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Pseudoatoms in Diatomic Molecules: Restricted Radial Functions*

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Molecular charge-density functions for several diatomic molecules of first-row atoms have been analyzed by the least-squares method with pseudoatoms that have restricted radial functions. Multipole expansions up to quadrupoles on the two centers with single exponential radial functions provide qualitative descriptions of the molecular charge densities. They do not provide accurate values of molecular electrostatic properties, however. Extension to octupoles and hexadecapoles does not improve the representation of physical properties. Variations of the valence exponents proved to be the most critical parameters for goodness of fit as well as for retrieval of physical properties. For the selected examples in this work it appears that the valence exponent is more sensitive to the atom type than to the bonding environment; the exception is the hydrogen pseudoatom.

Introduction

In a previous paper (Stewart, 1976) it was proposed that accurate X-ray diffraction data be analyzed for static charge-density information with rigid pseudoatoms. The pseudoatom is spanned by a small finite multipole expansion about its nuclear center. The multipoles serve as basis functions for an electron population analysis. The Fourier transforms of these bases, the generalized X-ray scattering factors, are used in a least-squares analysis of kinematic structure factors. The model is intended to retrieve (or measure) the static charge density in the asymmetric part of the crystallographic unit cell. It has also been proposed (Stewart, 1972, 1976) that the results of the least-squares analysis can be used to determine a variety of physical properties of the crystalline material.

The multipole model advocated for X-ray structure analysis is restricted to single exponential representations for the radial density functions of the pseudoatom. In the present paper, we give results for fits of these restricted functions to known one-electron density functions for several diatomic molecules. These relatively simple systems can serve to establish the limitation of single exponentials for the representation of the molecular density functions and of the several molecular averages. In this study we hope to establish prospects of these density functions for application to real diffraction data of first-row-atom materials.

Least-squares calculations and static charge properties

Projection studies of the one-electron density function, $\varrho(\mathbf{r},R)$, are carried out by the method of least squares. The molecular form factor, $F_0(\mathbf{S},R)$, is computed from a molecular wavefunction by methods previously published (Bentley & Stewart, 1973). A model molecular form factor $F_c(\mathbf{S},R)$ is assigned population and exponential parameters to be determined by least squares:

$$F_c(\mathbf{S},R)=\sum_{p=1}^{2}[C_{c,p}f_{\mathrm{core},p}(S)+\sum_{l=0}^{L_p}C_{l,p}(i)^l f_{l,p}(\alpha_p,S)P_l(\eta)\exp[(-1)^p iSR\eta/2]\,, \quad (1)$$

where $\eta=\mathbf{S}\,.\,\mathbf{R}/|\mathbf{S}|\,|\mathbf{R}|$, $i=\sqrt{-1}$, $\mathbf{S}$ is the Bragg vector with $|\mathbf{S}|=4\pi\sin\theta/\lambda$ and $\mathbf{R}$ is the internuclear vector from center 1 to center 2. The coefficients $C_{l,p}$ for pseudoatom p are electron population parameters. The sum over l implies a multipole expansion for the valence shell on center p. The function $P_l(\eta)$ is an lth order Legendre polynomial and the valence radial scattering factor

$$f_{l,p}(\alpha_p,S)=[\alpha_p^{n_p+3}/(n_p+2)!]\times\int_0^\infty r_p^{n_p+2}\exp(-\alpha_p r_p)j_l(Sr_p)\mathrm{d}r_p\,. \quad (2)$$

The details for the choice of n_p in (2) and for the core density function for $f_{\mathrm{core},p}(S)$ are given below. The least-squares function for the projection studies is

$$\varepsilon(S_{\max}\mathbf{C},\boldsymbol{\alpha})=\int_0^{S_{\max}}\int_{-1}^{1}\int_0^{2\pi}|F_0(\mathbf{S},R)-F_c(\mathbf{S},R)|^2S^2\mathrm{d}\varphi\mathrm{d}\eta\mathrm{d}S\,, \quad (3)$$

where φ is the azimuthal angle of the Bragg vector about the internucleus vector $\mathbf{R}$ and $S_{\max}$ is the limit of the sphere of diffraction data. Note that (3) and (1) constitute a model study for a non-vibrating diatomic molecule. When $S_{\max}$ is infinite then (3), by the Fourier integral theorem, is

$$\varepsilon(\infty,\mathbf{C},\boldsymbol{\alpha})=(2\pi)^3\int[\varrho_{\mathrm{mol}}(\mathbf{r},R)-\varrho_c(\mathbf{r},R)]^2\mathrm{d}\mathbf{r}\,, \quad (4)$$

where $\mathbf{r}$ is the vector from the origin (the midpoint of

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$\mathbf{R}$) to an infinitesimal volume element of the charge density in the diatomic molecule. Many of the results in this paper come from minimization of (4) with respect to $\mathbf{C}$ and $\boldsymbol{\alpha}$. By minimization of (3) the influence of $S_{\max}$ on the results has been determined as well.

The quality of fit of F_c to F_0 (or ϱ_{mol} to ϱ_c) is judged in several ways. A least-squares figure of merit is the relative root-mean-square error,

$$R_w = |\varepsilon(S_{\max}, \mathbf{C}, \boldsymbol{\alpha})/\int_{|S_{\max}|} |F_0(\mathbf{S}, R)|^2 d\mathbf{S}]^{1/2} . \qquad (5)$$

Other criteria are found by comparison of physical properties calculated from $\varrho_c(\mathbf{r}, R)$ with those from $\varrho_{\text{mol}}(\mathbf{r}, R)$. In this work we concentrate on molecular quadrupole moments, dipole moments, total charge, and electric fields and electric field gradients at each nucleus.

If $\varrho(\mathbf{r}, R)$ is known, the molecular average for an electrostatic operator, $A(\mathbf{r})$, is

$$\langle A \rangle = \int A(\mathbf{r}) \varrho(\mathbf{r}, R) d\mathbf{r} . \qquad (6)$$

For a diatomic molecule the properties of interest are: Dipole moment:

$$\mu = \tfrac{1}{2}(Z_B - Z_A)R - \langle z \rangle . \qquad (7)$$

Quadrupole moment (mass center):

$$Q_{AB} = (Z_A m_B^2 + Z_B m_A^2)R^2/(m_A^2 + m_B^2) - \langle r^2 P_2(\cos\theta) \rangle . \qquad (8a)$$

Quadrupole moment (center A):

$$Q_{AH} = Z_H R^2 - \langle r_A^2 P_2(\cos\theta_A) \rangle . \qquad (8b)$$

Electric field at nucleus A:

$$e_A = -Z_B/R^2 + \langle r_A^{-2} P_1(\cos\theta_A) \rangle . \qquad (9)$$

Electric field gradient at A:

$$q_A = 2Z_B/R^3 - 2\langle r_A^{-3} P_2(\cos\theta_A) \rangle . \qquad (10)$$

Z_A and m_A are the atomic number and mass of nucleus A respectively, $\langle z \rangle$ is taken with respect to the midpoint between nuclei and $\langle r^2 P_2(\cos\theta) \rangle$ is evaluated with the origin at the center of mass. When $\varrho(\mathbf{r}, R)$ is given by a multiple expansion with single exponentials all integrals are simple analytical expressions.

The formulas given in (7)–(10) are derived with the normalization condition,

$$\int \varrho(\mathbf{r}, R) d\mathbf{r} = Z_A + Z_B . \qquad (11)$$

For the present study, $\varrho_c(\mathbf{r}, R)$ is not constrained to satisfy (11). The sum of the variable monopole population coefficients is compared to the total number of electrons in the molecule. When the ratio differs greatly from unity it is indicative of a deficient pseudoatom density model. For calculations of (7)–(10), the variable monopole population coefficients are renormalized to satisfy (11). In the minimization of (3) and/or (4) $\varrho_c(\mathbf{r}, R)$ is also not constrained to be positive definite for all $\mathbf{r}$. We find in practice that this degree of freedom is not serious and that all $\varrho_c(\mathbf{r}, R)$ investigated are effectively positive definite.

Molecular wavefunctions for the diatomic molecules

The molecules studied in this work are the diatomic hydrides AH (A = B, C, N, O and F) and the 14 electron family, N_2, CO ($^1\Sigma$) and BF. The wavefunctions of near Hartree–Fock quality, are taken from Cade & Huo (1967) for the hydrides, Cade, Sales & Wahl (1966) for N_2 (wavefunction 2*D*) and Huo (1965) for CO and BF (wavefunctions at experimental R_e). For these molecular wavefunctions, the molecular orbitals were spanned by extensive sets of Slater-type functions and were determined by solving the Hartree–Fock–Roothaan equations of motion for the electrons (Roothaan, 1951).

Core monopole studies

It is generally assumed that the coherent X-ray scattering by the atomic-core electron density is invariant to chemical bonding. Our previous studies of the monopole scattering factors for pseudoatoms in diatomic molecules cogently support this assumption (Bentley & Stewart, 1975). There is some ambiguity, however, in the choice of a core density function. For example, it has been suggested that the $(1s)^2$ SCF orbital product of a first-row atom be defined as the core-electron atomic density function (Stewart, 1968). But the electron density on or near the nucleus of an isolated atom has a contribution from the $(2s)^2$ SCF orbital product as well as from $(1s)^2$. Thus a $(\chi_{1s})^2$ density populated with two electrons does not give all the charge on or near the nucleus in the isolated atom. This may also be true for the pseudoatom in a molecule. To add more flexibility to the monopole of the pseudoatom, a variable electron population parameter is assigned to the Hartree–Fock 1*s* orbital product in the pseudoatom density model, $p_c(\mathbf{r}, R)$.

Extensive studies have been done with a $(\chi_{1s})^2$ whereby the electron population is fixed at two or allowed to vary. Results from solutions to the least-squares equations (3) and (4) show that a doubly occupied $(\chi_{1s})^2$ function is not an adequate representation of the core density. The total electron charge from the fixed-core-population model is 2–3% lower than the total charge determined with both variable core and valence population. The figure of merit, R_w from (5), was larger by a factor of 1·5 to 2·5 for the fixed-core model than for the variable-core electron function. The differences in R_w are smaller when $(\sin\theta/\lambda)_{\max}$ is restricted to a sphere of 0·7 Å^{-1} or 1·4 Å^{-1}, but core charges are essentially the same. Molecular dipole and quadrupole moments from the variable-core model are generally in closer agreement with the starting molecular density values than results from the fixed-core case. Electric fields and field gradients are essentially insensitive to the core monopole representation.

The results reported below include a variable population for the core density function. The average core population is 2·10 with a trend for smaller populations for nuclei with smaller charge and larger than 2·1 for O and F atoms. If this trend is also true for organic molecular crystals, then the variable scale factor, as proposed by Stewart (1976), will be too large by ~5%.

Valence density representations

The major results are based on expansions up through quadrupole terms for each pseudoatom in the diatomic molecule. For first-row atoms the valence radial functions for each multipole are of the form, $r^2 \exp(-\alpha r)$ so that α is a variable parameter and shared among the first three multipoles. These functions plus the core monopole are assigned electron population parameters. For the hydrides, the hydrogen pseudoatom is expanded with the radial basis, $\exp(-\alpha_H r)$, $r\exp(-\alpha_H r)$ and $r^2\exp(-\alpha_H r)$ for the monopole, dipole and quadrupole functions respectively. All three multipoles are given a variable electron population parameter and the variable exponential parameter α_H. In addition to variable α parameters, we also report results for standard molecular exponents (Hehre, Stewart & Pople, 1969). In this case the α parameter is fixed at twice the standard molecular exponent value. These exponents are average values from parameters which minimize the energies in minimal basis-set molecular-orbital calculations. Exponents obtained by an energy criterion need not be the best least-squares exponents for fitting of charge densities.

Results

Figs. 1 and 2 summarize the trends for the diatomic hydrides whereby (4) was minimized with both standard molecular exponents (SM) and with variable exponents (LS). In Fig. 1 it can be seen that R_w is dramatically improved for BH and CH by minimization with respect to the exponential parameters in addition to the electron population coefficients. Note that R_w, however, is between 0·02 and 0·01 for all the diatomic hydrides when the model employs restricted radial functions of a single exponential type. By contrast, unrestricted radial functions with expansions up to quadrupolar terms on both centers of the hydrides have an R_w of 0·002 (Bentley & Stewart, 1975). The total charge for the hydrides (see Fig. 1) is rather close to the total number of electrons (3% or better) when the exponential parameters are varied in addition to the electron population parameters. For fixed exponents at standard molecular values the total charge is rather less. The dipole moments of the diatomic hydrides are reproduced much better with the LS model than the SM model. The one exception is for FH. The quadrupole moments from the LS bases are closer to the SCF values as well. As illustrated in Fig. 2 the electric fields at the heavy atoms of the hydrides depart markedly from the SCF values. This is primarily due to the core charge deformation (Bentley & Stewart, 1974) which is not included in the model here.

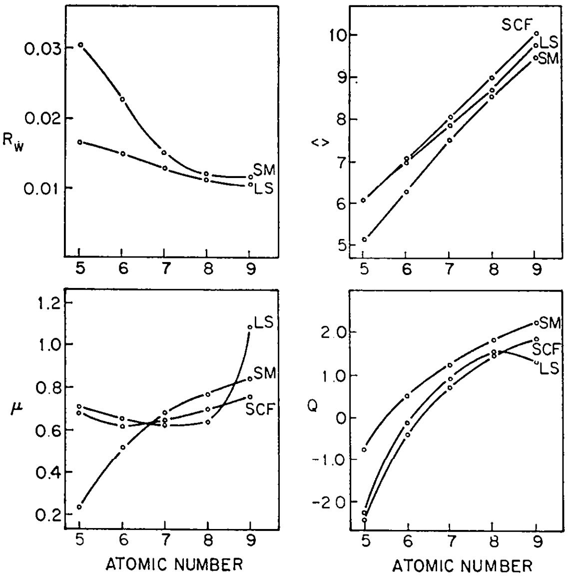

Fig. 1. Properties for diatomic hydrides, BH to FH. Values displayed are R_w (relative root-mean-square error), $\langle\ \rangle$ (total charge), μ (dipole moment) and Q (quadrupole moment with origin at the heavy atom). LS is for variable valence exponents; SM is for standard molecular exponents; SCF is molecular average property. All units are a.u.

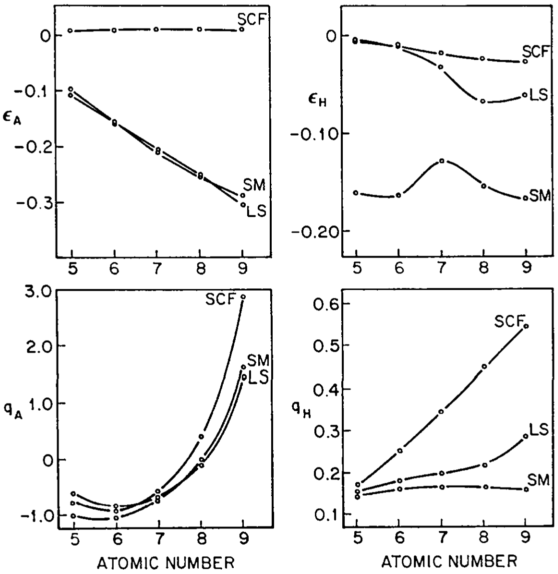

Fig. 2. Electric fields and electric field gradients for diatomic hydrides, BH to FH. ε_A and ε_H are electric fields at the heavy atom and hydrogen atom respectively. q_A and q_H are similarly the electric field gradients. LS, SM, and SCF defined in caption for Fig. 1. All units are a.u.

If a core deformation density function with the exponent taken from Bentley & Stewart (1974) is included in the charge density model, then the SCF values for the electric fields at the heavy-atom nucleus are closely reproduced. Other physical properties are not changed with inclusion of the core dipole density function. The LS model reproduces reasonably well the electric fields at the protons, however. In this case, the model does include a relatively flexible dipole density function for the hydrogen pseudoatom. The electric field gradients at the heavy atoms are correctly given to within a few tenths of atomic units. On the other hand, the field gradients at the protons are very poorly given. Although the H pseudoatom does include a quadrupole term, the restricted radial density model is still unsatisfactory for a reliable estimate of hydrogen-atom electric field gradients in these diatomic hydrides.

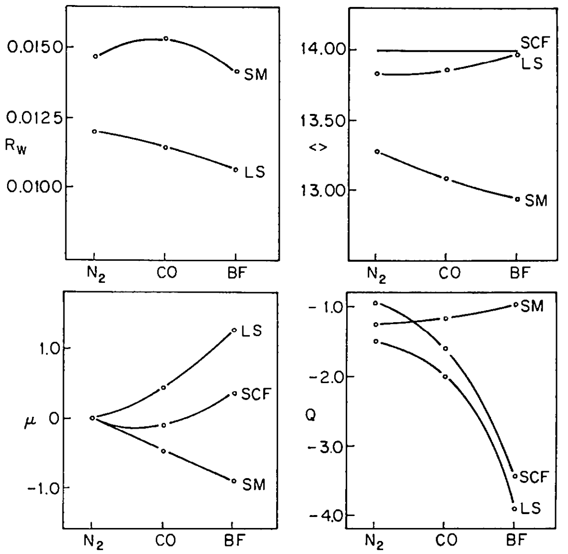

Fig. 3. Properties for the 14-electron series, BF, CO and N_2. Values displayed are R_w (relative root-mean-square error), $\langle\ \rangle$ total charge, μ (dipole moment) and Q (quadrupole moment with origin at center of mass). LS, SM and SCF defined in caption for Fig. 1. All units are a.u.

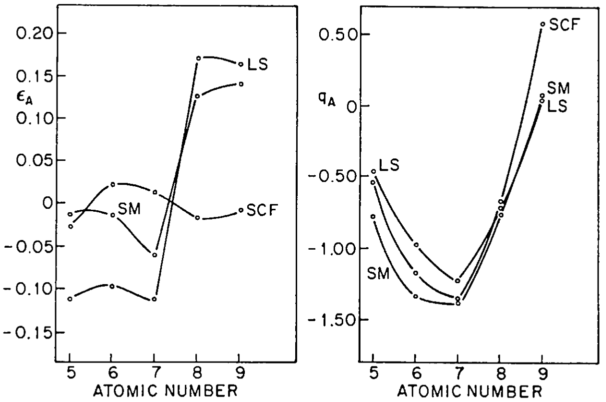

Fig. 4. Electric fields (ε_A) and field gradients (q_A) at the atoms in BF, CO and N_2. For O and F the field is with respect to center B. LS, SM and SCF defined in caption for Fig. 1. All units are a.u.

Figs. 3 and 4 summarize the results for the 14-electron series BF, CO($^1\Sigma$), and N_2. A sin the diatomic hydride series, the LS model affords a rather smaller relative root-mean-square error (R_w) and a total electron charge that is closer to a neutral molecule than what the SM model gives. Both LS and SM models give rise to poor dipole moments for both CO and BF but the former model reproduces the SCF quadrupole moments rather well. In Fig. 4 are shown the electric fields and electric field gradients at B, C, N, O and F for BF, CO and N_2. [The electric-field results for O and F, atomic numbers 8 and 9, are shown for center B so that in equation (9) the symbols A and B are interchanged.] Both LS and SM models give electric fields with sizeable discrepancies from the SCF starting values. As with the hydrides, inclusion of dipole core-deformation functions from Bentley & Stewart (1974) brings the least-squares results into satisfactory agreement with the molecular values. The electric field gradients are reproduced with a quality comparable to the heavy atoms in the diatomic hydrides.

Up to now the discussion has focused on those results which minimized the least-squares function (4). A finite Ewald sphere [equation (3)] may influence the molecular properties and pseudoatoms somewhat. Studies were restricted to spheres with $(\sin\theta/\lambda)_{\max}$ at 0·7 Å^{-1} and at 1·4 Å^{-1}. It was generally found that the physical properties showed some dependence on $S_{\max}$, but these variations were very small compared to the differences from the SCF expectation values. The major conclusion to be drawn is that the Fourier coefficients of the molecular density function within a sphere of 1·4 Å^{-1} in $\sin\theta/\lambda$ are probably adequate for a detailed charge density analysis. The limiting feature for electrostatic physical properties is the single exponential radial density function model for the pseudoatom rather than an inaccessibly infinite Ewald sphere.

Table 1. *Valence exponents for first-row atoms*

	B	C	N	O	F
α_A from AH	2·39	3·05	3·75	4·46	5·25
α_A from AB	2·34	3·04	3·72	4·43	5·16
α_A from Hartree–Fock atom	2·36	3·05	3·77	4·47	5·16
Standard molecular value*	3·00	3·44	3·90	4·50	5·10
α_H from AH	2·10	2·24	2·29	2·13	1·76

* Taken from Hehre, Stewart & Pople (1969).

For almost all cases variable exponential parameters in the least-squares equations afford physical properties in closer agreement with the molecular averages. In Table 1 we list the values of the exponential parameters found in this work. These restricted radial bases give a reasonably qualitative description of charge density in diatomic molecules, and electrostatic properties which have the correct trends, if not the correct values. The exponent parameters for isolated Hartree–Fock atoms are also listed in Table 1. These were obtained by fitting

$$\varrho^{c}_{\text{atom}}=(4\pi)^{-1}[C(\chi_{1s})^2+Mr^2\exp(-\alpha r)] \qquad (5)$$

to the Hartree–Fock atomic density with C, M and α as variable least-squares parameters. The Hartree–Fock atomic densities were taken from the SCF wavefunctions of Clementi (1965). Note that the molecular α_A values are rather close to the isolated-atom values and that for B, C and N the valence radial functions are considerably more diffuse than the energy-optimized values which are shown in Table 1 under standard molecular values. The similarity between the valence exponents in various bonding situations suggest that they are characteristic of the atom regardless of atomic environment. This may mean, for example, that all nitrogen atoms in an organic molecular crystal could share the same valence exponent as a refinable least-squares parameter without unwarrantable restriction of the model.

For comparison the α_H values are also listed in Table 1. Except for H in HF, the pseudoatoms are contracted compared to the isolated H atom. Also note that the α_H value depends markedly on the diatomic hydride from which it was extracted.

In closing this section we mention that inclusion of hexadecapole and octupole deformation functions in the least-squares model led to very marginal improvement. This indicates that the restricted, single exponential radial functions are the limiting feature in the present density model.

Conclusion

Projections of near Hartree–Fock one-electron density functions for diatomic molecules into finite multipole expansions for the pseudoatoms with single exponential radial functions reproduce qualitative features of charge density, but do not consistently provide accurate values for physical properties. Total charge and electric field gradients for the first-row atoms are most accurately retrieved. Electric fields, without a core-deformation model, are very poorly represented. The basic limitation is the inflexibility of the radial function. Stewart, Bentley & Goodman (1975) have shown that minimization of (4) with unrestricted radial functions leads to functional equations that automatically satisfy all molecular properties discussed in this paper if each pseudoatom is expanded up to the quadrupole level. Thus a small, finite multipole expansion can satisfy several static-charge properties, but a single exponential radial density function is severely limited. It is also clear from this work that valence exponents should be made a variable least-squares parameter in a charge-density analysis of structure factors. However, it appears that one can restrict this degree of freedom to the type of atom rather than to all atoms. If it is not feasible or practical to refine the exponent, then the values in Table 1 for the first two rows are probably better than standard molecular values.

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