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THE INTERPRETATION OF MOLECULAR WAVE FUNCTIONS: THE DEVELOPMENT AND APPLICATION OF ROBY'S METHOD FOR ELECTRON POPULATION ANALYSIS

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An extensive investigation has been made of Roby's (*Molec. Phys.* **27**, 81 (1974)) projection-density method for electron population analysis, particularly as applied to extended basis molecular wave functions. In the developed method maximum possible populations are ascribed to atomic s.c.f. orbitals and minimum possible populations to polarization functions. Roby populations are reported for a range of diatomic and simple polyatomic molecules. For a given coordination number, the Roby atomic population n_A reflects the electronegativities of an atom and its ligands. By equipartition of shared populations, atomic charges q_A may also be defined. The two-centre shared populations $s_{AB} = n_A + n_B - n_{AB}$ are found to be coherent indicators of bond strengths. For conventional single bonds, s_{AB} can often be roughly interpreted as $s_{AB} \approx 2S_{ab}$, where S_{ab} is the overlap integral between the two hybrid atomic orbitals defined by a localized molecular orbital representing the A–B bond. Multiple bonds can be interpreted similarly.

Multi-centre shared populations s_{ABC}, s_{ABCD} are helpful in descriptions of the bonding in B_2H_6 and P_4. The Roby projector technique is particularly useful in determining the unique effects of polarization functions. Several wave functions for NF_3 and SO_3 are examined in detail, and the sulphur d functions are confirmed as the most important polarization functions. Various technical aspects of the Roby method are also explored, and the method is shown to have some significant advantages over the widely used Mulliken (*J. chem. Phys.* **23**, 1833 (1955)) method of population analysis.

1. INTRODUCTION

(*a*) *Background*

In the last 30 or so years enormous strides have been made in the theory and calculation of molecular wave functions and of associated molecular properties. Thanks to the speed and power of modern computers, and to the development of theories and methods of calculation, it is now possible to compute the molecular geometry, multipole moments, force constants, ionization potentials, dissociation energies, etc. of the ground and excited states of many small- and medium-size molecules. The degree of accuracy depends on the property, the electronic state, the size of the molecule, the method used and the amount of computer time available.

Despite this progress in the direct calculation of molecular properties, there remains a need for the characterization of wave functions in terms of bond orders, charges and allied quantities. Links are needed with descriptive chemistry, since it is with concepts such as these that chemists have been so successful in rationalizing many aspects of molecular structure and bonding. Often the size of a molecule precludes the calculation of a wave function at other than a single geometry; consequently no direct calculation of some properties is possible. Often comparisons of wave functions in different molecules are required. Every wave function is a mathematical description of a molecule and contains a vast amount of information; for many purposes summaries of that information are required. Electron population analysis is a tool for such summaries and comparisons.

The concepts of bond orders, overlap populations and net electron populations go back to the earliest days of molecular orbital theory in the 1930s, and were developed by a number of authors. In 1955 when the first all-electron l.c.a.o. wave functions were beginning to become available, these earlier notions were brought together and codified by Mulliken (1955) in an important paper on electron population analysis. The overlap populations and gross atomic charges defined by Mulliken have been much used since that time, and have provided valuable insight into the bonding and antibonding characteristics and the polarities of molecular orbitals. As more accurate wave-function calculations have become available, so certain drawbacks in Mulliken's procedures have become more apparent and a variety of modifications have been proposed.

Roby (1974*a*, *b*, 1973) has approached the problem of electron population analysis in a very different way. His method of population analysis for molecular wave functions is based on population projection operators which act on molecular electron density operators. Populations of individual atoms or groups of atoms, and populations shared between two or more atoms, are derived by methods stemming from basic concepts of probability in quantum mechanics. Projection operators are set up to represent subspaces (atomic orbitals, atoms, groups of atoms, etc.) of the molecular Hilbert space, and the probabilities of occupancy of these subspaces are calculated.

The present paper reports an extensive investigation of Roby's projection-density approach. The aim has been to explore its utility in discussions of chemical bonding, and through results for simple reference molecules to provide guides by which results for other molecules can be interpreted. A development of Roby's original method has been devised to overcome major difficulties which could arise as atomic basis sets increase in size. Associated with this is a technique to determine the unique contribution of any polarization function to the molecular wave function.

The developed Roby method of population analysis has some significant advantages over the widely used Mulliken method. The Roby shared populations are often better indicators of bond strengths than the Mulliken overlap populations (which are sometimes small or negative for quite normal chemical bonds). The various Roby populations are less dependent on the size and degree of balance in basis sets. The Roby method allows definition and calculation of multi-centre shared populations, for which there are no counterparts in the Mulliken method.

The main formulae of Roby's method are summarized in the following subsection 1 (*b*). If this presents initial difficulties to the reader, it may be found helpful to pass on to the simple applications discussed in §2 and to re-read §1 (*b*) later. The essential procedure for wave functions calculated with non-minimal basis sets is set out in §3.

A method of population analysis having some features in common with that of Roby was presented in an earlier paper by Davidson (1967). In an extension of the work of Davidson and Roby, Heinzmann & Ahlrichs (1976) have introduced a method based on modified atomic orbitals. This method is considered in §10.

(*b*) *Projection formulae*

The simplest application of the Roby projection operators to a one-electron problem shows that the occupation probability for a normalized atomic or basis orbital $|\mu\rangle$ when the electron is in a molecular orbital (m.o.) $|i\rangle$ is

$$n_\mu = \langle i|\mu\rangle\langle\mu|i\rangle = |S_{\mu i}|^2, \tag{1.1}$$

where S is the overlap integral between the basis orbital and the m.o. This simple result, involving the square of the overlap integral, serves also to introduce the basis orbital projector $P_\mu = |\mu\rangle\langle\mu|$. A version of the proof runs on the following lines. The application of P_μ to $|i\rangle$,

$$P_\mu|i\rangle = |\mu\rangle\langle\mu|i\rangle, \tag{1.2}$$

gives the projection of $|i\rangle$ along $|\mu\rangle$. Premultiplication by the conjugate vector $\langle i|\mu\rangle\langle\mu|$ gives the magnitude of the projection as required:

$$\langle i|\mu\rangle\langle\mu|\mu\rangle\langle\mu|i\rangle = \langle i|\mu\rangle\langle\mu|i\rangle. \tag{1.3}$$

The general result, based on Gleason's (1957) theorem, is that when D is the density operator for a many-electron molecule (represented in a whole Hilbert space) and P is the projector for some sub-space, the probability of occupation of the sub-space is

$$\mathrm{tr}(DP) = \sum_j \langle\psi_j|DP|\psi_j\rangle, \tag{1.4}$$

where tr denotes the trace, and the set $|\psi_j\rangle$ is any complete orthonormal set.

To express (1.2) in a more convenient form, it is helpful to introduce Löwdin's (1955) molecular one-density operator

$$\rho = \sum_i |i\rangle\,\lambda_i\langle i|, \tag{1.5}$$

where the $|i\rangle$ are the natural spin orbitals for the given molecular wave function, and the λ_i are probabilities such that $\Sigma_i\lambda_i = 1$. For a given projector operator P it can then be shown that the occupation number for the subspace is given by

$$n = N\,\mathrm{tr}\,(\rho P) = N\sum_i \langle i|\rho P|i\rangle, \tag{1.6}$$

where N is the number of electrons in the molecule. In particular for the basis function $|\mu\rangle$

$$n_\mu = N\,\mathrm{tr}\,(\rho P_\mu), \tag{1.7}$$

with $P_\mu = |\mu\rangle\langle\mu|$.

When $|i\rangle$ is a m.o. with $\lambda_i = 1/N$, the occupation probability for $|\mu\rangle$ in this orbital is

$$\begin{aligned} n_{i\mu} &= N\,\mathrm{tr}\,(\rho_i P_\mu) \\ &= N\lambda_i\,\mathrm{tr}\,(|i\rangle\langle i|\mu\rangle\langle\mu|) \\ &= \langle i|i\rangle\langle i|\mu\rangle\langle\mu|i\rangle + \langle i^\perp|i\rangle\langle i|\mu\rangle\langle\mu|i^\perp\rangle + \ldots, \end{aligned} \tag{1.8}$$

where $|i^\perp\rangle$ stands for the functions orthogonal to $|i\rangle$. Since $\langle i|i^\perp\rangle = 0$, only the first term is nonzero and

$$n_{i\mu} = |\langle\mu|i\rangle|^2$$

as stated earlier.

For the complete molecular one-density operator ρ, the occupation number for atomic orbital (a.o.) $|\mu\rangle$ is

$$n_\mu = \sum_i n_{i\mu} = N\sum_i \lambda_i|\langle\mu|i\rangle|^2. \tag{1.9}$$

For an atom A described by several orthonormal a.os, we introduce the projector

$$P_A = \sum_{\mu} |\mu\rangle\langle\mu|. \tag{1.10}$$

The occupation number for the atom is then

$$n_A = N \operatorname{tr}(\rho P_A) = N \sum_{i} \sum_{\mu} \lambda_i |\langle\mu|i\rangle|^2. \tag{1.11}$$

If a reference set includes a number of functions centred at A and others at B, the occupation number for the sub-space spanned by the functions centred at A and B is

$$n_{AB} = N \operatorname{tr}(\rho P_{AB}), \tag{1.12}$$

with

$$P_{AB} = \sum_{\mu} \sum_{\nu} |\mu\rangle (S_{AB}^{-1})_{\mu\nu} \langle\nu| \tag{1.13}$$

where $|\mu\rangle$ and $|\nu\rangle$ each run through all the functions centred at A and B. The matrix elements of S_{AB}^{-1} are found from the inverse overlap matrix derived from this limited set of functions, *not* by selection from the inverse overlap matrix of the whole molecular reference set. The formula used for calculation is

$$n_{AB} = N \sum_{i} \sum_{\mu} \sum_{\nu} \lambda_i \langle i|\mu\rangle (S_{AB}^{-1})_{\mu\nu} \langle\nu|i\rangle. \tag{1.14}$$

It will be realized that (1.14) reduces to (1.11) when all the functions $|\mu\rangle$ are orthogonal.

If the reference set is complete and runs through functions centred at A, B, ..., Y, Z the total electron population is of course

$$n_{AB\ldots Z} = N \operatorname{tr}(P_{AB\ldots Z}) = N. \tag{1.15}$$

By considering the population associated with the centres A, B, ..., Y we see that the unshared, or unique, population of the functions centred at Z is

$$u_Z = N - N \operatorname{tr}(P_{AB\ldots Y}). \tag{1.16}$$

The calculation of these unshared populations is non-trivial, since each different unshared population requires the inversion of a different large matrix.

The application of (1.14) for n_{AB} is not restricted to situations conceived as involving a pair of atoms, but may be used to find the occupation number of any set of functions $|\mu\rangle$, whether situated at one, two or several centres. Similarly in (1.16) for u_Z, Z can denote any group of functions, provided AB ... Y denotes the remainder. Equation (1.16) proves particularly useful when Z denotes one or more polarization functions.

2. Simple applications

(*a*) *Homonuclear diatomic molecules*

A first understanding of the Roby method of population analysis is most easily obtained by considering the approximate m.o. for the one-electron molecule H_2^+ constructed from two 1s-type a.os, $|a\rangle$ and $|b\rangle$, centred at the nuclei A and B. With an internuclear distance of 1.06 Å† and a small-basis Gaussian representation of an a.o. giving $\langle a|b\rangle = 0.459$, the normalized m.o. is

$$|i\rangle = 0.585\,(|a\rangle + |b\rangle). \tag{2.1}$$

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† Å $= 10^{-10}$ m $= 10^{-1}$ nm.

Hence the atomic population

$$n_A = \langle a|i\rangle^2 = [\langle a|0.585\ (|a\rangle+|b\rangle)]^2 = 0.729 = n_B. \tag{2.2}$$

By definition the joint population $n_{AB} = 1.000$. Roby defines a shared population as

$$s_{AB} = n_A+n_B-n_{AB}. \tag{2.3}$$

In this case $s_{AB} = 0.729+0.729-1.000 = 0.458$. Thus of the one electron, a population of 0.729 is assigned to $|a\rangle$ and the same to $|b\rangle$, and 0.458 of the electron is regarded as shared.

The unshared population of $|a\rangle$ is

$$u_A = 1-n_B = 0.271. \tag{2.4}$$

Hence with this simple molecular wave function, a population of 0.271 electrons is unique to $|a\rangle$, 0.271 electrons unique to $|b\rangle$, and the remaining 0.458 electrons form the shared population.

If the calculation is done algebraically in terms of the overlap integral $\langle a|b\rangle = S_{ab}$, the result is that the Roby population n_A for the simple bonding m.o. $c(|a\rangle+|b\rangle)$ is

$$n_A = \tfrac{1}{2}+\tfrac{1}{2}S_{ab}. \tag{2.5}$$

The shared population is thus

$$s_{AB} = 2(\tfrac{1}{2}+\tfrac{1}{2}S_{ab})-1 = S_{ab}, \tag{2.6}$$

which is an attractively simple result.

For the antibonding m.o. $c'(|a\rangle-|b\rangle)$, one finds $n_A = \tfrac{1}{2}-\tfrac{1}{2}S_{ab}$, and hence $s_{AB} = -S_{ab}$. Thus the simple antibonding m.o. has a negative shared population. (Roby (1974*a*) originally claimed that s_{AB} was always non-negative. The supposed proof in his Appendix B has an error at equation (B 21).)

For the ground state of the hydrogen molecule where both electrons are in the bonding m.o., $n_A = n_B = 1+S_{ab}$, and $s_{AB} = 2S_{ab}$. In a typical small-basis calculation at the experimental internuclear distance of 0.741 Å, $n_A = n_B = 1.732$ and $s_{AB} = 1.464$. The shared population is more than twice that in H_2^+ because the overlap integral is larger on account of the shorter distance. An artificially short distance would lead to an artificially large shared population for H_2.

The ground state of the hypothetical four-electron molecule He_2 will have two electrons in a bonding m.o. and two in an anti-bonding m.o. In a simple minimum-basis treatment, the contributions to the shared population will cancel and $s_{AB} = 0$ for all internuclear distances.

For the nitrogen molecule N_2, numerical calculations with a [2, 1] minimum basis give $n_N = 8.38$ and $s_{NN} = 2\times 8.38-14.00 = 2.76$. Thus the conventional N≡N triple bond corresponds to a large shared population, which arises mainly from the valence orbitals. The Roby population n_N of each nitrogen atom lies between 7 (the atomic number) and 10 (the population if each a.o. was doubly occupied).

(*b*) *Introduction of polarization functions*

Let us return to H_2^+ and improve the m.o. (2.1),

$$|i\rangle = 0.585\ (|a\rangle+|b\rangle),$$

by introducing two pσ polarization functions centred at A and B. Let $|p\sigma\rangle$ denote this normalized pair. With typical values, the energy-optimized m.o. becomes

$$|i'\rangle = 0.553\ (|a\rangle+|b\rangle)+0.118|p\sigma\rangle. \tag{2.7}$$

The Roby population of $|a\rangle$ is now

$$n_A = \langle a|i'\rangle^2 = 0.721, \tag{2.8}$$

which is little changed from the earlier 0.730. The Roby population of $|p\sigma\rangle$ is

$$n_p = \langle p\sigma|i'\rangle^2 = 0.267. \tag{2.9}$$

This is quite a large value and one might be tempted to say that the polarization function is of major importance. However the unshared population of $|p\sigma\rangle$ is only

$$u_{p\sigma} = 1-\mathrm{tr}\,(\rho P_{ab}) = 0.012, \tag{2.10}$$

so that only a small part of the molecular wavefunction $|i'\rangle$ is uniquely derived from $|p\sigma\rangle$. This small unique population may be compared with the small 2.4% decrease in energy obtained on introducing $|p\sigma\rangle$ into the basis set.

It is instructive to consider the effect of an alternative kind of polarization function, namely the introduction of a bond polarization function $|s\rangle$ which is a 1s function placed at the mid-point of the molecule. It is now found that the energy-optimized m.o. is

$$|i''\rangle = 0.489\,(|a\rangle+|b\rangle)+0.174|s\rangle. \tag{2.11}$$

Though the coefficient of $|a\rangle$ is now 16% smaller than in $|i\rangle$, the value of $n_A = \langle a|i''\rangle^2 = 0.726$ is practically the same. The Roby population of $|s\rangle$,

$$n_s = \langle s|i''\rangle^2 = 0.905, \tag{2.12}$$

is very large and reflects the fact that $|s\rangle$ has very large overlaps with $|a\rangle$ and $|b\rangle$. However, the unshared population of $|s\rangle$ is very small,

$$u_s = 1-\mathrm{tr}\,(\rho P_{ab}) = 0.004, \tag{2.13}$$

so that this bond polarization function is of less importance, at least for some purposes, than the $|p\sigma\rangle$ polarization function. Its introduction produces a 1.8% decrease in the energy of the simple m.o.

The above analysis is not of course the only way of assessing the value of polarization functions. The three approximate m.os may be written in the forms

$$|i\rangle = 0.585\,(|a\rangle+|b\rangle), \tag{2.14}$$

$$|i'\rangle = 0.582\,(|a\rangle+|b\rangle)+0.107\,|p\sigma^o\rangle, \tag{2.15}$$

$$|i''\rangle = 0.584\,(|a\rangle+|b\rangle)+0.064\,|s^o\rangle, \tag{2.16}$$

where $|p\sigma^o\rangle$ is that combination of $|p\sigma\rangle$ and $(|a\rangle+|b\rangle)$ which is orthogonal to $(|a\rangle+|b\rangle)$, and $|s^o\rangle$ is the corresponding orthogonalized form of $|s\rangle$. Because of the orthogonalities the Roby populations $n(p\sigma^o)$ and $n(s^o)$ are immediately calculated as

$$n(p\sigma^o) = (0.107)^2 = 0.012 = u_{p\sigma}, \tag{2.17}$$

and

$$n(s^o) = (0.064)^2 = 0.004 = u_s. \tag{2.18}$$

(c) *Comparison with the Mulliken method*

Consider a single electron in a m.o. $|i\rangle$ formed from two normalized a.os $|a\rangle$ and $|b\rangle$,

$$|i\rangle = c_a|a\rangle+c_b|b\rangle. \tag{2.19}$$

The normalization condition

$$1 = c_a^2 + 2c_a c_b S_{ab} + c_b^2 \tag{2.20}$$

expresses the result that the total probability of finding the electron is unity. In Mulliken's (1955) method of electron population analysis c_a^2 is the contribution from this m.o. to the *net* population of atom A. The *overlap* population is $2c_a c_b S_{ab}$, and this is divided equally between the two atoms to yield $c_a^2 + c_a c_b S_{ab}$ as the contribution from the m.o. to the *gross* population of atom A.

For the orbital (2.19) the Roby population of atom A is

$$n_A = c_a^2 + 2c_a c_b S_{ab} + c_b^2 S_{ab}^2. \tag{2.21}$$

In comparison with the Mulliken method, not only is the whole of Mulliken's overlap population $2c_a c_b S_{ab}$ regarded as belonging to atom A, but a further contribution arises from $c_b^2 S_{ab}^2$ because of the non-orthogonality of $|a\rangle$ and $|b\rangle$. Roby's atom population n_A may be regarded as the *maximum* number of electrons that can be properly associated with atom A.

The Roby shared population is

$$\begin{aligned} s_{AB} &= n_A + n_B - n_{AB} \\ &= 2c_a c_b S_{ab} + (c_a^2 + c_b^2) S_{ab}^2. \end{aligned} \tag{2.22}$$

This is larger than the Mulliken overlap population by the term $(c_a^2 + c_b^2) S_{ab}^2$.

For a homonuclear molecule $c_a^2 = c_b^2 = \frac{1}{2}(1 + S_{ab})$, whence $n_A = \frac{1}{2} + \frac{1}{2} S_{ab}$ and $s_{AB} = S_{ab}$, whereas the Mulliken overlap population is $S_{ab}/(1 + S_{ab})$.

For a heteronuclear molecule with $c_b = g c_a$, the Roby shared population is

$$s_{AB} = S_{ab} \frac{2g + (g^2+1) S_{ab}}{(g^2+1) + 2g S_{ab}}. \tag{2.23}$$

Note that $s_{AB}(g) = s_{AB}(1/g)$, and that when $g = 1$, $s_{AB} = S_{ab}$ as stated. If we write $s_{AB} = S_{ab} M(g)$, the multiplier function $M(g)$ is close to unity over an appreciable range of g and positive S_{ab}, e.g. even for $g = 2$ and $S = 0.5$, $M(g) = 0.93$.

TABLE 1. ROBY POPULATIONS IN NF_3 OBTAINED BY USING ALL FUNCTIONS AT EACH CENTRE

basis	n_N	n_F	s_{NF}
N, F: [2, 1]	8.060	9.571	0.914
N, F: [4, 3]	10.158	10.350	1.923
N, F: [5, 3]	10.387	10.695	2.262
N: [5, 3, 2], F: [5, 3]	13.038	10.700	3.381
N, F: [5, 3, 1]	12.541	11.416	3.813
N, F: [∞, ∞, ...]	34	34	34

3. NON-MINIMAL BASIS SETS: ATOMIC ORBITALS AND POLARIZATION FUNCTIONS

In this paper the notation [5, 3, 1] will be used to indicate that for the given atom the contracted Gaussian basis involved 5 independent combinations of s functions, 3 sets of p functions, and 1 set of d functions. In most of those calculations in which d functions were used, each set of d functions comprised five d functions proper plus a sixth function of s-type arising from the $x^2 + y^2 + z^2$ combination.

Table 1 shows the Roby populations in a series of single-determinant s.c.f. calculations for the 34-electron molecule NF_3. In these analyses all the basis functions of each centre are regarded as contributing to the population of that centre. The results $n_N = 8.060$, $n_F = 9.571$, and s_{NF} = 0.914 for the [2, 1] minimum basis are sensible enough. But as the basis size is increased all the populations increase, and in the limiting case of an infinite and complete basis centred on each nucleus, all the electrons of the molecule are shared by all the atoms. Clearly little useful information can be obtained if the populations are markedly dependent on basis size.

TABLE 2. ROBY POPULATIONS IN NF_3 ANALYSED BY ATOMIC S.C.F. ORBITALS AND POLARIZATION FUNCTIONS

	atomic orbitals				Mulliken overlap
basis	n_N	n_F	s_{NF}	polarization population	population
N, F: [2, 1]	8.060	9.571	0.914	0	0.336
N, F: [4, 3]	7.964	9.586	0.915	0.088	0.211
N, F: [5, 3]	7.954	9.582	0.910	0.098	0.192
N: [5, 3, 2], F: [5 3]	7.903	9.592	0.915	0.132	0.321
N, F: [5, 3, 1]	7.891	9.596	0.918	0.143	0.314

The following procedure, which is a development of one proposed by Roby (1974*a*), has been found useful. Take all the basis functions centred at a given nucleus, and use these to determine s.c.f. a.os for that atom. These s.c.f. a.os are combinations of the basis functions (and hence vary with the basis). The remaining combinations at that centre may be orthogonalized to the a.os at that centre and can be regarded as polarization functions in the molecular s.c.f. calculations. Thus with a [5, 3] basis for N we determine the corresponding 1s, 2s and 2p s.c.f. a.os for the ^{5}S ground state, and then find three s-type and two sets of p-type orthogonal polarization functions. In the Roby population analysis of the molecular wave function, the s.c.f. a.os are assigned their normal Roby populations from (1.11) and (1.14), while only the unshared (unique) populations from (1.16) are assigned to the polarization functions. In other words, *maximum possible populations are ascribed to the atomic s.c.f. functions, and minimum possible populations are ascribed to the non-atomic polarization functions.*

Table 2 shows what happens for NF_3 when the molecular wavefunction is determined with the five different basis sets. Even with the [5, 3, 1] basis only 0.143 of the 34 electrons in the molecule have to be assigned to the unshared population of the set of 60 polarization functions, while 33.857 of the electrons can be assigned to the set of 20 s.c.f. a.os. It can be seen that the atomic populations are not strongly dependent on the basis size; this independence is shown to a greater degree by the shared population s_{NF} of each N–F bond. The populations remain sensible even when an unbalanced basis is used with two sets of d functions on nitrogen and none on the fluorines. The slight drop in n_N as the basis size increases is largely due to the rising polarization population. A possible way of partitioning the polarization population between the atoms will be considered in §9. The Mulliken N–F overlap populations are also given in table 2, and they can be seen to be somewhat basis dependent.

The largest polarization population we have found is 0.546 electrons in SO_3 which are assigned to the set of 73 polarization functions in a calculation with a [6, 4, 2] basis for sulphur and a [4, 3, 2] basis for each oxygen. The unshared populations of individual polarization functions are in general very small. We shall discuss in §7 how the polarization function populations can be used to identify which polarization functions are of most significance in a good molecular wave function.

4. Applications to hydrides and fluorides

We now apply the Roby method with projection on to s.c.f. a.os to some series of simple molecules. Table 3 gives results for the hydrides and fluorides AX_n of second- and third-row elements. The calculations were done at experimental geometries with a [3] basis and a scale factor of 1.41 for H, [5, 3] bases for C, N, O and F, and [6, 4] bases for Si, P, S and Cl (Dunning 1974, Dunning & Hay 1977). No d functions were included. The unshared polarization function populations for the hydrides range from 0.032 in ClH to 0.099 in NH_3, and for the fluorides from 0.007 in F_2 to 0.214 in CF_4 (a molecule with 42 electrons). Thus by far the largest part of the electron population in each molecule can be described by the populations projected on to the atomic s.c.f. orbitals. (The hydrogen 1s orbital is that determined from the scaled [3] basis. It is not a scaled s.c.f. orbital.)

Table 3. Populations for hydrides and fluorides AX_n

molecule	Roby populations n_A	n_X	s_{AX}	Mulliken overlap population	Roby polarization population
CH_4	9.124	1.657	1.461	0.760	0.088
NH_3	9.367	1.509	1.341	0.685	0.099
OH_2	9.616	1.346	1.201	0.562	0.077
FH	9.832	1.174	1.048	0.462	0.042
CF_4	7.560	9.727	1.045	0.530	0.214
NF_3	7.954	9.582	0.910	0.192	0.098
OF_2	8.550	9.441	0.732	0.036	0.033
F_2	9.300	9.300	0.608	0.014	0.007
SiH_4	16.409	1.772	1.387	0.723	0.081
PH_3	16.855	1.700	1.323	0.672	0.060
SH_2	17.348	1.613	1.312	0.580	0.054
ClH	17.719	1.502	1.253	0.519	0.032
SiF_4	14.425	9.876	0.868	0.440	0.183
PF_3	15.193	9.828	0.855	0.152	0.155
SF_2	16.095	9.744	0.807	−0.126	0.086
ClF	17.076	9.625	0.722	−0.130	0.022

If the second-row hydride series were completed by the isoelectronic neon atom, the atom would have the population $n_{Ne} = 10.000$. In the series it can be seen that population n_A rises towards 10.000 as the central atom becomes more electronegative. However even for carbon in methane the a.os have a population of more than nine electrons. In the corresponding fluoride series, the central atom populations n_A are significantly smaller owing to the greater electron-withdrawing power of fluorine as compared with hydrogen. In CF_4 the population n_C has dropped to 7.560.

As would be expected, the trends in the ligand populations are in the opposite sense to those for the central atom. The population of the hydrogen 1s orbital n_H falls from 1.657 in CH_4 to 1.174 in FH, while the population $n_F = 9.727$ in CF_4 is nearly as large as the $n_F = 9.832$ in FH. The lowest n_F is 9.300 in F_2.

In the two series with third-row central atoms the effects of the lower third-row electronegativities are clearly shown. Whereas C in CF_4 was 2.440 (= 10.000 − 7.560) electrons short of a completely filled outer shell, Si in SiF_4 is 3.575 electrons short of a complement of 18 electrons. Conversely fluorine in SiF_4 with $n_F = 9.876$ has an almost filled outer shell. The values of n_H for the third-row hydrides are larger than for the second-row; in particular H with $n_H = 1.502$ in ClH has an appreciably larger population than the $n_H = 1.174$ in FH.

Table 3 also shows the Roby populations, $s_{AX} = n_A + n_X - n_{AX}$, shared between the central atom and one of the ligands. In each series the AX_4 molecule shows the largest value of s_{AX}. Overall the values range from 1.461 in CH_4 (nearly the same as that in H_2), through 1.048 and 1.045 for FH and CF_4, to 0.608 in F_2. For comparison the table also shows the Mulliken overlap populations (calculated by using all the basis functions at each centre). For the two hydride series the Roby shared populations are about twice the Mulliken values, and in each series both sets of values exhibit reasonable trends. However amongst the fluorides the Mulliken overlap populations are small or negative for OF_2, F_2, SF_2 and ClF. The Roby values are much more in keeping with conventional ideas of single bonds.

Table 4. Populations for diatomic molecules

molecule basis	n_A	n_B	$s_{\sigma AB}$	$s_{\pi AB}$	s_{AB}	Roby polarization population	Mulliken overlap population
H_2: [3]	1.714	1.714	1.450	—	1.450	0.021	0.805
HeH^+: [3]	1.924	0.917	0.884	—	0.884	0.042	0.203
F_2: [5, 3]	9.300	9.300	0.609	0.000	0.608	0.007	0.014
O_2: [5, 3]	8.738	8.738	1.102	0.441	1.543	0.066	0.147
N_2: [5, 3]	8.412	8.412	1.547	1.383	2.930	0.106	0.969
BF: [5, 3]	5.678	9.829	1.017	0.553	1.570	0.062	0.320
CO: [5, 4]	7.161	9.324	1.421	1.170	2.590	0.105	0.842
CO_2: [5, 4]	7.668	9.386	1.406	0.746	2.152	0.191	0.935
SiO: [6, 4]; [4, 3]	14.169	9.391	n.a.	n.a.	1.635	0.075	0.709
SO: [6, 4]; [4, 3]	16.379	9.057	1.065	0.441	1.506	0.070	0.115
Cl_2: [6, 4]	17.434	17.434	0.875	0.000	0.875	0.006	0.021
S_2: [6, 4]	16.795	16.795	1.177	0.451	1.627	0.038	0.191
P_2: [6, 4]	16.264	16.264	1.407	1.178	2.584	0.056	1.028
P_4: [6, 4]	16.496	16.496	—	—	1.112	0.074	−0.058

5. Some diatomic molecules

(a) *Results*

Results for some diatomic molecules, together with CO_2 and P_4, are presented in table 4. The separation contributions of σ and π orbitals to s_{AB} are identified. The calculations were done at experimental geometries. In the series F_2, O_2 and N_2 the progression through single, double and triple bonds can be clearly seen. In N_2 s_{AB} rises to 2.930. Both BF and CO have sizeable values of $s_{\sigma AB}$, but $s_{\pi AB}$ is much the larger in CO.

The calculations for O_2, SO and S_2 were for the triplet ground states by the unrestricted Hartree–Fock method with separate m.os for electrons of α and β spin. The values of $s_{\sigma AB}$ and $s_{\pi AB}$ are very similar in each molecule.

In F_2, O_2, and N_2 the Roby atomic populations n_A are 9.300, 8.738 and 8.412, which are respectively 0.300, 0.738 and 1.412 electrons above the atomic numbers. These excesses, doubled and with the small polarization populations added, yield the shared populations s_{AB} of 0.608, 1.543 and 2.930. The Roby populations of the individual a.os of F, O and N are given in table 5. The chief reason for $s_{\sigma AB}$ in N_2 (1.547) being substantially greater than in F_2 (0.609) is that the 2pσ population of each N is larger than that of each F by 0.454. On the other hand since there are only four π-electrons in N_2 as compared with eight in F_2, the smaller

$2p\pi$ population of 1.343×2 for each N as compared with $1.999_6 \times 2$ for each F results for N_2 in a large $s_{\pi AB}$ of 1.383 ($= 0.343 \times 4 + 0.010$ [polarization]) as compared with 0.000 for F_2.

The contributions to s_{AB} of the individual m.os in F_2, O_2 and N_2 are analysed in table 6. The values for F_2 and N_2 correspond to two electrons per orbital; for oxygen the α and β electrons are shown separately. The orbitals are listed in the reverse sequence of energy eigenvalues for F_2. For N_2 and O_2 (β spin) the $3\sigma_g$ orbital is calculated as just below $1\pi_u$. In each molecule, the largest individual contribution to s_{AB} comes from the $2\sigma_g$ orbital.

Table 5. Roby populations of a.os in F_2, O_2 and N_2

molecule	1s	2s	$2p\sigma$	$2p\pi$	total
F_2	2.000	1.994	1.308	$1.999_6 \times 2$	9.300
O_2	2.000	1.973	1.555	1.605×2	8.738
N_2	2.000	1.964	1.762	1.343×2	8.412

Table 6. Values of s_{AB} for individual m.os in F_2, O_2 and N_2

m.o.	F_2	O_2(α spin)	O_2(β spin)	N_2
$1\sigma_g$	0.001	0.004	0.004	0.029
$1\sigma_u$	0.001	0.003	0.003	0.026
$2\sigma_g$	0.491	0.559	0.583	1.581
$2\sigma_u$	-0.094	-0.014	0.022	0.194
$1\pi_u$	0.221×2	0.221×2	0.222×2	0.692×2
$3\sigma_g$	0.210	-0.021	-0.042	-0.282
$1\pi_g$	-0.221×2	-0.223×2	—	—

It can be seen that s_{AB} changes sign across the series for the $2\sigma_u$ and $3\sigma_g$ orbitals, and that s_{AB} for $2\sigma_g$ in F_2 is only one third of its value in N_2. Besides effects of internuclear distances and sizes of a.os, these results are chiefly related to the gap in energy between the 2s and 2p a.os. This gap is greater for F than N, so that the $2\sigma_g$ and $2\sigma_u$ orbitals of F_2 contain relatively small amounts of $|2p\rangle$. The leading terms for atom A in the m.os are:

$$\begin{array}{lll} F_2 & 2\sigma_g & 0.65|2sA\rangle - 0.09|2pA\rangle + \ldots \\ & 2\sigma_u & 0.75|2sA\rangle + 0.06|2pA\rangle - \ldots \\ & 3\sigma_g & 0.21|2sA\rangle + 0.65|2pA\rangle + \ldots \\ N_2 & 2\sigma_g & 0.49|2sA\rangle - 0.24|2pA\rangle + \ldots \\ & 2\sigma_u & 0.80|2sA\rangle + 0.22|2pA\rangle - \ldots \\ & 3\sigma_g & 0.39|2sA\rangle + 0.58|2pA\rangle + \ldots \end{array}$$

It is at first surprising that the $2\sigma_u$ orbital of N_2 (which has a nodal plane through the midpoin of the molecule) should have a positive shared population s_{AB}. However, in the operation of the projector on the density operator the interactions between $|2sA\rangle$ and $|2pB\rangle$, and between $|2pA\rangle$ and $-|2sB\rangle$, give positive contributions which, together with contributions from polarization components in the density operator, outweigh the negative contributions between $|2sA\rangle$ and $-|2sB\rangle$, and between $|2pA\rangle$ and $|2pB\rangle$.

In the [4, 2] double zeta basis of Snyder & Basch (1972) the Mulliken overlap population are:

F_2	$2\sigma_g$	0.311;	$2\sigma_u$	-0.279;	$3\sigma_g$	0.126.
N_2	$2\sigma_g$	0.760;	$2\sigma_u$	-0.573;	$3\sigma_g$	0.028.

The $2\sigma_u$ and $3\sigma_g$ Mulliken overlap populations for N_2 are of opposite signs to the corresponding Roby shared populations. Indeed the total Mulliken σ overlap population of 0.211 is much smaller than the π overlap population of 0.969. The ratio of the Roby σ and π values of 1.547 and 1.383 is in better accord with conventional descriptive accounts of the bonding in N_2.

For F_2 Snyder & Basch give the Mulliken π overlap populations as 0.19×2 for $1\pi_u$ and -0.25×2 for $1\pi_g$. It is the effect of the $1+S$ term in the denominator of the analytical approximation $S/(1+S)$ for the Mulliken overlap population which causes the antibonding contribution from $1\pi_g$ with negative overlap to outweigh the bonding contribution from $1\pi_u$. This overweighting of antibonding orbitals in the Mulliken method is evidently the chief reason for the negative Mulliken overlap populations in ClF and SF_2. As shown by table 6 the Roby shared populations for the $1\pi_u$ and $1\pi_g$ orbitals in F_2 cancel each other.

Table 7. Roby populations for individual m.os in CO and BF

	carbon monoxide			boron fluoride		
m.o.	n_C	n_O	s_{CO}	n_B	n_F	s_{BF}
1σ	0.021	2.000	0.021	0.012	2.000	0.012
2σ	2.000	0.029	0.029	2.000	0.018	0.018
3σ	1.480	1.908	1.418	0.967	1.977	0.952
4σ	0.306	1.812	0.145	0.210	1.911	0.150
1π	0.835 × 2	1.741 × 2	0.585 × 2	0.317 × 2	1.955 × 2	0.277 × 2
5σ	1.684	0.094	−0.192	1.856	0.013	−0.116
totals	7.161	9.324	2.590	5.678	9.829	1.570

Table 8. Values of s_{AB} for individual m.os in Cl_2, S_2, P_2 and SO

m.o.	Cl_2	S_2(α spin)	S_2(β spin)	P_2	SO(α spin)	SO(β spin)
inner total	0.014	0.020	0.020	0.073	0.016	0.015
$4\sigma_g$	0.655	0.512	0.542	1.295	0.484	0.532
$4\sigma_u$	−0.078	−0.015	0.012	0.099	0.040	0.047
$5\sigma_g$	0.284	0.057	0.029	−0.059	−0.027	−0.041
$2\pi_u$	0.286 × 2	0.225 × 2	0.226 × 2	0.588 × 2	0.175 × 2	0.221 × 2
$2\pi_g$	−0.286 × 2	−0.226 × 2	—	—	−0.176 × 2	—

The contributions of the individual m.os to the Roby populations in CO and BF are shown in table 7. Despite the heteronuclear character of the molecule, the individual shared populations in CO are very similar to those of N_2. In general the shared populations of BF are rather smaller. The orbital 4σ is mainly the lone pair on F, while 5σ is mainly the lone pair on B. The problem of assigning effective point charges in heteronuclear molecules will be considered in §9.

The contributions of the individual valence m.os to s_{AB} for Cl_2, S_2, P_2 and SO are shown in table 8. They are very similar to the individual contributions for the second row molecules given in table 6, though there are small differences in the details. For instance, whereas the $2\sigma_g$ m.o. contributes 0.491 for F_2 and 1.581 for N_2, the corresponding $4\sigma_g$ m.o. contributes 0.655 for Cl_2 and 1.295 for P_2. The sign changes found across the second row series for $2\sigma_u$ and $3\sigma_g$ are also found for $4\sigma_u$ and $5\sigma_g$ across the third row series.

The tetrahedral molecule P_4 has also been studied in a [6, 4] basis, primarily for examination of the multi-centre shared populations. The various populations for P_4 are shown at the end of table 4. Each atom is involved in bonds to three other atoms. For each pair of atoms the shared population is $s_{PP} = 1.112$. In comparison with $s_{PP} = 2.584$ in P_2, this is a reasonable value for a single bond. The Mulliken overlap population is negative.

(*b*) *A simple interpretation*

A somewhat rough-and-ready interpretation can be given for the values of the Roby shared populations. The analysis of § 2 (*c*) for a homonuclear diatomic molecule with *two* electrons in a common m.o. shows that $s_{AB} = 2S_{ab}$, where S_{ab} is the overlap integral between the appropriate hybrid a.os on each atom. Now for any molecule the Roby molecular populations are invariant to unitary transformations both of the m.os and of the projector orbitals on a given atom. It may be possible to transform the canonical m.os to another set that includes just one localized molecular orbital (l.m.o.) representing a two-electron bond between the atoms A and B. In such a case we might have $s_{AB} = 2S_{ab}$, where S_{ab} is the overlap integral for the atomic hybrids defined by the l.m.o. Such a result would be true if, for instance, (*a*) there are no significant atomic overlap integrals between the l.m.o. hybrids on either A or B and the atomic hybrids implicit in any of the other orbitals of the transformed set, (*b*) the bond is homopolar, and (*c*) polarization populations can be neglected. The analysis of (2.23) shows that $s_{AB} \approx 2S_{ab}$ may also be a rough approximation for bonds that are not excessively heteropolar. For molecules where two or three l.m.os occur to represent double or triple bonds, s_{AB} will be twice the sum of the corresponding overlap integrals.

The approximate interpretation $s_{AB} \approx 2S_{ab}$ is supported by calculations on F_2, N_2 and CO with Boys' (1960) method for finding l.m.os. For F_2 the valence l.m.os represent one σ-bond pair and three tetrahedral-type lone pairs on each fluorine. The leading terms for atom A in the σ-bond l.m.o. are $0.19|2sA\rangle - 0.59|2pA\rangle + \ldots$. This l.m.o. has $s_{AB} = 0.708$, while each of the six lone pairs contributes only -0.017. Thus the l.m.o. bond pair provides the major constituent of the F_2 total $s_{AB} = 0.608$.

For N_2 with total $s_{AB} = 2.930$, three l.m.o. 'banana' bonds each contribute 0.978, while the two lone pairs contribute only -0.010 each. If the three 'banana' bonds are transformed to one σ-bond and two π-bond l.m.os, the π bonds contribute 0.692×2 to s_{AB} as in table 6. The σ-bond l.m.o. has $s_{AB} = 1.550$, and the leading terms for atom A in this l.m.o. are $0.38|2sA\rangle - 0.36|2pA\rangle + \ldots$. This is close to sp hybridization and explains why the σ overlap integral, and hence $s_{\sigma AB}$, is much larger for N_2 than for F_2. For CO with total $s_{AB} = 2.590$, three l.m.o. 'banana' bonds each contribute 0.868 and the carbon σ lone pair -0.026, with smaller amounts from the oxygen σ lone pair and the inner shells. Similar results are implicit in the results reported by Roby (1974*b*) in his tables 1 and 2 for the l.m.os of HF and CO obtained by the localization methods of Magnasco & Perico (1967) and Edmiston & Ruedenberg (1963). In the former method the triple bond of CO is represented by one σ-bond and two π-bond l.m.os.

Through the approximation $s_{AB} \approx 2S_{ab}$ one can understand why s_{AB} for a conventional single bond never exceeds 2.0, and the trends of the s_{AB} values in tables 3 and 4 are intelligible in terms of the overlap integrals of plausible hybrid a.os. For example the low $s_{AB} = 0.6$ in F_2 can be rationalized in terms of the relatively large F–F distance and the fairly small 2s coefficients in the two atomic hybrids forming the σ-bond l.m.o., whereas the much larger

$s_{AB} = 1.5$ in CH_4 is due to the 2s, 2p mixing in carbon and the consequent large overlap integral for the C–H bond. Similar reasons explain why the shared population is larger in Cl_2 than in F_2, and the large size of the silicon 3s, 3p a.os relative to hydrogen 1s may explain why s_{AB} is slightly lower in SiH_4 than in CH_4. The $s_{AB} = 2.6$ for the conventional triple bond in P_2 can be understood in terms of three l.m.os: a σ bond ($s_\sigma = 1.4$) with a large hybrid overlap integral and two π bonds ($s_\pi = 0.6 \times 2$) with smaller overlap integrals.

This method of interpretation of s_{AB} values through hybrid overlap integrals should be regarded at present as rather approximate and as something of a mnemonic. Although the relation $s_{AB} = 2S_{ab}$ for a two-electron minimum-basis calculation was understood near the start of this work, it was not realized until almost all the calculations had been completed that a similar relation might hold rather generally for single bonds if the canonical m.os were transformed into localized m.os. It is known that the wave functions for saturated molecules can usually be transformed into l.m.os representing bond pairs, lone pairs and inner shells, but these l.m.os often have small tails extending into other parts of the molecules. Such tails affect the accuracy of the approximation $s_{AB} \approx 2S_{ab}$. The non-zero s_{AB} contributions from the six lone pairs in F_2 are an example of this effect. Further work will be needed to establish the most suitable method of localization and the conditions of validity of the approximation. There are some types of molecule that cannot possess suitable l.m.os.

It must be stressed that molecular geometries are determined by energy minima not by maximation of shared or overlap populations. In a minimum-basis treatment of H_2, s_{AB} tends uniformly to 2.000 as $r \rightarrow 0$. The position of r_e cannot be found by examination of $s_{AB}(r)$. The Roby populations provide an interpretation of an electronic wave function whose nuclear coordinates have been selected by other means.

6. Multi-centre shared populations

(a) *Tri-hydrogen cation and neutral molecule*

Roby defines a shared population for three centres as

$$s_{ABC} = n_A + n_B + n_C - n_{AB} - n_{BC} - n_{AC} + n_{ABC}. \tag{6.1}$$

We now present results for calculations with [3] bases on the ground state of two configurations of H_3^+. The equilateral triangular form had $r_{AB} = 0.873$ Å and total energy $-1.280\,E_h$; the linear form with nucleus A at the centre had $r_{AB} = 0.820$ Å and total energy $-1.224\,E_h$. In each case there is a single m.o. with two electrons of opposite spin. In the triangular form, the values $n_H = 1.464$ and $s_{HH} = 1.160$ are somewhat smaller than the 1.714 and 1.450 in H_2, as would be expected for two electrons spread around three centres. In the linear form the central hydrogen has $n_H = 1.879$ (not far short of the possible maximum of 2.000), while the outer hydrogens have the low values of $n_H = 1.094$. The shared population for two adjacent centres $s_{HH} = 1.073$ is only slightly less than in the triangular form. The population shared between the two outer hydrogens is $s_{HH} = 0.464$ (the positive value is expected since the m.o. has no spatial nodes). The three-centre shared populations s_{HHH} are 0.988 for the triangular form and 0.490 for the linear form. The higher shared population for the triangular form is consistent with its lower energy.

S.c.f. calculations for linear neutral H_3 were run with the same basis functions at $r_{AB} = 0.926$ Å. The unrestricted Hartree–Fock method was used for two electrons of α spin (eigenvalues $\epsilon = -0.690\,E_h$ and $-0.401\,E_h$) and one electron of β spin ($\epsilon = -0.586\,E_h$); the total energy was $-1.595\,E_h$. The populations are shown in table 9. When allowance is made for the slightly larger r_{AB} in H_3, the populations for the $1\sigma_g(\alpha)$ and $1\sigma_g(\beta)$ m.os are similar to those for a one-electron m.o. in linear H_3^+. However, the results for the $1\sigma_u(\alpha)$ m.o. are at first surprising. This orbital has the form

$$1\sigma_u(\alpha) = 0.789\,(|b\rangle - |c\rangle) + \text{polarization functions.}$$

The negative value of -0.196 for s_{BC} is close to that expected for an antibonding orbital in H_2^+ with $r = 1.852$ Å. It is the value of -0.259 for s_{AB} which is remarkable. A value $s_{AB} = 0$ might have been expected as the coefficient of $|a\rangle$ in the m.o. is zero. The result is however correct. Since $|a\rangle$ is not orthogonal to either $|b\rangle$ or $|c\rangle$, the projected (length)^2, i.e. population, of $1\sigma_u(\alpha)$ in the space formed by $|a\rangle$ and $|b\rangle$ is greater than the projected (length)^2 in the space of $|b\rangle$ only. Consequently $n_{AB} > n_B$, and s_{AB} is negative. This also causes s_{ABC} to be negative. The result can also be understood by considering a normalized hybrid $|y\rangle$ formed from $|b\rangle$ and $k|a\rangle$, where k is negative and fairly small. On projecting $1\sigma_u$ into the space of $|y\rangle$, $n_Y = \langle y|1\sigma_u\rangle^2$ will be greater than $n_B = \langle b|1\sigma_u\rangle^2$, despite $n_A = 0$.

Table 9. Populations for linear H_3

m.o.	n_A	$n_B = n_C$	s_{AB}	s_{BC}	s_{ABC}
$1\sigma_g(\alpha)$	0.843	0.560	0.511	0.183	0.231
$1\sigma_g(\beta)$	0.958	0.488	0.476	0.160	0.171
$1\sigma_u(\alpha)$	0.000	0.402	−0.259	−0.196	−0.518
totals	1.802	1.450	0.728	0.147	−0.116

When the total populations for the three orbitals of H_3 are considered, we find $s_{AB} = 0.72$ (which, reasonably, is about half that in H_2) and $s_{BC} = 0.147$, while $s_{ABC} = -0.116$ is slightl negative. Negative values of s_{ABC} will be encountered again later for other molecules that hav m.os with zero or small coefficients for a central atom and are antibonding with respect to th outer atoms.

A further comment on the triangular form of H_3^+ may be made. The argument of §2(c showed that for a two-electron homonuclear diatomic molecule $s_{AB} = 2S$ in a minimum-basi calculation, where S is the overlap integral. An extension of this argument to the two-electro symmetric bonding orbital of triangular H_3^+ shows

$$n_H = \frac{2(1+2S)}{3}, \quad s_{HH} = \frac{4S(1+2S)}{3(1+S)} \quad \text{and} \quad s_{HHH} = \frac{4S^2}{1+S}. \qquad (6.2$$

With $S = 0.64$, we get $n_H = 1.52$, $s_{HH} = 1.19$ and $s_{HHH} = 1.00$. These values are close t the 1.46, 1.16 and 0.99 actually found in the non-minimum-basis calculation for H_3^+. Th formula for s_{HHH} shows that the three-centre shared population for a symmetric m.o. has leading dependence on S^2.

(b) *Diborane*

Diborane B_2H_6 is the classic molecule for any examination of multi-centre bonding. S.c. calculations were carried out with a [5, 4] basis for boron and a [3] basis for hydrogen. Th numbering of the atoms is shown in table 10. The assumed geometry was $r(B_1B_2) = 1.755$ $r(B_1H_1) = 1.196$ Å, $r(B_1H_5) = 1.339$ Å, $r(H_1H_3) = 2.061$ Å, $r(H_5H_6) = 2.005$ Å. The ato populations were found to be $n(B) = 8.233$, $n(H_1) = 1.766$, and, marginally lower, $n(H_5)$ 1.750 in the bridge. The two-centre shared populations are $s(B_1H_1) = 1.496$, $s(B_1H_5) = 1.1$

(which is distinctly lower), and $s(B_1B_2) = 1.979$. The corresponding Mulliken overlap populations are 0.857, 0.349 and 0.170. The Roby analysis clearly places much greater emphasis on the boron–boron interaction.

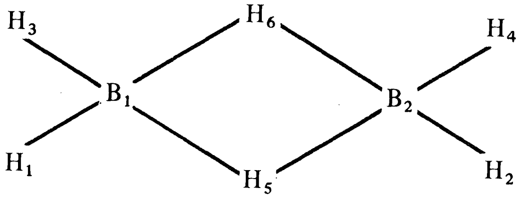
Table 10 shows the shared populations in the $B_1B_2H_5H_6$ bridging region in terms of the two main bonding orbitals for the region, $2a_g$ and $1b_{3u}$. The former is the symmetric orbital giving positive shared populations for all bonds in the molecule. The latter may be described approximately as

$$c_1\{|B_1(2p_y)\rangle + |B_2(2p_y)\rangle\} + c_2\{|H_6(1s)\rangle - |H_5(1s)\rangle\},$$

where the y-axis is parallel to H_5H_6 and the x-axis is perpendicular to the $B_1B_2H_5H_6$ plane. It can be seen from table 9 that these two orbitals provide the main contributions to the overlap populations for B_1H_5 and B_1B_2. (The shared population $s(B_1B_2)$ does have contributions $+0.578$ from $1b_{2u}$ and -0.569 from $1b_{3g}$. So far as the B_1B_2 bond is concerned these are the π_{ux} and π_{gx} orbitals, and their contributions to $s(B_1B_2)$ effectively cancel in the same way as for the corresponding orbitals in F_2 (see table 6).)

Table 10. Shared populations in the bridging region of diborane

m.o.	$s(B_1H_5)$	$s(B_1B_2)$	$s(B_1H_5B_2)$	$s(H_5H_6)$	$s(B_1H_5H_6)$	$s(B_1B_2H_5H_6)$
$2a_g$	0.811	1.362	0.765	0.233	0.248	0.262
$1b_{3u}$	0.331	0.531	0.055	−0.280	−0.358	−0.436
other m.os	0.049	0.086	0.055	0.025	0.035	0.045
totals	1.191	1.979	0.875	−0.022	−0.075	−0.129



The important three-centre shared population involving the two borons and one bridging hydrogen is $s(B_1H_5B_2) = 0.875$, a value that conforms nicely with the idea of a 'three-centre bond'. Much the largest part of this shared population comes from the $2a_g$ orbital, but there are small positive contributions also from $1b_{3u}$ and $3a_g$. The $2a_g$ orbital also gives a positive contribution to the four-centre shared population $s(B_1B_2H_5H_6)$, but this is outweighed by the negative contribution from the $1b_{3u}$ orbital. It will be seen that $s(H_5H_6)$ has the small negative value of -0.022; by comparison $s(H_1H_3) = 0.011$.

The various other three-centre shared populations in the molecule are all small, though $s(B_1H_5H_6)$ reaches -0.075 as shown in table 10.

In the isoelectronic molecule ethylene $s(CC) = 2.333$, of which 0.690 comes from the π bonding orbital. These values are similar but somewhat greater than the diborane values $s(BB) = 1.979$, of which 0.531 comes from the $1b_{3u}$ orbital. In qualitative terms, the Roby analysis thus supports a picture of B_2H_6 as analogous to C_2H_4, with the pair of non-hydrogen atoms strongly linked by two 'banana' bonds but with a proton (the bridge hydrogen) placed in the middle of each 'banana'. If ethylene is described in terms of a σ-bond and a π-bond, the shared populations in table 10 show that the analogous picture for diborane requires both bridge hydrogens to partake in each of the 'σ-bond' $2a_g$ and 'π-bond' $1b_{3u}$ orbitals.

(*c*) *Non-bonded and multi-centre shared populations*

We now examine the two-centre shared populations for pairs of atoms that are normally regarded as non-bonded, e.g. s_{HH} in CH_4. The molecules considered are CO_2, and the hydrides and fluorides of table 3, together with BF_3, OO_3, SO_3, O_3, SO_2, NSF, NSCl, HNSO, NSF_3, ONF_3, OPF_3 and $FClO_3$. The bonding populations in the latter molecules will be discussed in a later paper. The results given here are for bases without d functions.

The s_{HH} values are slightly positive and lie in the range 0.002 to 0.021, except for a value of -0.003 in SiH_4. The s_{OH} and s_{SH} in HNSO are also slightly positive.

The s_{FF}, s_{OO}, s_{NF}, s_{NCl}, s_{NO} and s_{OF} values are all slightly negative and lie in the range -0.002 to -0.032. In O_3 the non-bonded s_{OO} is -0.052. None of the s_{FF} values are less than -0.016.

We now turn to three-centre shared populations. Those not involving a central atom are all very small. The various s_{FFF}, s_{OOO}, s_{FFO}, s_{FOO} and s_{FFN} values lie between 0.001 and -0.002. The s_{HHH} values lie between 0.011 in NH_3 and -0.001 in SiH_4.

The three-centre shared populations involving a central atom and two hydrogens are quite small, and range from $s_{OHH} = 0.032$ in H_2O to $s_{PHH} = -0.010$ in PH_3.

However, the three-centre shared populations involving a central atom and two non-hydrogen ligands have significant negative values. The least of these (i.e. the one with the largest magnitude) is $s_{COO} = -0.341$ in CO_2. Of this value -0.442 comes from the $1\pi_{gx}$ and $1\pi_{gy}$ m.os. These orbitals have zero coefficients for carbon basis functions, but for the reasons explained for the $1\sigma_u(\alpha)$ orbital of H_3 their contributions to s_{CO} and s_{COO} are negative. The value of $s_{OO} = -0.013$ is in the normal range.

The value of s_{SOO} in SO_2 is -0.291; of this -0.144 comes from the $2b_1$ m.o. which has only fairly small sulphur coefficients and -0.124 from the $1a_2$ m.o. which has zero sulphur coefficients. Other values of s_{XOO} are -0.220 in SO_3, -0.164 in $FClO_3$, -0.060 in $O.O_3$, and -0.082 in ozone O_3. The values of s_{XOF} are -0.164 in OPF_3, -0.083 in ONF_3 and -0.074 in $FClO_3$. However, the values of s_{XFF} are less than -0.100 only in BF_3 (-0.148) and SiF_4 (-0.104). In NF_3 (-0.035) and OF_2 (-0.015) the values are quite small. In NSCl s_{NSCl} is -0.197, while in NSF and NSF_3 the s_{NSF} are -0.171 and -0.188.

There seem to be two essential requirements for the occurrence of substantial negative s_{ABB}. There must be an occupied m.o. whose behaviour near A is unlike any of the projector a.os allowed for centre A. This m.o. will make zero contribution to n_A, but may have $n_{AB} > n_B$ if there is on A an a.o. that can hybridize with appropriate a.os of B to provide a greater projection n_{AB} for the m.o. The negative values of s_{ABB} would often disappear if functions of higher azimuthal quantum number were admitted as a.os of A, e.g. d functions for carbon in CO_2 or for sulphur in SO_2.

The four- and five-centre shared populations spanning all the centres of a four- or five-atom molecule are all very small numerically, except for $s_{NHHH} = 0.013$ in NH_3 and $s_{SOOO} = 0.038$ in SO_3. In $FClO_3$ the four-centre term s_{ClOOO} reaches 0.020, but the other four-centre terms and the five-centre term (-0.001) are insignificant.

(*d*) *Strained ring molecules*

We now discuss multi-centre populations in some ring compounds regarded conventionally as single but strained. The compounds considered are the 24-electron molecules C_3H_6, C_2H_4O,

$CH_2(NH)_2$ and cyclic O_3, together with tetrahedral P_4 and the triplet state of square cyclic $(CH)_4$. The dimensions for the first three molecules were taken from Snyder & Basch (1972). For the other molecules the dimensions used were O–O = 1.435 Å, P–P = 2.21 Å, C–C = 1.440 Å and C–H = 1.080 Å. The bases were [3] for H, [5, 3] for C, N and O and [6, 4] for P.

The values of s_{ABC} for the rings were 0.384 in C_3H_6, 0.259 in C_2H_4O, 0.266 in $CH_2(NH)_2$ and 0.153 in cyclic O_3. The three-centre shared populations decrease with increasing electronegativity of the ring atoms and with decreasing two-centre shared populations. These fall from $s_{CC} = 1.463$ to $s_{OO} = 0.807$ in O_3 (these values are close to those typical for the respective single bonds in open chain molecules). In P_4, where each $s_{PP} = 1.112$, $s_{PPP} = 0.175$ for each three-membered ring and $s_{PPPP} = 0.095$. In C_4H_4 $s_{CCC} = 0.174$ (of which the π contribution is 0.075) and $s_{CCCC} = 0.210$ (π contribution 0.092). These positive values may be contrasted with the negative values for a central atom and two non-hydrogen ligands discussed for non-cyclic molecules in the previous subsection (especially $s_{OOO} = -0.082$ for normal ozone). The results suggest that multi-centre electron sharing is of some importance for the bonding in these cyclic molecules, even though it does not reach the diborane level of $s(B_1H_5B_2) = 0.875$.

The contributions from the individual m.os are most easily understood for cyclic O_3. The symmetric 2a′ orbital (with $\epsilon = -1.654\ E_h$ and which contributes 0.671 to the total 0.807 for each s_{OO}) gives the main contribution of 0.435 to s_{OOO}. This is the in-phase σ-bonding orbital. The other five σ valence orbitals 2e′ (-0.068×2), 3a′ (0.068) and 3e′ (-0.108×2) contribute a total of -0.282, while the contributions of the 1a″ (0.079) and 1e″ (-0.039×2) π orbitals cancel almost exactly.

7. THE UNIQUE CONTRIBUTIONS OF POLARIZATION FUNCTIONS

In this section we consider how the Roby method of population analysis can be used to assess the unique contribution of any polarization function. The distinction between a.os and polarization functions was explained in §3. The polarization functions at a centre are those combinations of basis functions at that centre which are orthogonal to the s.c.f. a.os determined with the given basis.

(a) *Nitrogen trifluoride*

Table 2 of §3 showed how the total polarization population for NF_3 varied with size of basis. It is instructive to analyse the populations in terms of unique contributions from different types of polarization function. Table 11 analyses the four non-minimum-basis molecular wave functions in two ways: (*a*) by the unique contributions from the polarization functions centred at each nucleus; (*b*) by the unique contributions from all s, all p, and all d polarization functions. In the largest basis, [5, 3, 1], there are 20 s.c.f. a.os (whose projectors yield the atomic populations) and 60 polarization functions. Of the latter 16 are of s-type (including the spherically symmetrical contributions from the $x^2+y^2+z^2$ pseudo-d-functions), 24 of p-type and 20 of d-type. In this basis the total polarization population is 0.143. The population unique to the 15 polarization functions on nitrogen is $u(N) = 0.023$, whereas $u(F) = 0.007$. The sum $u(N)+3u(F)$ is substantially less than 0.143 because of the non-orthogonality of the polarization functions on different centres. In fact there is not much redundancy between the three sets of fluorine polarization functions since $u(F_1F_2F_3) = 0.022$, but there is considerable overlap between the functions on nitrogen and those on the fluorines since $u(NF_1) = 0.051$, $u(NF_1F_2) = 0.089$ and $u(NF_1F_2F_3) = 0.143$.

For the same basis, the analysis by s, p and d polarization functions yields $u(\mathrm{s}) = 0.017$, $u(\mathrm{p}) = 0.022$ and $u(\mathrm{d}) = 0.038$. The d functions make the largest total contribution. If the d contribution is broken down by atoms, it is found that $u(\mathrm{N, d^4}) = 0.008$ and $u(\mathrm{F, d^5}) = 0.003$. The individual d functions have u values ranging from 0.002_0 to 0.001_2 on nitrogen, and 0.001_3 to 0.000_6 on fluorine. If the s and p contributions are broken down by atoms, it is found that $u(\mathrm{N, s^4}) = 0.001_4$, $u(\mathrm{F}, s^4) = 0.000_2$, $u(\mathrm{N, p^6}) = 0.006_8$ and $u(\mathrm{F, p^6}) = 0.001_7$.

Table 11. Polarization populations in NF$_3$

basis	number of polarization functions	total polarization population	u(N)	u(F)	u(s)	u(p)	u(d)
N, F: [4, 3]	32	0.088	0.030	0.003	0.017	0.060	—
N, F: [5, 3]	36	0.098	0.022	0.003	0.023	0.058	—
N: [5, 3, 2], F: [5, 3]	48	0.132	0.051	0.003	0.028	0.039	0.027
N, F: [5, 3, 1]	60	0.143	0.023	0.007	0.017	0.022	0.038

Thus for the [5, 3, 1] wave function of NF$_3$, the analysis shows that the order of importance of the polarization functions in the electron population analysis is d > p > s, while functions on nitrogen are more important than those on fluorine. The importance of the d polarization functions on nitrogen is consistent with the central position of nitrogen in the molecule. The unique unshared populations of individual polarization functions are very small (the largest is only 0.002_0) because of the high degree of redundancy. In the [4, 3] wave function with fewer polarization functions one of the nitrogen p functions has $u = 0.009_2$.

The unique contributions of the polarization functions on the fluorines differ little between the [5, 3] and [5, 3, 2], [5, 3] calculations, but in the latter with d functions added to nitrogen alone, the u(N) value increases significantly to 0.051. However, this value is small compared with the total population of 34 electrons in the molecule. On re-examining table 2 it can be seen that this small increase in u(N) on change of basis is related to the small decrease from 7.954 to 7.903 in the atomic population n_{N}.

(*b*) *Sulphur trioxide*

The largest polarization population we have met is 0.546 electrons in the calculations for SO$_3$ with two sets of d functions for each atom, namely a [6, 4, 2] basis for sulphur and a [4, 3, 2] basis for each oxygen. This polarization population is about four times that in the [5, 3, 1] calculation for NF$_3$. It occurs for hexavalent sulphur, and is evidently related to the high 'charge' on sulphur. Wave functions and density difference maps for SO$_3$ will be considered in detail in another paper (Cruickshank *et al.* 1982), but some aspects of three wave functions for SO$_3$ are relevant here.

Table 12 shows the polarization populations for the calculations on SO$_3$ in the same manner as table 11 did for NF$_3$. The first wave function omitted any d polarization functions, the second included them only on sulphur, and the third included two sets on each atom. (In the third, but not the second, calculation the function of s-type arising from the $x^2+y^2+z^2$ contribution was excluded, so that each d set comprised only five d functions proper.) It is apparent from table 12 that the order of importance of the polarization functions is again d > p > s, and that the functions on sulphur are more important than those on oxygen. If one compares for SO$_3$ and NF$_3$ the calculations in which d functions are placed only on the central atom, one sees that the d functions on sulphur are almost ten times as important as those on nitrogen. Even so the unique d population of S reaches only 0.258.

In the third calculation for SO_3 with two sets of d polarization functions on each atom, there is considerable redundancy between the functions on the various centres. As compared with the calculation with d functions only on sulphur, the unique polarization population for S drops to 0.129, of which 0.005 is unique to sulphur s functions, 0.023 to p functions, and 0.097 to d functions. The unique polarization population for any O is 0.012, of which 0.010 is unique to oxygen d functions. Clearly of all the polarization functions used, the sulphur d functions are the most important, but a satisfactory description of the bonding in SO_3 can be given without regarding these d functions as basic a.os. The shared atomic populations s_{SO} in the three calculations of table 12 are 1.331, 1.350 and 1.372. The first value may be compared with the value of 1.506 given in table 4 for the SO molecule with the same s, p basis.

TABLE 12. POLARIZATION POPULATIONS IN SO_3

basis	number of polarization functions	total polarization population	u(S)	u(O)	u(s)	u(p)	u(d)
S: [6, 4], O: [4, 3]	33	0.279	0.097	0.009	0.055	0.148	—
S: [4, 3, 1], O: [3, 2]	22	0.499	0.320	0.020	0.008	0.134	0.258
S: [6, 4, 2], O: [4, 3, 2]	73	0.546	0.129	0.012	0.014	0.064	0.279

As just remarked, in the [6, 4, 2], [4, 3, 2] calculations for SO_3 the unique sulphur d population is 0.097 and the unique d population for each oxygen is 0.010. If all the d functions had been classified as atomic rather than as polarization functions, the Roby maximum populations n(d) as calculated by (1.11) would have been 4.06 for sulphur and 0.69 for each oxygen. Such values would have greatly exaggerated the distinct contributions of the d functions to the total wave function. The Mulliken gross populations for the d functions are 0.93 for sulphur and 0.06 for oxygen; these also overestimate the unique contributions.

In NF_3 in the [5, 3, 1] basis the corresponding populations for d functions are; Roby unique, 0.088 for N and 0.003 for each F; Roby maximum, 2.14 and 0.53; Mulliken, 0.21 and 0.03.

(c) *Hydrogen species and outer polarization functions*

Atomic populations n_A and shared populations s_{AB} and s_{ABC} for H_3^+ and H_3 with [3] bases were reported in §6. By comparison with the 34-electron molecule NF_3, the unshared polarization populations for H_3^+ are large: 0.101 for the triangular form and 0.055 for the linear. The polarization populations for neutral H_3 and H_2 are much smaller: 0.016 and 0.021, respectively. The large polarization populations for the cations are due to the substantial contractions in their orbitals. The [3] basis (Dunning 1974) with a scale factor of 1.41 involves three functions: G_1, a combination of three Gaussians with exponents 67.28, 10.116 and 2.294; G_2, a single Gaussian with exponent 0.6422; and G_3 a single Gaussian with exponent 0.2026. In this basis the s.c.f. a.o. for H is $0.118\ G_1 + 0.282\ G_2 + 0.698\ G_3$. For H_2 the contribution to the normalized m.o. from one hydrogen is $0.091\ G_1 + 0.221\ G_2 + 0.299\ G_3$. In triangular H_3^+ the contribution from one hydrogen is $0.074\ G_1 + 0.251\ G_2 + 0.125\ G_3$. The relative contribution from the most diffuse Gaussian G_3 is clearly much reduced in triangular H_3^+.

The process can be studied also through the Roby populations. At each centre the polarization functions are found by orthogonalization to the s.c.f. a.o. An inner polarization function

P_i is found by orthogonalizing G_1 to the a.o. by the Schmidt method: $P_i = 1.141\,G_1 - 0.200\,G_2 - 0.493\,G_3$. An outer polarization function P_o is found by orthogonalizing G_3 to the a.o.: $P_o = -0.432\,G_1 - 1.034\,G_2 + 1.240\,G_3$. For simplicity, P_i and P_o were not redefined for mutual orthogonality.

For any one centre in triangular H_3^+, the unshared polarization population $u(P_iP_o) = 0.016_2$ (this is much less than one third of the total polarization population of 0.101 because of overlapping from the three centres). The individual unshared contributions are $u(P_i) = 0.000_3$ and $u(P_o) = 0.006_9$. The ratio of these values shows that the outer polarization function is much the more important. A similar conclusion applies to linear H_3^+ and to neutral linear H_3 and H_2.

This conclusion about the importance of outer polarization functions has been confirmed for a number of polyatomic molecules, namely SiO, NF_3, NF_3O, NSF, NSCl, NSF_3, and SO_3. For instance for NF_3 in the [4, 3] basis with a total polarization population of 0.088, the unique contribution of the s and p inner functions is 0.002 whereas that from the s and p outer polarization functions is 0.053.

(*d*) *An alternative method of ranking polarization functions*

The earlier discussion has compared the relative importance of different polarization functions in terms of the unique population of each function as calculated by (1.16). Because of redundancy among polarization functions this may not always be a satisfactory basis for comparison, and as the number of polarization functions increases, the unique population of any one of them is liable to become smaller. An alternative method of ranking polarization functions is to continue to project out any redundancy with respect to a.os, but to maximize the population of each polarization function as a component of the total polarization population. If A, B, ..., M are the complete set of a.os, and r, s, t, ... are the polarization functions, we could define an intermediate polarization population of r as

$$i(r) = N\,\mathrm{tr}\,(\rho P_{\mathrm{AB}\ldots\mathrm{M}r}) - N\,\mathrm{tr}\,(\rho P_{\mathrm{AB}\ldots\mathrm{M}}). \tag{7.1}$$

Such intermediate polarization populations would be less dependent on the total basis. For example, the intermediate population i(d) for a set of sulphur d functions in SO_3 would have much the same value whether or not the oxygens had d functions, whereas the unique sulphur d population drops from 0.258 to 0.097 between the second and third calculations of table 12.

8. THE PROBLEM OF VALENCE SHELL EXPANSION

(*a*) *Some compounds of* Li *and* Be

As described in §3 the Roby method of population analysis yields consistent results if s.c.f. a.os are determined from the given basis functions and are used as projectors to give atom populations in the molecular wave functions. To this stage the definition of a.os has been fairly obvious. However, consider compounds of Li and Be, say LiF and BeH_2. Are Li and Be atoms to be regarded as containing solely 1s and 2s a.os? Are 2p orbitals of Li and Be to be regarded as a.os or as non-atomic polarization functions?

Table 13 illustrates a variety of analyses of the molecular wave function for LiF constructed by Hinchliffe & Dobson (1976) from a largish basis set, [4, 3] for Li and [5, 4, 2] for F, and with r(Li–F) = 1.581 Å. The top line shows the populations with the limited definition of a.os 1s, 2s and 2p for F, but only 1s and 2s for Li. The unshared polarization population of 0.091

includes contributions from Li (2p) orbitals. The next line shows the effect of changing the status of the Li (2p) orbitals from polarization functions to a.os. (The 2p orbital was defined through an s.c.f. calculation of the atomic $(1s)^2$ (2p) state.) With the wider definition n_{Li} increases from 2.187 to 2.940, and s_{LiF} from 0.186 to 0.897 (of this the σ and π contributions are 0.590 and 0.307 respectively). The population n_{F} remains unaltered at 9.909, since there has been no change in either the molecular wave function or the definition of the fluorine a.os.

Table 13. Alternative population analyses for LiF

projector functions	n_{Li}	n_{F}	s_{LiF}	polarization population
Li (1s, 2s), F (1s, 2s, 2p)	2.187	9.909	0.186	0.091
Li (1s, 2s, 2p), F (1s, 2s, 2p)	2.940	9.909	0.897	0.049
Li^+ (1s), F^- (1s, 2s, 2p)	2.000	9.963	0.001	0.038
Li (1s, 2s, 2p), F^- (1s, 2s, 2p)	2.940	9.963	0.931	0.028

The third line shows the populations when the ionic model is used in the projector analysis. The analysing functions are now those from Li^+ and F^- s.c.f. calculations; the outer orbitals of F^- are more diffuse than those of F. As expected the analysis yields $n_{\mathrm{Li}} = 2.000$, while n_{F} rises to the remarkably high value of 9.963. The unshared polarization population is down to 0.038. Evidently the simple ionic picture $\mathrm{Li}^+\mathrm{F}^-$ is quite a good summary of the molecular wave function. The lowest polarization population of 0.028 is given with a somewhat artificial set of projector orbitals from F^- and Li (1s, 2s, 2p).

Table 14. Population analyses for LiH and Li_2

molecule	projector functions	n_{A}	n_{B}	s_{AB}	polarization population
LiH	Li (1s, 2s), H (1s)	2.824	1.766	0.666	0.076
	Li (1s, 2s, 2p), H (1s)	3.557	1.766	1.330	0.007
Li_2	Li (1s, 2s)	3.530	3.530	1.119	0.058
	Li (1s, 2s, 2p)	3.830	3.830	1.663	0.002

Table 14 shows population analyses for LiH and Li_2, with Li (2p) regarded (*a*) as a polarization function and (*b*) as an atomic function. The wave functions were calculated with Li:[4, 3] and H:[3, 2] bases, $r(\text{Li–H}) = 1.595$ Å and $r(\text{Li–Li}) = 2.673$ Å. Table 14 shows that the inclusion of Li (2p) among the atomic projector functions reduces the total polarization populations very markedly and increases the shared populations substantially. With Li (2p) regarded as atomic, the individual a.o. populations for Li are 1s, 2.000, 2s, 0.824, 2p, 0.733 in LiH, and 2.000, 1.530 and 0.300 in Li_2.

Table 15. Population analyses for BeH_2

projector functions	m.o.	n_{Be}	n_{H}	n_{BeH}	s_{BeH}	polarization population	s_{BeHH}
Be (1s, 2s), H (1s)	$1\sigma_g$	2.000	0.018	2.000	0.018	0.000	0.002
	$2\sigma_g$	1.616	0.909	1.747	0.778	0.008	0.187
	$1\sigma_u$	0.000	0.903	1.228	−0.325	0.115	−0.651
	totals	3.616	1.830	4.975	0.471	0.123	−0.462
Be (1s, 2s, 2p), H (1s)	$1\sigma_g$	2.000	0.018	2.000	0.018	0.000	0.001
	$2\sigma_g$	1.616	0.909	1.809	0.716	0.008	0.064
	$1\sigma_u$	1.446	0.903	1.715	0.634	0.002	−0.065
	totals	5.062	1.830	5.524	1.368	0.010	0.000

Table 15 shows two analyses of a molecular wave function for BeH_2 calculated from a [5, 2] basis for Be and a [3] basis for H, with r(Be–H) = 1.344 Å. If the analysis is in terms of the $(1s)^2\,(2s)^2$ s.c.f. orbitals of Be and the (1s) s.c.f. orbital of H, the population of Be, $n_{Be} = 3.616$, is below its atomic number, and the shared population, $s_{BeH} = 0.471$, is well below that for a typical single bond. The unshared population for the 2p and other polarization functions is 0.123, of which the unique contribution of 2p is 0.090. The latter value is quite large for a single function participating in a single m.o. If the definition of a Be atom is widened to include the 2p orbital obtained in a $(1s)^2\,(2s)(2p)$ atomic s.c.f. calculation, n_H remains the same at 1.830 but n_{Be} rises to 5.062 and s_{BeH} to 1.368. The polarization population drops to 0.010.

The increase of n_{Be} on inclusion of the 2p orbital as atomic arises solely from the $1\sigma_u$ m.o. where the 2p orbital has a population of 1.446. The joint population n_{BeH} rises from 4.975 to 5.524, mostly as a result of the effect of 2p in the $1\sigma_u$ orbital, but there is also a slight increase in the contribution to n_{BeH} from the $2\sigma_g$ orbital. Though the coefficient of 2p in this m.o. is zero, the inclusion of 2p increases the projected $(\text{length})^2$ of the m.o. in the enlarged joint space of Be and H for the reasons discussed in §6. The three-centre shared populations s_{BeHH} are also shown in table 15. The total s_{BeHH} changes from -0.462 to 0.000 on treating Be(2p) as an atomic function.

For the four molecular wave functions considered in this section the Mulliken overlap populations are Li–F 0.151, Li–H 0.754, Li–Li 0.818, and Be–H 0.718.

(*b*) *Polarization populations and difference maps for* LiF

Whereas in §7 various wave functions for a given molecule were examined to find the importance of different polarization functions, in §8(*a*) various Roby projectors were used to analyse in different ways a given wave function. As shown by table 13, the projector functions for atomic Li (1s, 2s) and atomic F (1s, 2s, 2p) capture all but 0.091 of the 12 electrons in the LiF molecular wave function. However, the use of ionic s.c.f. orbitals in the projectors Li^+ (1s) and F^- (1s, 2s, 2p) does even better, and only 0.038 electrons are left to the polarization functions.

This support for the ionic model as a good approximation to whole wave function is related to the conclusions drawn by Bader & Henneker (1965) from their studies of electron density difference maps. They calculated difference maps (i) between LiF and Li and F atoms, and (ii) between LiF and Li^+ and F^- ions. The contours in the second map were of substantially smaller magnitude, and were taken to show that LiF approximates the ionic density quite closely.

The two techniques for assessing models, Roby population analyses and difference maps, are not however directly comparable. In the latter specific atomic or ionic configurations with defined populations are subtracted from the molecular density. In case (i) the F atom configuration was $(1s)^2\,(2s)^2\,(2p\sigma)^1\,(2p\pi)^4$ with *atomic* orbitals, and in case (ii) the F^- ion configuration was $(1s)^2\,(2s)^2\,(2p\sigma)^2\,(2p\pi)^4$ with *ionic* orbitals. In the Roby method the populations of the individual orbitals are determined by the projection process, and the variations in n_F and the polarization populations arise from the different matchings of the atomic or ionic orbitals to the molecular wave function. The populations of the *F atomic* orbitals for the wave function of table 13 are 2s 1.996, 2pσ 1.975, 2pπ 1.969 × 2, but with *ionic* orbitals as projectors the populations are even closer to 2.000, namely 2s 1.999, 2pσ 1.980, 2pπ 1.992 × 2. The Roby technique yields two main results. First, because of the smaller polarization population, the form of the molecular wave function is better matched by the forms of the ionic orbitals. Second, the populations of the orbitals are very near to closed shell values and are thus consistent with the ionic approximation.

The fit of the ionic model is not perfect. If it were, not only would the polarization population be zero but Bader & Henneker's ionic difference map (ii) would be featureless.

Table 16. Polarization populations in LiF

projector functions	total polarization population	u(Li)	u(F)	u(s)	u(p)	u(d)
Li, F	0.091	0.012	0.029	0.001	0.077	0.003
Li with 2p, F	0.049	0.006	0.029	0.001	0.040	0.003
Li^+, F^-	0.038	0.012	0.013	0.001	0.016	0.003
Li with 2p, F^-	0.028	0.006	0.013	0.000_5	0.014	0.003

Some details of the polarization populations remaining after the various projections are shown in table 16. These values also serve as an illustration of the effects of redundancy, or overlap, among basis functions. As already discussed, the ionic projectors Li^+ (1s) and F^- (1s, 2s, 2p) pick up all but 0.038 of the molecular electrons. If the Li (2s, 2p) orbitals are added to the projectors, the polarization population decreases by only 0.010 to 0.028, yet these orbitals (2s 0.187, 2pσ 0.409, 2pπ 0.172×2) have a Roby population of 0.940. However, 0.930 of these electrons are shared with the F^- ion. Until one appreciates the degree of redundancy and sharing, it may seem surprising that the Li (2s, 2p) functions contribute so little (0.010) to the reduction of the polarization population. Other functions, especially the polarization functions on F, pick up the remaining 0.028 electrons. The need for the latter is consistent with the arrangement of peaks and troughs in the ionic difference map of Bader & Henneker, and in the separate σ and π difference maps given by Dobson (1974), and Hinchliffe & Dobson (1976).

(c) *Which are atomic orbitals?*

So far no direct answer has been given to the question posed at the beginning of §8 as to whether the 2p orbitals of Li and Be are to be regarded as a.os or as non-atomic polarization functions. Population analyses for several molecules have been presented for both possible definitions. Indeed for LiF a third possibility emerged, the use of ionic orbitals.

Of the molecules considered in §8(*a*), BeH_2 is the strongest candidate for regarding the 2p function as an a.o. By so doing, the polarization population drops from 0.123 to 0.010, the change of 0.113 occurring solely in the $1\sigma_u$ m.o. For comparison, in the 34-electron molecule NF_3, where there is no dispute about the definition of a.os, the total polarization population is 0.098 in the [5, 3] calculation, with a largest population of 0.017 in the $4a_1$ orbital. In BeH_2 if 2p is classified as an a.o., it has a Roby population $n(2p)$ of 1.446, and s_{BeH} increases from 0.471 to 1.368. The latter value is similar in magnitude to the $s_{BH} = 1.496$ for the terminal bonds in B_2H_6 and to the $s_{CH} = 1.461$ in CH_4. It is thus not unreasonable to choose to regard Be (2p) as an a.o. The widened definition corresponds to that implicit in the simple description of the molecular binding as arising from Be(sp) digonal hybrid orbitals.

One advantage of treating Be (2p) as an a.o. in the projector is that it avoids the large negative value for s_{BeHH} shown in the upper part of table 15. Similarly the negative $s_{\mathrm{SOO}} = -0.291$ in SO_2 might be avoided if S(3d) orbitals were to be regarded as atomic. However, such a line of thought can have its pitfalls since $s_{\mathrm{COO}} = -0.341$ in CO_2, and to eliminate this one would have to treat C (3d) oribtals as atomic.

In LiH and Li_2 the choice about Li (2p) is rather open. Elementary descriptions of the bonding with reasonable shared populations can be provided without regarding Li (2p) as an a.o. However it is then an important polarization function, distinctly more so than H(2p) in H_2, where with a [3, 2] basis the total s, p polarization population is 0.023. On the other hand, with Li (2p) treated as an a.o., the shared populations in LiH and Li_2 are 1.330 and 1.663, which are not unacceptably large values.

The decision whether to regard Li (2p), Be (2p) or S (3d), say, as an a.o. in the projector is basically arbitrary. With either choice the Roby procedure leads to a population description of a molecule. Which is preferable depends on simplicity, utility and consistency through related series of molecules. But one must be cautious in admitting as atomic those orbitals which are appreciably higher in energy than the upper orbital of the atomic ground state.

9. ATOMIC CHARGES AND THE PARTITIONING OF SHARED POPULATIONS

(a) *Method*

The charge on an atom in a molecule is an attractive and useful concept, but one that is very elusive of satisfactory universal definition. An essential requirement is that the sum of the atomic charges should equal the molecular charge (if any). In Mulliken's scheme for a diatomic molecule half the overlap population is added to each net atomic population to give the gross electron population of each atom. The gross atomic charges are then obtained by subtracting the gross electron populations from the atomic numbers Z_{A}. For a homonuclear diatomic neutral molecule the Mulliken method sensibly yields zero gross charges on each atom.

A similar method of assigning charges in the Roby scheme can be illustrated by considering the [2, 1] minimum basis calculation for N_2. The Roby populations given in §2(*a*) are $n_{\mathrm{N}} = 8.38$ and $s_{\mathrm{NN}} = 2.76$. By dividing the shared population equally between the two centres, we obtained a partitioned population $p_{\mathrm{N}} = 8.38-(2.76/2) = 7.00$ and hence a charge $q_{\mathrm{N}} = 0.00$ on each atom. In the minimum basis calculation of Ransil (1960) for NH, quoted by Roby (1974*a*), the populations are $n_{\mathrm{N}} = 7.87$, $n_{\mathrm{H}} = 1.25$ and $s_{\mathrm{NH}} = 1.12$. If the shared population is equally divided between the two centres, the partitioned populations are $p_{\mathrm{N}} = 7.31$ and $p_{\mathrm{H}} = 0.69$. Thus the charges are $q_{\mathrm{N}} = +0.31$ and $q_{\mathrm{H}} = -0.31$.

It has to be stated at once that the partitioning of shared populations is not part of the fundamental quantum theoretical basis of Roby's projector methods. Nevertheless we have made such calculations and have often found the results useful.

For heteronuclear molecules the equipartitioning of shared populations is an obvious point for debate. It could be suggested that shared populations should be divided so as to preserve some dipole moment parameter, say, in a fashion analogous to the Löwdin–Daudel partitioning of the overlap density (Löwdin 1953, Daudel *et al.* 1952). However, a consistent procedure is not easily devised for polyatomic molecules, and we prefer at this stage to present results obtained from equipartitioning. In any case if exact dipole or multipole moments are required, they are usually available as part of the output from molecular s.c.f. programmes.

In a partitioning scheme for the Roby populations of polyatomic molecules with non-minimum-basis sets, the analysis must account for all the multi-centre shared atomic populations and for the division of the polarization population. The partitioned population assigned to atom A is

$$P_A = \alpha_A + \beta_A, \tag{9.1}$$

where α_A is derived from the Roby atomic populations and β_A from the polarization population. Here

$$\alpha_A = n_A - \tfrac{1}{2}\sum_{B} s_{AB} + \tfrac{1}{3}\sum_{B,C} s_{ABC} - \dots, \tag{9.2}$$

since in the partition, n_A must be reduced by equipartition of all the two-centre shared population s_{AB} with due elimination of redundant counting of the higher order multi-centre shared populations. Similarly

$$\beta_A = u_A - \tfrac{1}{2}\sum_{B} \sigma_{AB} + \tfrac{1}{3}\sum_{B,C} \sigma_{ABC} - \dots, \tag{9.3}$$

where

$$\sigma_{AB} = u_A + u_B - u_{AB}, \tag{9.4}$$

$$\sigma_{ABC} = u_A + u_B + u_C - u_{AB} - u_{BC} - u_{AC} + u_{ABC}, \tag{9.5}$$

and u_A is the unique population given by (1.16) of the polarization functions centred at A, and u_{AB} is the corresponding population of the polarization functions at A and B taken as a group. Note that σ_{AB} will often be negative.

The sum of the partitioned populations p_A over all centres A, B, ..., Z must equal N, the number of electrons in the molecule. With the above formulae

$$\sum_{A} p_A = \sum_{A} (\alpha_A + \beta_A) = n_{AB\dots Z} + u_{AB\dots Z} = N. \tag{9.6}$$

(*b*) *Results*

Table 17 compares the atomic charges in NF_3 and NSF obtained by equipartitioning in the Roby and Mulliken methods. Results for wave functions calculated with a variety of basis sets are shown. The Mulliken charges are markedly anomalous when the basis set is unbalanced and include d polarization functions only on the central atom. On the other hand the Roby charges with unbalanced bases are similar to those with balanced bases. This is a result of the procedure of dividing the basis functions into atomic s.c.f. functions and polarization functions, with maximum possible populations ascribed to the s.c.f. functions and minimum possible populations ascribed to the polarization functions. The approximate independence of the Roby charges from basis size suggests that Roby charges can be regarded as consistent to about ± 0.1 electrons in different calculations. It will be noted however that with balanced bases, increase of basis size results in a slight decrease in the numbers of electrons assigned to the central atoms in both the Roby and Mulliken partitionings.

Table 18 for balanced s, p bases compares the Roby and Mulliken charges for the hydrides, fluorides, diatomic molecules, etc. previously discussed. It can be seen that there is agreement about the trends in the two series, but that the Roby charges are typically between 50 % and 70 % of the Mulliken charges. Both methods agree in assigning a large positive charge to Si in SiF_4, and a small negative charge to H in SiH_4. For CO the small Roby charges of ± 0.07 are in better accord with the small experimental dipole moment than the Mulliken charges of ± 0.31.

The lower Roby charges are consistent with the comparison of the Roby and Mulliken methods given in §2(*c*) for a one-electron diatomic molecule. With no polarization functions, and use of (2.21) and (2.22), the Roby partitioned population p_A is

$$p_A = n_A - \tfrac{1}{2}s_{AB} = c_a^2 + c_a c_b S_{ab} - \tfrac{1}{2}(c_a^2 - c_b^2)\, S_{ab}^2. \qquad (9.7)$$

On the right hand side the first two terms are equal to the Mulliken gross population. For a bonding orbital with c_a, c_b and S_{ab} positive, p_A will be greater than p_B when $c_a > c_b$. In such circumstances the last term of (9.7) is negative, and Roby charges in neutral molecules will tend to be smaller than Mulliken charges.

TABLE 17. CHARGES GIVEN BY EQUIPARTITIONING OF SHARED POPULATIONS FOR NF_3 AND NSF

		Roby charges			Mulliken charges		
molecule	basis	q_N		q_F	q_N		q_F
NF_3	N, F: [2, 1]	0.332		−0.111	0.484		−0.161
	N, F: [4, 3]	0.388		−0.130	0.574		−0.191
	N, F: [5, 3]	0.396		−0.132	0.536		−0.179
	N: [5, 3, 2], F: [5, 3]	0.420		−0.140	0.098		−0.033
	N, F: [5, 3, 1]	0.454		−0.152	0.667		−0.222
		q_N	q_S	q_F	q_N	q_S	q_F
NSF	S: [7, 4], N, F: [4, 3]	−0.389	0.837	−0.449	−0.471	0.983	−0.512
	S: [7, 4, 1], N, F: [4, 3]	−0.424	0.875	−0.452	−0.162	0.554	−0.392
	S: [7, 4, 2], N, F: [4, 3, 2]	−0.467	0.939	−0.472	−0.539	1.047	−0.508

TABLE 18. COMPARISON OF ROBY AND MULLIKEN CHARGES FOR AB_n MOLECULES

	Roby charges		Mulliken charges	
molecule	q_A	q_B	q_A	q_B
CH_4	−0.27	0.07	−0.76	0.19
NH_3	−0.43	0.14	−0.92	0.31
OH_2	−0.46	0.23	−0.78	0.39
FH	−0.32	0.32	−0.47	0.47
CF_4	0.60	−0.15	0.98	−0.25
NF_3	0.40	−0.13	0.54	−0.18
OF_2	0.17	−0.08	0.21	−0.10
SiH_4	0.33	−0.08	0.52	−0.13
PH_3	0.11	−0.04	0.04	−0.01
SH_2	−0.06	0.03	−0.18	0.09
ClH	−0.10	0.10	−0.20	0.20
SiF_4	1.41	−0.35	2.25	−0.56
PF_3	1.09	−0.36	1.63	−0.54
SF_2	0.68	−0.34	0.96	−0.48
ClF	0.27	−0.27	0.37	−0.37
BF	0.05	−0.05	0.39	−0.39
CO	0.07	−0.07	0.31	−0.31
CO_2	0.50	−0.25	0.64	−0.32
SiO	0.60	−0.60	0.90	−0.90
SO	0.33	−0.33	0.52	−0.52
B_2H_6	−0.13	−0.01 (H_1)	−0.14	0.06 (H_1)
	—	0.16 (H_5)	—	0.02 (H_5)

For LiF, LiH and BeH_2, as would be expected from the discussion of §8, the Roby charges depend strongly on whether the Li and Be 2p orbitals are included as projectors for the atomic populations n_A. With atomic projector functions Li (1s, 2s), F (1s, 2s, 2p) the Roby charges in LiF are ±0.87, which are close both to the Mulliken charges of ±0.87 and to the point charges ±0.84 equivalent to the experimental dipole moment. With Li 2p added as an atomic projector and hence an increased shared population, the Roby charges drop to ±0.50. With ionic projector functions Li^+ (1s), F^- (1s, 2s, 2p) the Roby charges are ±0.98.

For LiH the Roby charges are ±0.45 or ±0.10 according to whether Li 2p is excluded or included in the atomic projector functions. The Mulliken charges are ±0.12, and the experimental dipole moment is equivalent to ±0.76. For BeH_2 the Roby charge on Be is +0.89 or +0.30 depending on whether Be 2p is excluded or included as an atomic orbital. The Mulliken charge on Be is +0.56. Clearly Roby charges should be used with caution when applied to atoms for which there is ambiguity in the definition of the valence shell.

(c) *Approximations*

Except for B_2H_6, the Roby charges shown in tables 17 and 18 were calculated with the full formulae (9.2) and (9.3), but the higher-order multi-centre terms become cumbersome and are often quite small. Usually the main contribution to p_A is $n_A - \frac{1}{2}\Sigma\, s_{AB}$, where the summation is over the atoms regarded as bonded to A. If we define $y = \Sigma n_A - \Sigma\, s_{AB}$, where the first summation is over all centres and the second is over all bonds in the molecule counted once, it is often found that $N-y$ is a fairly small quantity, comparable in magnitude with the total polarization population. As a rough approximation one may divide $N-y$ by the number of bonds b in the molecule, and then for each bond assign $(N-y)/2b$ electrons to each of the two atoms participating in the bond. This gives as an approximate formula for the partitioned population

$$p_A = n_A - \tfrac{1}{2}\sum_{\text{bonds}} s_{AB} + a(N-y)/2b, \tag{9.8}$$

where a is the number of bonds in which atom A participates. This formula is much simpler to apply for multi-atom molecules than (9.2) and (9.3), and often leads to values of p_A within about 0.05 of the exact values. It is somewhat inaccurate when three-centre shared populations are appreciable, as in CO_2 where $s_{COO} = -0.341$. The approximate formula (9.8) can then be improved by including the larger $\frac{1}{3}s_{ABC}$ terms.

As an example of the approximation, consider the partitioned population for Si in SiF_4. With $a = b = 4$, $N = 50$ and $y = 50.46$, the simplest formula (9.8) reads

$$\begin{aligned} p_{Si} &= 14.42 - \tfrac{1}{2}\times 4 \times 0.87 + [4(50\text{–}50.46)/(2\times 4)] \\ &= 14.42 - 1.74 - 0.23 = 12.45. \end{aligned}$$

Thus the approximate charge on Si is 1.55, as compared with 1.41 in the complete calculation given in table 18. The slight error is due mainly to the three-centre shared populations $s_{SiFF} = -0.10$. Extension of y and (9.8) to include these terms gives the improved approximate charge as 1.45.

The Roby charges in B_2H_6 at the end of table 18 were calculated by an extension of (9.8) which included all those leading s_{AB}, s_{ABC} and s_{ABCD} terms mentioned in §6 (*b*) and table 10. Somewhat remarkably the Roby and Mulliken charges on the boron atoms, −0.13 and −0.14, are practically the same. This is probably an accident since the Mulliken method has no counterpart of the large Roby $s(B_1H_5B_2) = 0.875$, and the Roby $s(B_1B_2) = 1.979$ is very different from the Mulliken B_1B_2 overlap population of 0.170. The Roby partitioning makes the bridge hydrogens, H_5 and H_6, distinctly more positive than the Mulliken method.

(*d*) *Atomic populations, charges and electronegativities*

In §4 on AX_n hydrides and fluorides it was shown that the Roby atomic populations n_A and n_X vary in a manner consistent with the electronegativities of the atoms. Thus n_C which is 9.12 in CH_4 drops to 7.56 in CF_4, and n_S which is 17.35 in SH_2 drops to 16.10 in SF_2. The same trends are shown by the Roby charges in table 17: q_C changes from -0.27 in CH_4 to 0.60 in CF_4, and q_S changes from -0.06 in SH_2 to 0.68 in SF_2. Similarly q_H changes from -0.08 in SiH_4 to 0.32 in FH.

The problem of multiple valence states of a given atom will be considered in a later paper, but some preliminary remarks are relevant here. SII in SO has $n_S = 16.38$, while SVI in SO_3 (in the calculations with the [6, 4] basis shown in table 12) has $n_S = 16.25$. Thus in SO and SO_3 the sulphur atomic populations are much the same. However in SO the sulphur is bonded to just one oxygen with a shared population $s_{SO} = 1.51$, whereas in SO_3 sulphur shares $s_{SO} = 1.33$ electrons with each of three oxygens. The equipartition of these shared electrons (and other higher order terms) leads to charges $q_S = 0.33$ in SO and 1.82 in SO_3. It is the latter value, rather than n_S, which reflects conventional descriptions of the point charge distribution in SO_3 where sulphur is bonded to three electronegative oxygens.

As another example, CII in CO with $n_C = 7.16$ has a lower Roby population than CIV in CO_2 with $n_C = 7.67$. However, in CO the carbon shares in one bond with $s_{CO} = 2.59$, whereas in CO_2 the carbon shares in two bonds each with $s_{CO} = 2.15$. The end result is that CIV with $q_C = 0.50$ appears more positively charged than CII with $q_C = 0.07$.

In general terms where variable coordination numbers and several valence states are involved, it is Roby charges q_A rather than atomic populations n_A which show correlations with such properties as the e.s.c.a. chemical shifts of core levels in molecules.

10. DISCUSSION

The present paper has been concerned with the development and application of the Roby (1974*a*) projection-density method of population analysis. Parts of the paper have sought understanding of the method by the examination of very simple systems; other parts have explored more technical aspects, e.g. the explanation of the apparent paradox that non-zero shared populations can occur for m.os in which one atom has zero coefficients. Overall the investigation has shown that the developed Roby method yields very useful and coherent summary descriptions of molecular wave functions. The main features of the method are as follows.

(*a*) *Two-centre shared populations.* Roby shared populations s_{AB} are more consistent indicators of bond strengths than Mulliken overlap populations, which are often unsatisfactorily small or negative for electronegative elements and are rather basis dependent. The Roby s_{AB} are positive for bonded atoms and are large for conventional multiple bonds. They are small for non-bonded atoms and are negative for anti-bonding m.os. Strained ring molecules often have s_{AB} values close to those for normal bonds. If a molecular wave function can be transformed to a set of l.m.os that are well localized, the equation $s_{AB} \approx 2S_{ab}$ may provide a rough-and-ready interpretation of the shared population in an A–B single bond in terms of the overlap integral of the hybrid a.os defined by the A–B l.m.o. Indeed this interpretation provides a bridge between molecular wave mechanics and descriptive chemistry, since it is closely related to the long-established criterion of maximum overlap (Pauling 1931; Slater 1931) and the use of overlap integrals as measures of hybridization and bonding (Mulliken 1950; Maccoll 1950).

(*b*) *Multi-centre shared populations*. The Roby method can characterize multi-centre bonding directly through the multi-centre shared populations s_{ABC}, s_{ABCD}, … . In triangular H_3^+, s_{HHH} has the appreciable value of 0.99. The Roby description of diborane is satisfactory: substantial shared populations for the B–H (terminal) bonds, and shared populations s_{BHB} of 0.88 for each of the B–H–B bridges, with a total s_{BB} of 1.98. A subsequent paper (Chablo & Cruickshank 1982) will show how multi-centre shared populations s_{BBB} s_{BBC} and s_{BCC} are helpful in describing the bonding in other boranes and in carboranes.

(*c*) *Polarization function populations*. The Roby projector technique enables the unique effects of polarization functions to be identified free of any redundancy with the atomic basis functions. The examples of the pσ and mid-point 1s polarization functions for H_2^+ are instructive. In the energy optimized m.os these functions have appreciable coefficients. The Roby projector technique eliminates the redundancy with the a.o. set and shows the unshared polarization contribution to the electron population to be quite small (though of course important in terms of the differences between the minimum-basis wave function and the exact s.c.f. m.o.). In an extended basis calculation for NF_3 0.14 of the 34 electrons have to be assigned to polarization functions. In a similar calculation for SO_3 0.55 of the 40 electrons form the polarization population and of the various polarization functions the sulphur d functions are much the most important. Even so a satisfactory description of the bonding in SO_3, with acceptable shared populations s_{SO}, is obtained without reclassifying the sulphur d functions as a.os. Polarization populations are complementary to the study of electron density difference maps.

(*d*) *Atomic populations and charges*. For given coordination numbers, the Roby atomic populations n_A reflect the electronegativities of an atom and its ligands, and show to what extent the atomic environment approaches a complete noble gas shell. The populations n_A cannot be used for estimation of any electrical properties since Σn_A does not equal the number of electrons in the molecule. By equipartition of shared populations Roby charges q_A can be found which are useful but approximate indicators of the molecular charge distribution. They tend to be smaller in magnitude than Mulliken charges and are less sensitive to lack of balance in the basis set. It is hoped that Roby charges will correlate with charges determined from X-ray crystallographic experiments by Hirshfeld's (1977) method, which uses free atom densities to proportion the experimental molecular density among the constituent atoms. A preliminary comparison is encouraging.

It should be realized that the Roby method of electron population analysis requires more computation than the Mulliken method. The Mulliken populations can be obtained by simple matrix multiplications of orbital coefficients and overlap integrals. However, the Roby populations n_{AB} and u_Z given by (1.14) and (1.16) require also the inversion of a different selected overlap matrix for each distinct population n_{AB}, n_{CD}, n_{ABC}, …, $n_{AB\ldots Y}$.

It must be stressed that the Roby method of electron population analysis for molecules depends on the definition of an 'atom'. The 'atoms' define the projectors by which the molecular density is analysed. In Roby's (1974*a*) original paper most of the applications were to molecular wave functions calculated with minimum bases, and the definition of an atom was self-evident. In large-basis calculations the method leads to nonsense if all the basis functions at a given centre are regarded as belonging to the atom. Roby was well aware of this problem and he analysed large-basis molecular calculations for HF in terms of atomic s.c.f. orbitals obtained in other large-basis calculations. We have suggested that the most sensible definition of an 'atom' is obtained by using the s.c.f. a.os found from the given molecular basis set.

A possible sophistication would be to use radially contracted a.os, or in a molecule such as SO_3, where the indicated charge on sulphur is close to $+2$, to use a.os obtained from s.c.f. calculations on S^{2+}. Apart from an alternative (Li^+, F^-) analysis of LiF, we have preferred to use the s.c.f. orbitals from neutral atoms, and to realize as in §7 (*c*) that the contractions or expansions are chiefly absorbed in the populations of the outer polarization functions.

A method of population analysis based on occupation numbers of modified atomic orbitals (m.a.os) has been proposed by Heinzmann & Ahlrichs (1976). This is rather similar to the present development of the Roby method, but the atomic projectors are obtained by minimizing $\epsilon = N - \mathrm{tr}\,(DP)$, where D is the molecular density operator and P is the projector for a minimal set of m.a.os. Each m.a.o. is a linear combination of all the basis functions of appropriate symmetry at a given centre, and the coefficients are determined by minimizing ϵ. In our terminology, the m.a.os are chosen so as to minimize the polarization population. A considerable reduction is certainly achieved. The polarization population in a [5, 3] calculation for N_2 by Heinzmann & Ahlrichs comes down to 0.001 (cf. 0.106 in table 4). For the [3] calculations for the two-electron molecules H_2 and H_3^+ discussed in §7 (*c*) the polarization population would reduce to zero exactly, but with significantly different m.a.os for the two molecules. Evidently the problem of molecular formation can usefully be studied by examining the differences between m.a.os and s.c.f. a.os in different situations. However, it is uncertain as to how far m.a.os can legitimately be described as atomic, even though their component functions are all based on the centre in question.

The m.a.os determined by Heinzmann & Ahlrichs for different atoms are not independent. This is shown by their minimization for CO. In comparison with a calculation by Davidson (1967), their process while reducing ϵ from 0.16 to 0.001 also decreased the carbon population by 0.30 and increased the oxygen population by 0.22. If the m.a.o. treatment were applied to NF_3 or SO_3, say, it would reduce considerably our s and p polarization populations but would leave unaltered the unique d populations, provided d functions were not admitted to the m.a.os. In our calculations we have preferred to use the same method to measure the populations of both the non-atomic d functions and the modifications of the s and p function sets.

Our version of the Roby method has already been used in several publications: the charge distribution in the cyclohexadienyl anion (Burdon *et al.* 1979), the examination of possible cyclic structures for O_3, N_2O, N_2O^+, etc. (Chablo & Cruickshank 1981), and the interpretation of the photoelectron spectra of SOF_2, SF_4 and SOF_4 (Costa *et al.* 1981). Other papers are in preparation on: (i) multi-centre bonding in boranes and carboranes; (ii) molecules with atoms in higher valence states, including compounds of Cl, S, P and N, with detailed analyses of polarization functions and difference maps for SO_3 and NF_3O; (iii) single and multiple bonds in hydrocarbons and other simple molecules containing nitrogen, oxygen or fluorine; (iv) aromatic and related hydrocarbons, where Roby shared populations for model molecules with equal C–C lengths give good correlations with experimental bond lengths.

It should be noted that the Roby method of electron population analysis is not restricted to single determinant molecular wave functions. As may be seen from Roby's (1974*a*) original discussion in terms of natural orbitals, both the molecular density and atomic projector operators can be based on multi-determinant wave functions.

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After this paper had been accepted for publication, we learned with regret of the untimely death of Keith Roby on 8 November 1981 at the age of 39. We therefore dedicate the paper to his memory.

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