Liversidge Research Lecture

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WHERE ARE THE ELECTRONS?

R. D. BROWN

The Royal Society of New South Wales

Ronald Drayton Brown

RONALD DRAYTON BROWN 1927 - 2008

Ronald Drayton Brown was born on October 14 1927 at Melbourne. After secondary education at Wesley College, he studied at the University of Melbourne, graduating B.Sc. in 1946. He then worked under the supervision of Dr. F. N. Lahey on acridone alkaloids and graduated M.Sc. in 1948. In 1950 he went with a National University Travelling Fellowship to King's College, London to work with C.A. Coulson on theoretical physics (effect of dielectric media on electronic spectra) and graduated Ph.D. in 1952. From 1952 to 1953 he held an assistant lectureship at University College (London) where he devised the Z-index theory of electrophilic substitution and, with J.H. Ridd, established the mechanism of diazonium coupling of imidazole. He then returned to the University of Melbourne to take up a position as Senior Lecturer in Chemistry, where he continued his experimental studies of diazonium coupling, and created a theoretical chemistry research group. In 1959 he was promoted to the position of Reader, and in 1959 he was appointed to the Foundation Chair of Chemistry at Monash University where he remained Head of the Department until 1992. He was also Director of the Centre for High-Resolution Spectroscopy and Opto-Electronic Technology. In 1964, study leave was spent in the USA, where he visited all of the leading centres of microwave spectroscopy research, and some theoretical chemistry groups.

His research interests have included developing theories of chemical reactivity for π-electron systems and this led to the VESCF method still used in molecular mechanics software. The extension to all-valence-electron calculations and properly antisymmetrised wavefunctions, originally developed to help understand the weak central bond in N_2O_4, slightly predated Pople's CNDO publications. A major school of microwave spectroscopy evolved in the 1960s and, in the 1970s, spread to embrace studies of molecules in space via radioastronomy. The latter led to both independent and collaborative astronomical studies involving radiotelescopes located at Kitt Peak (USA) , Arecibo (Puerto Rico), Onsala (Sweden), and Nobeyama (Japan). Among many discoveries perhaps the most interesting were the detection of gas-phase tricarbon monoxide and benzyne, the former also being detected in space. He retired in 1993 with the title Emeritus Professor, and has maintained research interests in collaboration with Dr. Peter Godfrey.

Ron Brown's extramural activities included Chairmanship of the National Committee for Chemistry and of the Committee on Science Policy. He also served as a member of the Sub-Committee on Chemical Education, and of UNESCO's Australian National Advisory Committee's specialist Committee. In 1963 he was President of the Victorian Branch of the RACI. In 1982 he was appointed by the International Astronomical Union to an international panel of consultants to advise on the desirability of creating a new commission on bioastronomy. He subsequently served as a member of the Organizing Committee of the commission (1982-1997), and was President for Commission 51

(Bioastronomy) from 1991-1993. He also served in various capacities for the International Union of Pure and Applied Chemistry between 1987 and 1997.

Honours and Awards (Pre-2001)

1948 Masson Medal, Royal Australian Chemical Institute (RACI)

1951 Rennie Medal, RACI

1959 H.G. Smith Medal, RACI

1959 David Syme Prize for research, University of Melbourne.

1961 Edgeworth-David Medal, Royal Society of New South Wales

1965 FAA

1969 Liversidge Research Lecture, Royal Society of New South Wales

1977 Royal Society of Victoria Medal

1988 Matthew Flinders Lecture, Australian Academy of Science

Biographical Source: personal communication

Obituary: F.P. Larkins, "Ronald (Ron) Drayton Brown AM, FRACI, FAA 14 October 1927 to 31 October 2008," *Chemistry in Australia*, 2009, **76** (1), 21-22.

Biographical Memoir: P.D. Godfrey, F.P. Larkins, J.M. Swan, **"**Ronald Drayton Brown 1927-2008", *Historical Records of Australian Science*, 2010, **21**, 191-220.

Scientific Publications of R.D. Brown

Between 1948 and 2000, R.D. Brown published some 312 papers: in recent years most of these were on microwave spectroscopy.

WHERE ARE THE ELECTRONS?*

R. D. BROWN

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When chemists come to interpret their observations in terms of the atomic molecular theory of matter one of the first questions to be settled is: where are the electrons? This may arise at a relatively elementary level in balancing a redox equation or using the octet rule to derive a structural formula. At more sophisticated levels of valency theory the interpretation of virtually all chemical and physical properties of compounds depends heavily on a knowledge of how the electrons are distributed over a molecule.

This knowledge of the distribution of electrons being so basic to chemistry, it is instructive to consider how profound is this knowledge. There is much to suggest that chemists are fairly well informed on this matter. For example, many papers in the current literature contain confident pictures of electron distributions in molecules (as portrayed by drawing in covalent bonds, charges on atoms, etc.) and of electronic shifts accompanying chemical reactions. Basic textbooks describe ionic and covalent bonds, and more advanced texts discuss bonds in transition element compounds with synergic back donation of π-electrons strengthening the metal ligand σ-bond and simultaneously ameliorating its polarity. What is rarely pointed out is that all of these descriptions of electron distributions are based upon sets of rather sweeping assumptions, the validity of which is open to question. Indeed, when looked into closely it is surprising how little we know beyond reasonable doubt about where the electrons are in molecules. I propose to try to illustrate the current fight with ignorance and to do it at two levels. Firstly, I want to consider how much we know about the gross distribution of electrons when we merely try to assess the net charges that should be associated with each atom. Secondly, I want to consider to what extent we can distribute the atomic electron densities among the different atomic orbitals associated with each atomic nucleus. Thus at the first level I shall consider the overall distribution of electrons in formaldehyde and other molecules. At the second level I shall touch on questions such as: are the 3d orbitals of sulphur used to any appreciable extent to accommodate valence electrons in SF_6? Let us start with the problem of gross charges.

If we are interested in the charge distribution in formaldehyde, for example, a textbook is likely to indicate the electronic structure as shown in Fig. 1. We should first ask what this means. The only aspect of charge distribution that is observable in principle is the total

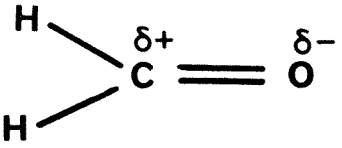

FIGURE 1. - Typical textbook representation of the charge distribution informaldehyde.

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*Liversidge Lecture delivered before the Royal Society of New South Wales, July 17th, 1968. Reproduced by permission of the Royal Society of New South Wales from *J. Proc. Roy. Soc. N.S.W.*, 1968-9, **102**, 73-81.

electron density at various points in space, $|\varphi^2|$; in practice only certain derived quantities that I shall mention later have been observed.

Very accurate, theoretical information is available for some diatomic hydrides (Bader *et al.*, 1967), as shown in Fig. 2. To gain some impression of the changes that accompany bonding, it is useful to inspect the differences between these charge distributions and those for the separate uncharged atoms. Figure 3 shows the difference maps.

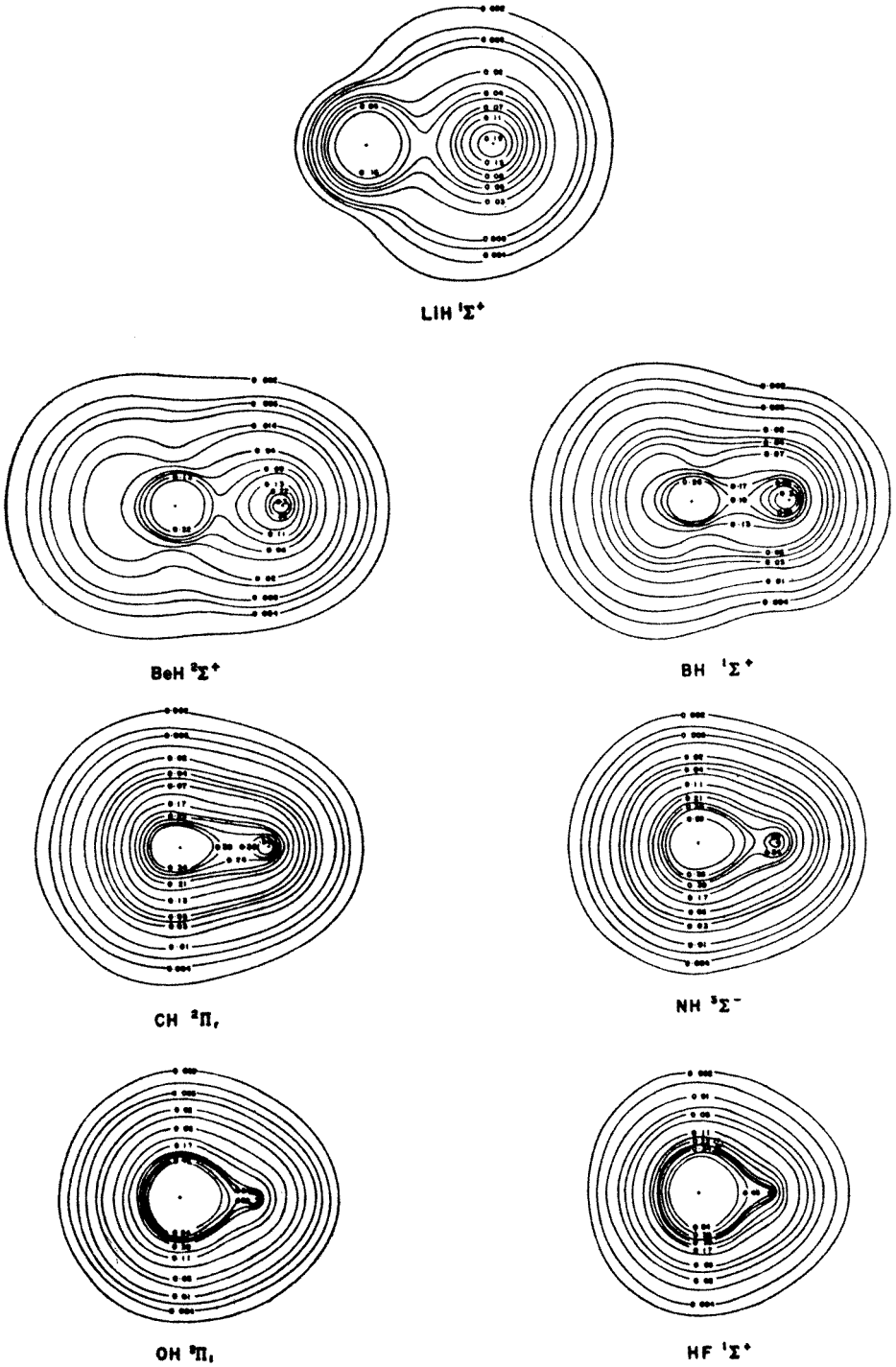


FIGURE 2 - Total molecular charge density contours for the first-row diatomic hydrides (atomic units; H nucleus is on the right in each case). The innermost contours encircling the heavy nucleus have been omitted for the sake of clarity.
(Reproduced, with permission, from Bader *et al.*, 1967.)

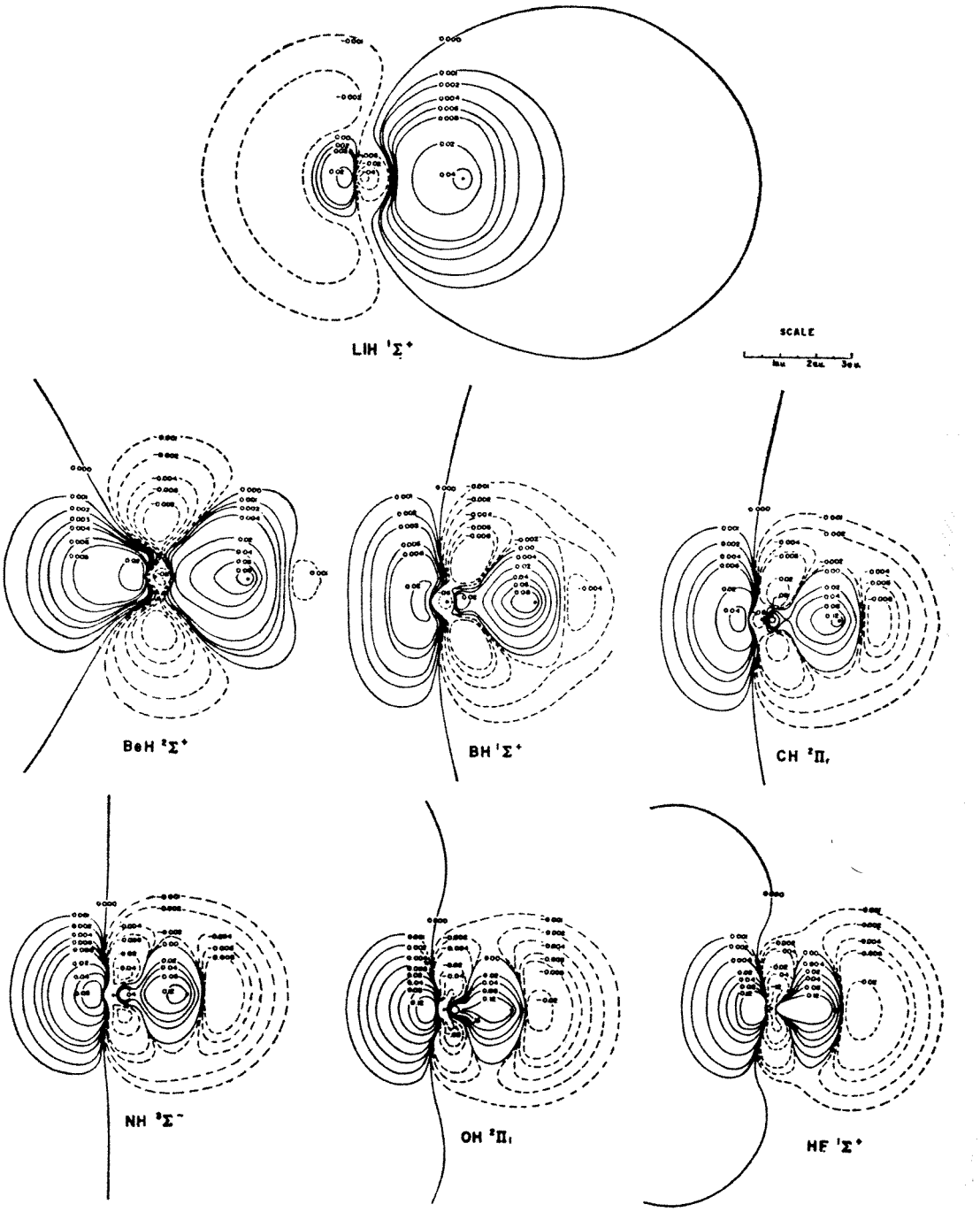


FIGURE 3. Contour maps of the electron density difference (molecule-separate atoms) in atomic units for the first-row diatomic hydrides (H on right in each case).
(Reproduced, with permission, from Bader *et al.*, 1967.)

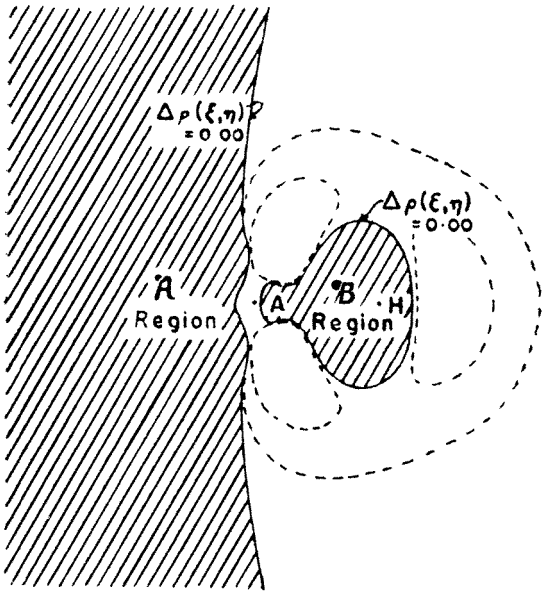


FIGURE 4. Definitions of A and B regions.

Figure 4 shows an analysis into integrated charge transferred to bonding and to lone pair regions. We note that these data parallel our classical views that LiH is mainly ionic and that bonding becomes more and more covalent as we proceed across the periodic table. However, the appearance of the opposite ionic character, e.g. in HF, is hard to discern. One does not know just how this would reveal itself in the charge density contour maps - HF looks like the fluoride ion with a "pimple" representing the hydrogen.

*Total Charge Migration in Diatomic Hydrides as Determined by Density Difference Maps**

AH	Charge Increase in Region A	Charge Increase in Region B
LiH	0.01	0.55
BeH	0.11	0.35
BH	0.20	0.16
CH	0.20	0.16
NH	0.20	0.16
OH	0.22	0.19
HF	0.24	0.22

*These figures were obtained by numerical integration using a grid of 0.02 a.u. Regions A and B are defined in Figure above.

Reproduced from J. *Chem. Phys.*, 1967, **47**, 3381, Fig. 2 (6) and Table 11.

In order to associate different portions of the integrated charge density with different atoms, we must have some agreed scheme of partitioning. One could perhaps imagine surfaces dividing up all space into regions and associating each region with one of the atoms, but this presents difficulties in deciding where to place the partitions. However, instead it has proved more convenient to construct approximations of ψ using sets of functions associated

with each of the atoms. We have become accustomed to call these functions atomic orbitals. It is straightforward to dissect the approximate $|\psi^2|$ algebraically in a way that yields occupation numbers for each of the atomic orbitals, and if we add up the occupation numbers for all of the orbitals on a particular nucleus we obtain the electron density for that atom. I do not want to go into details about this analysis, but rather to make two points. Firstly, there is wide freedom in choosing the sets of atomic orbital functions used to represent ψ and it is even permissible to go to the extreme of using functions centred on only one of the atomic nuclei. In the latter case one might deduce that all the electrons are on one atom! The lesson to be learned is that the conclusion that we draw about electron distributions will depend to some extent on the kind of atomic orbitals that we decide to use to build up the molecular eigenfunction. Secondly, if we use only a relatively simple set of atomic orbitals to obtain an approximate ψ the resultant analysis of electron distribution will be affected to some extent because we have not analysed the exact wave function.

Let me now give you a survey of what some of the best available current wavefunctions for various small molecules have to say about charge distributions as analysed in terms of molecular orbitals, so that you can compare these with the popular mythology of textbooks. While I am doing this you may be asking how reliable are these wavefunctions, and later in this talk I shall point out some experimental data that can be used to test these wavefunctions.

First let us look at formaldehyde. The calculated electron distribution (Peters, 1963; Cook and McWeeny, 1968) is shown in Fig. 5.

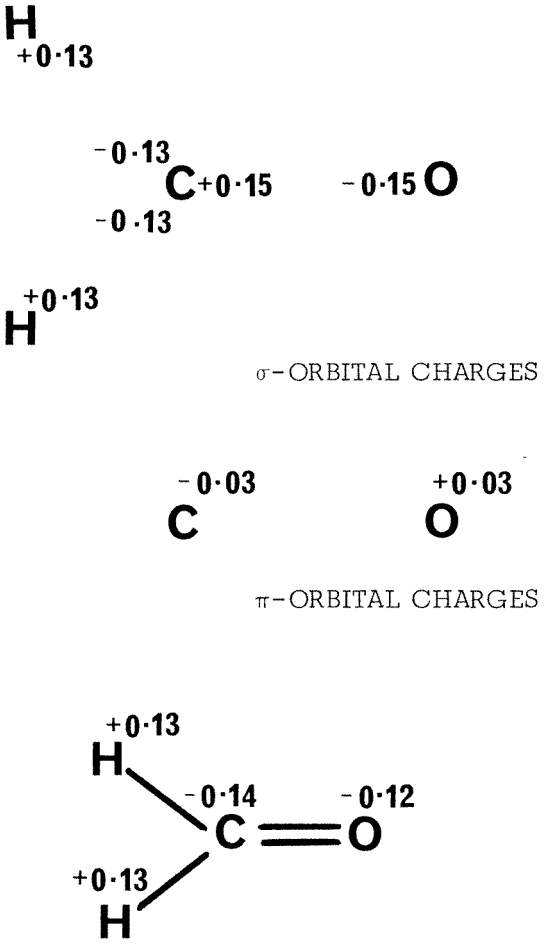


FIGURE 5. Charge distribution in formaldehyde (Peters, 1963)

Notice that the qualitative trends do not agree with popular belief as represented in textbooks because the total carbon charge (-0.14) is more negative than the oxygen charge (-0.12). The overall polarity must be largely laid at the door of the positive net charges on the hydrogens, with an additional contribution from the atomic dipole of the oxygen. The carbonyl polarity is not that normally believed. It is possible that this is an artifact of the particular wavefunction used here, but several other recent approximate wavefunctions for formaldehyde display the same qualitative result.

As a second example (Veillard *et al.*, 1967), let us consider the prototype of the so-called dative bond BH_3<---NH_3 (Fig. 6). From comparison with analogous calculations on BH_3 and on NH_3 separately, we see an interesting electron drift accompanying the association of the parts, quite different from that deduced by octet rule methods. In particular, the net charge on the boron is virtually unchanged by bond formation and a rather curious alternating drift of electrons, involving the hydrogens attached to boron, has occurred.

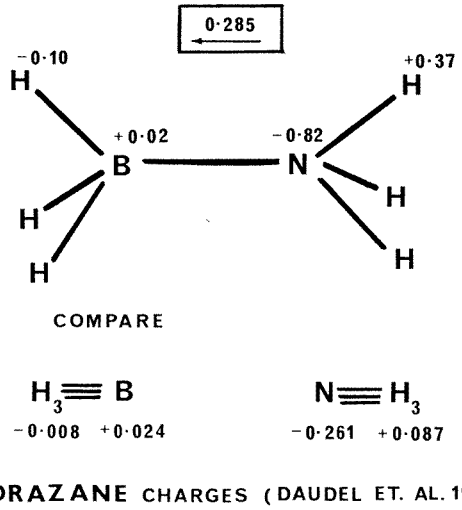


FIGURE 6 - Charge distribution in borazane (Daudel *et al.*, 1967).

Somewhat similar distributions of electrons have been found in other saturated systems (Pople and Gordon, 1967). Thus when a fluorine substituent is introduced into a saturated hydrocarbon (Fig. 7) the immediate effect is to generate a net positive charge on the attached carbon, but the more distant influences seem to alternate in sign, not to fall monotonically! It is possible that a new set of rules for σ-electrons drifts will be called for in place of the beloved inductive shifts of organic chemistry.

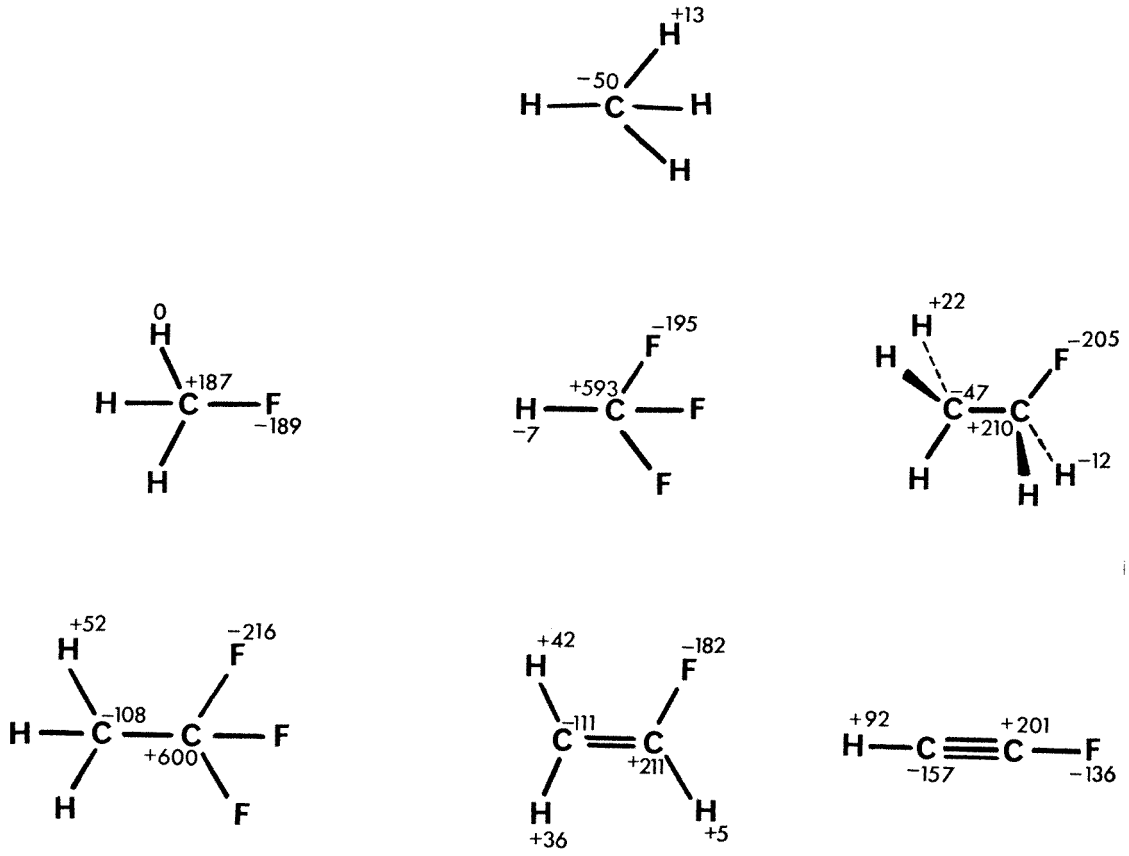
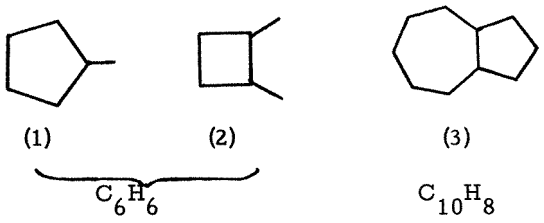


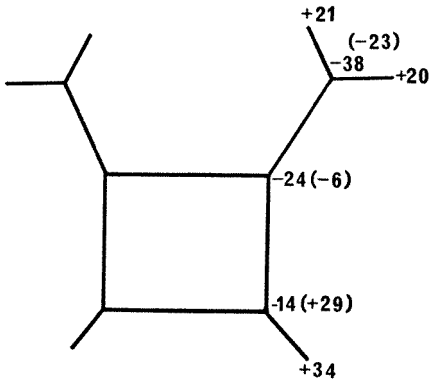
FIGURE 7. Charge distribution in fluorocarbons (milliprotonic units).

Let me now turn to another example that has been of particular interest to us at Monash: that of non-alternant hydrocarbons. The interest centres largely around three conjugated cyclic hydrocarbons: fulvene (1), dimethylenecyclobutene (2) and azulene (3) :



All three hydrocarbons have a substantial dipole moment - of the order of ten times the magnitude of analogous aromatic hydrocarbons. We ask: to what should the polarity be attributed?

The initial proposal was that for conjugated hydrocarbons containing odd membered rings - so-called non-alternants - the distribution of π-electrons is non-uniform (Coulson and Rushbrooke, 1940), and this leads to the appreciable polarity. More recently it has been predicted (Brown and Burden, 1966), and then confirmed experimentally (Brown *et al.*, 1967), that dimethylenecyclobutene, though an alternant, should have an uneven distribution of π-electrons and so be polar. In attempting to account in more detail for the polarity, it has been suggested that the σ-electrons also contribute to the polarity, particularly because the hydrogen atoms are appreciably charged. Let us see now what the best available wave functions imply, first with dimethylenecyclobutene (Fig. 8).



DIMETHYLENE CYCLOBUTENE net charges (e/1000)
π net charges in parentheses

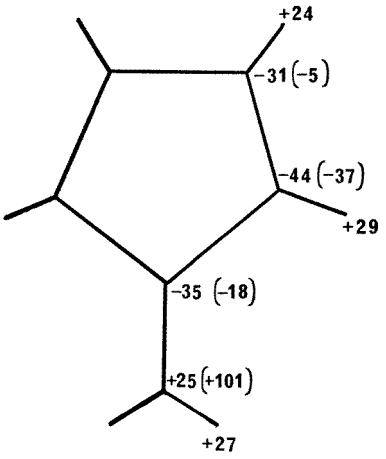
Dipole moment

σ densities	0.254 D	↑
σ hybridization	0.231	↓
π densities	0.607	↓
TOTAL	0.584 D	↓
experiment:	0.61_8 D	

FIGURE 8. Dimethylenecyclobutene.

Here the implication is that the polarity must be ascribed primarily to π-electrons, the total σ-electron effect being a minor contribution. The agreement of the calculated value with the observed dipole moment is impressive. However, let us next turn to fulvene (Fig. 9). Here the qualitative story is similar to that of dimethylenecyclobutene, but the agreement with the experimental dipole moment data is less satisfactory. Hitherto the value, deduced from measurements in solution on substituted fulvene, was 1.1D. We have been engaged in a precision measurement on fulvene vapour by microwave methods and now find that the dipole moment is 0.44D.

In the case of azulene, the story is still less satisfying. The theoretical computations again imply that the polarity stems essentially from a non-uniform π-electron distribution (Fig. 10) but the theoretical value of the moment is depressingly far from a recent precise experimental value for azulene vapour (Tobler *et al.*, 1965). Thus it is clear that the presently available electronic wavefunctions for molecules like azulene are not all that we would like; but perhaps the qualitative indication of the relative polarity contributions from σ- and, π-electrons are sound.

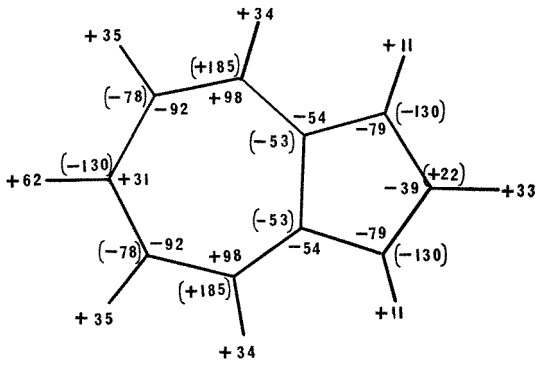


FULVENE net charges (e/1000)
π net charges in parentheses

Dipole Moment

σ densities	0.260 D	↑
σ hybridization	0.086	↓
π densities	1.061	↓
TOTAL	0.887 D	↓
experiment:	0 44 D	

FIGURE 9. Fulvene



AZULENE NET CHARGES (e/1000)
π net charges in parentheses

Dipole Moment

σ density	0.809 D	→
σ hybridization	0.589	←
σ total	0.220	→
π density	3.446	←
TOTAL	3.226 D	←
experiment	0.79_6 D	

FIGURE 10. Azulene.

Now let us move on to somewhat more complex systems involving larger atoms. First, a few words about SF_6, PF_5, etc. Textbooks will sometimes describe the bonding as involving sp^3d^2 or sp^3d hybrids on the central atom these hybrids being used to form somewhat polar covalent bonds with the fluorine ligands. Alernatively, a structure involving ionic-covalent resonance among the various ligand positions and only the s and p orbitals on the S (or P), has sometimes been advocated. On close analysis, it proves difficult to decide whether the d-orbitals of the central atom are involved in the bonding because of the variety of functional forms that can be written down as representing a d-orbital. However, if we agree that by

orbitals we mean the various functions that are obtained by solving the H-atom problem so that

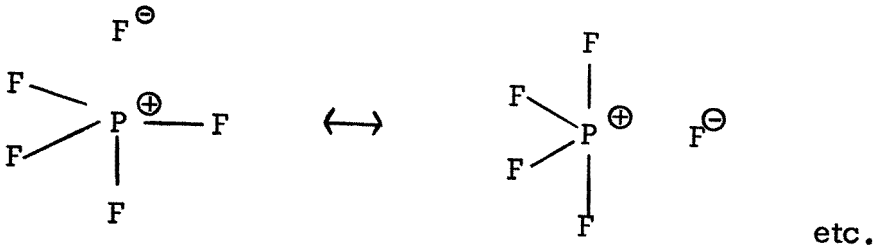
$$f_{3d} = N.\rho^2 e^{-\rho/3}.Y_{2m}(\theta,\phi) \qquad (\rho = \zeta r/\mathrm{a})$$

(Y_{2m} : Spherical harmonic of order 2)

then the best function that has so far been derived for these molecules (by Dr. Peel) implies (Table 1) that the 3d orbitals are insignificantly occupied in SF_6, PF_5, SF_4, CIF_3, etc.

TABLE 1
Orbital Occupation Numbers

	PF_5	SF_4	CIF_3
3s	1.09	1.53	1.75
3p	2.15	2.67	3.80
3d	0.13	0.22	0.19



Another example involving a transition element atom is the electronic structure of the permanganate ion. In recent years a number of investigations of the electronic structure of tetrahedral anions have been published. The most elaborate of these (Table 2), obtained by Mr. James at Monash, implies that the 4s and 4p orbitals of Mn are but little occupied, the central atom using its 3d orbitals almost exclusively to accommodate valence electrons.

TABLE 2
Orbital Occupation Numbers

	MnO_4^-		CrO_4^{2-}	
	MCZDO	CNDO	MCZDO	CNDO
3d	5.70	6.71	5.84	6.56
4s	0.08	0.10	0.04	0.10
4p	0.00	0.02	0.00	0.15

These calculations on systems containing larger atoms are necessarily rather less rigorous than those on smaller systems and it is possible that the picture could be changed somewhat by still more elaborate calculations. However, it seems unlikely that the qualitative description will be noticeably altered. The overall picture that we are left with is one rather different from the classical description in current textbooks.

Returning now to smaller systems, let us consider what kind of experimental tests can usefully be applied to molecular wavefunctions. Because of the widespread use of the variation theorem for computing wavefunctions, a habit of mind has grown of asking what kind of energy expectation value derives from the function ψ.

$$\langle E \rangle = \left\langle \psi \middle| \hat{H} \middle| \psi \right\rangle / \langle \psi | \psi \rangle$$

The more negative $\langle E \rangle$ is the better function ψ is considered to be. However, the energy test depends critically on how well ψ accounts for electron correlation. If we are interested in electron distribution this correlation effect is less important and so functions that give only moderate values of $\langle E \rangle$ can sometimes give a good picture of the overall electron distribution in the molecule. It therefore seems better to apply different tests, namely the following:

$\langle r \rangle = \left\langle \psi \middle| \hat{r} \middle| \psi \right\rangle / \langle \psi | \psi \rangle$ derived from dipole moment.

$\langle r^2 \rangle$ - relative to molecular centre of gravity - derived from molecular g factor and susceptibility.

$\langle 1 / r \rangle$ - relative to a nucleus with $I \neq 0$ - derived from spin rotation constant and chemical shift for a nucleus of non-zero spin.

Etc.

Most of these quantities are particularly taxing to determine experimentally, but values are starting to emerge for a few simple molecules as a result of the efforts of Flygare and his co-workers at Illinois. Values that he has just published for formaldehyde (Hüttner *et al.*, 1968) are shown in Tables 3 and 4. These provide a very stringent test of electronic wavefunctions, and so far even the best published wavefunctions for formaldehyde show deficiencies. However, further experimental work of this kind and further computational effort on wavefunctions must surely produce a steady increase in our knowledge of how the electrons are distributed in molecules.

TABLE 3

Experimental Mean Values for Electrons in Formaldehyde

$\langle x^2 \rangle$	$3.2 \pm 0.3 \times 10^{-16}$ cm.^{2}
$\langle y^2 \rangle$	$5.2 \pm 0.3 \times 10^{-16}$ cm.^{2}
$\langle z^2 \rangle$	$11.4 \pm 0.3 \times 10^{-16}$ cm.^{2}

TABLE 4

Experimental Values (A.U.) of Various Electronic Properties of Formaldehyde

q_{zz}(O)	-0.703
q_{yy}(O)	-1.687
$r_0 \cos\theta$	19.495
x^2	11.3
y^2	18.7
z^2	40.8
z_O/r^3_O	1.261
z_C/r^3_C	1.262
$q_{\alpha\alpha}$(D)	-1.446
$q_{\alpha\beta}$(D)	-0.178
$q_{\beta\beta}$(D)	0.650
α_D/r^3_D	2.059
β_D/r^3_D	0.266
$1/r_H$	6.12

Maybe if you are kind enough to invite me again to Sydney some years hence to talk on "Where Are the Electrons?" I may be able to give you more confident answers such as textbooks now give. At present the honest answer is: "We do not know for sure but we have some suspicions!"

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