Chemical Interpretations of Molecular Wavefunctions

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1 Introduction

The calculation of reasonably accurate wavefunctions for moderately large-sized molecules is now completely routine. For many authors the primary aim of performing such wave-mechanical calculations is to evaluate physical properties such as the dipole moment of a molecule, the electric field gradient at a nucleus, spectroscopic constants, and the like. However, from the early days of quantum mechanics others have repeatedly attempted to 'interpret' the wavefunction Ψ (or to be rigorous Ψ^2: the reader will recall that whilst Ψ itself has no direct physical meaning, $\Psi^2 \, \mathrm{d}V$ is taken to represent a *probability*). When Ψ is a many-electron wavefunction, $\Psi^2 \, \mathrm{d}V$ becomes $\Psi^2 \, \mathrm{d}\mathbf{r}_1 \, \mathrm{d}s_1 \, \mathrm{d}\mathbf{r}_2 \, \mathrm{d}s_2 \ldots \mathrm{d}\mathbf{r}_n \, \mathrm{d}s_n$ (where $\mathbf{r}$ and s indicate space and spin variables of the n electrons) and gives the probability of an instantaneous configuration of *all* electrons. The most common physical properties, however, depend on the probability per unit volume of finding a *single* electron (no matter which) at a given point $\mathbf{r}$ in space: this is given[1] by

$$P(\boldsymbol{r}) = n \int_{\boldsymbol{r}_1 = \boldsymbol{r}} |\Psi|^2 \, \mathrm{d}s_1 \, \mathrm{d}\boldsymbol{r}_2 \, \mathrm{d}s_2 \ldots \mathrm{d}\boldsymbol{r}_n \, \mathrm{d}s_n \tag{1}$$

The factor n arises because the n electrons are indistinguishable. The quantity P is often referred to as the 'electron density' since for many purposes the electron distribution may be treated as a smeared-out charge of density P (electrons per unit volume).

The aim of such an investigation is to try to recover chemically useful information from Ψ, to see why it takes a particular form for a given molecule, and to rationalize how Ψ changes from molecule to molecule; in other words, to obtain by reliable techniques answers to the questions posed by elementary descriptive valence theory. In this review we shall describe some of the more popular methods available for such an investigation, and then show by means of two examples what sort of chemical information wave-mechanical calculations can give. We could mention here that some methods lead to information that can be directly compared with experiment (such as electron-density maps) whilst others, such as population analysis, do not. In general there is no single 'best' method of analysis: the different methods tend to be complementary.

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[1] R. McWeeny and B. T. Sutcliffe, 'Methods of Molecular Quantum Mechanics', Academic Press, New York. 1971.

2 Techniques

Density Maps.—For a preliminary survey of the electron density in a molecule one can make a pictorial representation of the calculated electronic charge density. The most common choice is a contour diagram (a map with lines joining points of equal electron density), although such diagrams do not usually give much information; Figure 1 shows a contour map calculated from a Self Consistent Field Molecular Orbital (SCF-MO) wavefunction for the tetrahedral molecular ion $LiNH_3^+$; this shows the electron density surrounding the Li

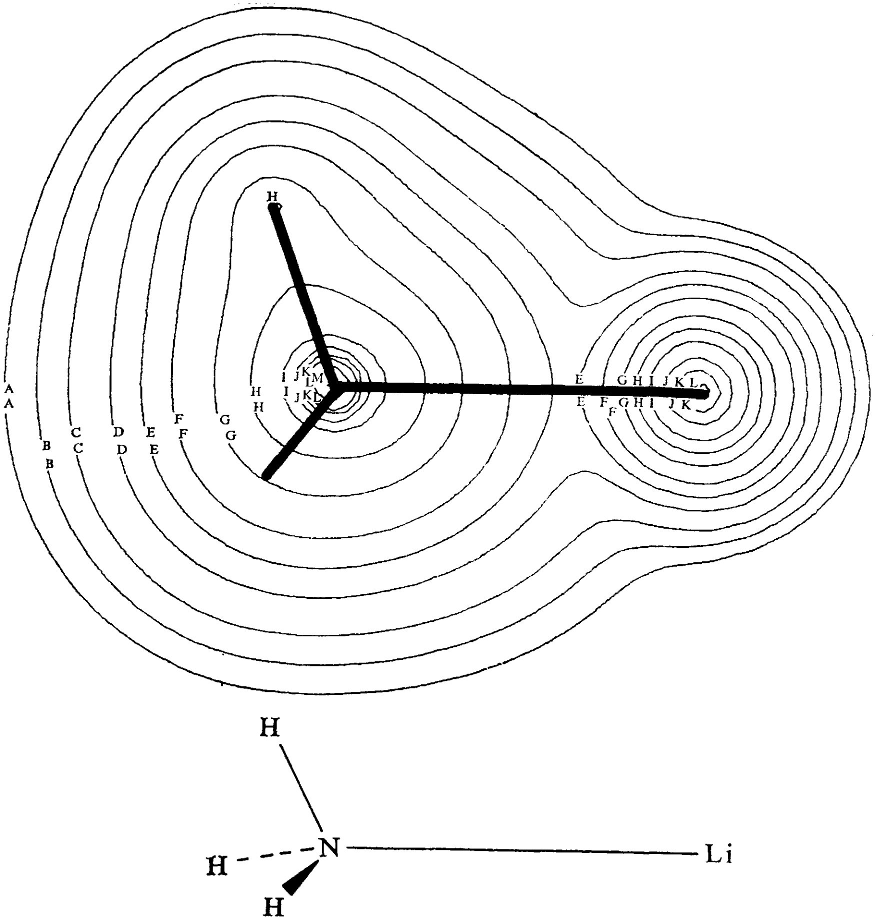

Figure 1 *Total SCF-MO electron density map for the molecular ion* H_3NLi^+ *drawn in a plane containing* N, Li, *and one of the* H *atoms. Contours are drawn corresponding to values of the electron density as follows:* A = 0.002, B = 0.004, C = 0.008, D = 0.020, . . ., N = 20.000 *electrons*

nucleus overlaps relatively little of the electron density surrounding the N; thus the Li—N bond is weak. The H nucleus, on the other hand, is closely embedded in the contour rings surrounding the N atom. A qualitative examination of the diagram therefore reveals that it is difficult and probably pointless to attempt to identify a fragment corresponding to a free H atom, but an Li^+ fragment can be identified quite readily.

These electron-density maps provide a theoretically calculated quantity which can be compared with the results of *X*-ray diffraction. A whole volume of the *Transactions of the American Crystallographic Association*[2] is devoted to reporting a symposium on the subject. Among other papers, Cade discusses the probable accuracy of quantum-mechanical calculations and Coppens gives alternative choices of theoretical and experimental quantities to compare.

MO Density Diagrams.—Many molecular wavefunctions are currently calculated using the SCF-MO scheme, where the total electron density is the sum of the densities in the occupied MO's. Thus one can attempt to understand the total electronic density by examining density diagrams for the individual MO's.

A good example is the discussion by Buenker and Peyerimhoff[3] of the geometries of H_2X molecules. They were testing the theory of Walsh,[4] according to which the apex angle and bond length of such molecules can be predicted by considering the variation of a loosely defined theoretical quantity often referred to as an 'orbital energy' with the apex angle. Walsh's arguments are based on simple concepts pertaining to the effect of atomic orbital (AO) mixing on the energy of the MO; conclusions about the geometry are then made easily on the basis of which orbitals are occupied in a particular electronic configuration. The theory *does* give gross features correctly but cannot explain, for example, why the isoelectronic molecules BH_2^- and NH_2^+ should have very different bond lengths. By looking at the orbital density plots (amongst other things) Buenker and Peyerimhoff were able to rationalize the experimental facts much more convincingly.

Obvious disadvantages of this kind of approach are (i) the number of orbitals can quickly become unmanageable, many MO's often being involved in the bonding with even inner shells having to be considered, and (ii) MO's are often delocalized over the entire molecule, making conclusions about particular bonding regions difficult to obtain unless one is prepared to transform such MO's into localized MO's.

Density Difference Maps.—The electronic rearrangement which takes place when atoms combine to form molecules is rather subtle. It is natural to attempt to depict this rearrangement by subtracting the superimposed free-atom electron densities from the molecular density. Bader, Keaveny, and Cade[5] have developed

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[2] *Trans. Amer. Cryst. Assoc.*, 1972, **8.**

[3] R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, 1966, **45**, 3682.

[4] A. D. Walsh, *J. Chem. Soc.*, 1953, 2260.

[5] R. F. W. Bader, I. Keaveny, and P. E. Cade, *J. Chem. Phys.*, 1967, **47**, 3381.

this technique in a large number of systematic applications, but there is a major conceptual difficulty in the not-infrequent case that one or more of the atoms has a partially filled shell in its electronic ground state. A typical example is NF$_3$; the N atom has a unique ^2S ground state but the F atoms each have orbital configurations s^2p^5 which give spatially degenerate ^2P states. Apart from the spin degeneracy there is thus a 3^3-fold spatial degeneracy. Which combination of these spatial wavefunctions should one take as reference states in evaluating the atomic densities?

Figures 2a and 2b, which show two density difference maps for NF$_3$ in a plane

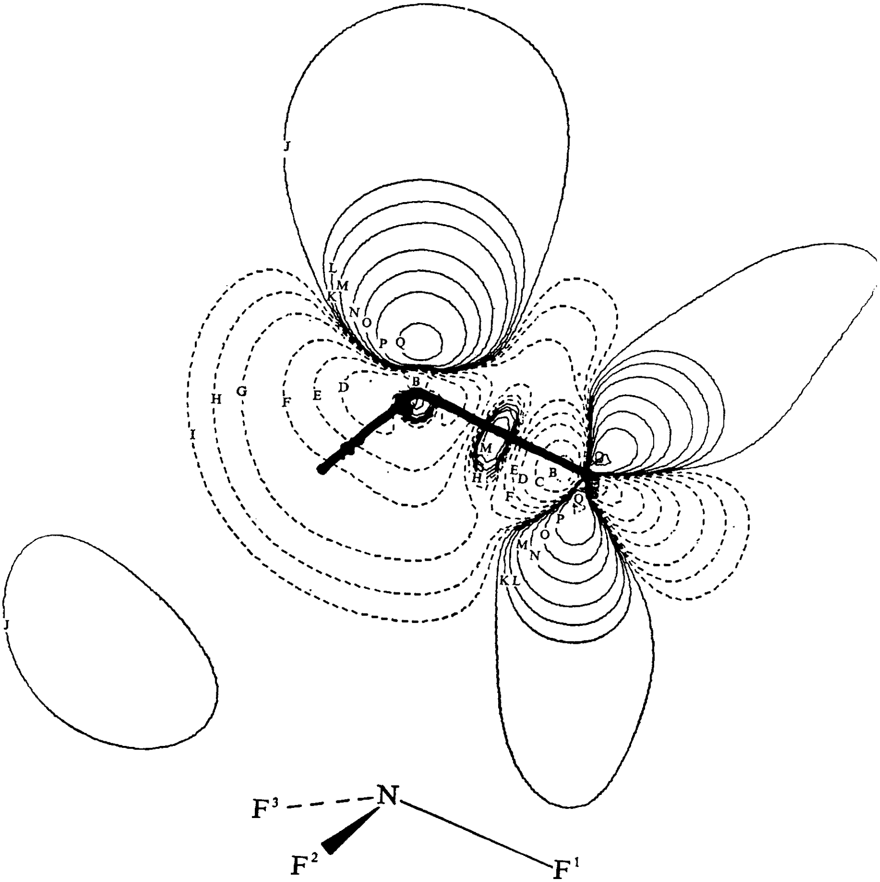

Figure 2a *SCF-MO density difference map for* NF$_3$ (*with pyramidal geometry*) *drawn in a plane containing the* N *and one of the* F *atoms. This map is the electron density of the molecule minus that of 'spherically averaged' atoms. Contours are drawn corresponding to values of the electron density as follows:* A = −0.800, B = −0.400, C = −0.200, D = −0.800, . . ., J = 0, . . ., S = +0.800 *electrons*

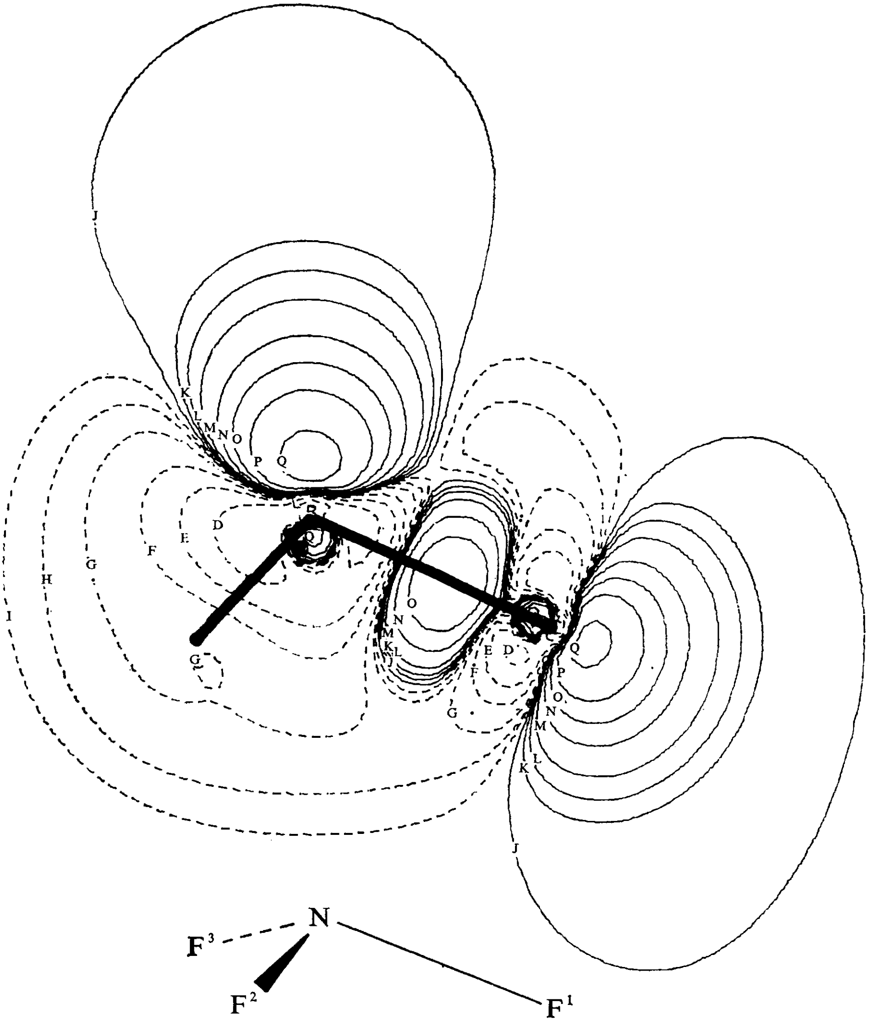

Figure 2b *As for Figure* 2a, *except that this map is the electron density of the molecule minus valence states*

containing the N and one F atom (F^1) illustrates the problem; the top map has as reference state a 'spherical average' of the P_1, P_0, and P_{-1} states for each F whilst the bottom map has a 'valence state' in which the p_0 orbital on each F is singly occupied (we should mention that a *valence state* is not necessarily a true spectroscopic state, rather the state of an atom 'in the molecule').

The top map shows how electron density is built up in the p_π orbital on F^1 at the expense of the p_σ orbitals, the bottom map telling a very different story as there is now a substantial build-up of electron density between N and F_1. The two maps are thus quite different and the decision as to which reference state to use is clearly subjective: it depends on one's preconceived ideas about the bonding in a molecule. One obvious class of compound for which this choice is rather more objective is ionic molecules such as Li_2S, when one naturally compares the molecular density with that of the superimposed *ions*, Li^+ and S^{2-} in this case.

Integration over a Region of Space.—Our qualitative discussion of Figure 1 suggested that in favourable circumstances, one might expect to identify spatial regions corresponding to atomic fragments. Several recent attempts to achieve this quantitatively deserve mention: Bader and Beddall,[6] for example, divide up the total electron density into atomic regions in which the Virial Theorem $\langle V\rangle = -2\langle T\rangle$ is satisfied by the kinetic T and potential V energy operators over the region. They have reported results for LiF, LiO, and LiH, together with their positive ions, the aim being to find atomic 'invariants' such as an atomic charge density and potential which can be transferred from molecule to molecule.

Ransil and Sinai[7] have suggested two ways in which the electron density can be partitioned numerically: in the first, contours enclosing one nucleus only (see for example Figure 1) are taken as defining 'atomic' regions, those enclosing two or more nuclei regions of 'delocalization'. In their second scheme regions are classified according to the density difference map and the population in each region is found by numerical integration.

Such techniques are not widely used presumably because of the difficulty of performing the numerical integrations. Another method, which avoids such integrations, will now be described.

Population Analysis.—The aim of population analysis is to divide up molecules into 'atoms' and 'overlap regions' which can be easily characterized by the amount of electronic charge density they contain. If the wavefunction was calculated using a set of atomic orbitals (a so-called *basis set*) which are well localized in space on atoms A, B, . . . then it is useful to split up the charge density P into atom and overlap terms

$$P(\boldsymbol{r}) = \sum_{\mathrm{A}} P^{\mathrm{A}}(\boldsymbol{r}) + \sum_{\mathrm{A<B}}\sum P^{\mathrm{AB}}(\boldsymbol{r}) \qquad (2)$$

where P^{A} is the *net density* of atom A and P^{AB} the *overlap density* of the atoms A and B. These densities are defined in terms of the atomic orbitals and a matrix P which readers familiar with the Hückel treatment of π-electron molecules will recognize as the matrix of charges and bond orders, with the sums running only

$$P^{\mathrm{A}}(\boldsymbol{r}) = \sum_{k}\sum_{l} \Phi_k(\boldsymbol{r})\, P_{kl}\, \Phi_l(\boldsymbol{r}) \qquad (3)$$

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[6] R. F. W. Bader and P. M. Beddall, *J. Chem. Phys.*, 1972, **56**, 3320.

[7] B. J. Ransil and J. J. Sinai, *J. Chem. Phys.*, 1967, **46**, 4050.

over those AO's Φ_t which are centred on atom A. There is a related formula for P^{AB}. To obtain the amounts of electronic charge in the atom and overlap regions these densities are integrated to give the corresponding *populations* p^{A} and p^{AB}. Given a MO wavefunction and the values of the overlap integrals between the AO's (which have to be calculated anyway, as part of the SCF-MO procedure) it is an easy matter to calculate the populations p^{A} and p^{AB}.

The three basic assumptions of population analysis are as follows: (i) the partitioning described by equation (2) is chemically useful; (ii) useful information is retained when the densities are integrated to give populations; (iii) it is valid to divide the overlap population p^{AB} into parts and assign the parts to the two atoms contributing

$$p^{AB} = \nu_A{}^{AB} + \nu_B{}^{AB} \qquad (4)$$

For a given atom A the sum of the fractions $\nu_A{}^{AB}$, $\nu_A{}^{AC}$, . . . with reference to all other atoms B, C, . . . is called the *valence population* ν_A, the sum of ν_A and the atom population p_A being the *gross population* q_A. In the Mulliken scheme,[8a] which is the most widely used, the fractions of equation (4) are assumed equal: *i.e.* the electron density in a given overlap region is allotted equally to the two atoms involved. (It is interesting to note that this approximation was used in 1952 by McWeeny,[8b] in a crystallographic application; he showed that *X*-ray scattering from an aggregate of bonded atoms could be dealt with in exactly the same way theoretically as when no interactions were present by replacing the atomic scattering factor by 'effective' scattering factors. In the example given, H_2, the effective scattering factor related to a charge distribution characterized by the Mulliken gross population of each H atom).

Figure 5 (p. 92) shows a contour map of the overlap density function $P^{LiF}(\mathbf{r})$ for LiF. It can be seen that the Mulliken assumption is not very realistic for such a molecule, as the overlap density is very unequally shared. There are, however, alternative schemes such as one we will refer to as the Löwdin–Daudel scheme[8c] in which the overlap population is divided up according to the bond dipole – the bigger the bond dipole the more unequal the sharing of p^{AB}.

Population analysis tends to be used in two main ways and the relative importance of assumptions (i), (ii), and (iii) is different in either case. Often the 'atomic charges' $Z_A - q_A$, where Z_A is the nuclear charge number and q_A the gross population, of atom A are taken as a succinct description of the major features of the charge distribution and in particular its polarity. A good example is the study by Veillard[9] of lithium acetylene, LiCCH, where the gross populations of the σ- and π-electrons are presented separately and compared with those in acetylene. The molecule is predicted to be highly ionic with no definite Li—C bond but rather an ionic association between the Li^+ ion, carrying a positive charge of 0.78, and the CCH^- ion. There is also a small back-donation of electron

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[8] (*a*) R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833; (*b*) R. McWeeny, *Acta Cryst.*, 1952, **5**, 463; (*c*) P.-O. Löwdin, *J. Chem. Phys.*, 1953, **21**, 374; (*d*) R. Daudel, A. Laforgue, and C. Vroelant, *J. Chim. phys.*, 1952, **49**, 545.

[9] A. Veillard, *J. Chem. Phys.*, 1968, **48**, 2012.

density from C to Li *via* the π-electrons. When population analysis is used in this way assumption (i) is less important than (ii), *e.g.* it is impossible from the gross populations to distinguish an atom whose electron density is approximately spherical (*e.g.* Li^+ in Figure 1) from one that is not: population analysis can say nothing about the lone-pair in ammonia.

The second main use of population analysis is to discuss the nature and strength of bonding, p^{AB} being taken as a measure of how the strength of a bond can be attributed to contributions from atoms A and B. An example is the study by Cruickshank *et al.*[10] on KrF_2 where the overlap populations p^{KrF} and some component MO populations are discussed. In this use of population analysis assumption (iii) is not required but (i) and (ii) are vital.

Population analysis is a particularly simple process to perform but the indices calculated depend directly on the atomic orbitals used in the calculation, as equation (3) shows. This can give rise to the problem of basis set dependence. It sometimes happens that two basis sets give strikingly different population indices but otherwise give results in good agreement with each other. Mulliken[11] has discussed this problem and given criteria for choosing basis sets which are likely to lead to 'reasonable' populations. A basis set is said to be *physically balanced* if it has sufficient flexibility to describe all parts of the molecule well, and *formally balanced* if each atom has an adequate number of atomic orbitals centred on it. Only formally balanced basis sets are likely to lead to numerical populations that are meaningful (thus a wavefunction for HF calculated using only F atomic orbitals could be physically balanced if enough atomic orbitals were used, but it is not formally balanced and one would not attach much importance to the resulting gross populations of 10 for F and 0 for H).

There are, however, examples in the literature of bad disagreement between calculations on the same molecule using rather similar basis sets of AO's.[12]

As an alternative to dividing up the overlap population between two contributing atoms one can reject assumptions (ii) and (iii) and just investigate the net and overlap densities P^A and P^{AB} directly rather than their integrals. Bader and Henneker[13] have used this approach to study the degree of ionicity in LiF: a 'classical' model of the ionic bond was taken as two charged spheres each slightly polarized by the electric field of the other, this electron density distribution then being compared with an SCF-MO one by calculating the forces exerted by the two distributions on the nuclei.

Again, Roby[14] argues that it is not very useful to attempt to split up the electron density in the bonding region at all: the electron density is genuinely *shared* by the participating atoms. Thus he is able to give a very different definition for the atomic charges *etc.*, which seem to have none of the disadvantages of the Mulliken-type schemes.

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[10] G. A. D. Collins, D. W. J. Cruickshank, and A. Breeze, *Chem. Comm.*, 1970, 884.

[11] R. S. Mulliken, *J. Chem. Phys.*, 1962, **36**, 3428.

[12] R. S. Mulliken and P. Politzer, *J. Chem. Phys.*, 1971, **55**, 5135.

[13] R. F. W. Bader and W. Henneker, *J. Amer. Chem. Soc.*, 1965, **87**, 3063.

[14] K. R. Roby, *Mol. Phys.*, 1974, **1**, 81.

Summary.—The methods discussed can be conveniently classified into those which investigate electron densities directly (total densities, difference densities, and the like) and those methods which attempt to characterize regions of space numerically, usually by the amount of electron density contained within the regions. Population analysis is probably the easiest method to use as the calculation is rather simple. For this reason it is almost certainly the most widely used method; it *can* give useful information when applied to a series of related molecules or when used in conjunction with other methods of analysis, but its predictive value is small when used in isolation on a single molecule.

In Section 3 we show how the different methods are used together to give information about the bonding in LiF, then in Section 4 the differences between the electronic structures of NH_3 and $LiNH_3^+$ are discussed.

3 How Ionic is LiF?

Throughout this section all calculations refer to an *isolated* LiF molecule, *i.e.* LiF(g) and not LiF(c). Before giving any quantitative results it is useful to discuss what might be expected, in line with the general aim of the review.

Clearly LiF will be strongly ionic, approximating to Li^+F^-, and so to get any insight into its bonding it is necessary to compare LiF with Li^+ and F^- ions since a comparison with the neutral atoms would show a predominant charge transfer from Li to F and consequent expansion of the fluorine L shell, which would mask any more subtle effects.

We could imagine then a 'zero-order' description of LiF comprising two undistorted (spherical) ions at their equilibrium distance: a better approximation would result if polarization of the charge clouds were admitted, *i.e.* the spherical ions would distort owing to their mutual repulsions. In orbital language the AO's of Li^+ would be allowed to vary owing to the nearby F^- ion and *vice versa*, but no MO formation would be allowed at this stage. Finally a covalent interaction could be allowed in which MO's were formed. We can summarize this as follows

1 spherical Li^+ and F^- ions (at equilibrium separation)
$\downarrow$ polarization
2 distorted Li^+ and F^- ions
$\downarrow$ covalence
3 LiF molecule

However, the problem of basis set dependence (see p. 86) must be remembered: if the Li^+ and F^- basis sets were sufficiently large the zero-order wavefunction would be a rather good approximation and we would ascribe nearly all improvements on going from 1 to 3 above to polarization and few to covalence. On the other hand, if we had used a very small basis set of AO's comprising 1*s* orbitals on Li and F with 2*s* and 2*p* on F we would find no polarization effects whatever.

This qualitative discussion suggests a number of questions: (i) how closely does a good SCF-MO wavefunction for LiF resemble the 'zero-order' model? (ii) is the polarization of Li^+ and F^- ions the same as one would find from classical electrostatics? (iii) is it possible to distinguish between polarization and covalence effects? With these questions in mind we now examine the various methods of analysis.

Ransil and Sinai[7] have calculated an electron-density map for LiF using an accurate SCF-MO wavefunction and by numerical integration over the closed contours around the Li and F nuclei (*i.e.* those contours which only encircle one atom) obtained the amounts of electron density in each atomic region. A comparison with the free-atom values shows that there has been a substantial amount of charge transfer on forming the molecule from F and Li *atoms*. An SCF-MO density difference map of the molecule minus undistorted ions is shown in Figure 3. Bader and Henneker[13] have discussed a similar map, together with one of the molecular density minus that of the free *atoms*. On comparing the two maps it turns out that the contours of Figure 3 are very much smaller than those on the (molecule – atoms) map, showing that LiF is much more nearly ionic than covalent. It should be remembered that Figure 3 is a density *difference* map

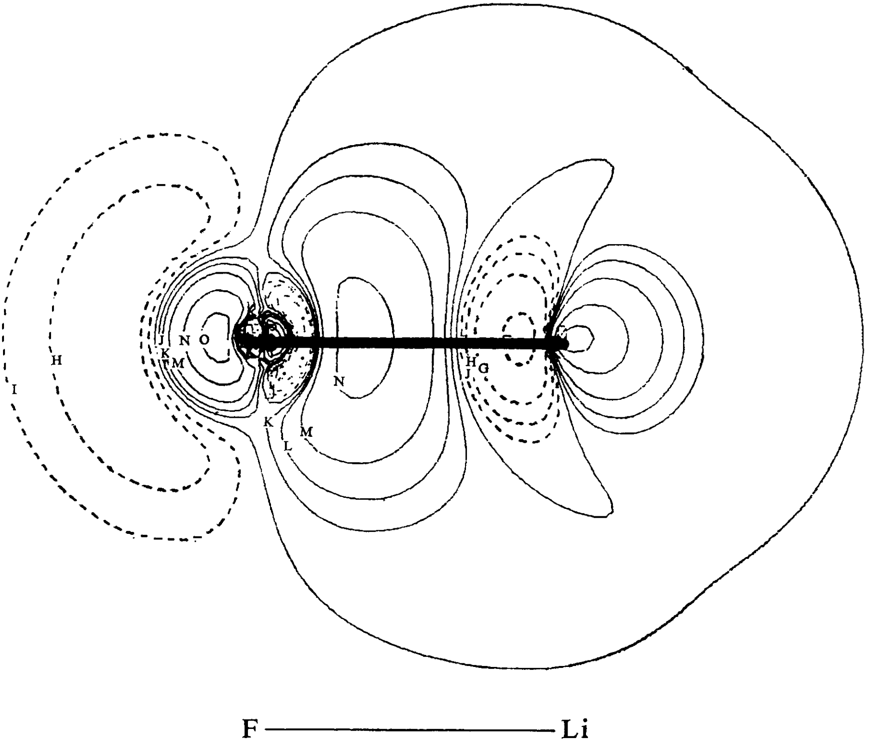

Figure 3 *Total SCF-MO density difference map for* LiF *with respect to free ions. Contours as Figure* 2a

and so a large positive contour around the F is not due to the initially greater amount of charge on that centre. It can be seen that electron density has been removed from the region in front of the Li^+ ion (*i.e.* the region close to Li and in between Li and F) and increased in the region behind it. We call this a dipole polarization. Overall the F electron density is slightly more contracted than that of a free F^- ion as the outer parts of the F density are negative, and is polarized towards the Li nucleus. The Li approximates very closely to a Li^+ ion slightly polarized away from F^-.

It is interesting to examine the density difference map for the π-electrons separately (Figure 4). Comparing Figures 3 and 4, and noting that both the shape

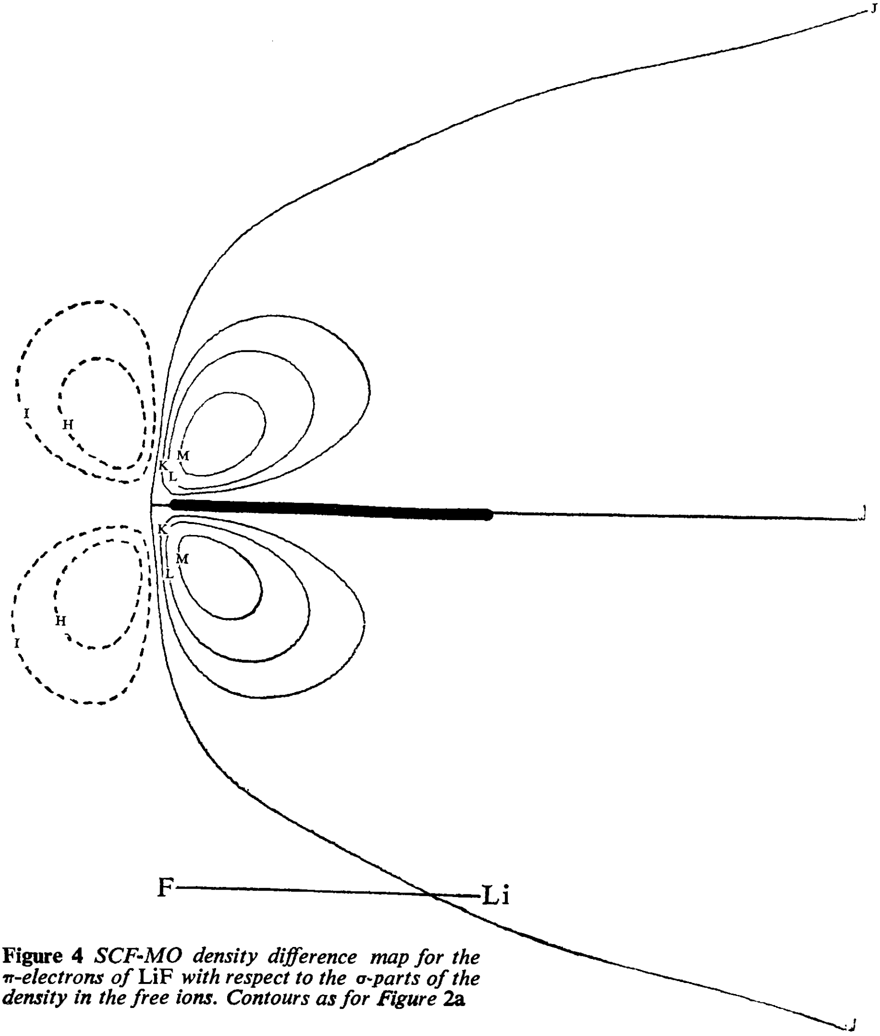

Figure 4 *SCF-MO density difference map for the π-electrons of* LiF *with respect to the σ-parts of the density in the free ions. Contours as for Figure* 2a

of the positive contours stretching out from F to Li and also the π-map contours are very similar in magnitude to the total, one might guess that the π-orbitals are more important than the σ-orbitals in moving electron density into the bonding region.

Some of the more significant statistics from population analysis studies of LiF with the SCF-MO wavefunctions used to calculate Figures 3 and 4 are shown in Table 1. Clearly, LiF is rather close to $Li^+(1s^2)$ $F^-(1s^22s^22p^6)$ as the gross populations show. The d-orbital gross population is very small but this does not mean that such polarization functions are unimportant. The overlap population p^{LiF} is small at 0.147 when compared with more typical values of *ca.* 0.7 for covalent molecules like NH_3; the σ contribution (0.059) turns out to consist of a negative term (due to overlap of Li s with F p_σ orbitals) close to Li and a positive term (mainly Li p_σ:F p_σ) rather polarized towards F. In the Mulliken scheme this overlap population is divided equally between Li and F as shown, but when the Löwdin–Daudel scheme is used, the σ-valence population of Li is negative (−0.009). Because of this very unequal sharing of the overlap density one would

Table 1 *Some indices from a population analysis study of an SCF-MO wavefunction for* LiF

<table>
<tr><th></th><th></th><th>Löwdin–Daudel</th><th>Mulliken</th></tr>
<tr><td colspan="4">(<i>a</i>) <i>Overall indices</i></td></tr>
<tr><td>p^{LiF}</td><td>σ</td><td colspan="2">0.059</td></tr>
<tr><td></td><td>π</td><td colspan="2">0.088</td></tr>
<tr><td></td><td>total</td><td colspan="2">0.147</td></tr>
<tr><td colspan="4">valence population of Li with respect to F</td></tr>
<tr><td></td><td>σ</td><td>−0.009</td><td>0.030</td></tr>
<tr><td></td><td>π</td><td>0.034</td><td>0.044</td></tr>
<tr><td>F</td><td>valence population</td><td>0.123</td><td>0.074</td></tr>
<tr><td></td><td>gross population</td><td>9.922</td><td>9.873</td></tr>
<tr><td>Li</td><td>valence population</td><td>0.025</td><td>0.074</td></tr>
<tr><td></td><td>gross population</td><td>2.078</td><td>2.127</td></tr>
<tr><td></td><td>atomic charge</td><td>0.922</td><td>0.873</td></tr>
<tr><td colspan="4">(<i>b</i>) <i>Gross populations</i></td></tr>
<tr><td>F</td><td>s</td><td>3.992</td><td>3.970</td></tr>
<tr><td></td><td>p_σ</td><td>1.971</td><td>1.956</td></tr>
<tr><td></td><td>p_π</td><td>3.953</td><td>3.942</td></tr>
<tr><td></td><td>d_σ</td><td>0.001</td><td>0.001</td></tr>
<tr><td></td><td>d_π</td><td>0.004</td><td>0.004</td></tr>
<tr><td>Li</td><td>s</td><td>1.984</td><td>2.014</td></tr>
<tr><td></td><td>p_σ</td><td>0.050</td><td>0.060</td></tr>
<tr><td></td><td>p_π</td><td>0.044</td><td>0.053</td></tr>
</table>

hesitate to ascribe to it any 'covalent' interaction: it represents rather a reorganization within the electron density of the F^- ion. On the other hand, the π overlap density is more nearly equally shared on the Löwdin–Daudel scheme with a valence population of F of 0.054 and Li 0.034, so one might tentatively suggest that there is evidence for a weak π-bond.

To re-emphasize the point regarding the allocation of overlap density between two atoms by equation (4), Figure 5 is a contour map for the overlap density $P^{FLi}(\mathbf{r})$. It shows that the electron density in the bonding region is really very unequally shared: there is a region of negative overlap near the Li nucleus and a smaller one near F. The region of positive overlap is well towards the F end of the bond and extends some distance from the internuclear axis as one might expect from the relative importance of the π-contribution.

By studying the gross populations in Table 1 of the individual atomic orbitals on F and comparing with similar quantities for a free F^- ion one can show that the outermost part of the F charge density has contracted considerably in going to LiF, both for $2s$ and $2p$ orbitals. On the other hand, the inner $1s$ orbital is not significantly affected.

To conclude, very good agreement between the descriptions of LiF is given by the various methods and the following points can be made. The electron density is reasonably well approximated by the superposition of ions but there are considerable distortions from the spherical shape. The polarization of the F^- ion is not exactly what one would expect classically, since the σ- and π- parts need to be considered separately and, whilst the distortion of the σ-density is essentially a polarization towards Li^+ and contraction, that of the π-density can best be described as a weak covalent bond.

4 How does $LiNH_3^+$ differ from NH_3? [15]

We have already discussed the total electron-density map (Figure 1) calculated for $LiNH_3^+$ from an accurate SCF-MO wavefunction (see p. 80), and decided that to a good approximation the molecule can be regarded as a combination of NH_3 with Li^+. The dipole moment μ calculated for the molecule at the particular geometry chosen for the SCF-MO calculation is 2.591 atomic units and if we write

$$\mu(LiNH_3) = \mu(NH_3) + \alpha R(Li—N) \tag{5}$$

where R(Li—N) is the Li—N bond distance, then α would be exactly 1 if no charge transfer or polarization had taken place. In fact $\alpha = 0.872$, showing that there has been a substantial charge transfer to Li from N. The atomic charges are calculated from a Löwdin–Daudel population analysis to be 0.937 (1.0), -0.345 (-0.187), and 0.136 (0.062) for Li, N, and H, respectively, with the corresponding free Li^+ and NH_3 values in parentheses. This shows the polarization of the NH_3 fragment, whilst the overlap population in the NH bond hardly changes, being 0.702 in $LiNH_3^+$ and 0.733 in NH_3. Again, the valence population of H is almost

[15] A. Hinchliffe and J. C. Dobson, *Theor. Chim. Acta*, 1975, **39**, 17.

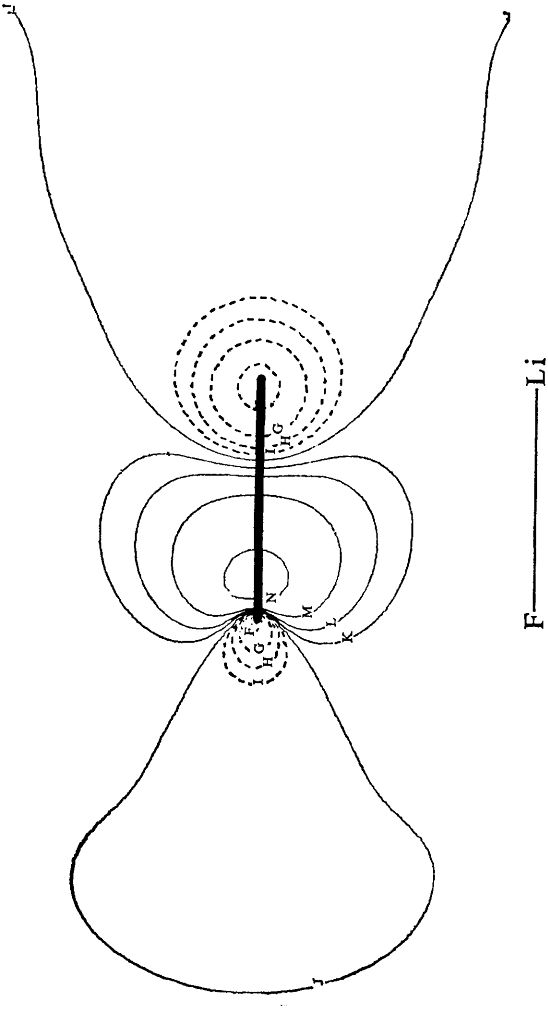

Figure 5 *SCF-MO overlap density function* $P^{\mathrm{LiF}}(\mathbf{r})$ *for* LiF. *Contours as for Figure* 2a

constant at 0.569 as compared with 0.594 in NH_3. That the Li—N bond is weak is shown by the overlap population of 0.108.

A density difference map calculated from the same SCF-MO wavefunction of molecule minus (NH_3 + Li^+) fragments is shown in Figure 6; like Figure 1 it is

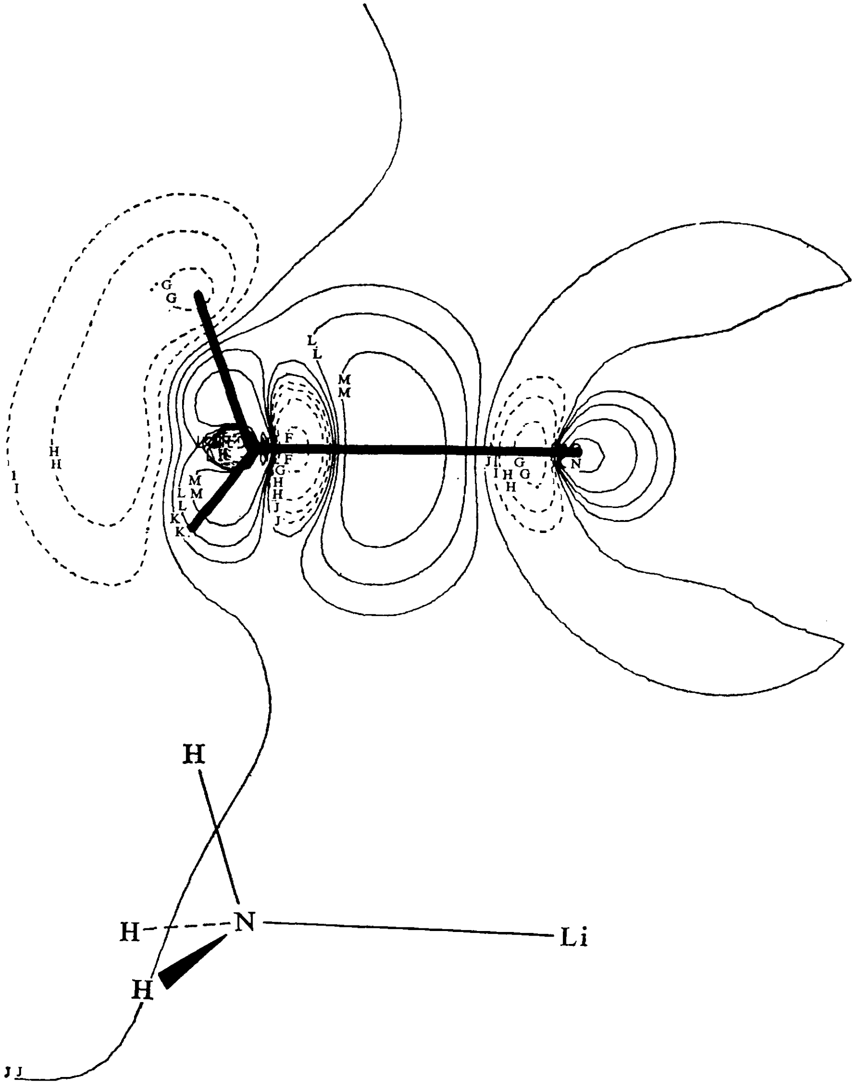

Figure 6 *SCF-MO density difference map of the molecular ion* H_3NLi^+ *with respect to* NH_3 and Li^+, *drawn in the same plane as Figure* 1. *Contours as for Figure* 2a

drawn in a plane containing Li, N, and one of the H atoms. It can be seen that the Li^+ exhibits the same dipole polarization as the Li in LiF (see Section 3), since electron density is removed from 'in front' of the Li nucleus as demonstrated by the dotted contours, and redistributed behind the nucleus. The N atom, on the other hand, shows a quadrupolar polarization: electron density is removed from the regions on either side of the nucleus and transferred to regions above and below. Such a polarization turns out to be common for atoms which bond mainly through *p*-electrons,[16] and a closer examination of the density difference map for LiF shows the same feature. The zero-contour line (J on the map) is rather close to the N—H bond, supporting the assertion that the overlap density in the N—H bond hardly changes on molecule formation.

5 Conclusions

In this review we have tried to show how useful chemical information can be recovered from wavefunctions. There is no 'best' method of analysis. The use of density difference maps can draw attention to electronic rearrangements different from those expected on preconceived ideas of bonding, whilst Löwdin–Daudel population analysis is, we believe, a useful guide for intepreting the density difference maps. In conjunction with a knowledge of the polarity of atomic densities, population analysis helps in an understanding of the origin of dipole and quadrupole moments.

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