general absence of spatially localized electron pairs did little to increase the rapport between myself and Ron Gillespie, which had been buoyed up with our initial findings of the strong pairing present in the ionic hydrides [12].

3. The physical basis of electron localization

The papers by Bader and Stephens [13,14] did, however, accomplish something very positive. By focusing their attention on the pair density, they established that the physical requirement for the spatial localization of electrons is a corresponding localization of their Fermi correlation. The formation of α,β pairs is a consequence of the pair density being antisymmetric with respect to the exchange of the space and spin coordinates of every pair of electrons, as required by the Pauli exclusion principle. The ‘exclusion’ is a result of the Fermi hole that is created in the pair density by the antisymmetrization requirement. The Fermi hole, as discussed below, has a simple physical interpretation: it may be viewed as a description of how the density of an electron of given spin, the so-called reference electron, is spread out in space, thereby excluding the presence of an identical amount of same-spin density [14]. It is to be understood that all physical measures of the localization or delocalization of an electron are determined by the corresponding localization or delocalization of its Fermi hole [15]. Since this behaviour is obtained separately for an α and a β electron in a closed-shell system, the density of the Fermi hole determines the spatial pairing of the electrons. It is this property of the electron distribution that enables one to determine the average number of electron pairs that are localized to a given atom or region of space and to determine also, the number of pairs that are shared between atoms [16]. It is these ideas that ultimately provide the physical underpinnings of the Lewis electron pair model and of the VSEPR model of molecular geometry.

3.1. The role of the Fermi hole in localising an electron

In what follows we shall restrict the discussion to the Hartree–Fock level of theory where the only correlation is the Fermi correlation. The addition of the Coulomb correlation, while altering the numerical results, does not alter any of the physical interpretations or the understanding of electron localization [16]. At the Hartree–Fock level, there is no correlation between electrons of different spin and the pair density is simply the product of the α and β spin densities multiplied by a factor of one-half (so as not to count the same pair twice), or

$$\rho^{\alpha\beta}(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1/2)\rho^{\alpha}(\boldsymbol{r}_1)\rho^{\beta}(\boldsymbol{r}_2) \tag{5}$$

(One interprets the pair density as one does the density itself, the quantity $\rho^{\alpha\beta}(\boldsymbol{r}_1, \boldsymbol{r}_2)\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2$ determining the number of α,β pairs that are formed between the two infinitesimal volume elements $\mathrm{d}\boldsymbol{r}_1$ and $\mathrm{d}\boldsymbol{r}_2$.) For same-spin electrons however, the density at $\boldsymbol{r}_2$, $\rho^{\alpha}(\boldsymbol{r}_2)$, is reduced in value by the density of the Fermi hole $h^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ [6], a negative quantity, and the number of same spin pairs is correspondingly reduced, Eq. (6),

$$\rho^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1/2)\rho^{\alpha}(\boldsymbol{r}_1)[\rho^{\alpha}(\boldsymbol{r}_2) + h^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2)] \tag{6}$$

The density of the Fermi hole is identical, except for the sign, with the exchange charge density introduced by Slater in his discussion of the Hartree–Fock equations [17],

$$h^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2) = -\sum_{i}^{\alpha}\sum_{j}^{\alpha}[\phi_i^*(\boldsymbol{r}_1)\phi_i(\boldsymbol{r}_2)\phi_j^*(\boldsymbol{r}_2)\phi_j(\boldsymbol{r}_1)]/\rho^{\alpha}(\boldsymbol{r}_1) \tag{7}$$

The density distribution of the Fermi hole is a function of the position of the coordinate $\boldsymbol{r}_1$ assigned to the reference electron labelled e*. However, e* is not localized to $\boldsymbol{r}_1$. Instead the Fermi hole describes how the density of e* is spread out from this point into the space of another same-spin electron described by the coordinate $\boldsymbol{r}_2$, excluding an equivalent amount of density at each $\boldsymbol{r}_2$ [14]. The value of the Fermi hole is equal to the negative of the same-spin density when $\boldsymbol{r}_2 = \boldsymbol{r}_1$, thereby totally excluding all other same-spin electrons from the reference point. If this total exclusion of same-spin density persists as $\boldsymbol{r}_2$ is displaced from $\boldsymbol{r}_1$, then the hole will describe a region of space from which all other same-spin electrons are excluded. In this situation, the Fermi hole is maximally localized and its density excludes the density of all other same-spin electrons, up the amount of one electronic charge, from the vicinity of e*. In a closed-shell molecule, the same behaviour will be obtained for an electron of opposite spin and the result will be a region of space occupied by the density of a single α,β pair of electrons. If this total degree of exclusion is maintained for motion of the pair of reference electrons over the region of exclusion, the result is a spatially localized electron pair. Thus, the requirement for the localization of an electron of either spin to a given region of space, and hence for the formation of a localized pair, is that the density of their Fermi holes be completely contained within the region, thereby excluding all other electrons of either spin [14].

This degree of localization of the Fermi hole density, hereafter referred to as the Fermi density, can be approached but never achieved, except for an isolated system. The approach to complete localization is found only for core electrons and ionic systems. For valence electrons in general, the hole is delocalized and the magnitude of its density is less than the same-spin density for positions other than the coordinate of e*. Thus, the exclusion is less than complete, the density from other same-spin electrons is found within the Fermi hole of e* and it in turn is delocalized into the Fermi holes of the other same-spin electrons. Clearly, the extent of localization or delocalization of the density of an electron is determined by the corresponding localization or delocalization of its Fermi hole [14].

The Fermi density integrates to minus one, corresponding to the removal of the density of one electron for any one position of the reference electron [6]. By weighting the density of the Fermi hole by the density of the reference electron and then integrating over the space of both electrons, one obtains a measure of the total Fermi correlation which must correspond to the removal of all N^{α} electrons, as indicated in Eq. (8)

$$\int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 \rho^{\alpha}(\boldsymbol{r}_1) h^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2) = -N^{\alpha} \tag{8}$$

If the same integration scheme is applied to a region A of space, one obtains a measure of the total Fermi correlation for the α-electrons contained within that region, a quantity labelled $F^{\alpha\alpha}(\mathrm{A}, \mathrm{A})$ [14],

$$F^{\alpha\alpha}(\mathrm{A}, \mathrm{A}) = \int_{\mathrm{A}} d\boldsymbol{r}_1 \int_{\mathrm{A}} d\boldsymbol{r}_2 \rho^{\alpha}(\boldsymbol{r}_1) h^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{9}$$

At the Hartree–Fock level of theory, it follows from Eq. (7) that $F^{\alpha\alpha}(\mathrm{A}, \mathrm{A})$ is simply the double integration of the exchange density, which reduces simply, to the product of overlaps of the spin orbitals over the region A, as given in Eq. (10),

$$F^{\alpha\alpha}(\mathrm{A}, \mathrm{A}) = -\sum_{i}^{N_{\alpha}}\sum_{j}^{N_{\alpha}} S_{ij}^{2}(\mathrm{A}) \tag{10}$$

We denote the total Fermi correlation for electrons of both spins by the symbol $F(\mathrm{A}, \mathrm{A}) = F^{\alpha\alpha}(\mathrm{A}, \mathrm{A}) = F^{\beta\beta}(\mathrm{A}, \mathrm{A})$ and from this point on refer to the correlation for both spins in a closed-shell system. $F(\mathrm{A}, \mathrm{A})$ appears in the expression for the average number of electron pairs in a region A [14], an expression obtained by the double integration of the pair density $\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$, Eq. (11),

$$D_2(\mathrm{A}, \mathrm{A}) = \int_{\mathrm{A}} d\boldsymbol{r}_1 \int_{\mathrm{A}} d\boldsymbol{r}_2 \rho(\boldsymbol{r}_1, \boldsymbol{r}_2) = [N(\mathrm{A})^2 + F(\mathrm{A}, \mathrm{A})]/2 \tag{11}$$

where $N(\mathrm{A})$ is the population of the region A. This expression demonstrates that the net effect of the Fermi correlation is to ensure that the pair density integrates to the correct number of pairs formed between a set of identical spin electrons by correcting for the self-pairing of the electrons. When A equals all space, $F(\mathrm{A}, \mathrm{A}) = -N$ thereby reducing the number of pairs from $\frac{1}{2}N^2$ which includes self-pairing, by $N/2$ to $\frac{1}{2}N(N-1)$. Similarly, if $F(\mathrm{A}, \mathrm{A})$ attains its limiting value of $-N(\mathrm{A})$ for a region A, the self-pairing correction would be complete within A and the $N(\mathrm{A})$ electrons, now necessarily an integer number, would form a distinct set, separate from the remainder of the molecule—they would be totally localized to A and $P_{N(\mathrm{A})}(\mathrm{A})$ would be unity. In general, $|F(\mathrm{A}, \mathrm{A})| < N(\mathrm{A})$, indicating that the Fermi density for electrons referenced to A extends into the remainder of space and they are not completely localized to A. The ratio $|F(\mathrm{A}, \mathrm{A})|/N(\mathrm{A})$ determines the fraction of the maximum attainable localization. In ionic systems such as LiH or NaCl, this ratio for atoms defined by zero-flux interatomic surfaces equals or exceeds 0.95, i.e. the contained Fermi correlation is at least 95% of that required for complete localization of the electrons to either atom.

The relation between the fluctuation in a population of a region A and its contained Fermi correlation is given by the expression [13,14]

$$\Lambda(\mathrm{A}) = N(\mathrm{A}) + F(\mathrm{A},\ \mathrm{A}) \tag{12}$$

Clearly, when the contained Fermi correlation attains its limiting value of $-N(\mathrm{A})$, corresponding to the complete localization of the $N(\mathrm{A})$ electrons to the region A, the fluctuation in the average population of A vanishes. In general, a region will exhibit a minimum in the fluctuation in its population only if the localization index $|F(\mathrm{A},\ \mathrm{A})|/N(\mathrm{A})$ is in excess of 80%.

For someone unfamiliar with the pair density, it is important to note that $D_2(\mathrm{A},\ \mathrm{A})$ is the average number of pairs formed within the region A by all of the electrons in the molecule, a number that is not to be confused with a counting of the number of Lewis pairs. The limiting value for this number of pairs is $(1/2)N(\mathrm{A})[N(\mathrm{A})-1]$. For example, the Na atom in NaF, for which $N(\mathrm{Na}) = 10.06$, has an average pair population equal to 45.6 and the ratio of $|F(\mathrm{Na},\ \mathrm{Na})|/N(\mathrm{Na}) = 99.5$ indicates that all but 0.5% of the Fermi correlation needed for complete localization is present. The (unattainable) ionic limit corresponds to precisely ten electrons being totally localized within the basin of the Na atom, yielding a pair population of $10 \times 9/2 = 45$. The remarkable extent to which the number and pair populations approach their limiting ionic values should dispel any lingering doubts about the lack of physical relevance of Mulliken populations which are incapable of predicting ionic like populations.

This work [14] established the physical requirement for the spatial localization of electrons of either spin and hence the requirement for the spatial pairing of electrons. At this time in my laboratory however, all of our efforts were being placed on the development of the theory of atoms in molecules [18–20] through the use of Schwinger's principle of stationary action [21]. As a consequence, no more work was done in the area of electron localization until 1983 when we discovered the remarkable properties exhibited by the Laplacian of the electron density.

4. Laplacian of the density as a measure of electron localization

The Laplacian of the electron density, the quantity $\nabla^2\rho(\boldsymbol{r})$, has played an important role throughout the development of the theory of atoms in molecules [22], including the observations made in the original work regarding the transferability of the kinetic energy density [11]. The Laplacian also appears in the local expression of the virial theorem and in the constraint that leads to the theory of atoms in molecules [19,22].

It is useful to define a quantity proportional to the negative of the Laplacian, as $L(\boldsymbol{r}) = -\nabla^2\rho(\boldsymbol{r})$ [23]. The Laplacian of the density, a scalar quantity, has the important property of determining where the density is locally concentrated, regions where $L(\boldsymbol{r}) > 0$, and where it is locally depleted, regions where $L(\boldsymbol{r}) < 0$. Where $L(\boldsymbol{r}) > 0$, $\rho(\boldsymbol{r})$ is greater than its value averaged over an infinitesimal sphere centred at $\boldsymbol{r}$, with the reverse being true for $L(\boldsymbol{r}) < 0$ [22]. Because of this mathematical property, the Laplacian brings to the fore variations in the spatial properties of the density that are not revealed in the topology of $\rho(\mathbf{r})$ itself. It is this property of the Laplacian that reflects the extent of spatial pairing of electrons, as we first noted empirically and have since, because of our collaboration with Ron Gillespie, demonstrated theoretically.

It was noted early on that the topology of the Laplacian reveals the shell structure of an atom, by displaying pairs of regions with $L(\mathbf{r}) > 0$ and $L(\mathbf{r}) < 0$, for each quantum shell, with the innermost region of charge concentration being a spike-like maximum in $L(\mathbf{r})$ at the position of the nucleus [11]. This shell structure persists when the atom is bound within a molecule, unless of course, the outermost shell of charge concentration is transferred to neighbouring atoms. The shell structure exhibited by $L(\mathbf{r})$ has been shown to recover the shell structure determined by the pair density through the conditional pair density for same-spin electrons, a topic discussed later in the paper. The outer shell of charge concentration is referred to as the valence shell charge concentration (VSCC) [22].

The bond critical point denotes the point of minimum density along a uniquely defined line of maximum density that links two neighbouring nuclei—the bond path [22]. The Laplacian of the density at a bond critical point along with other properties defined at this point, proved to be invaluable in the classification of atomic interactions [24]. All types of interactions were considered in the paper presenting this classification scheme: shared (covalent), polar and closed-shell including ionic and hydrogen bonding, as well as van der Waals interactions. The hydrogen bonding examples consisted of the dimers of HF and H_2O and one afternoon viewing the diagrams of the Laplacian distribution for these dimers, Fig. 3 of the paper, my students and I noticed that the O–H or F–H axis of the donor molecule was directed at what appeared to be a maximum in $L(\mathbf{r})$ in the VSCC of the oxygen or fluorine atom in the acceptor molecule. Could it be that the VSCC exhibited local maxima–maximum concentrations of electronic charge—in those positions where lone pairs of electrons were presumed to reside? What about bonded pairs? We decided on the spot to investigate these possibilities [25]. I immediately worked out the expressions needed to determine critical points in $L(\mathbf{r})$ and Douglas Morgan wrote the necessary programs. It was Preston MacDougall's idea to apply this analysis to a density obtained for the T-shaped molecule ClF_3, knowing that it was a classic example in illustrating the predictive power of the VSEPR model. The result is shown in Fig. 1 and the rest, as they say, is history. Preston pasted a large copy of this diagram on the door to Ron Gillespie's office and we finally got his favourable attention.

One must appreciate that displayed here in the topology of the Laplacian, a measurable property of a system, was the first physical evidence, albeit initially empirical, for the basic tenets underlying the VSEPR model. The correspondence between these tenets and the properties of the maxima exhibited by the VSCC of the Cl atom is no less than remarkable [25]. (a) There are five local maxima in accordance with the five electron pairs assumed to be present in the valence shell of the Cl atom, three are bonded (i.e. situated on bond paths linking each F to Cl) and two are non-bonded lying in the equatorial plane. (b) The non-bonded maxima are

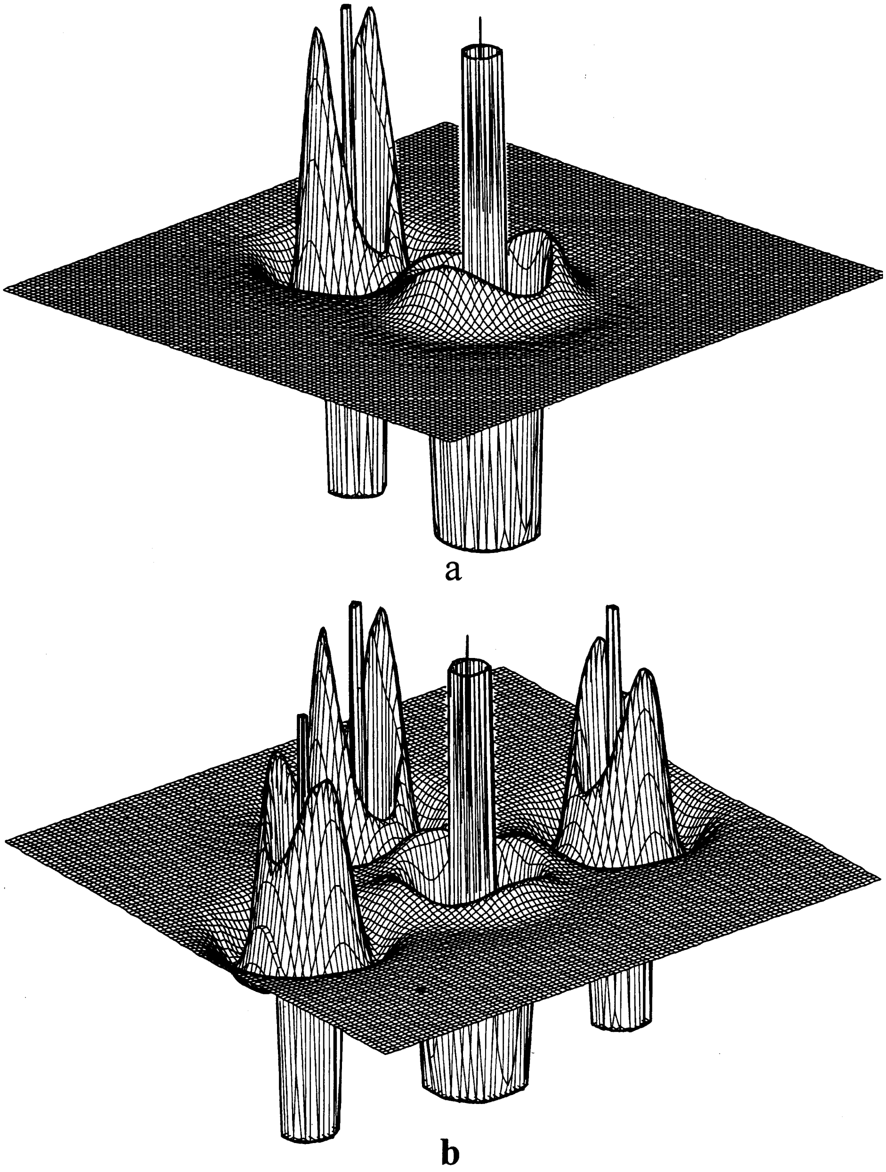

Fig. 1. Relief maps of $L(\mathbf{r})$ for (a) the equatorial plane and (b) a plane containing the axial, as well as the equatorial fluorines, of ClF_3 for the T-shaped equilibrium geometry. Each fluorine atom exhibits two shells of charge concentration, the chlorine atom, three such shells. The equatorial plane shows the presence of two non-bonding and one smaller bonding CC. In the axial plane there are three bonding CCs, (3, − 3) CPs in $L(\mathbf{r})$, and a fourth apparent maximum. This latter feature is actually another view of the (3, − 1) CP between the two non-bonding CCs which appears as a saddle point in (a). Thus, the VSCC of chlorine possesses two non-bonding and three bonding CCs.

considerably larger in magnitude and spatial extent than the bonded maxima and the equatorial bonded maximum is larger than are the axial bonded maxima (the axial bonds are longer than the equatorial bond and the axial fluorines more ionic, as predicted by VSEPR). (c) The angle between the non-bonded maxima opens to 148° while the angle between an axial and the equatorial bonded maxima is 84°. The relative dispositions and sizes of the bonded and non-bonded maxima are those required to account for the observed T-shaped geometry. Furthermore, other geometries yielding one or two axial non-bonded pairs give patterns for $L(\mathbf{r})$ in which the bonded and non-bonded or the two non-bonded maxima are brought into closer contact than found for the T-shaped geometry, violating a basic tenet of VESPR that the favoured geometry is the one that maximizes the separation between the electron pair domains. Ron Gillespie is acknowledged at the end of this first paper on the topology of $L(\mathbf{r})$ 'for many useful discussions and for his constant encouragement in our search for evidence of 'lone pairs' in the properties of the electronic charge distribution [25]'.

The VSCC of a free atom exhibits a sphere over which the electronic charge is maximally and uniformly concentrated. The topology of $\nabla^2\rho$ is classified in terms of its critical points (CPs), points where $\nabla(\nabla^2\rho) = 0$ and the function exhibits extrema. Each point on this surface is a (1, -1) CP when classified by (rank, signature): the two curvatures tangent to the surface are zero, reducing the rank from three to one, and the curvature perpendicular to the surface is negative since $L(\mathbf{r})$ is a maximum on the surface of the sphere, yielding a signature of -1. In general, this surface persists for an atom in a molecule, but the sphere is distorted and the surface is no longer one of uniform concentration, as the two tangential curvatures assume either positive or negative values to yield CPs of rank 3. The topology of $L(\mathbf{r})$ on this surface is equivalent to the description of the hills and valleys of a surface terrain. If the two tangential curvatures assume negative values the result is a (3, -3) CP, a local maximum, in $L(\mathbf{r})$; if they assume positive values a local minimum is formed on the surface and the result is a (3, $+1$) CP in $L(\mathbf{r})$; if they assume values of opposite sign a saddle point is formed on the surface and $L(\mathbf{r})$ exhibits a (3, -1) CP. The local maxima formed within a VSCC are referred to as charge concentrations or CCs. The CCs are linked together by paths emanating from the intervening (3, -1) CPs and the result is a polyhedron, with each edge containing a (3, -1) CP and each face containing a (3, $+1$) CP, a local minimum in $L(\mathbf{r})$. In ClF_3 for example, the CCs in the VSCC of Cl are linked to form a (distorted) trigonal bipyramid with two fluorines adjacent to the two axial CCs and one fluorine adjacent to one of the three equatorial CCs, the remaining two representing non-bonded pairs of the VSEPR model.

Thus, the VSCC of a bound atom exhibits not only local maxima or CCs on its surface of charge concentration, but also local minima or 'holes' and these properties taken together provide a basis for the Lewis acid–base model: the maxima representing base sites, the minima the acid sites. It has been demonstrated that the initial approach geometry of reactants can be predicted by aligning the maxima on an atom in one reactant with a minimum or 'hole' on an atom of the second reactant. Thus, the topology of $L(\mathbf{r})$ appears to recover all aspects of the

Lewis model of the electron pair, raising the question of its relationship to the pair density [22,25].

4.1. The concept of partial pair condensation

This faithful mapping of the number and properties of electron pair domains assumed in the VSEPR model, onto the number and properties of the CCs displayed in $L(\boldsymbol{r})$ as found in our initial investigation [25], forced us to rethink the earlier conclusions of Bader and Stephens regarding the general absence of regions dominated by single electron pairs outside of core regions or ionic systems. It is clear from the work of Bader and Stephens [14] that the domains occupied by the CCs in $L(\boldsymbol{r})$ found in the valence region of the Cl atom for example, cannot represent regions with average populations of two whose contained Fermi correlation is maximized, the requirements for the limiting case of a completely localized electron pair.

There could, however, be a localization of the Fermi density which, while less than that required for the near complete localization of an electron pair, is sufficient to result in partial condensation of the pair density to yield a spatial region with a greater than average probability of occupation by a single pair of electrons, that is, a region exhibiting a peaking in the value of $P_2(\Omega)$. In general, the electron density in any region of space will be the result of contributions from many pairs of electrons, as opposed to just one. The density in the region of an atomic core which integrates to give an average population of two, is very close to being the result of the occupation by a single pair of electrons, the average pair population for Li in LiF for example, equalling 1.1 pairs. The region of space associated with a non-bonded pair on N in NH_3, on the other hand, while also having an average population of two, is the result of the occupation of the region by an average 3.0 pairs of electrons [14]. However, there are ten electrons in ammonia which form $10 \times 9/2 = 45$ distinct pairs of electrons, or 28 if one excludes the pair localized within the core on N, so that a region with an average pair population of 3 is well below that obtained from a distribution with a random pairing of electrons throughout the molecule. Thus, while the non-bonded region on N in ammonia does not meet the requirements for a single, spatially localized electron pair, it does represent a region where the contributing number of pairs is greatly reduced from the random level, a situation termed ‘partial pair condensation’.

In 1988 Ron Gillespie, Preston MacDougall and I presented the first evidence tying the topology of $L(\boldsymbol{r})$ to the pair density via the properties of the Fermi density, looking for evidence of partial pair condensation [26]. The paper used the molecule $ClOF_3$ to illustrate the relation of the topology of $L(\boldsymbol{r})$ to the VSEPR model. This molecule, like ClF_3, has five electron pair domains, one being associated with the doubly bonded pair shared with oxygen. According to the VSEPR model, the oxygen should occupy what corresponds to an equatorial site in ClF_3 to accommodate the relatively large doubly bonded pair domain. This predicts a distorted trigonal bipyramid geometry of C_s symmetry, in agreement with the observed and calculated minimum energy geometries. All the nuances of VSEPR are again recovered for this molecule. The non-bonded equatorial CC on Cl is larger than the CC associated with the doubly bonded oxygen, which in turn is larger than the bonded CC associated with the equatorial F, which in turn is larger than the bonded CCs associated with the two axial fluorines, as predicted for the corresponding electron domains of VSEPR [2,27].

This paper [26] and a further review paper by the same authors [28] demonstrated that the existence of the CCs in the VSCC of a central atom is indeed a result of partial pair condensation. This finding was obtained through displays of the Fermi density for given positions of the reference electron. It was found that the Fermi hole obtained when the reference electron is placed at a corresponding bonded or non-bonded maximum in the VSCC of the central atom is the most localized and least mutually overlapping. The effect is most pronounced for the geometries that in the VSEPR model maximize the separation of the electron pair domains, or equivalently, maximize the separations between the CCs in the VSCC of the central atom. It should be emphasized, that the use of the locations of the CCs in $L(\boldsymbol{r})$ to position the reference electron is crucial to obtaining the correspondence between maximizing the localization of the density of the Fermi hole and the VSEPR model. This study, while admittedly qualitative in nature, convinced us that the presence of the number and properties of the CCs in the VSCC of a central atom were a manifestation of a corresponding spatial localization of the Fermi density leading to partial pair condensation.

5. The use of the Laplacian to explain apparent VSEPR failures

The large number of examples subsequently investigated left no doubt of the overall correspondence that exists between the predictions of the VSEPR model with regards the electron pair domains and the number and properties of the CCs found in the VSCC of the central atom. The VSEPR model can however, fail to predict the correct geometry when a transition metal atom is the central atom for the location of the electron pair domains. The Lewis model has not been applied to transition metals and there were no models that could be used to justify any particular arrangement of electron pair domains within the basin of a transition metal atom. Gillespie et al had commented on this problem with the statement “the 3d electrons cannot be clearly identified as either valence shell electrons or as core electrons. This special nature of the 3d electrons is responsible for most of the unusual properties of the transition metals [29]”. A study of the topology of $L(\boldsymbol{r})$ in the outer shell of a transition metal atom, a shell whose quantum number is definitely established, removes this uncertainty.

The topology of the Laplacian provides a model-free determination of the spatial localization of the electrons that is present in any system and its use offers the possibility of determining the patterns of pair condensation characteristic of a bound transition metal atom. Ron Gillespie suggested that we investigate the topology for $L(\boldsymbol{r})$ for a transition metal molecule with the hope of extending the empirical rules of the VSEPR model, thereby making possible its extension to molecules containing metal atoms. At this time we were looking for a topic as a basis for a paper to contribute to an issue of *Canadian Journal of Chemistry* that was to be published in his honour in 1989 so we carried out his suggestion by studying the molecule $VOCl_3$ [30].

Failures of the VSEPR model can take one of two forms, which Ron Gillespie refers to as qualitative and quantitative, receptively. In a qualitative failure, the model predicts the correct geometry but the relative sizes of the bond angles subtended at the central nucleus are in the wrong order. In a quantitative failure, the model predicts the wrong geometry. In our first paper on this subject we investigated an example of a qualitative failure found in the molecule $VOCl_3$. The failure of the model is best understood by contrasting the geometry of $VOCl_3$ with that of related main group molecules. In POX_3 with $X = F$ and Cl, VESPR predicts that, because of the greater size of the electron domain associated with the doubly bonded pair, the XPO angle should be greater than the XPX angle in these tetrahedral-like molecules, as is indeed observed. Similarly in the related SO_2X_2 molecules, the OSO angle is found to be greater than the XSX angle. The relative sizes of the four electron pair domains predicted by VSEPR in these tetrahedral-like molecules are faithfully recovered in the sizes of the four bonding CCs found in the VSCCs of the P and S atoms, the doubly bonded domains associated with the oxygens being the largest. In corresponding molecules containing transition metal atoms, the reverse ordering of the bond angles is found, with the ClVO angle less than the ClVCl angle in $VOCl_3$ and the OCrO angle smaller than the XCrX angle in CrO_2X_2 with $X = F$ and Cl.

First, one uses the ability of $L(\boldsymbol{r})$ to define shell structure to show that there is no shell of charge concentration corresponding to the fourth quantum shell for the V atom in $VOCl_3$, a result that was later to prove to be general for transition metal molecules. Whether or not such a shell is present in the free atom, the point remains that when bound in a molecule, the shell structure exhibited by $L(\boldsymbol{r})$ unequivocally determines that the third quantum shell forms the VSCC of a bound transition metal atom with the configuration $3d^n4s^2$. The net charges on these atoms are generally of the order of $+2$ or greater, ($q(\mathrm{V}) = +2.41$ in $VOCl_3$) indicating that the 4s electrons have indeed been transferred to the ligands. (The charges reported here are the physical charges of the atoms in a molecule, determined by an integration of the density over an atomic basin, as required by the principle of stationary action [22].) We found [30] that the locations of the CCs in the VSCC of the V atom were indeed different from those found for a main group atom, a finding that has since proved to be general and to provide a rationalisation for the differing geometrical properties of molecules containing metal atoms.

The VSCC of V in $VOCl_3$ also exhibits four principal CCs but they are in each case opposed to rather than adjacent to the ligands. The simplest way of picturing this arrangement and contrasting it with that found in the main group counterpart is in terms of the (distorted) tetrahedron formed by the four CCs. In the main group molecule, a ligand is placed at each apex of the tetrahedron, i.e. adjacent to a CC and the CCs behave as bonding CCs. In $VOCl_3$, each ligand is placed adjacent to a face of the tetrahedron and is thus, opposite to a CC. The local charge concentrations are in this case referred to as ligand opposed CCs. The CC opposed to the oxygen is, as in the main group elements, by far the largest. However, since in this case it is a ligand opposed CC, it lies within the VCl_3 pyramid and consequently the ClVCl angles are increased at the expense of the OVCl angle. Thus, while the CCs for transition metal atoms are found to display some of the same properties found for the main group elements, they differ in one important respect in that the CCs are opposed to rather than adjacent to the position of the ligand.

In some relatively rare instances, a CC of small magnitude appears in the face adjacent to a ligand in the polyhedron formed by the CCs, and the ligand is associated with both a bonded and a ligand opposed CC. Such a CC is found only for relatively ‘soft’ ligands like a doubly bonded oxygen or a methyl carbon atom and one appears in the face adjacent to the oxygen in $VOCl_3$.

This paper was followed by one co-authored with Ron Gillespie in which another apparent qualitative exception to the VESPR model found in certain main group molecules was also shown to be explicable in terms of the Laplacian distribution [31]. The molecules of concern are of the general form YSF_4 ($Y = OH$, NH, CH_3) and are treated as exceptions because of the unexpected increase in the $Y–S–F_{eq}$ angle in the series OSF_4, $NHSF_4$ and H_2CSF_4. This paper demonstrated that the shape of a CC can be of importance in determining relative geometries. The CC associated with the double bond domain in these molecules exhibits a considerable ellipticity, that is, the curvature of $L(\boldsymbol{r})$ at the position of the local maximum in the equatorial plane is smaller than that in the second plane perpendicular to the bond path. Thus, both the electron density and its concentration is more spread out in the equatorial plane and the result is a charge distribution with a pronounced ellipsoidal nature in a cut through a plane perpendicular to the Y=S bond. As anticipated on the basis of relative electronegativities and hence tightness of binding of the density, the ellipticity is greatest for the C=S interactions and least for the O=S interaction. The same elliptical nature of the CC associated with the lone pair domain in the series of molecules AF_4E ($A = P$, S, Cl; $E =$ a lone pair), together with the relative sizes of the CCs associated with the bonded domains, demonstrated that their geometrical features are in complete agreement with the VSEPR model.

5.1. Distortions of metal atom cores

In 1994 we turned to the problem of the quantitative failure of VSEPR to predict the geometries of molecules containing metal atoms found in the third and following periods. Specifically, we considered the diflourides and dihydrides of Ca, Sr and Ba which experimentally are know to be bent and not linear as anticipated on the basis of the VSEPR model [32]. The VSEPR model assumes the inner core of electrons to be spherical and nonparticipatory in determining the geometry. Gillespie had already noted in his first book that the core of some of the heavier main group elements and some transition metals may be sufficiently polarizable so that, in certain molecules, it is distorted to a nonspherical shape that may influence the geometry of the molecule [2]. In the research that followed, we were led to invoke the phrase 'core distortions' to describe the cores of the Ca, Sr and Ba atoms

We review the findings only briefly here. The charges on the metal atoms vary from + 1.6 to + 1.8 e and the outer shell of charge concentration in every case corresponds to the $n-1$ quantum shell where n is the period in which the metal atom is found. Thus, in BaH_2 and BaF_2, the shell structure of the Laplacian indicates that it is the fifth quantum shell, or the outer shell of the core, that exhibits the CCs induced by the presence of the ligands. Here again one finds that two of the CCs found in the outer shell of the core are opposed to the ligands, the remaining two behaving as non-bonded CCs. Thus, one has a picture in which the four CCs form a tetrahedron with the ligands disposed opposite two of its faces, rather than being located at two of the apexes. The contrasting topology exhibited by the VSCC of a metal atom, as illustrated for BaH_2, and for a main group element for an approximately tetrahedral arrangement of CCs, is illustrated in Fig. 2.

In the linear geometries of the metal dihydride and difluoride molecules, each ligand is necessarily adjacent to a CC, a situation that, unlike that in main group molecules, is apparently destabilising. Instead, the most stable geometries for these molecules and those containing transition metal atoms is one in which the negatively charged ligands are adjacent to a face, or in some cases to an edge, of the polyhedron of CCs. A face contains a (3, + 1) CP in $L(\boldsymbol{r})$ and represents a position of minimum charge concentration in the surface of the polyhedron. A (3, − 1) CP defining an edge, is the next most deficient region of charge concentration. Thus, it is an empirical observation (the experimentally determined Laplacian distributions exhibiting the same behaviour [33]) that negatively charged ligands in transition metal and heavy metal molecules, seek out positions of minimum charge concentration in the VSCC of the metal atom.

This work was followed by a more extensive investigation, wherein the distortions present in the metallic cores of the fluorides, oxofluroides, hydrides and methanides of vanadium(V), chromium(VI) and molybdenum(VI) were determined [34]. To illustrate the general findings, we consider only VF_5 which exhibits the VSEPR anticipated trigonal bipyramid geometry, and VH_5 and VMe_5 which possess square pyramidal geometries. In the trigonal bipyramid geometries of all three molecules, the five CCs present in the VSCC of vanadium are arranged in the form of a trigonal bipyramid. While the axial ligands are necessarily adjacent to a CC in this arrangement, the equatorial ligands are not so restricted and instead one finds the three equatorial CCs to be ligand opposed in all cases. The bonding is more ionic in VF_5 than in the hydride and methanide molecules and the CCs found in the fluoride are correspondingly smaller and more tightly bound. Apparently because of the larger size of the CCs in the more covalently bonded hydride and methanide molecules, these molecules adopt the square pyramide geometry in which all five of the CCs are ligand opposed. In this case, the CCs are arranged in the form of a square pyramid but the ligands are adjacent to the faces of the pyramid, i.e. adjacent to the regions of charge depletion. Since the normals to the faces also exhibit a square pyramidal arrangement, inverted with respect to that defined by the CCs, the result is a square pyramidal geometry. Not only are the CCs opposed to the hydrogens and methanide groups larger than those associated with the fluorines, the VSCCs of both the hydrogen and carbon atoms themselves possess CCs of relatively large magnitude. For hydrogen, the CC corresponds to one localized on the proton and for a carbon, to a CC within its VSCC on the bonded side. Thus, C and H appear as donor atoms and are ligand opposed, while F which does not have a bonded CC in its own VSCC, can appear adjacent to a CC on the metal atom.

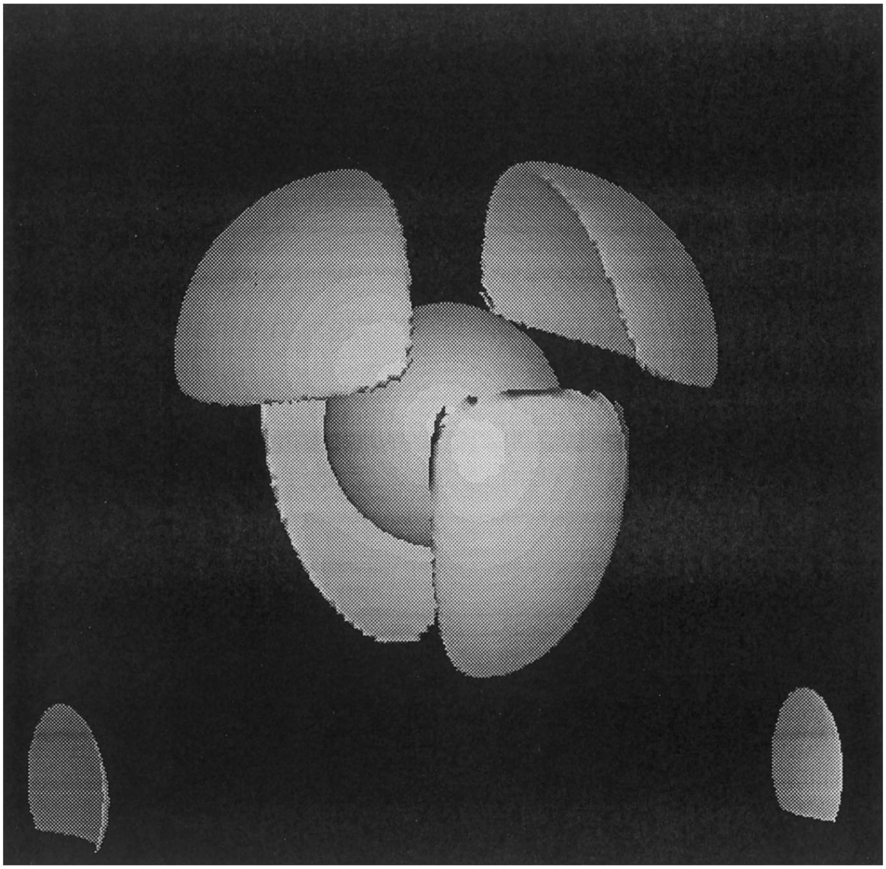

Fig. 2. Envelope map of $L(\boldsymbol{r})$ for BaH_2. The envelopes are for a constant value of $L(\boldsymbol{r})$ and define regions within which electronic charge is concentrated, i.e. $L(\boldsymbol{r}) > 0$. The inner sphere envelops the (essentially undistorted) outermost shell of charge concentration of the inner core, i.e. the fourth quantum shell of the Ba atom. The envelopes in the VSCC of Ba, its fifth quantum shell, define four CCs with an approximately tetrahedral arrangement, two of which are opposed to the protons whose positions are denoted by the partial envelopes that appear in the two lower corners of the diagram. For a main group molecule with four CCs in the VSCC of the central atom, such as H_2O or H_2S, the protons would appear in the two upper corners and the same two CCs would then be bonding CCs and the remaining two, non-bonding CCs.

It has been found that the geometries of some transition metal molecules can be predicted using an effective core potential for the metal atom. This procedure would appear to contradict the principal finding obtained from the topology of $L(\boldsymbol{r})$ that the distortions of the core of the metal atom is the determining factor in fixing the geometry of such molecules. However, this apparent contradiction has been resolved [35] by noting that one must distinguish between the definition of a core using the shell structure defined by $L(\boldsymbol{r})$ and one based on the orbital model employed in the construction of an effective core potential.

The topology of $L(\boldsymbol{r})$ has established that the outer shell of the core is the valence shell—the shell where the chemistry occurs—for a transition metal or heavy metal atom. It has also shown that like main group molecules, the VSCC of a bonded metal atom exhibits a characteristic number of CCs and that the geometrical arrangement of these CCs appears to determine the most stable geometry of the molecule using a set of VSEPR-like rules. That is, the most stable geometry is the one which maximizes the separation between the CCs or between the ligands and the CCs, just as for the main group molecules, but with one most important difference; what correspond to bonded CCs in the VSCC of a main group atom, are now situated so as to be opposed to rather than adjacent to the ligands. In main group molecules, the ligands are adjacent to some or all (depending on the number of unshared pairs of electrons) of the apexes of the characteristic polyhedron defined by the CCs within the VSCC of the central atom. In molecules containing a metal atom, the ligands are adjacent to some or all of the faces of the same polyhedron, the sites of local charge depletion within the VSCC of the metal atom. Through the continuing study of the topology of $L(\boldsymbol{r})$ we are gaining familiarity with the form of the core distortions and developing a VESPR-like model to predict and rationalise the observed geometries of molecules containing metal atoms. What is lacking is a complete understanding of why the minimum energy geometry of a main group molecule is determined by attaching ligands to the vertices of the polyhedron of CCs, while in a metal containing molecule, the energy is minimized with the ligands appearing in the faces of the polyhedron.

6. The relation between L(r) and the pair density

The electron localization function (ELF) of Becke and Edgecombe [36] is also used to determine and display the spatial localization of electrons. It is based on a function $\Delta(\boldsymbol{r}) \geq 0$, that equals the difference between the positive definite form of the kinetic energy density, and the kinetic energy density calculated in terms of the electron density $\rho(\boldsymbol{r})$ assuming the density to describe a one-electron system [37]. In other words, $\Delta(\boldsymbol{r})$ is a function that vanishes when the kinetic energy at $\boldsymbol{r}$ behaves as though only one electron of each spin contributed to the density at that point. Tal and Bader [36] had earlier shown that the requirement for $\Delta(\boldsymbol{r})$ to vanish for a region of space is the same as that required to maximally localise the density of the Fermi hole and thus, create a localized electron pair. Becke [38] was able to relate $\Delta(\boldsymbol{r})$ to the conditional pair density for same-spin electrons, a quantity discussed below, and ELF was created as an empirical function to embody the measure of electron localization provided by $\Delta(\boldsymbol{r})$. ELF varies between zero and one: when ELF equals unity (obtained when $\Delta(\boldsymbol{r}) = 0$), one electron pair contributes at $\boldsymbol{r}$ and when ELF approaches zero, many pairs contribute. Since ELF, through $\Delta(\boldsymbol{r})$, has a direct tie to the pair density, a comparison of the topologies of ELF and $L(\boldsymbol{r})$ would determine whether $L(\boldsymbol{r})$ bore the same relation to the pair density as does ELF. An extensive comparison of the topologies of $L(\boldsymbol{r})$ and ELF, covering a wide spectrum of interactions including transition metal molecules, demonstrated that in nearly all cases, the two functions predict the same topological structures—that they are homeomorphic in terms of the number and relative arrangement of the electron domains they define [15]. Thus, as indicated earlier by the correlation found between the magnitude of the CCs within the VSCC with the degree of localization of the Fermi density [26], the CCs denote regions of partial condensation of the pair density, but a direct relationship with the pair density was still lacking.

Finding the direct relationship between the topology exhibited by $L(\boldsymbol{r})$ and the pair density grew out of a discussion held over lunch between Professor Gillespie and myself. We had returned once again to the original work of Lennard-Jones on the pair density [4] and its relationship to the paper just completed on the comparison of the topologies of ELF and $L(\boldsymbol{r})$ which used a pair function called the conditional same-spin pair density, $\delta^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2)$. This is the density obtained by dividing the same-spin pair density $\rho^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ in Eq. (6), by $\rho^{\alpha}(\boldsymbol{r}_1)$, the spin density of the reference electron at $\boldsymbol{r}_1$. The result is the density of α,α pairs between the points $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ when one α electron is known to be at $\boldsymbol{r}_1$. As seen from Eq. (6) this density is given by the difference between the spin density at $\boldsymbol{r}_2$ and the magnitude of the density of the Fermi hole $h^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2)$, i.e. $\delta^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \rho^{\alpha}(\boldsymbol{r}_2) - |h^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2)|$. On thinking about this function we realised that it should reflect the very spatial localisations of the pair density that were discussed and pictured by Lennard-Jones and used by Ron in his early papers on the VESPR model. Assuming that $\delta^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ did exhibit maxima, such maxima should show where the density of the other α electrons is most likely to be found, relative to some fixed position of the reference electron. In a closed-shell system the conditional pair densities for both spins are identical and a localization of α density implies an equal localization of β density. From this point on the symbol $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ will denote the sum of the conditional densities for both spins.

Within a short time Dr Platts wrote the program for the display of the same-spin conditional pair density and Dr Heard wrote one for determining its critical points. The core electrons of the central atom are very localized and their spin density dominates the display of $\delta^{\alpha\alpha}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ for any positioning of e* outside of the core. Thus, in this initial investigation, the core orbitals were omitted from the calculations. The investigation demonstrated that the topology of the conditional same-spin pair density defined in this manner is so successful in recovering the geometrical models associated with differing numbers of electron pairs, that we proposed that the function be called the Lennard-Jones function or LJF [39]. The digonal, trigonal, tetrahedral, bipyramidal and octahedral patterns of the local maxima displayed by LJF demonstrate that these patterns are indeed the most probable arrangements for corresponding numbers of electron pairs, as proposed in the VSEPR model and as recovered in the topology of $L(\boldsymbol{r})$. We thus, observed a remarkable similarity in the patterns of spatial pairing of electrons exhibited by the maxima in $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ for given positions of the reference electron and $L(\boldsymbol{r})$, including the patterns generated by the ligand opposed CCs found in transition metal molecules. In addition, in those cases where differences were found between the topologies of ELF and $L(\boldsymbol{r})$ [15], the topology of $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ agreed with that displayed by $L(\boldsymbol{r})$. Since ELF is an empirical expression, the predicted positions of its maxima, while exhibiting the same angular behaviour as those in $L(\boldsymbol{r})$, are always predicted to occur at larger distances from the nucleus. The CCs in $L(\boldsymbol{r})$ and the maxim exhibited by $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ on the other hand, exhibit nearly identical radii.

In retrospect, $L(\boldsymbol{r})$ and $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$, when referred to the total density, must exhibit the same defining behaviour for the number and location of the regions of partial pair condensation. The agreement between the topology of $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ away from the position of the reference electron, and $L(\boldsymbol{r})$ is greatest when the reference electron is placed near a CC of $L(\boldsymbol{r})$ or in its vicinity along the line linking it to the nucleus, the line determining its angular orientation with respect to the remainder of the density [38]. Under these conditions of maximum localization of the Fermi hole of the reference electron, $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ approaches the total density in regions removed from the region of localization centred on $\boldsymbol{r}_1$. That is, when the Fermi density is strongly localized about a given position $\boldsymbol{r}_1$, the conditional density for electrons removed from this position will simply reduce to the sum of the two spin densities at $\boldsymbol{r}_2$, i.e. to $\rho(\boldsymbol{r}_2)$. Under these conditions, the Laplacian of $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$, including the core contributions, in regions removed from $\boldsymbol{r}_1$, must approach the Laplacian of the density and the local maxima evident in the Laplacian of $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ should coincide with the CCs of $L(\boldsymbol{r})$. This is illustrated in Fig. 3 which displays the Laplacian of the electron density in PH_3 and the Laplacian of $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ including the core orbitals, for the reference electron placed at a proton where $L(\boldsymbol{r})$ exhibits a maximum. This figure is taken from work currently in progress by G. Heard and myself [40]. While $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ with core orbitals included, does not in general exhibit local maxima, its fine structure is revealed by its Laplacian, as is that of the density. The plane illustrated shows that the Laplacian of $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ exhibits local maxima at positions nearly coincident with those of the bonded and non-bonded CCs of $L(\boldsymbol{r})$. While the form of $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ and its Laplacian change as the position of the reference electron is changed, $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ leaves its fingerprint in the density, i.e. whatever form the density assumes when $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2) \Rightarrow \rho(\boldsymbol{r}_2)$, that form remains. One could imagine using $\delta(\boldsymbol{r}_1, \boldsymbol{r}_2)$ to determine $\rho(\boldsymbol{r}_2)$ throughout space by varying the position $\boldsymbol{r}_1$ of e*. Thus, the two-electron information regarding the spatial pairing of electrons is transmitted to the Laplacian of the one-electron density $\rho(\boldsymbol{r})$ and we have established that the Laplacian of the density provides a mapping of the essential pairing information from six- to three-dimensional space.

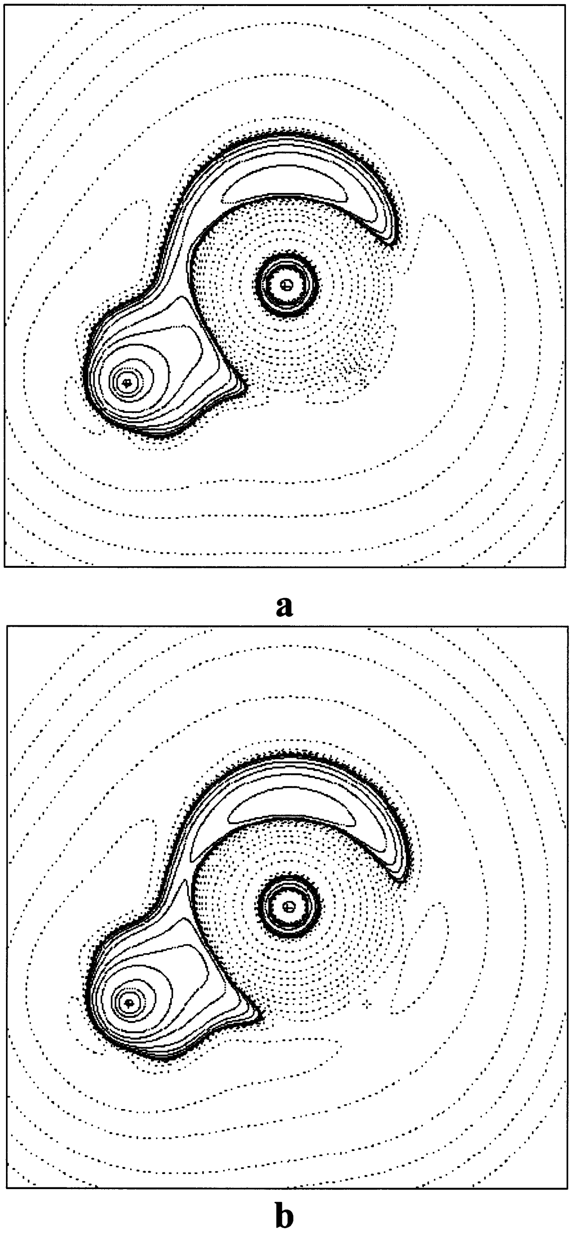

Fig. 3. Maps of the Laplacian of the electron density and (a) of the conditional pair density for electrons of both spins, (b) for a plane of the PH_3 molecule containing a single proton, a σ_v symmetry plane. The solid contours are for regions where each function is concentrated, i.e. $L(\boldsymbol{r}) > 0$ in the case of the density, the dashed contours for regions where the functions are depleted. The reference electron for the conditional density display is placed at the position of an out-of-plane proton, where $L(\boldsymbol{r})$ exhibits a very pronounced local maximum, as demonstrated in (a). Thus, when the Fermi density of the reference electron is very localized, as it is in this case, then the conditional density approaches the electron density outside of the region of localization and the Laplacians of the two functions not only display the same local maxima at the same locations, but approach one another in value.

7. In retrospect

My intellectual journey with Professor Gillespie, that started so long ago and unfortunately did not begin in earnest until some years later, has been exciting and rewarding. It is not overly romantic to associate a scientist's life with a quest for an understanding of some part of nature's behaviour, one that can carry through his or her professional life. I have had, and continue to have the privilege of sharing such a quest with Professor Gillespie in our combined efforts to relate chemistry to the properties of the one- and two-electron densities. Professor Gillespie now makes extensive use of both densities in his continuing research directed at obtaining an understanding of molecular geometry, research that has recently resulted in the formulation of the ligand close-packing model [41] (with charges defined by the theory of atoms in molecules [22]).

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