gène, ce qui est très important du point de vue théorique, il nous semble donc absolument nécessaire de vérifier ce point expérimentalement. A cet effet, des mesures de diffusion des rayons X aux petits angles, qui sont particulièrement adaptées au cas de VO_2 dopé au niobium, seront entreprisent prochainement.

Nous tenons à exprimer notre gratitude à J. P. Pouget, H. Launois, et F. Dénoyer pour de nombreuses discussions, et à L. Descamps pour son assistance technique toujours très compétente et trés appréciée.

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Core Deformation Studies by Coherent X-ray Scattering

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'Core' deformation scattering factors have been determined for a series of diatomic molecules. These are defined as the difference between scattering factors calculated from corresponding molecular and atomic core orbital products. The core deformation scattering factors are too small to be measured by current X-ray diffraction methods. The core deformation scattering factors have been expanded in multipolar series about the nuclei. The major component of core deformation is a dipolar term, which is transferable for the same atom in different diatomic molecules. The multipole-expansion terms can be well represented by the Fourier–Bessel transforms of simple density-deformation multipole functions. The dipole density function makes a sizeable contribution to certain molecular physical properties (*e.g.* electric fields at the nuclei). Even though features of the core density deformation function are also present in the valence molecular orbital products, it is unlikely that total core deformation will be determined by X-ray diffraction measurements. The generalization of these findings to polyatomic systems is discussed.

Introduction

The approximation that coherent X-ray scattering by a core-electron distribution function is invariant to molecular formation is found in several models for electronic structure analysis of X-ray diffraction data (Stewart, 1968; Coppens, 1971). Previous theoretical studies (Groenewegen, Zeevalkink & Feil, 1971; Bentley & Stewart, 1971) have suggested that core deformation effects are too small to be easily detected by X-ray diffraction intensity measurements. In the present report we will extend and, to some extent, modify these conclusions.

In order to study 'core' or 'valence' properties, we need some criterion by which to define core and valence contributions to molecular (or atomic) one-

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electron density functions. An experimental criterion is ionization potential. Koopmans' theorem (Koopmans, 1934) has often been used to relate the ionized electron to a state function, which is characterized as either an atomic or a molecular orbital. The Hartree–Fock–Roothaan equations (Roothaan, 1951),

$$\mathsf{F}\mathbf{c}_i = \varepsilon_i \mathsf{S}\mathbf{c}_i, \tag{1}$$

provide a basis for differentiation of core and valence orbitals. In (1) F is the Fock Hamiltonian operator matrix, S is a matrix of overlap integrals among members of the atomic orbital basis set, $\mathbf{c}_i$ is the ith eigenvector of the expansion coefficients and ε_i the corresponding eigenvalue. The molecular or atomic orbitals of the system are

$$\psi_i = \sum_\mu c_{i\mu}\chi_\mu = \mathbf{c}_i^t \boldsymbol{\chi}, \tag{2}$$

where $\boldsymbol{\chi}$ is a vector of basis functions. Once the basis $\boldsymbol{\chi}$ is specified, $\mathbf{c}_i$ and ε_i are unique solutions to (1). For a first-row atom, the eigenvector with lowest eigenvalue is often called the core orbital. It is highly localized about the nucleus compared to the other atomic orbitals. For a diatomic molecule comprised of first-row atoms, the eigenvectors with the two lower eigenvalues are designated the core-electron orbitals. Except in cases of symmetry with respect to internuclear exchange (*e.g.* N_2), these core orbitals are rather localized in space about one of the nuclei; specifically, the eigenvector with the lower eigenvalue is localized about the nuleus of higher atomic number.

It was pointed out by Fock (1930) that a single determinant wavefunction is invariant to any unitary transformation of the atomic of molecular orbitals. Thus there are an infinite number of possible descriptions of the electronic structure in terms of orbitals. Several schemes have been proposed to transform the canonical molecular orbitals [*i.e.* the solutions to (1)] into localized molecular orbitals which correspond to chemical concepts of inner-shell electrons, lone pairs of electrons and bonds. Two intrinsic localization methods, which depend only on the self-consistent field wavefunction, are the energy localization procedure of Edmiston & Ruedenberg (1963) and the density localization method of von Niessen (1972*a*). The latter approach is very appealing for partitioning the one-electron density function in a study of coherent X-ray scattering. Von Niessen's results for homonuclear diatomic molecules show that 96% of the density-localized inner-shell orbital products are comprised of the canonical, core molecular-orbital products (von Niessen, 1972*b*). Although the valence molecular-orbital products possess only 4% of the core features (density with a large contribution near or on the nucleus), neglect of them could result in a large error for the estimate of an electrostatic force on the nucleus or of the electric field gradient on the nucleus. We will return to this point later.

In the present study we compare X-ray scattering factors calculated from canonical, core molecular-orbital products and the corresponding canonical core atomic-orbital products for the isolated atom. The difference may be called the core deformation scattering factor; it is analyzed for possible contribution to molecular charge densities and physical properties obtainable from X-ray diffraction data. From the discussion above we expect the general conclusions to be the same from a similar analysis of localized molecular-orbital products.

Computational procedure and molecular wavefunctions

The molecules studied in the present paper are the first-row diatomic hydrides XH (X = B, C, N, O and F) and the 14-electron series N_2, CO, and BF. Diatomic molecules have been chosen because (i) existing wavefunctions are of higher quality than those for polyatomics, (ii) their X-ray scattering factors are more easily computed than those of polyatomics, and (iii) interpretation of results is more straightforward. The wavefunctions employed are those of Cade & Huo (1967) for the hydrides, Cade, Sales & Wahl for N_2 [wavefunction 2*D* of Cade, Sales & Wahl (1966)], and Huo for CO and BF [wavefunctions at experimental R_e from Huo (1965)]. The atomic core orbitals are taken from the spin-restricted Hartree–Fock wavefunctions of Clementi (1965). For all of these wavefunctions, the atomic or molecular orbitals are linear combinations of Slater-type atomic-orbital basis functions, for which the expansion coefficients have been determined by the self-consistent field technique of Roothaan (1951). The computation of X-ray scattering factors for these wavefunctions reduces to evaluating the Fourier transforms of one- and two-center products of Slater-type orbitals (STO's). We have used the methods reported by Stewart (1969) and Bentley & Stewart (1973) for the one- and two-center integrals respectively.

The function of interest is the core difference scattering factor

$$\Delta f_\mu(\mathbf{S}) = f_{\mu,\,\mathrm{mol}}(\mathbf{S}) - f_{\mu,\,\mathrm{atom}}(\mathbf{S}) \tag{3}$$

with

$$f_{\mu,\,\mathrm{mol}}(\mathbf{S}) = 2\int \psi_\mu^*(\mathbf{r}) \exp{(i\mathbf{S}\,.\,\mathbf{r})}\psi_\mu(\mathbf{r})\mathrm{d}\mathbf{r} \tag{4}$$

and

$$f_{\mu,\,\mathrm{atom}}(\mathbf{S}) = 2\int \varphi_\mu^*(\mathbf{r}) \exp{(i\mathbf{S}\,.\,\mathbf{r})}\varphi_\mu(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{4$'$}$$

In (3), (4) and (4′) $\mathbf{S}$ is the Bragg vector, $[|\mathbf{S}| = 4\pi \sin \theta/\lambda]$, $f_{\mu,\,\mathrm{mol}}$ and $f_{\mu,\,\mathrm{atom}}$ are the respective scattering factors from the molecular and atomic core orbital products, $\psi_\mu^*\psi_\mu$ and $\varphi_\mu^*\varphi_\mu$. ψ_μ and φ_μ are corresponding orbitals in the sense that their corresponding eigenvalues have the same ordering when comparing the molecule to the isolated atoms. The orbitals are also localized in the same region of space; for instance, the electron-density distribution from $|\psi_{1\sigma}|^2$ of CO closely resembles $|\varphi_{1s}|^2$ of the isolated oxygen atom, and $|\psi_{2\sigma}|^2$ corresponds to $|\varphi_{1s}|^2$ of the isolated carbon atom.

For this reason the scattering factors (3), (4) and (4′) are computed by assigning the origin to the nucleus of localization. An exception is the case of N_2; the charge-density distribution $|\psi_{1\sigma_g}|^2+|\psi_{1\sigma_u}|^2$ must be compared to $|\varphi_{1s_a}|^2+|\varphi_{1s_b}|^2$ where the origin for the appropriate form factors is chosen to be the bond mid-point. As defined in (3), $\Delta f_\mu(\mathbf{S})$ is the change in core scattering induced by bond formation. Since φ_μ and ψ_μ give rise to similar density functions, we expect $\Delta f_\mu(\mathbf{S})$ to be small. For this reason ψ_μ and φ_μ should be as accurate as possible and close to each other in overall quality. All the wavefunctions used in this work are alleged to be near the restricted Hartree-Fock limit. Because of this, we feel able to make quantitative interpretations of Δf_μ, (3), with some confidence. The numerical accuracy of the wavefunctions is about one part in 10^5.

Results

For all the molecules examined, there is core deformation, as indicated by the non-zero values of $|\Delta f_\mu(\mathbf{S})|$, which for given $|\mathbf{S}|$ are generally much larger for $\mathbf{S}$ parallel to the internuclear vector $\mathbf{R}$ than for other orientations; see Fig. 1 for $|\Delta f_{1\sigma}(\mathbf{S})|$ for NH and Fig. 2 for $|\Delta f_{1\sigma}(\mathbf{S}) \exp(+i\mathbf{S}\,.\,\mathbf{R}/2)+\Delta f_{2\sigma}(\mathbf{S}) \exp(-i\mathbf{S}\,.\,\mathbf{R}/2)|$ for CO. The molecules are the middle members of the hydride and 14-electron series and their Δf_μ's illustrate features common to all members of the series.

The magnitude of Δf_μ can serve as a guide as to whether such deformation effects can be easily measured by X-ray diffraction. For NH and CO the maximum values are

$$|\Delta f_{1\sigma}|_{\max} \simeq 3\times 10^{-3}$$

and

$$|\Delta f_{1\sigma} \exp(+i\mathbf{S}\,.\,\mathbf{R}/2) + \Delta f_{2\sigma} \exp(-i\mathbf{S}\,.\,\mathbf{R}/2)|_{\max} \simeq 6\times 10^{-3},$$

both at $\sin\theta/\lambda \sim 0{\cdot}75$ Å^{-1} where the total core scattering factors of the molecules are about 1·5 and 3·0 respectively. We conclude in agreement with earlier studies (Groenewegen, Zeevalkink & Feil, 1971; Bentley & Stewart, 1971) that core deformation will be quite difficult to detect with current accuracy of X-ray diffraction.

Chemical trends in $|\Delta f_{1\sigma}|$ are evident. Among the hydrides it is largest for BH (about 1·4 times the corresponding values for NH) and least for FH (about 0·5 times the corresponding NH result), as if the core were more difficult to polarize in the more electronegative atoms. For $\mathbf{S}$ parallel to $\mathbf{R}$ the maximum of $|\Delta f_{1\sigma}|$ shifts from a $\sin\theta/\lambda$ of 1·0 Å^{-1} for FH to 0·55 Å^{-1} for BH: the deformation density, which gives rise to $\Delta f_{1\sigma}$, is progressively more diffuse as one moves to lighter members of the series (Fig. 3).

Similar trends can be seen for the 14-electron series. Because the core molecular orbitals in BF and CO are relatively localized, it is instructive to display $|\Delta f_{1\sigma}|$, for the heavier atom, and $|\Delta f_{2\sigma}|$, for the lighter

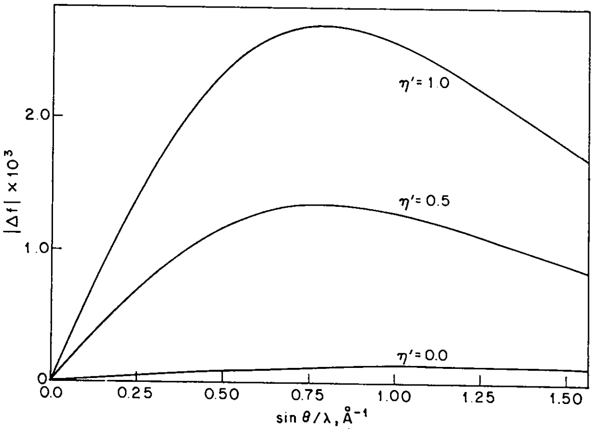

Fig. 1. $|\Delta f_{1\sigma}(\mathbf{S})|$ for NH at selected orientations of $\mathbf{S}$ relative to $\mathbf{R}$. $\eta'=\mathbf{S}\,.\,\mathbf{R}/|\mathbf{S}|\,|\mathbf{R}|$.

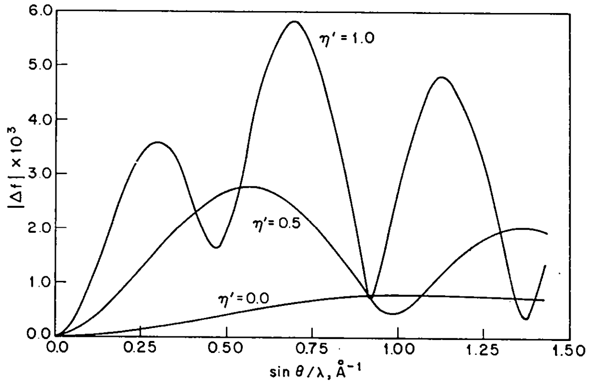

Fig. 2. $|\exp(+ic\eta')\Delta f_{1\sigma}(\mathbf{S})+\exp(-ic\eta')\Delta f_{2\sigma}(\mathbf{S})|$ for CO at selected orientations of $\mathbf{S}$ relative to $\mathbf{R}$. $c=(\frac{1}{2})|\mathbf{S}|\,|\mathbf{R}|$, $\eta'=2\mathbf{S}\,.\,\mathbf{R}/c$.

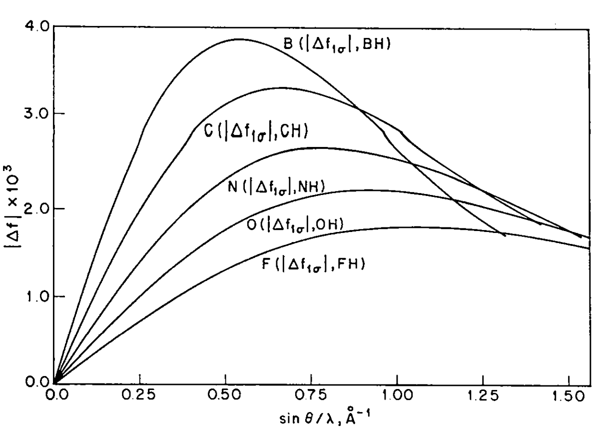

Fig. 3. $|\Delta f_{1\sigma}(\mathbf{S})|$ for the diatomic hydrides with $\mathbf{S}$ parallel to $\mathbf{R}$.

atom. These curves (Fig. 4) are closely similar to the hydride curves of Fig. 3. It is important to note that each core molecular-orbital product [*e.g.* $|\psi_{1\sigma}|^2$ for oxygen in CO] has a small contribution from one-center STO products on the opposite center as well as contributions from a variety of two-center STO products. Nonetheless, this decomposition, *i.e.* $\Delta f_{1\sigma}$ for O and $\Delta f_{2\sigma}$ for C, affords us the same chemical interpretation that we found for the diatomic hydrides, where contributions from the STO's centered on the hydrogen nucleus are small. For example, $\Delta f_{1\sigma}$ for CO is about equal to $\Delta f_{1\sigma}$ on OH, as is $\Delta f_{2\sigma}$ in CO (origin at C) to $\Delta f_{1\sigma}$ for CH. The phases of these core deformation form factors are all nearly the same. When the angle between **S** and **R** is less than 70°, the functions are predominantly imaginary. For CO, at **S** parallel to **R**, $\Delta f_{1\sigma}$ decreases monotonically from a phase of 90 to 77·9° as $\sin\theta/\lambda$ varies from 0 to 1·41 Å^{-1}. The range of phase for $\Delta f_{1\sigma}$ of OH over the same domain of $\sin\theta/\lambda$ is 90 to 84·4°. By comparison $\Delta f_{2\sigma}$ for CO falls from 90 to 69·6° whereas the phases for $\Delta f_{1\sigma}$ for CH drop from 90 to 83·7° as $\sin\theta/\lambda$ varies from 0 to 1·42 Å^{-1}. Since both amplitudes (Figs. 3 and 4) and phases are comparable, we infer that there is a core deformation density function, roughly characteristic of the atom, which is transferable among diatomic molecules. The preponderance of the imaginary component in the Δf_μ's is analyzed in the next section.

Interpretation of core deformation factors

One possible representation of the difference scattering factors, $\Delta f_\mu(\mathbf{S})$, includes atomic monopole, dipole and quadrupole scattering factors (Stewart, 1971),

$$\Delta f_\mu(\mathbf{S}) \simeq P_0(\eta')g_0(S) \pm iP_1(\eta')g_1(S) - P_2(\eta')g_2(S) \quad (5)$$

where i is $\sqrt{-1}$, P_l is the lth order Legendre polynomial in the direction cosine of **S** with respect to **R** (*i.e.* η') and $g_l(S)$ are the Fourier coefficients of the radially dependent multipole deformation electron-density function. The upper sign for the dipole term $[P_1(\eta')]$ pertains to the $\Delta f_\mu(\mathbf{S})$ on center a as the origin (which we take as the origin of **R**) and the lower sign applies to those $\Delta f_\mu(\mathbf{S})$ (BF and CO, only) with origin on center b (which we take as the terminus of **R**). By the method of least squares, the functions $g_0(S)$, $g_1(S)$ and $g_2(S)$ have been determined for selected values of S. Integration of the trial function (5) on the $\Delta f_\mu(\mathbf{S})$ over η' and φ_0 (the azimuthal angle about the internuclear axis) has been done analytically. Thus the explicit solutions are:

$$g_0(S) = \int_{-1}^{1} \Delta f_\mu(\mathbf{S})\mathrm{d}\eta'/2,$$

$$g_1(S) = \pm \int_{-1}^{1} f_\mu(\mathbf{S})\eta'\mathrm{d}\eta'/(\tfrac{2}{3}) \quad (6)$$

and

$$g_2(S) = -\int_{-1}^{1} f_\mu(\mathbf{S})P_2(\eta')\mathrm{d}\eta'/(\tfrac{2}{5}).$$

[For the ease of doing these integrals, see Stewart (1969) and Bentley & Stewart (1973).] Note that the atomic core scattering factor, (4'), makes no contribution to $g_1(S)$ and $g_2(S)$. For the special case of N_2, the following set of linear equations must be solved for each value of S:

$$\begin{aligned}
\int_{-1}^{1} \Delta F_{\text{core}} \cos(c\eta')\mathrm{d}\eta' &= [j_0(2c)+1]g_0(S) \\
&\quad + j_1(2c)g_1(S) + j_2(2c)g_2(S) \\
\int_{-1}^{1} \Delta F_{\text{core}} P_1(\eta') \sin(c\eta')\mathrm{d}\eta' &= +j_1(2c)g_0(S) \\
&\quad + (\tfrac{1}{3})\,[1 - j_0(2c) + 2j_2(2c)]g_1(S) \\
&\quad - (\tfrac{1}{5})\,[2j_1(2c) - 3j_3(2c)]g_2(S) \qquad (7) \\
\int_{-1}^{1} \Delta F_{\text{core}} P_2(\eta') \cos(c\eta')\mathrm{d}\eta' &= +j_2(2c)g_0(S) \\
&\quad - (\tfrac{1}{5})\,[2j_1(2c) - 3j_3(2c)]g_1(S) + (\tfrac{1}{35})\,[18j_4(2c) \\
&\quad - 10j_2(2c) + 7(j_0(2c)+1)]g_2(S)
\end{aligned}$$

where $\Delta F_{\text{core}} = \Delta f_{1\sigma_g} + \Delta f_{1\sigma_u}$, $c = (\tfrac{1}{2})|\mathbf{S}|\,|\mathbf{R}|$ and the $j_n(2c)$ are spherical Bessel functions.

As anticipated from the large imaginary component, in all cases studied here, $g_1(S)$ accounted for most of the amplitude of Δf_μ over the range of $\sin\theta/\lambda$ considered ($0 \le \sin\theta/\lambda \le 1{\cdot}5$ Å^{-1}). A plot of several $g_1(S)$ is shown in Fig. 5 where the curves labeled C and O are extracted from $\Delta f_{2\sigma}$ and $\Delta f_{1\sigma}$, respectively, of the CO molecule; the curve for N is from $\Delta f_{1\sigma}$ of NH. Note how the maximum of each reflects a more localized dipole density function as the atomic number of the atom increases. The Fourier coefficients of the monopole density function, $g_0(S)$, are about an order of magnitude smaller than $g_1(S)$, and $g_2(S)$, the Fourier transform of a radial quadrupole density function,

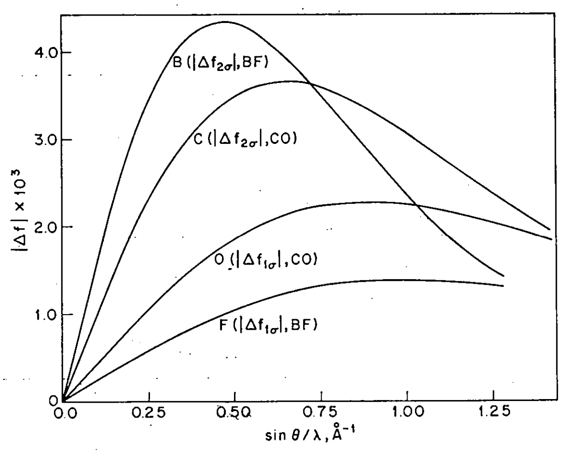

Fig. 4. $|\Delta f_{1\sigma}(\mathbf{S})|$ and $|\Delta f_{2\sigma}(\mathbf{S})|$ for CO and BF with **S** parallel to **R**.

ranges from slightly smaller than $g_0(S)$ to negligible. A representative set of $g_0(S)$ and $g_2(S)$ are plotted in Fig. 6. These results are the solutions of (6) for CO and NH. The same prominent chemical trend is not so evident as in the dipole case (see Fig. 5).

Coefficients of a multipolar expansion in reciprocal space are the Fourier–Bessel transforms of the corresponding density functions in direct space. Thus we may interpret the $g_l(S)$ in terms of density deformation functions, $\varrho_l(r)$, which give rise to them. In this sense, g_0 is the scattering difference induced by an overall expansion or contraction of the spherically symmetrical component of the core density, g_1 is the scattering due to dipole polarization of core charge density along the bond axis, and g_2 arises from a density shift to the region along the molecular axis from a π-like toroid surrounding the nucleus in question. The function $g_0(S)$ is negative for all S for all core orbital products examined (see Fig. 6). This indicates that the core orbital product is slightly more diffuse in a molecule than in the corresponding free atom. From other studies of density-difference contour maps for the diatomic hydrides (Bader, Keaveny & Cade, 1967) and for the 14-electron series (Bader & Bandrauk, 1968), it is evident that the total charge density, within a sphere of 0·1 Å or less about the first-row atom nucleus, is greater for the isolated atom than for the molecule. The $g_0(S)$ functions here reflect the core-density contributions to this feature. This rather general redistribution of charge on formation of a chemical bond may affect the Debye–Waller parameters that are determined in routine structure analysis. For an example with powdered-diamond diffraction data, see Stewart (1973*b*).

We find that $g_1(S)$ is positive for all core orbital products investigated and, further, that it can be well represented analytically by the function,

$$g_1(S)=8CZS/(Z^2+S^2)^3 \tag{8}$$

where C and Z are parameters characteristic of each core orbital product. The dipolar term $iP_1(\eta')g_1(S)$ with $g_1(S)$ given by (8) corresponds to scattering by the density function

$$\varrho_1(\mathbf{r})=(4\pi)^{-1}CP_1(\cos\theta)r\exp(-Zr)\,. \tag{9}$$

Note that (9) is the form of a $1s2p_\sigma$ STO product.

The function $g_2(S)$ is positive (or effectively zero) for all S for the orbital products considered. This corresponds to an increase of density along the molecular axis at the expense of the off-axis regions. We find that $g_2(S)$ can be reasonably represented analytically by the simple function

$$g_2(S)=48DXS^2/(X^2+S^2)^4 \tag{10}$$

where D and X are parameters characteristic of each core orbital product. The density function that corresponds to $-P_2(\eta')g_2(S)$ is

$$\varrho_2(\mathbf{r})=(4\pi)^{-1}DP_2(\cos\theta)r^2\exp(-Xr)\,. \tag{11}$$

Such a function can arise from a $2p_\sigma 2p_\sigma$ or a $1s3d_\sigma$ STO product. In Table 1 the parameters Z, C, X, and D from (8) and (10) are listed for the diatomics studied in this work. With the exception of B in BH and BF, Z and X are characteristic of the atom to which they refer and are almost independent of molecular environment. It is these parameters [Z from (8) and X

Table 1. *Parameters of core deformation density functions*

The terms Z, C, X and D are defined by equations (8)–(11).

	B	C	N	O	F
Z	8·05*	9·90	12·0	13·7	15·5
	6·75	9·23	10·7	12·6	15·0
C	7·92	15·4	27·8	37·5	50·1
	4·27	12·9	17·0	26·9	34·8
X	5·34	7·34	8·65	9·44	–†
	6·23	7·80	8·1	9·75	–
D	0·121	0·463	0·545	0·296	–†
	0·994	2·81	1·17	0·855	–

* The upper quantity is appropriate for the atom in question (here B) bound to hydrogen; the lower for the atom bound to another first-row atom (B to F, C to O, N to N).

† Neither FH nor BF exhibits a significant quadrupolar deformation at F.

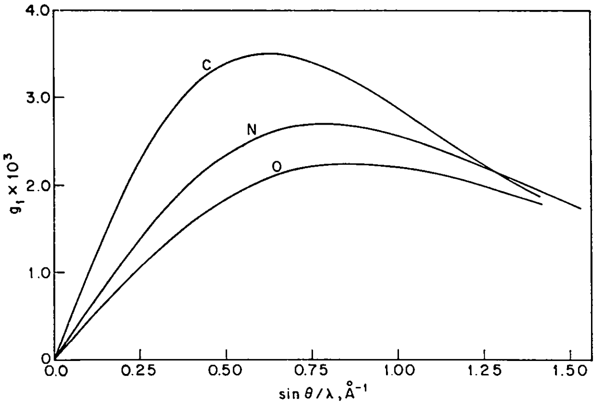

Fig. 5. The dipolar radial X-ray scattering component [g_1(S)] for N in NH and C and O in CO.

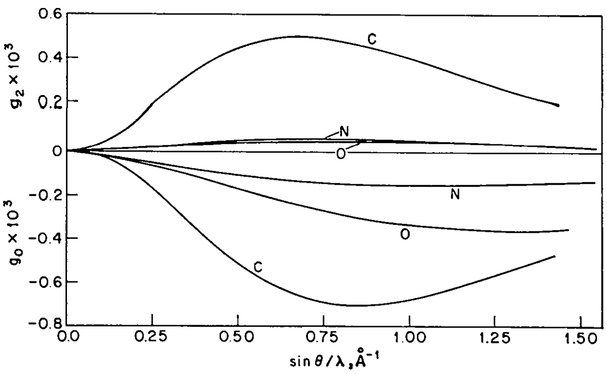

Fig. 6. The spherical and quadrupolar radial X-ray scattering components [g_0(S) and g_2(S)] respectively for N in NH and C and O in CO.

from (10)] which determine the shape of g_1 and g_2. Of special interest, the $g_1(S)$ 'dipole' scattering factors have maxima at much larger $\sin\theta/\lambda$ values than the corresponding valence dipole scattering factors (Stewart, 1971). For example, a nitrogen-atom valence dipole scattering factor peaks at 0·21 Å^{-1} in $\sin\theta/\lambda$, but our nitrogen dipole form factor has a maximum at 0·77 Å^{-1}. We name $g_1(S)$ a core density dipole scattering factor. Similarly we can characterize $g_2(S)$ as a core quadrupole density function.

Molecular properties in core deformation

Several molecular, physical properties can be determined from electron-density functions that are extracted from X-ray diffraction data (Stewart, 1972). From the density functions of (9) and (11), we can compute core-deformation contributions to physical properties. Two properties which depend on local atomic dipole density functions are the local dipole moment, μ, and the local electric field, ε. The corresponding core deformation contributions, in terms of (9), are

$$\mu(\text{core})=8C/Z^5 \text{ in units of } ea_0 \qquad (12)$$

and

$$\varepsilon(\text{core})=C/3Z^2 \text{ in units of } ea_0^{-2} \qquad (13)$$

where e is $1{\cdot}602\times10^{-19}$ coulomb, and a_0 is $0{\cdot}529167\times10^{-10}$ m. For all cases studied, μ(core) is less than 0·0025 ea_0, which is negligible compared to the local molecular dipole moments, which are of the order of 0·5 ea_0. We find that ε(core) lies between 0·03 and 0·07 ea_0^{-2}. The total electric field at any nucleus should vanish for a Hartree–Fock wavefunction at the nuclear configuration for which the Hartree–Fock energy is a minimum (Hurley, 1954; Hall, 1961). The near Hartree–Fock wavefunctions employed here do not satisfy this theorem exactly, but give residual fields at the nuclei between 0·006 and 0·03 ea_0^{-2}. It is evident that if the core contribution is omitted from an electric-field calculation, the resultant field will be comparable in magnitude and opposite in direction to the core component. The force on a nucleus is proportional to the field at that nucleus. For the diatomic molecules studied here, neglect of core contributions gives rise to *apparent* forces which would, if they were real, tend to stretch each molecule *out of* its equilibrium configuration.

Properties that depend on the local quadrupole density function are the local quadrupole moment Q and the local electric field gradient, q. The core contributions to these properties, in terms of the density function (11), are

$$q(\text{core})=2D/5X^2 \text{ in units of } ea_0^{-3} \qquad (14)$$

and

$$Q(\text{core})=144D/X^7 \text{ in units of } ea_0^2. \qquad (15)$$

Q(core) is less than 0·00025 ea_0^2 for all core orbital products considered; this is negligible in comparison to total local quadrupole moments for these molecules which range from several tenths to several ea_0^2. On the other hand, q(core) can be as large as 0·02 ea_0^{-3}, which is rather small in comparison with total local electric-field gradients where the magnitudes lie between 0·40 and 2·87 ea_0^{-3}. Values of ε(core) and q(core) for the core orbital products considered are given in Table 2.

Table 2. *Core contributions to local electric fields and their gradients*

Values are calculated from equations (13) and (14) with the parameters of Table 1.

Atom	B	C	N	O	F
Electric field	0·0407*	0·0524	0·0644	0·0666	0·0695
(ea_0^{-2})	0·0312	0·0505	0·0495	0·0565	0·0516
Electric field gradient	0·0017	0·0034	0·0036	0·0013	–†
(ea_0^{-3})	0·0102	0·0185	0·0071	0·0036	–†

* The upper quantity is appropriate for the atom in question (here B) bound to hydrogen; the lower for the atom bound to another first-row atom (B to F, C to O, N to N).

† F has no detectable quadrupolar core deformation, and thus no core contribution to the electric field gradient.

Implications of core deformation for valence density analysis

It appears from the results of the previous section that core deformations of the sort encountered here, while too small to be easily measured by single-crystal X-ray diffraction techniques, cannot be neglected if reliable values of certain physical properties are sought. In order to discover whether the charge-density information implicit in Δf_μ is completely lost, we must determine the efficiency with which the density functions (8) and (10) project into the basis functions that span the valence charge density. In the valence model we have been investigating (Stewart, 1971, 1973*a*), both the dipolar and the quadrupolar radial density functions are given by

$$\varrho_v(r)=(4\zeta\ /3)r^2\exp(-2\zeta r) \qquad (16)$$

where ζ is a standard molecular value recommended by Hehre, Ditchfield, Stewart & Pople (1970). A measure of the linear dependence of (8) or (10) on ϱ_v of (16) is given by the projection coefficient

$$p_1=\int_0^\infty \varrho_1(r)\varrho_v(r)r^2\mathrm{d}r/\left[\int_0^\infty(\varrho_1)^2r^2\mathrm{d}r\int_0^\infty(\varrho_v)^2r^2\mathrm{d}r\right]^{1/2} \qquad (17)$$

and a corresponding expression for p_2 where ϱ_2 is substituted for ϱ_1. If we set $a=Z/2\zeta$ and $b=X/2\zeta$, where X and Z are from Table 1 and ζ is a standard molecular exponent, then

$$p_1(a)=(5/6)^{1/2}a^{5/2}[2/(1+a)]^6 \tag{18}$$

and

$$p_2(b)=b^{7/2}[2/(1+b)]^7. \tag{19}$$

Maximum and minimum values of $p_1(a)$ are 0·453 (for B in BF) and 0·217 (for F in FH); the average $p_1(a)$ is 0·271. For p_2, 0·564 is the minimum (for C in CO) and 0·752 the maximum (for B in BH), and 0·625 the average. A summary of results is given in Table 3. The figures indicate that a substantial part of the quadrupole core deformation will be represented by the valence quadrupole term in a least-squares analysis, but that the content of $\varrho_1(r)$, (8), will, for the most part, be lost. As pointed out in other studies on density basis functions (Stewart, 1971, 1973*a*), analysis with generalized X-ray scattering factors, where the maximum in $\sin\theta/\lambda$ is restricted to the Ewald sphere, will usually lead to somewhat larger projection coefficients than those shown in Table 3.

Table 3. *Core vs. valence density function projection coefficients*

The quantities ζ, a, b, p_1 and p_2 are defined by equations (18) and (19) and their accompanying text. The ζ values are taken from Hehre, Ditchfield, Stewart & Pople (1970).

Atom	B	C	N	O	F
ζ	1·50	1·72	1·95	2·25	2·55
a	2·68*	2·88	3·08	3·04	3·04
	2·25	2·68	2·74	2·80	2·94
b	1·78	2·13	2·22	2·10	–†
	2·08	2·27	2·08	2·17	–†
p_1	0·277	0·241	0·211	0·217	0·217
	0·376	0·277	0·265	0·255	0·231
p_2	0·752	0·613	0·581	0·624	–†
	0·632	0·564	0·632	0·599	–†

* The upper quantity is appropriate for the atom in question (here B) bound to hydrogen; the lower for the atom bound to another first-row atom (B to F, C to O, N to N).

† No values are determined here because F has no significant quadrupole deformation.

There is another point which was mentioned in the Introduction and which must now be dealt with. The separation of electron density into core and valence parts, as we have done here *via* (3), (4) and (4′), is a formal rather than a physical partitioning. Each of the wavefunctions studied here contains in its valence orbital products terms that give rise to a density distribution similar to that obtained by a Fourier analysis of g_1 [equation (6)]. This density component will fail to project into the valence model (16) in the same way that $\varrho_1(r)$ failed. An estimate of the dipole core density function [such as (8)] was made by projecting *all* $1s2p_\sigma$ type STO products on the same center into the dominant core deformation function, (8), in order to weight the contribution of each one (eight in all for each diatomic hydride). We find that the valence orbital products ($|\psi_{2\sigma}|^2$ and $|\psi_{3\sigma}|^2$ for the hydrides) *taken together*, have a density component, like (8), with an electron population somewhat less than the core orbital product alone. This means, for example, that the electric field values in Table 2 should be multiplied by 1·5 to 2, *since the core dipole component from the valence molecular-orbital products has the same parity as the main component from* $|\psi_{1\sigma}|^2$.

The foregoing considerations indicate that the present valence scattering model (Stewart, 1971, 1973*b*) sacrifices an important charge density feature (which is distributed among both the core and valence orbital products) for want of a $1s2p_\sigma$ density basis function. If such a function were to be added to the model, the representation of physical properties in diatomic molecules would be improved, provided, of course, that the model contains no more serious deficiencies.

The results and discussions in this paper are applicable to diatomics consisting of first-row atoms, but we make some generalizations to more complex systems. The carbon atom in methane or in diamond has $T_d(\bar{4}3m)$ site symmetry; local dipole and quadrupole polarizations are symmetry forbidden. In the ethane molecule, the charge about the carbon atom has an approximate tetrahedral environment [actually it is $C_{3v}(3m)$ for both the staggered and the eclipsed configurations], so it will probably have less dipole core deformation than CH. We visualize a polarization vector from one carbon toward the other, and another vector from the carbon toward the geometric center of the methyl protons; these opposing vectors will partly cancel. For most atoms forming two or more chemical bonds among nonhydrogen atoms, the exact or approximate site symmetry of the potential (largely due to neighboring nuclei, screened by other electrons) will force the dipole deformation function to vanish or at least be smaller than in a comparable diatomic molecule. One case of multipole bonding where dipole core polarization will probably *not* diminish is that of terminally bonded atoms, of which the most prominent example is a carbonyl oxygen. Such atoms will probably require the $1s2p$ density function discussed above for a more appropriate representation of charge density and local physical properties. It may be worth while to incorporate this feature into the generalized X-ray scattering factors for electron population analysis of organic molecular crystals (Stewart, 1971). The rather small amplitude of scattering compared to the total scattering will most likely make it difficult to detect the core dipole density electron population from present-day X-ray diffraction data.

Conclusion

The products of canonical core molecular orbitals of first-row diatomics closely resemble the canonical core atomic orbital products of their constituent isolated atoms. When the X-ray scattering amplitudes of these density functions are compared and analyzed, we find that (i) the spherically symmetric component of the molecular core charge is more diffuse than for the isolated atom, (ii) the molecular core charge has a dominant dipolar polarization which is clearly evident in the scattering amplitudes and phases, and (iii) a quadrupolar density function, with a much smaller electron population than the dipolar term, gives rise to a small part of the structure in the core molecular density scattering factor. We have emphasized that these same core deformation terms are also present in products of the valence molecular orbitals and that the core molecular orbital product alone accounts for about one-half to two-thirds of the total of such features. The deformation terms have an amplitude of scattering which is no more than 1 % of the total molecular scattering for the range of $\sin\theta/\lambda$ studied in this work ($0 \leq \sin\theta/\lambda \leq 1{\cdot}5$ Å^{-1}). Nonetheless, these density deformations make appreciable contributions to certain physical and molecular properties (in particular electric fields). Quadrupole core deformations can, to some extent, be absorbed by a valence scattering model; dipolar deformation will not be accommodated by this model. We have argued that because of the increased effective site symmetry of a multiply bonded atom, most core deformation terms for it will be smaller than for an atom in a diatomic, whereas for a terminally bonded atom, such as an oxygen in a carbonyl or amide group, they will probably be about the same. We therefore mildly suggest that the density functions in Table 1 be tried for the construction of a dipole generalized X-ray scattering factor in the charge density analysis of a terminally bonded atom.

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On the Application of Phase Relationships to Complex Structures. VI. Automatic Interpretation of Electron-Density Maps for Organic Structures

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This paper describes a procedure for the automatic interpretation of electron-density maps of organic structures which makes use of the restrictions on the values of the intramolecular bond distances and angles. It is also shown how some chemical-data processing algorithms can be used as an efficient means of introducing chemical information in the process of structure determination.

The last step of a crystal structure determination by direct methods which requires human intervention is the interpretation of E maps. Though graphical display procedures make this easier it is still a time-consuming task, especially when no easily recognizable fragment can be found. We wish to report here some