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The Projection of Molecular Charge Density into Spherical Atoms.
I. Density Basis Functions for First-Row Atoms

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Electron population analyses of several molecular one-electron density functions have been studied by least-squares projection methods into several atomic-density basis functions. All studies have been restricted to spherically symmetrical functions, which have been fitted to the atomic-density functions for the ground-state atoms hydrogen through neon. It is found that when the atom-density basis functions are split into inner (K shell) and outer (L shell) parts, then the atomic charges reflect polarity of the molecule reasonably well and, moreover, are relatively independent of the orbital bases used in spanning the molecular wave function. The standard density basis sets given here can be used for a similar electron population analysis of accurate X-ray diffraction data.

1. Introduction

The concept of a local electronic charge on an atom in a molecule has been qualitatively valuable in correlating and interpreting a wide range of molecular properties. A unique, well defined procedure for partitioning a molecular electron density into atomic components has been proposed (Srebrenik & Bader, 1975). However, it has proved difficult to turn these virial fragments into simple X-ray scattering factors. Such a partition, if it could be achieved in a practical manner, would permit many qualitative discussions of electron distribution to be recast in more precise form.

In earlier work, atomic-density basis functions were used for electron population analysis of X-ray diffraction data (Stewart, 1970*a*). The atom-density functions consisted of a core part $(\varphi_{1s})^2$, and an L shell constructed from a standard STO (Hehre, Stewart & Pople, 1969). The core was frozen at two electrons and the L-shell functions were then used to analyze X-ray structure factors by least-squares projection methods. Reasonable atomic charges for the molecular crystals of *s*-triazine, cyanuric acid and uracil were found. The projection of F_o (or $\bar{\rho}$) into atomic density functions as a basis for determining the atomic charge has been employed by Coppens (1975) for molecular crystals and by Kurki-Suonio & Salmo (1972) for ionic crystals. In this case finite spheres with appropriate atomic radii are chosen as the atomic functions. It is desirable, however, to develop a standard set of atomic-density basis functions that can be easily used for atomic population analysis of molecular density functions derived from electronic wave functions as well as for a comparable analysis of X-ray diffraction data.

A density-partitioning technique frequently employed by theoretical chemists is Mulliken's (1955) population analysis. This starts with a molecular-orbital wave function, each orbital being expanded as a linear combination of basis functions centered at the atomic nuclei. By appropriate distribution of the total electron population among the basic functions, an atomic partition is achieved. The principal drawback of this method is that the populations depend on the details of the basis set used as well as on the density function that is to be represented. Two different basis sets, which lead to similar total electron density functions, may give quite different atomic electron populations by Mulliken analysis. Clearly, if the electron-density function is obtained in some other manner such as from X-ray diffraction data, then an approach in terms of a particular orbital basis set is quite inappropriate.

An alternative approach, which avoids these difficulties of Mulliken population analysis, is to represent the electron density $\rho(\mathbf{r})$ approximately by an expansion in terms of a separate basis set designed primarily for this purpose. Thus, if $\Omega_j(\mathbf{r})$ $(j = 1, 2\ldots)$ constitutes such a density basis set, an approximate expansion

$$\rho'(\mathbf{r}) = \sum_j p_j \Omega_j(\mathbf{r}) \tag{1}$$

can be obtained by least-squares fitting to $\rho(\mathbf{r})$, thereby leading to a set of populations p_j. The use of different orbital basis sets leading to the same density $\rho(\mathbf{r})$ would thus give the same population analysis in these terms.

Perhaps the simplest density basis expansion (1) is one in which there is a single spherically symmetric Ω function for each atom A in the molecule,

$$\rho'(\mathbf{r}) = \sum_{A}^{\text{atoms}} p_A \Omega_A(|\mathbf{r} - \mathbf{R}_A|), \tag{2}$$

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$\mathbf{R}_A$ being the position vector of the A nucleus. Further, $\Omega_A(\mathbf{r})$ may be chosen as the spherically averaged electron density for the isolated atom A. It may be noted that an electron density function such as (2) is implicitly assumed in most structure determinations by X-ray crystallography. The populations p_A are normally taken to be equal to the number of electrons in the neutral atoms and the $\mathbf{R}_A$ then adjusted to optimize the agreement between structure factors implied by (2) and those found experimentally.

If the parameters p_A in (2) are adjusted by least-squares fitting to the exact density $\rho(\mathbf{r})$, we have a well-defined set of total atomic populations. Even if $\rho(\mathbf{r})$ is not exact, such populations should converge to limiting values as the errors are removed. The p_A obtained in this way may be described as total atomic populations using a spherical-atom-density basis set.

Populations obtained directly from (2) will be subject to some drawbacks. One limitation is that the optimum p_A will not necessarily add up to the number n of electrons in the molecule. An alternative procedure is to introduce an electron-number constraint

$$\sum_j p_j = n \tag{3}$$

and vary p_j in (1) subject to this restriction.

Another feature that is not treated adequately by the approximate density function (2) is the tendency of atoms to expand or contract in a molecular environment. This can be incorporated into the treatment by generalizing (2) to

$$\rho'(\mathbf{r}) = \sum_A^{\text{atoms}} p_A s_A^3 \Omega_A(s_A|\mathbf{r}-\mathbf{R}_A|) \tag{4}$$

where s_A is a scale factor for atom A. If the s_A parameters are also varied in the least-squares fitting procedure, the density population analysis may be described as scaled. The scale factors s_A may or may not be associated with the electron-number constraint (3).

A further difficulty with population analysis based on (2) or (4) is that all parts of each atom are treated in a uniform manner. For example, a low population p_A for a particular atom in (2) implies that electrons are removed in similar proportions from inner shells and from the valence shell. In reality, most of the population variation from molecule to molecule takes place in the valence shell. To incorporate such additional flexibility into $\rho'(\mathbf{r})$, the density basis set must be expanded to more than one function per atom. The simplest extension would be to use two spherical functions, one for the inner shells and one for the valence shell.

The principal objective of this paper is to develop and test techniques for carrying out these various types of atomic population analysis. This will be carried out by developing Gaussian representations for spherical-atomic-density basis functions $\Omega_j(\mathbf{r})$. Subsequent least-squares variation of populations and scale factors can then be performed easily if the electron density $\rho(\mathbf{r})$ is available in Gaussian form. Since this is part of the normal output of a molecular-orbital wave-function calculation with a Gaussian orbital basis set, the technique is widely applicable.

In the next section, the general theory of the least-squares fitting with Gaussian density basis functions is outlined. This is followed by determination of Gaussian representations for the spherical atom densities $\Omega_A(\mathbf{r})$ which can then be used to determine the total populations defined by (2) or (4). In the later sections of the paper, corresponding methods are developed which allow for separate density basis functions for inner and valence shells of atoms beyond helium.

2. General theory of spherical Gaussian fits of electron density

In this section we consider the general problem of fitting a given density function $\rho(\mathbf{r})$ by a linear combination of spherical Gaussian functions using a least-squares criterion. Suppose that the density is represented approximately by an expansion (1) where p_j are population parameters to be determined and the density basis functions Ω_j are contracted Gaussian functions,

$$\Omega_j(\mathbf{r}) = \sum_k d_{jk} g_k(\gamma_k, \mathbf{r}-\mathbf{R}_j), \tag{5}$$

$$g(\gamma, \mathbf{r}-\mathbf{R}) = (\gamma/\pi)^{3/2} \exp[\gamma(\mathbf{r}-\mathbf{R})^2]. \tag{6}$$

All primitive Gaussian functions g_k constituting one Ω_j are taken to be at the same center $\mathbf{R}_j$. The basis functions will be normalized so that

$$\sum_k d_{jk} = 1; \quad \int \Omega_j(\mathbf{r})\,d\mathbf{r} = 1. \tag{7}$$

We determine population parameters p_j by minimization of

$$\varepsilon = \int (\rho - \rho')^2\,d\mathbf{r} \tag{8}$$

or

$$\varepsilon' = \varepsilon - \int \rho^2\,d\mathbf{r} = -2\int \rho\rho'\,d\mathbf{r} + \int \rho'^2\,d\mathbf{r}. \tag{9}$$

Substitution of (1) leads to

$$\varepsilon' = -2\sum_j w_j p_j + \sum_{jk} V_{jk} p_j p_k \tag{10}$$

where

$$w_j = \int \rho \Omega_j\,d\mathbf{r} = \sum_k d_{jk} \int \rho g_k\,d\mathbf{r} \tag{11}$$

and

$$V_{jk} = \int \Omega_j \Omega_k\,d\mathbf{r} = \sum_{lm} d_{jl} d_{jm} \int g_l g_m\,d\mathbf{r}$$

$$= \sum_{lm} d_{jl} d_{jm} \left[\frac{\gamma_l \gamma_m}{\pi(\gamma_l + \gamma_m)}\right]^{3/2} \times \exp\left[-\frac{\gamma_l \gamma_m}{\gamma_l + \gamma_m}(\mathbf{R}_j - \mathbf{R}_k)^2\right]. \tag{12}$$

If we write **p**, **w** and **V** for the vectors and matrices p_j, w_j and V_{jk}, unconstrained minimization of (10) with respect to **p** leads to the solution

$$\mathbf{p} = \mathbf{V}^{-1}\,\mathbf{w}. \tag{13}$$

This solution is unique, provided that **V** is non-singular.

As indicated in the *Introduction*, it is often preferable to minimize ε' subject to the electron-number constraint

$$\int \rho'\,d\mathbf{r} = \sum_i p_j = n \tag{14}$$

where n is the number of electrons. Using the method of Lagrange multipliers, define

$$\varepsilon'' = \varepsilon - \lambda \sum_j p_j. \tag{15}$$

Then the conditions $\partial\varepsilon''/\partial p_j = 0$ together with (14) lead to the constrained solution

$$\mathbf{p} = \mathbf{V}^{-1}\,\mathbf{w} + (\mathbf{i}^t\,\mathbf{V}^{-1}\,\mathbf{i})^{-1}\,(n - \mathbf{i}^t\,\mathbf{V}^{-1}\,\mathbf{w})\,\mathbf{V}^{-1}\,\mathbf{i}. \tag{16}$$

Here **i** and $\mathbf{i}^t$ are column and row vectors with unit elements.

The above analysis is general and makes no reference to the actual form of the density function $\rho(\mathbf{r})$. In molecular-orbital calculations, $\rho(\mathbf{r})$ is frequently obtained as a quadratic expression

$$\rho(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu}\,\varphi_\mu\,\varphi_\nu \tag{17}$$

where φ_μ, φ_ν are orbital basis functions and $P_{\mu\nu}$ is the one-electron density matrix. Equation (11) then becomes

$$w_j = \sum_k d_{jk}(\gamma_k/\pi)^{3/2} \sum_{\mu\nu} P_{\mu\nu} \int \varphi_\mu\,\varphi_\nu \exp[-\gamma_k(\mathbf{r}-\mathbf{R}_j)^2]\,d\mathbf{r}. \tag{18}$$

If the orbital basis functions φ_μ are themselves of Gaussian type, the integrals in (18) can be evaluated by elementary methods.

3. Optimized Gaussian fits to spherical atomic densities

In this section, we attempt to determine the best fits of a spherically averaged atomic density $\rho(r)$ by a linear combination of M uncontracted Gaussian basis functions Ω_j centered at the nuclear position ($M = 1, 2, 3, \ldots$). Thus, instead of (5) we use

$$\Omega_j = g_j(\gamma_j, r) \quad (j = 1, \ldots M) \tag{19}$$

the nucleus being placed at the coordinate origin. The M Gaussian exponents γ_j are then to be determined.

For a given set of γ_j, the individual populations p_j may be determined either directly (13) or with the total-electron constraint (16). In either case, the result is a residual $\varepsilon(\gamma_j)$. This can then be minimized with respect to all the γ_j by an appropriate search procedure. In practice, the optimum γ_j can be found by minimization of ε' (9), thereby avoiding computation of $\int \rho^2\,d\mathbf{r}$. For the H atom, we have obtained results with and without the total population constraint, using differentiation with respect to γ_j to locate the optimum fit. For other atoms, only the constrained solution has been considered and minimization of γ_j has been carried out by a version of the Fletcher & Powell (1963) search procedure. The results for H were then used as a suitable bench mark to test our search procedure for other atoms.

H *atom*

For the ground state of the H atom,

$$\rho(r) = \pi^{-1}\exp(-2r) \tag{20}$$

and the precise solution of the problem is possible. Equation (8) takes the form

$$\varepsilon = \int_0^\infty \left[\pi^{-1}\exp(-2r) - \sum_j p_j(\gamma_j/\pi)^{3/2} \times \exp(-\gamma_j r^2)\right]^2 4\pi r^2\,dr. \tag{21}$$

The extremum conditions

$$\partial\varepsilon/\partial p_j = \partial\varepsilon/\partial\gamma_j = 0, \quad j = 1 \ldots M \tag{22}$$

lead to

$$G_2(\tfrac{1}{4}\gamma_k) = 2\sum_j p_j\gamma_j^{3/2}(\gamma_j + \gamma_k)^{-3/2} \tag{23}$$

$$G_4(\tfrac{1}{4}\gamma_k) = 12\sum_j p_j\gamma_j^{3/2}(\gamma_j + \gamma_k)^{-5/2} \tag{24}$$

$$G_n(x) = \int_0^\infty t^n \exp(-t - xt^2)\,dt. \tag{25}$$

Evaluation of the functions $G_n(x)$ has been discussed previously (Stewart, 1969). Solution of (23) and (24) for (p_j, γ_j) then gives the unconstrained solution. Results up to $M = 6$ are listed in Table 1.

The unconstrained solutions to the H atom density have a simple relation to the corresponding solutions for small Gaussian fits to a 1*s* orbital. It can be shown that unconstrained γ_j and p_j in Table 1 are easily determined from α_j and d_j in Table 1 of Stewart (1970*b*) by the equations,

$$\gamma_j = 4\alpha_j \tag{26}$$

$$p_j = \sqrt{2}\left[\sum_{m=1}^{M} d_m\alpha_m^{3/4}\,G_2(\alpha_m)\right]\alpha_j^{-3/4}\,d_j \tag{27}$$

where $G_2(X)$ is given by (25).

If the variation is constrained so that the sum of populations p_j is unity, the function ε'' (15) is used and the appropriate extremum conditions are

$$\partial\varepsilon''/\partial p_j = \lambda; \quad \partial\varepsilon''/\partial\gamma_j = 0, \tag{28}$$

Table 1. *Density basis functions for hydrogen* [(*expansions for* $\pi^{-1}\exp(-2r)$]

	Unconstrained		Constrained	
M	γ_j	p_j	γ_j	p_j
1	1·083799	7·291582 (−1)	7·970093 (−1)	1·000000
2	3·407275	1·355567 (−1)	2·915943	1·764218 (−1)
	6·064932 (−1)	7·807701 (−1)	5·130127 (−1)	8·235782 (−1)
3	8·910642	2·368420 (−2)	8·017498	2·889780 (−2)
	1·623085	2·946506 (−1)	1·458517	3·410172 (−1)
	4·392700 (−1)	6·522254 (−1)	3·919576 (−1)	6·300850 (−1)
4	2·086738 (1)	4·601400 (−3)	1·926613 (1)	5·376900 (−3)
	3·818473	7·538720 (−2)	3·524518	8·660460 (−2)
	1·060814	4·035320 (−1)	9·780867(−1)	4·390733 (−1)
	3·520745 (−1)	5·050739 (−1)	3·230799(−1)	4·689452 (−1)
5	4·522255 (1)	1·005000 (−3)	4·241512 (1)	1·140900 (−3)
	8·286913	1·840230 (−2)	7·771840	2·075760 (−2)
	2·314594	1·399764 (−1)	2·170171	1·547741 (−1)
	7·902898 (−1)	4·557578 (−1)	7·403047 (−1)	4·776157 (−1)
	2·978109 (−1)	3·801028 (−1)	2·780168 (−1)	3·457117 (−1)
6	9·241213 (1)	2·434000 (−4)	8·759984 (1)	2·707000 (−4)
	1·694366 (1)	4·678900 (−3)	1·606086 (1)	5·190700 (−3)
	4·740226	4·153020 (−2)	4·492888	4·570000 (−2)
	1·628396	2·034963 (−1)	1·543057	2·191485 (−1)
	6·323537 (−1)	4·649442 (−1)	5·987529 (−1)	4·752435 (−1)
	2·604382 (−1)	2·830051 (−1)	2·459547 (−1)	2·544466 (−1)

leading to

$$G_2(\tfrac{1}{4}\gamma_k) = 2\left[\sum_j p_j\,\gamma_j^{3/2}(\gamma_j+\gamma_k)^{-3/2} - \pi^{3/2}\,\gamma_k^{-3/2}\,\lambda\right]$$

$$G_4(\tfrac{1}{4}\gamma_k) = 12\left[\sum_j p_j\,\gamma_j^{3/2}(\gamma_j+\gamma_k)^{-5/2} - \pi^{3/2}\,\gamma_k^{-5/2}\,\lambda\right]$$

$$\sum_j p_j = 1. \tag{29}$$

These equations have also been solved up to $M = 6$ for (p_j, γ_j), the results also being listed in Table 1.

Table 2. *Exponents for atomic d functions*

Atom	α_d
He	1·971
Li	4·560
Be	0·276
B	0·412
C	0·622
N	0·922
O	1·298
F	1·752
Ne	2·305

Atoms He *to* Ne

For heavier atoms, we have fitted spherical Gaussian density expansions to atomic electron density functions which make some allowance for electron correlation. Atomic wave functions were first obtained by the unrestricted Hartree–Fock procedure (Pople & Nesbet, 1954), *i.e.* the energy-optimized single determinant in which α and β electrons occupy different orbitals. The correlation correction of the electron density is then introduced by the Møller & Plesset (1934) perturbation scheme, terminated at second order (Seeger & Pople, 1975). For the atoms B, C, O and F, with p-type ground states, these atomic densities will not be spherically symmetric, but they can still be least-squares fitted by spherical expansions.

The atomic-orbital basis sets are based on those developed by van Duijneveldt (1971). For helium, we use his 10s Gaussian expansion. To take account of correlation, it is necessary to expand the basis set by including functions with higher angular quantum numbers. The full basis used is (10s,8p,1d). The p functions are chosen with exponents equal to those of the outermost eight s functions. The single set of d functions has a Gaussian exponent α_d = 1·971, obtained by energy optimization (Binkley & Pople, 1975). For Li and Be, we use (11s,7p,1d) orbital basis sets, constructed in the same manner as for He. The p exponents coincide with the outer seven s exponents and the d exponent is determined by optimization of the UMP2 (unrestricted Møller–Plesset, second-order) energy (Binkley & Pople, 1975) (Table 2). For B to Ne, the (11s,7p) set of van Duijneveldt (1971) is again supplemented by a single set of d functions obtained in the same way.

The atomic densities at the UMP2 level were fitted to the spherical expansions with total electron number constraint and with various values of M.†

4. Population analysis with one density basis function per atom

The atomic density representations obtained in the previous section can now be used to carry out molecular population analyses as indicated in the *Introduction*. One density basis function Ω_A is used for each atom, this being the contracted ($M = 5$) Gaussian function discussed in §3. In all cases we use the electron-number constraint within the atom and in the molecular analysis.

The population analysis was applied to density functions $\rho(\mathbf{r})$ obtained from a molecular-orbital calculation using the 6-31G* orbital basis set (Hariharan & Pople, 1973). This was first with the unrestricted Hartree–Fock (UHF) procedure (Pople & Nesbet, 1954) and then with the correlated density function obtained by applying the second-order Møller–Plesset correction (UMP2) (Seeger & Pople, 1975). The geometries used were those which minimized the corresponding energies.

Results for simple first-row hydrides are shown in Table 3, both with and without rescaling. In all cases, the results indicate very non-polar structures, the atomic populations being close to those of the neutral atoms. The optimized scaling factors for H are considerably greater than unity for some molecules, but the corresponding populations remain close to unity. These results are undoubtedly caused by the rigidity of the fit to the inner-shell region of the non-hydrogen atom and indicates that a satisfactory population analysis cannot be achieved unless the inner-shell electron density is separated from the valence part. This necessarily requires more than one density basis function per atom.

Table 3. *Population analysis with one density basis function per atom (based on* UMP2/6-31G* *molecular orbital calculations)*

	No rescaling		Rescaled			
Molecule	p_A	p_H	s_A	p_A	a_H	p_H
LiH	2·972	1·028	1·019	2·946	1·151	1·054
BeH	3·950	1·050	1·001	3·962	1·294	1·038
BH	4·976	1·024	1·004	4·977	1·402	1·023
CH	5·975	1·025	0·999	5·992	1·401	1·008
NH	6·965	1·035	0·996	6·995	1·327	1·005
OH	7·960	1·040	0·995	7·995	1·184	1·005
FH	8·962	1·038	0·994	9·000	1·018	1·000
BeH_2	3·950	1·025	1·001	3·963	1·316	1·019
BH_2	4·944	1·028	0·994	4·982	1·364	1·009
CH_2	5·941	1·030	0·988	6·005	1·318	0·997
NH_2	6·937	1·032	0·988	7·004	1·175	0·998
OH_2	7·951	1·025	0·991	8·008	1·141	0·996

5. Separation of inner and valence shell atomic densities

In this section we discuss the specification of more than one density basis function per atom (Li to Ne) in order

Table 4. *Shell density basis functions for* Li–Ne

	Shell	γ_j	p_j
Lithium	*K*	6·020625 (1)	6·347853 (−2)
		1·072344 (1)	6·835616 (−1)
		2·655235	1·252959
	L	7·232958 (−1)	−1·165096 (−1)
		1·049073 (−1)	1·116510
Beryllium	*K*	1·120053	6·197620 (−2)
		2·006076 (1)	6·828745 (−1)
		5·080061	1·255149
	L	8·525480	1·524275 (−1)
		3·634112	−2·793610 (−1)
		2·131764 (−1)	2·126933
Boron	*K*	1·793437 (2)	6·132441 (−2)
		3·222402 (1)	6·838936 (−1)
		8·256866	1·254782
	L	2·023289 (1)	8·467290 (−2)
		4·839469	−2·233350 (−1)
		3·630471 (−1)	3·138662
Carbon	*K*	2·623041 (2)	6·090121 (−2)
		4·722486 (1)	6·853655 (−1)
		1·217508 (1)	1·253733
	L	3·660348 (1)	6·778450 (−2)
		7·001496	−1·978088 (−1)
		5·612485 (−1)	4·130024
Nitrogen	*K*	3·608614 (2)	6·068809 (−2)
		6·505921 (1)	6·856238 (−1)
		1·687057 (1)	1·253688
	L	1·329521 (2)	2·081204 (−2)
		7·952781 (−1)	4·574772
		1·391511 (−1)	4·044154 (−1)
Oxygen	*K*	4·743946 (2)	6·062425 (−2)
		8·561050 (1)	6·870775 (−1)
		2·226712 (1)	1·252298
	L	1·790239 (2)	2·136481 (−2)
		1·139033	5·145554
		2·476962 (−1)	8·330810 (−1)
Fluorine	*K*	6·031480 (2)	6·061261 (−2)
		1·089292 (2)	6·884314 (−1)
		2·839467 (1)	1·250956
	L	2·352769 (2)	2·110218 (−2)
		1·560193	5·682882
		3·767315 (−1)	1·296016
Neon	*K*	7·470428 (2)	6·063671 (−2)
		1·350097 (2)	6·896739 (−1)
		3·525300 (1)	1·249689
	L	3·031421 (2)	2·033345 (−2)
		2·060714	6·197815
		5·268264 (−1)	1·781851

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† A list of the complete results for $M = 5$ has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33391 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

to incorporate more flexibility into the atomic-population description. One way to do this is to take the density fits discussed in § 3 and split them into inner and outer parts. For example, one might take the five-Gaussian fits of the table and use three Gaussian functions for an inner basis function and the outer two for the valence density. This does not, of course, correspond to a correct division of the atomic electrons into K and L shells since the sum of the lowest three populations for any atom is not equal to 2·0 so that it does not represent the inner shell precisely. Since it is useful to retain the description of two electrons in the K shell, we have obtained alternative basis sets which handle the two shells separately. The procedure consists of the following steps.

(1) An inner-shell density,

$$\rho_K = 2\psi_{1s}^2$$

is constructed for each atom using a restricted Hartree–Fock (RHF) procedure and the same orbital basis described in § 3.

(2) ρ_K is fitted by a set of three Gaussian functions using the procedure outlined in § 2. This defines a contracted K-shell density basis function Ω_K.

(3) The previously obtained unrestricted Hartree–Fock ρ_{UHF} are modified to give valence densities ρ_L by

$$\rho_L = \rho_{\mathrm{UHF}} - 2\Omega_K.$$

(4) The valence density ρ_L is then fitted by a further set of three Gaussian functions to give a contracted L-shell density basis function Ω_L. In the case of Li only two Gaussian functions were used for this fit since two of the exponents were found to collapse to a common value when optimization of three was attempted.

The resulting density basis functions are listed in Table 4. It should be noted that each is normalized to the number of electrons in the shell in the atomic ground state.

6. Population analysis with separated valence density basis

The atomic density basis functions obtained in the preceding section can be used to investigate the charge distributions in a number of simple molecules. Two density functions are used for each non-hydrogen atom; the single function for H is that with $M = 5$ from Table 1 (with electron-number constraint). Average molecular scaling factors were first determined by population analysis of the hydride series, LiH, BeH_2, BH_3, CH_4, NH_3, H_2O and HF. These molecular $\rho(\mathbf{r})$ were obtained from 6-31G* basis sets. For the heavy atoms, scaling was only applied to ρ_L. For H an average scale factor, $(1{\cdot}5)^{1/2}$, was found for the series B to F. (This value is not appropriate for LiH or BeH_2.) Scaling factors, listed as the square of s_A [see equation (4)], are given in Table 5. These factors were then used to scale the L-shell density functions in Table 4 and H in Table 1 ($M = 5$).

Table 5. *Average molecular scaling factors*

	s_A^2 [equation (4)]
Li	1·44
Be	1·25
B	1·26
C	1·08
N	0·91
O	0·92
F	0·95
H	1·5 (for B to F only)

The population analysis with the scaled density functions A, is applied to the Hartree–Fock densities

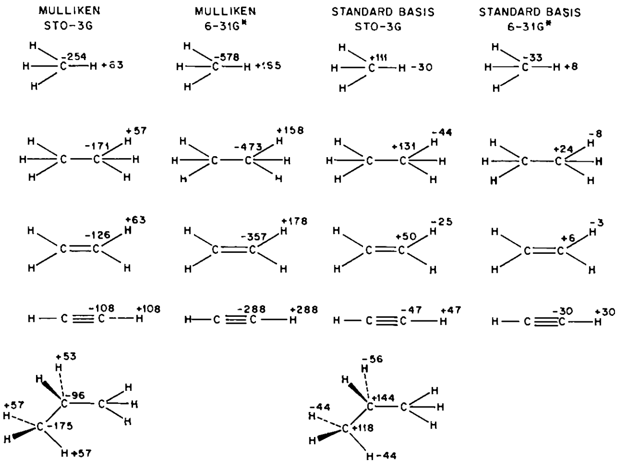

Fig. 1. Net charges (me) for hydrocarbons.

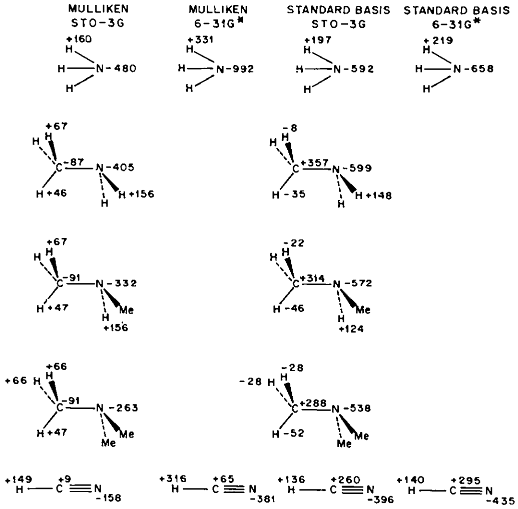

Fig. 2. Net charges (me) for nitrogen compounds.

$\rho(\mathbf{r})$ obtained from molecular-orbital calculations using the minimal STO-3G basis set and, for a smaller set of molecules, the polarized 6-31G* set. The populations obtained by our technique may be compared for the two basis sets, thereby giving some indication of the changes of electron distribution that occur when the orbital basis flexibility is increased.

The method has been applied to the set of molecules illustrated in Figs. 1–4, which give the results. All geometries are chosen according to a standard model described previously by Pople & Gordon (1967). The first two columns in each figure are based on Mulliken gross populations for the two orbital basis sets. The third and fourth columns give results with the standard density basis specified above.

The following features are apparent from the results. (*a*) The separation of the core and valence densities on the non-hydrogen atoms leads to more realistic charge distributions. This confirms the suggestion that the very non-polar electron distributions of Table 3 are due to including inner-shell electrons in the variable atom population. If the core density is treated separately, much larger variations are found in valence-electron populations.

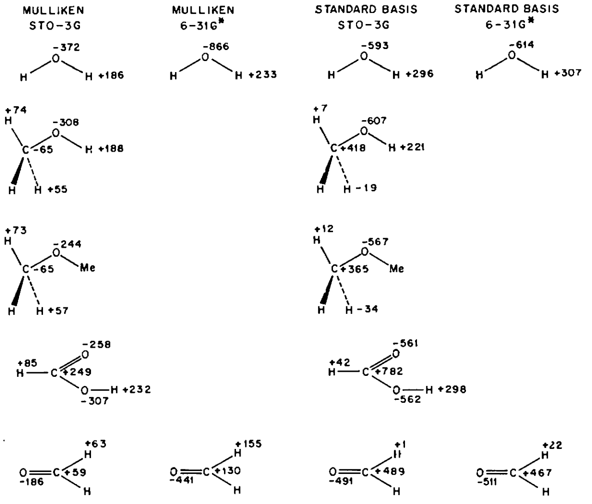

Fig. 3. Net charges (me) for oxygen compounds.

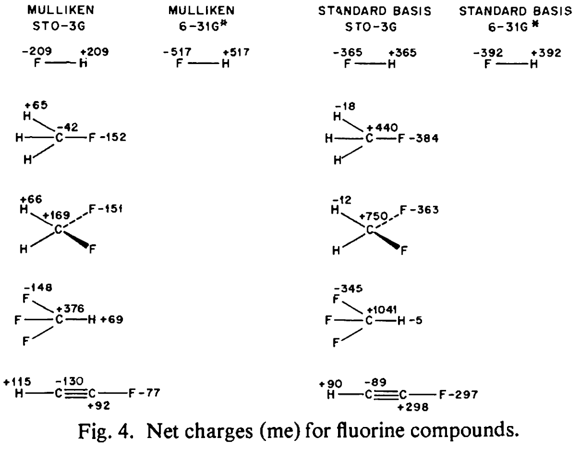

Fig. 4. Net charges (me) for fluorine compounds.

(*b*) For those molecules which have been examined with both STO-3G and 6-31G* basis sets, the populations obtained by our method do not differ very much. The differences are much less than the differences between the corresponding Mulliken populations. This indicates that the real differences between the two functions (using different orbital bases) are really less than would be suggested by the wide variations in Mulliken populations.

(*c*) The populations by density basis function analyses are generally closer to the Mulliken populations for the STO-3G orbital basis set than to the Mulliken populations for 6-31G*. This indicates that the high polarities implied by the Mulliken populations for extended orbital basis sets represent some lack of balance in the basis rather than real polarity in the full density function.

(*d*) Many expected qualitative trends are shown by the populations using the standard density basis set. The H atoms in acetylene are found to be more positive than in the other simple hydrocarbons methane, ethane and ethylene. The series of bonds to hydrogen C—H, N—H, O—H and F—H become increasingly polar.

7. Conclusion

The results described in this paper suggest that the technique of least-squares fitting of a density function to a small density basis set is a useful method of partitioning a total number of electrons into a set of well-defined populations. It is clear that inner-shell electrons have to be handled separately but, if this is done, the resulting valence-shell populations appear to reflect changes in atomic charge reasonably without too much detailed dependence on the orbital basis used.

The standard density basis sets given here may be easily converted to X-ray form factors which can serve as a basis for electron population analysis of X-ray diffraction data. Several applications will be given in a separate paper.

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The Projection of Molecular Charge Density into Spherical Atoms. II. An Application to X-ray Diffraction Data

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Standard density basis functions for hydrogen and the first-row atoms have been converted to *K*-shell and *L*-shell scattering factors. With the *K* shell fixed at two electrons, these scattering factors have been used for atomic-charge analysis of X-ray structure factors by the method of least squares. Results for cyanuric acid and uracil are given. The net charges for these cyclic amides are in reasonable agreement. It is recommended that scattering factors here be used for atomic-charge analysis of first-row atoms in routine structure refinements of chemically related molecular crystals.

Introduction

In the previous paper (Yáñez, Stewart & Pople, 1978), a set of atomic-density basis functions for first-row atoms were developed for a population analysis of molecular charge densities. These functions can be transformed into suitable scattering factors so that X-ray structure factors may be analyzed for atomic charges by the *L*-shell projection method (Stewart, 1970; Coppens, Pautler & Griffin, 1971).

We report below application of these form factors to atomic charge analysis of cyanuric acid and uracil. These two molecular crystals are closely related chemically since they are cyclic amides. In the present work the scattering factors have not been scaled, although this variation could be easily incorporated into the least-squares equations. The spirit of the approach is to use standard density basis functions for an atomic population analysis of chemically related molecules.

Refinement model and X-ray scattering factors

The atomic scattering factor is split into *K*-shell and *L*-shell functions for the first-row atoms. For the H atom, only a *K*-shell function is used. The outer shell is assigned a variable population parameter and the *K* shell is frozen with a charge content of two electrons. The structure factor model is

$$F_{\mathbf{h}} = \sum_{\text{sym}} \sum_{p=1}^{N} [kf_{pK}(S) + P_p f_{pL}(S)] \exp(2\pi i\mathbf{h}^t\mathbf{x}_p) \exp(-\tfrac{1}{2}\mathbf{S}^t\mathbf{U}_p\mathbf{S}) \quad (1)$$

where P_p, $\mathbf{x}_p$ and $\mathbf{U}_p$ are least-squares parameters for atom p and k is the overall scale factor. The charge of atom p is

$$q_p = 2 + P_p/k. \quad (2)$$

In the least-squares fit of (1) to observed structure factors, the inhomogeneous terms for the solution of P_q are,

$$I_q = \sum_{\mathbf{h}} W_{\mathbf{h}} F_{\mathbf{h}}^{\text{OBS}} f_{qL}(S) \exp(-\tfrac{1}{2}\mathbf{S}^t\mathbf{U}_p\mathbf{S}) \exp(-2\pi i\mathbf{h}^t\mathbf{x}_p) \quad (3)$$

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