J. Am. Chem. Soc. 1989, 111, 6933–6941

The desired correction vector $|\Delta\rangle$ for the parameters $W_l^B$ and $X_{mn}^B$ is then given by

$$|\Delta\rangle = -\sum_i |c_i\rangle\langle c_i|DI\rangle / e_i \qquad (36)$$

where the $i$ are restricted to those $e_i$ that are larger than some small positive constant $\delta$. This is done because if $e_i \approx 0$, this $|c_i\rangle$ represents a redundant linear combination of parameters and should be suppressed.

A program has been prepared for the analysis of theoretical molecular densities (where the thermal smearing need not be accounted for). The procedure consists of the following steps: 1. Read the molecular density, the atomic coordinates, the atomic SCF orbitals, and starting values for $W_l^B$ and $U_{mn}^B$. 2. Calculate the basic integrals (eq 16–18). 3. Perform the two- and four-index transformation (eq 20 and 21). 4. Calculate the Fock operators $F$ and $L$ (eq 25 and 33). 5. Construct the $DI$ vector and the $D^2I$ matrix (eq 32). 6. Diagonalize the Hessian (eq 34), determine improves values of $W_l^B$ and $U_{mn}^B$ (eq 30 and 36), and calculate the integrated squared residual density $I$ (eq 22). 7. Repeat steps 3–6 until self-consistency is reached.

The result is a promolecule uniquely defined as the density superposition of free atoms in their ground state which are optimally positioned *and* oriented in the molecule. This definition is in our opinion better suited for the purpose of analyzing chemical bonds than the choice of spherically averaged atoms.

**Acknowledgment.** We are grateful to J. D. Dunitz, D. Feil, R. Goddard, F. L. Hirshfeld, R. Jaquet, and E. N. Maslen for their constructive comments. W.H.E.S. expresses his cordial gratitude for the hospitality he has received at Iowa State University in Ames. We acknowledge financial support by NATO (Grant No. 298/83), by DFG (Grant No. 477/423), by Fonds der Chemischen Industrie (Grant No. 160273), and by the U.S. Department of Energy, Office of Basic Energy Science, Division of Chemical Sciences (Contract No. W-7405-ENG-82).

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# Chemical Deformation Densities.[†] 2. Small Molecules

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**Abstract:** The method described in the preceding paper[1] for deducing nonspherical, multipolar, oriented atomic ground-state reference density contributions to molecular densities is applied to the molecules $F_2$, HF, $H_2O$, $H_2O_2$, $^1CH_2$, $^3CH_2$, $CH_4$, and LiH. From these reference densities the chemical deformation densities (CDDs), which were also introduced in the preceding paper, are determined. They offer a consistent, interpretable picture for bond, lone-pair density, and charge-transfer deformations in these molecules. The CDDs of oxygen and fluorine compounds do not exhibit the exceptional peculiarities that appear when conventional difference densities, based on spherically averaged atomic reference densities, are examined. The eigenvalues of the orientation tensors are compared with the theoretical Mulliken populations.

## 1. Introduction

X-ray diffraction of crystals yields information on electron densities. There exists an interest in deducing chemical information from such densities without recourse to other information. A natural approach is first to determine atomic densities and then to subtract them from the molecular density to obtain interpretable difference densities (DDs).

In the preceding paper[1] the concept of the *chemical deformation density* (CDD) of a molecule was introduced as the difference between the molecular density $\rho_{mol}$ and the superposition of uniquely defined atomic reference densities $\rho_{at}$ representing appropriately *positioned and oriented unperturbed ground states* or near ground-state atoms in a molecule. A mathematical definition was formulated, and a computational algorithm was given for the quantitative determination of the orientation parameters of multipolar atomic ground-state densities $\rho_{at}$ and, hence, of the CDD, $\Delta\rho = \rho_{mol} - \rho_{at}$. While in conventional X-ray analysis, only the *positions* of the atoms of a molecule or unit cell are refined by using least-difference-squares techniques, the proposed method[1] extended this approach to the atomic *orientations*, i.e., the integrated squared difference density

$$\mathrm{IDD} = \int dr^3\,(\Delta\rho)^2$$

is also minimized with respect to the orientation tensors of degenerate atomic ground states.

An essential element of this approach is that in addition to the position, the orientation of a degenerate ground state (or possibly near-degenerate ground-state manifold) is the *only* adaptation of the atom to its environment. Energy changing hybridizations or other promotions are excluded. This limitation eliminates the arbitrariness introduced by other ways of "preparing" the atoms, and it makes a consistent interpretation possible.

In the present paper this method is successfully tested by applying it to the theoretically calculated density of several small molecules containing atoms that when free, have degenerate groundstates (C, O, F), namely, $F_2$, HF, $H_2O$, $H_2O_2$, $^1CH_2$, $^3CH_2$, $CH_4$, and, in addition, LiH. The examination of their theoretical chemical deformation densities leads to a number of conclusions regarding the meaning and utility of the "atomic orientations" and the "genuine chemical deformations" deduced from the

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[†] Partially presented at the International Workshop on the Interpretation and Uses of Electronic Distributions, Grenoble, 26–29 March 1985, and at the 5th International Conference on Quantum Chemistry, Montreal, 18–24 August, 1985.

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(1) Schwarz, W. H. E.; Ruedenberg, K.; Mensching, L. *J. Am. Chem. Soc.*, preceding paper in this issue.

**Table I.** Geometries and Total SCF Energies

| system | geometry | $-E$, hartrees |
|---|---|---|
| $F_2$ | $R = 1.42$ Å | 198.649 |
| HF | $R = 0.92$ Å | 100.006 |
| $H_2O$ | $R = 0.957$ Å, $\alpha = 104.5°$ | 76.015 |
| $H_2O_2$ (gas) | $R_{OH} = 0.95$ Å, $R_{OO} = 1.475$ Å, $\alpha_{HOO} = 95°$, $\gamma_{HOOH} = 120°$ | 150.751 |
| $H_2O_2$ (solid) | $R_{OH} = 0.99$ Å, $R_{OO} = 1.453$ Å, $\alpha_{HOO} = 103°$, $\gamma_{HOOH} = 90°$ | 150.752 |
| $CH_2(^1A_1)$ | $R = 1.11$ Å, $\alpha = 102°$ | 38.874 |
| $CH_2(^3B_1)$ | $R = 1.08$ Å, $\alpha = 134°$ | 38.914 |
| $CH_4$ | $R = 1.094$ Å | 40.157 |
| LiH | $R = 1.6$ Å | 7.981 |
| H ($^2$S) | | 0.499 |
| C ($^3$P) | | 37.669 |
| O ($^3$P) | | 74.765 |
| F ($^2$P) | | 99.348 |

molecular density distributions in this manner. They are summarized in section 9.

## 2. Details of the Calculations and Quantitative Results

The electron densities of the molecules $F_2$, HF, $H_2O$, $H_2O_2$ (gaseous and solid geometry), $CH_2$ (singlet and triplet), $CH_4$, and LiH were determined theoretically by using the SCF approximation and, in the cases of $F_2$, $CH_4$, and LiH, also with the MCSCF-FORS approach.[2] Standard Gaussian basis sets[3] of double-$\zeta$ polarization quality and experimental geometries[4] were used. The atomic orbitals of the free atoms were determined by the symmetry-restricted SCF method with the same basis sets, but fully uncontracted. The geometries and the total SCF energies are given in Table I.

In these molecules the populations and orientations of the "natural local" p orbitals of the atoms C, O, and F were determined by the method described in section 2 of the preceding paper,[1] and in doing so the atomic 1s and 2s orbitals were taken to be doubly occupied. The results are presented in Table II and in Figures 1–8. The orientations of the orbital axes are described in footnotes *a* and *b* of Table II. The results are discussed in the subsequent sections.

One may note that although the closed-shell SCF potential curves of $F_2$ and $(OH)_2$ have deep minima corresponding to the formation of covalent bonds, the minima are still higher than twice the open-shell SCF energies of the F atom and the OH radical, respectively. Nevertheless the SCF one-electron properties furnish an appropriate description of these bound systems (i.e., reasonable bond length, force constant, and molecular density; see, e.g., ref 2 and 6). While the MCSCF-FORS approach significantly improves the energy through the improvement of the two-electron density, the one-electron density is only slightly modified[5,7] (see also section 8 below).

The figures show difference-density (DD) contour plots in planes through the molecular axis. The separation of the contour lines is $0.04\ e/a_0^3 = 0.27\ e/Å^3$ except for LiH where $0.01\ e^2/a_0^3 = 0.067\ e/Å^3$ is used. Density increases ($\Delta\rho > 0$) are indicated by solid lines, density decreases ($\Delta\rho < 0$) by dashed lines. Instead of the zero-contour line ($\Delta\rho = 0$), two bond lines, one solid and one dashed, corresponding to $\pm 0.01\ e/a_0^3 = \pm 0.067\ e/Å^3$, respectively, are shown ($\pm 0.0025\ e/a_0^3 = \pm 0.017\ e/Å^3$ in the case of LiH). The value of $0.067\ e/Å^3$ is of the order of the optimal accuracy of experimental density determinations. The coordinate scales in the figures are in $a_0 = 0.529$ Å. In addition, total-density contour plots of spherically averaged and of oriented ground-state atoms are presented below the molecular DD plots. The different pertinent $\rho$ values of the contour lines are explicitely given in $e/a_0^3$.

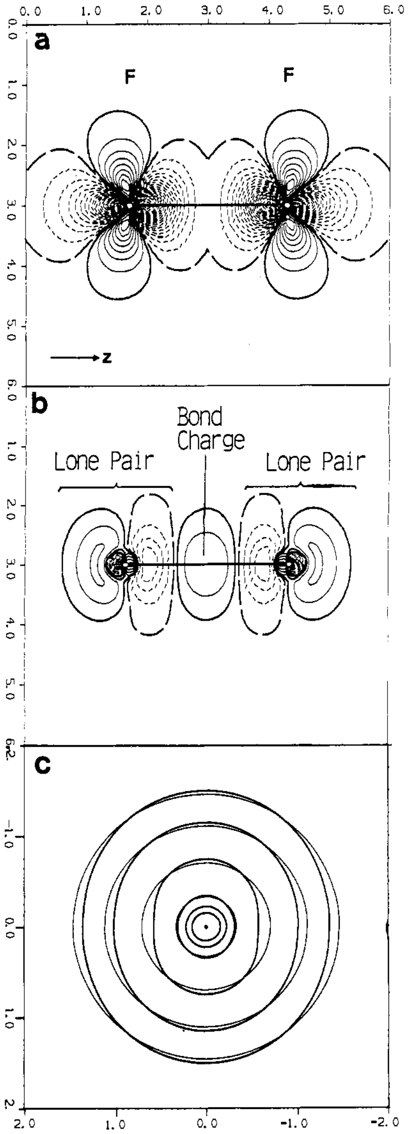

**Figure 1.** (a and b) SCF difference density maps of $F_2$ (for MCSCF maps see ref 8): thin solid line, $+0.04n\ e/a_0^3$; thin dashed line, $-0.04n\ e/a_0^3$ ($n = 1, 2, 3, ...$); bold solid line and bold dashed line $\pm 0.01\ e/a_0^3$. Unit of length $a_0 = 0.529$ Å. (a) TDD, molecular density minus sphericalized atoms ($F(1s^2\ 2s^2\ 2p_x^{5/3}\ 2p_y^{5/3}\ 2p_z^{5/3})$). (b) CDD, molecular density minus oriented atomic ground states ($F(1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1)$). (c) Total ground-state density of the fluorine atom; bold line, oriented F; thin line, spherically averaged F. Density values from outside to center: 0.1, 0.3, 1, 3, 10, 30 $e/a_0^3$ (note the different length scale).

## 3. Fluorine

The natural atomic p orbitals of F in $F_2$ are of $\sigma$ and $\pi$ type (see the second column of Table II) with populations 1.0 and 2.0 (see the third column). The total spherical and nonspherical atomic densities are plotted in Figure 1c in the direction of the molecular axis.

The difference density (DD) plots for the $F_2$ molecule are shown in Figure 1a,b. If we subtract the optimally populated F atoms ($2p_x^2\ 2p_y^2\ 2p_z^1$) from the $F_2$ molecule, we obtain the chemical deformation density map of Figure 1b. The CDD exhibits three chemically interesting features.

First, the constructive interference of the singly occupied valence AOs results in a *density contraction toward the overlap region* with a CDD maximum of 0.5 $e/Å^3$ at the bond center. This feature is typical for covalent bonds of second-row atoms. In a calculation including electron correlation[6,8] the "bond charge" is

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**Table II.** SCF Populations of Oriented Atomic Orbitals

| | | optimal pop. (this work) | | | Mulliken pop. | | | ICDD[e] |
|---|---|---|---|---|---|---|---|---|
| molecule | at. orbital[a] | pop. | %[c] | Δ%[d] | Δ%[d] | %[c] | pop. | (ITDD), $e^2/a_0^3$ |
| $F_2$ | F(pσ) | 1.000 | 20.0 | −13.3 | −13.0 | 20.3 | 1.018 | 0.0200 |
| | F(pπ) | 2.000 | 40.0 | +6.7 | +6.5 | 39.9 | 2.000 | (0.1923) |
| HF | F(pσ) | 1.414 | 28.3 | −5.1 | −5.7 | 27.7 | 1.531 | 0.0152 |
| | F(pπ) | 1.793 | 35.9 | +2.5 | +2.8 | 36.2 | 2.000 | (0.0263) |
| $H_2O$ | O($pa_1$(σ)) | 1.310 | 32.8 | −0.6 | +0.4 | 33.7 | 1.658 | 0.0259 |
| | O($pb_2$(σ)) | 1.116 | 27.9 | −5.4 | −7.7 | 25.6 | 1.259 | (0.0339) |
| | O($pb_1$(*n*)) | 1.574 | 39.3 | +6.0 | +7.3 | 40.7 | 2.000 | |
| $H_2O_2$[b] (gas) | O(p(OH)) | 1.401 | 35.0 | +1.72 | +1.1 | 34.4 | 1.555 | 0.0411 |
| | O(p(OO)) | 0.835 | 20.9 | −12.5 | −10.6 | 22.8 | 1.028 | (0.1097) |
| | O(p(*n*)) | 1.764 | 44.1 | +10.8 | +9.5 | 42.8 | 1.933 | |
| $H_2O_2$[b] (solid) | O(p(OH)) | 1.383 | 34.6 | +1.2 | | | | 0.0430 |
| | O(p(OO)) | 0.849 | 21.2 | −12.1 | | | | (0.1097) |
| | Op(n) | 1.768 | 44.2 | +10.9 | | | | |
| $CH_2$ ($^1A_1$) | C($pa_1$(σ)) | 1.112 | 55.6 | +22.2 | +26.4 | 59.7 | 1.509 | 0.0206 |
| | C($pb_2$(σ)) | 0.888 | 44.4 | +11.1 | +7.0 | 40.3 | 1.019 | (0.0549) |
| | O($pb_1$(*n*)) | 0.000 | 0.0 | −33.3 | −33.3 | 0.0 | 0.000 | |
| $CH_2$ ($^3B_2$) | C($pa_1$(σ)) | 0.496 | 24.8 | −8.5 | −4.3 | 29.0 | 0.829 | 0.0169 |
| | C($pb_2$(σ)) | 0.488 | 24.4 | −8.9 | +2.7 | 36.0 | 1.030 | (0.0218) |
| | C($pb_1$(*n*)) | 1.016 | 50.8 | +17.5 | +1.6 | 35.0 | 1.000 | |

[a] In $F_2$, HF, $H_2O$, and $CH_2$, the orientation of the p AOs is determined by symmetry. For $H_2O_2$ see footnote *b*. [b] In $H_2O_2$, the oriented p AOs $P_{OH}$ and $P_{OO}$ are approximately parallel to the bonds ($R_{OH}$, $R_{OO}$). The p AO p(*n*) is approximately perpendicular to these bonds. For gaseous (solid) $H_2O_2$ the values of the corresponding angles are ($P_n$, $R_{OH}$) = 89.3° (89.7°), ($P_n$, $R_{OO}$) = 89.8° (88.8°), ($P_{OH}$, $R_{OH}$) = 14.8° (22.5°), ($P_{OH}$, $R_{OO}$) = 80.0° (80.2°), ($P_{OO}$, $R_{OH}$) = 75.2° (67.5°), ($P_{OO}$, $R_{OO}$) = 10.0° (9.9°). [c] Distribution of p electrons over the three oriented p AOs in percent; a spherically averaged atom has 33.3%. [d] Percentage deviation of the optimized population from the average value of 33.3%. [e] ICDD = minimized integrated squared chemical deformation density for optimally oriented atoms; ITDD (in parentheses) = integrated squared total difference density with respect to spherically averaged atoms. See eq 19 of ref 1.

reduced to 0.3 e/Å$^3$. Such a low value is characteristic for a weak, elongated σ bond such as that in $F_2$.

Second, the Pauli repulsion between the doubly occupied orbitals results in a pronounced polarization of the $2s^2$ *lone pairs* from the bond side to the back side of the atoms. Often attention is paid only to the region of density increase "behind" the atomic core when considering lone-pair formation. However, it is evident from charge conservation that there must also exist a complementary region of density decrease. This is clearly shown in Figure 1b with extrema of −0.9 and +0.6 e/Å$^3$ on the bond and back sides, respectively, of the F atoms.

Third, the above-mentioned two features are clearly separated. This is typical for a comparatively long bond as in $F_2$, which is due to the nonbonded repulsions of the σ and π lone pairs. This interpretation has recently been substantiated in detail by a breakdown into orbital contributions.[7] Other detailed discussions are given in refs 9–12.

The three above-mentioned details become apparent *only* after appropriately orienting the F atoms. Without doing so, i.e., when using spherically averaged F atoms as reference density, one obtains the total difference density in Figure 1a. Here the dominant feature is the transfer of charge from the molecular axis (TDD extrema of −5 e/Å$^3$) toward toruses around the nuclei (TDD extrema of +2 e/Å$^3$). It represents nothing other than the fact that the bond in $F_2$ is due to the overlap of two singly occupied $2p_z$ AOs of the nonspherical ($2p_x^2\,2p_y^2\,2p_z^1$) $^2P_z$ ground states of the F atoms. The spherically averaged atomic density corresponds, however, to an orbital population of ($2p_x^{5/3}\,2p_y^{5/3}\,2p_z^{5/3}$) with two-thirds too many electrons in each $p_z$ AO and a corresponding deficiency in the $p_{x,y}$ AOs. Note that the deviation of the oriented F atom from the spherically averaged density (see Figure 1c) appears still small for the present case of maximal ground-state anisotropy. Nevertheless, it has a drastic effect on the $\Delta\rho$ maps.

The integrated squared total difference density (ITDD) has the value 0.19 $e^2/a_0^3$. This is 1 order of magnitude larger than that obtained for the optimal orientation: the integrated squared chemical deformation density is only ICDD = 0.02 $e^2/a_0^3$. The optimized populations $2p_x^2\,2p_y^2\,2p_z^1$ are exactly as expected. They agree with the Mulliken populations given in Table II.

## 4. Hydrogen Fluoride

Figure 2 displays three different DD plots, namely, (1) that obtained with the spherically averaged F atom $2p_x^{5/3}\,2p_y^{5/3}\,2p_z^{5/3}$ (Figure 2a), (2) that obtained with the "naive" choice of AO occupations $2p_x^2\,2p_y^2\,2p_z^1$ (Figure 2b), and (3) that obtained with the optimal occupations of the p AOs as listed in Table II, $2p_x^{1.8}\,2p_y^{1.8}\,2p_z^{1.4}$ (Figure 2c). The corresponding atomic anisotropy of F as exhibited by the plots in Figure 2d is even less pronounced than in $F_2$.

The chemical deformation density (Figure 2c) with the small ICDD value of 0.015 $e^2/a_0^3$ exhibits dipolar distributions around both nuclei. At the *fluorine* atom a density depression of −0.9 e/Å$^3$ on the bond side and a density accumulation of +0.6 e/Å$^3$ on the back side of the atomic core is typical for σ lone pair formation. The extrema values are very similar to those in $F_2$. The Mulliken populations of the F(2pπ) AOs are 2.0 as expected. However, the 2pσ population is larger than 1.0, namely, 1.53 (see Table II). The total Mulliken p population is thus 5.53, corresponding to a negative partial charge of $F^{-0.53}$, implying that F in HF is intermediate between a quadrupolar neutral F atom ($2p_x^2\,2p_y^2\,2p_z^1$) and a spherical negative $F^-$ ion ($2p_x^2\,2p_y^2\,2p_z^2$). By contrast, our optimized p populations are constrained to sum up to 5 as in neutral F. Therefore the best we can do is to compare our optimized values and the Mulliken populations with regard to the *relative* distribution of the *total p population* over 2pσ and 2pπ. These percentages of the p population are listed in Table II under the headings %. A spherically averaged atomic density corresponds to a relative population of 33.3% in each p AO. The percent deviation from this spherical average is given under heading Δ%. The relative p populations obtained of our density fit agree well with the corresponding relative Mulliken values.

The density distribution around the *hydrogen* is also of the dipolar type. The density increase in the overlap region (+0.6 e/Å$^3$) indicates the formation of a covalent bond. The density decrease on the backside of the proton (−0.2 e/Å$^3$) and practically no density increase at the nucleus is typical for what chemists call a positively charged hydrogen. By contrast, for prototypes of

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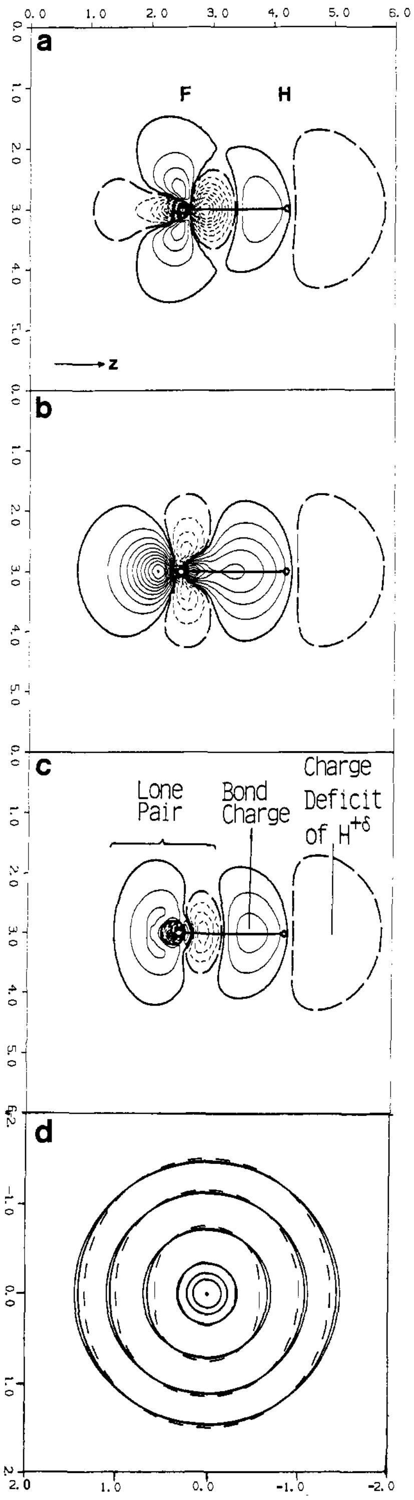

**Figure 2.** SCF difference density maps of HF (see legend of Figure 1). (a) TDD, molecular density minus sphericalized atoms (F($1s^2$ $2s^2$ $2p_x^{5/3}$ $2p_y^{5/3}$ $2p_z^{5/3}$)). (b) Naive DD, molecular density minus H(1s), F($1s^2$ $2s^2$ $2p_x^2$ $2p_y^2$ $2p_z^1$). (c) CDD, molecular density minus oriented atomic ground states (F($1s^2$ $2s^2$ $2p_x^{1.793}$ $2p_y^{1.793}$ $2p_z^{1.414}$)). (d) Total ground-state density of the fluorine atom; bold line, oriented F; dashed line, "naively oriented" F; thin line, spherically averaged F. Density values from outside to center: 0.1, 0.3, 1, 3, 10, 30 e/$a_0^3$ (note the different length scale).

neutrally bonded hydrogen atoms, such as in $H_2$[7] or in $CH_4$ (see section 8 below), one finds a strong positive difference density at and near the hydrogen nucleus.

Sphericalized reference populations of the nonbonding $\pi$ and the bonding $\sigma$ p AOs of fluorine (with $p^{5/3}$) yield a large negative difference density on the molecular axis both in the lone-pair region and in the bonding region (−2.4 e/Å$^3$; see Figure 2a), and a positive difference density in a torus around the atomic core (+0.9 e/Å$^3$). This quadrupolar distribution is similar to the one in $F_2$ (Figure 1a) although less pronounced. This is so because HF has a significant contribution from the ionic configuration $H^+F^-$ with $F^-$ having a spherical density, while $F_2$ is formed from neutral, strongly quadrupolar F atoms. Figure 2a demonstrates that a population of the $2p_z$ AO with $^5/_3$ e is still too large for describing the H(1s)–F(2p) bond. A population of the $2p_{x,y}$ AOs with $^5/_3$ e clearly is too small.

A "naive" alternative is a reference population of a single electron in the $2p_z$ AO and two electrons in each of the $2p_{x,y}$ AOs. This was first suggested by Bader et al.[13] The corresponding difference density, shown in Figure 2b, is also characterized by a strong quadrupolar distribution around the F atom, but now of opposite sign: unusually large density rises on the molecular axis in the bond region (+1.2 e/Å$^3$) and in the lone-pair region (+2.7 e/Å$^3$) and a density decrease in the $\pi$ region (−0.9 e/Å$^3$). The corresponding $I$ value is found to be 0.044 $e^2/a_0^3$ and is even larger than in the case of a sphericalized atomic reference density ($I$ = 0.026 $e^2/a_0^3$), while the CDD yields a low $I$ value of only 0.015 $e^2/a_0^3$ (see Table II).

The example of HF illustrates the difficulty of *guessing* at the optimal populations.

## 5. Water

The difference densities in the molecular $xz$ plane are shown in Figure 3a–d, those in the perpendicular $xy$ plane in Figure 3e–h.

As seen from Table II the optimized occupations of the O atom in $H_2O$ are $p_x^{1.12}$ $p_y^{1.57}$ $p_z^{1.31}$. The resulting oxygen density is shown in Figure 3i,k. The corresponding CDD (Figure 3d,h) yields a low $I$ value of 0.026 $e^2/a_0^3$. Since, in $H_2O$, oxygen has some spherical $O^{2-}$ character, the p occupations are not drastically different. The two oxygen lone pairs of 2s and $2p_y$ type are clearly seen as dipolar difference density features on the $z$ axis in Figure 3d ($xz$ plane) and in Figure 3h ($yz$ plane) with a minimum of −0.7 e/Å$^3$ and a maximum of +0.8 e/Å$^3$ on opposite sides of the nucleus. Because of the partial negative charge on O, the Mulliken p populations are higher than our optimized ones, which correspond to neutral $1s^2$ $2s^2$ $2p^{4.0}$ oxygen. Also a small amount of 2s–2p promotion contributes to the total Mulliken p-population value of 4.9. Nonetheless, as in HF, we find agreement within about 1% between our optimized populations and the Mulliken populations, when we examine the *relative* distribution of the total p population over the three p orbitals (see Table II).

In the O–H bond we find a difference density maximum of +0.7 e/Å$^3$. As in HF, a dipolar charge distribution exists around the hydrogen, indicating essentially charged hydrogens, although less so than in HF. Since O is less strongly electron withdrawing than F, a nonnegligible charge increase of 0.3 e/Å$^3$ is now observed at the proton. It is still much smaller, however, than that in $H_2$, where it is 0.8 e/Å$^3$. The density decrease "behind" the protons is still appreciable in $H_2O$. The density changes at the bond centers and behind the protons are only weakly diminished by correlation (by less than 0.1 $e^2/a_0^3$, see Figure 5a on p 35 of ref 5). Finally, we note the trigonal character of the chemical deformation density in the molecular plane around the oxygen (see Figure 3d).

Subtracting the density of a sphericalized oxygen atom corresponding to the atomic population $2p_x^{4/3}$ $2p_y^{4/3}$ $2p_z^{4/3}$ yields Figure 3a,e. It is obvious that the density in the $p_y$ AO is too small so that a significantly positive $\Delta\rho$ results on the whole $y$ axis (Figure 3f). The density in the $p_x$ AO is too large, while the $2p_z$ population of 1.33 is reasonable. Since oxygen is not very aspherical in $H_2O$, the ITDD value of 0.034 $e^2/a_0^3$ is only slightly larger than the minimized ICDD value of 0.026 $e^2/a_0^3$.

Bader[12] suggested the population $2p_x^{5/3}$ $2p_y^{5/3}$ $2p_z^{2/3}$. As Figure 3b,f shows the $p_y$ population of 1.67 is not unreasonable, but the $p_x$ population is now drastically large and the $p_z$ population is drastically low (large negative and positive $\Delta\rho$ values on the whole

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(13) Bader, R. F. W.; Keaveny, I.; Cade, P. E. *J. Chem. Phys.* **1967**, *47*, 3381.

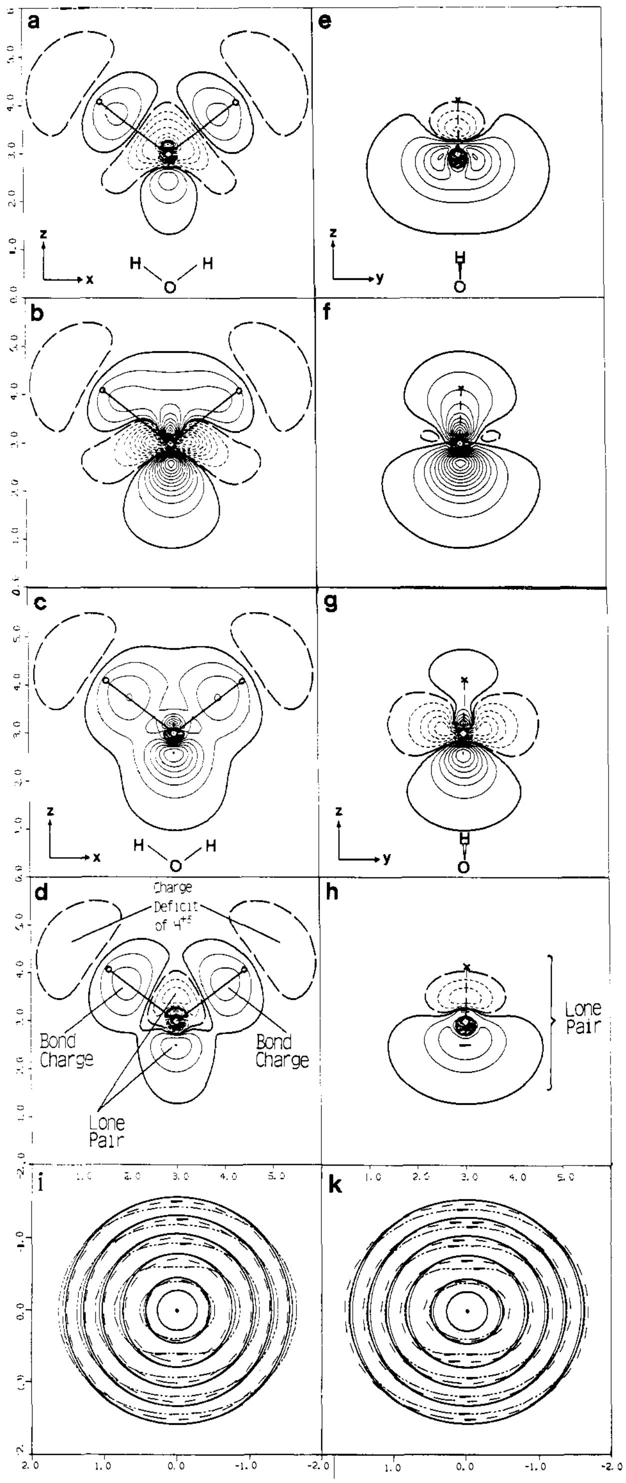

**Figure 3.** SCF difference density maps of $H_2O$ (see legend of Figure 1). (a, e) TDD, molecular density minus sphericalized atoms ($O(1s^2\ 2s^2\ 2p_x^{4/3}\ 2p_y^{4/3}\ 2p_z^{4/3})$). (b, f) Bader's DD, molecular density minus $2H(1s)$, $O(1s^2\ 2s^2\ 2p_x^{5/3}\ 2p_y^{5/3}\ 2p_z^{2/3})$. (c, g) Naive DD, molecular density minus $2H(1s)$, $O(1s^2\ 2s^2\ 2p_x^1\ 2p_y^2\ 2p_z^1)$. (d, h) CDD molecular density minus oriented atomic ground states ($O(1s^2\ 2s^2\ 2p_x^{1.116}\ 2p_y^{1.574}\ 2p_z^{1.31})$). (i, k) Total ground-state density of the oxygen atom; bold line, oriented O; dashed line, "naively oriented" O; dot–dash line, Bader's choice; thin line, spherically averaged O. Density values from outside to center: 0.075, 0.15, 0.3, 0.6, 1.2, 4.8 $e/a_0^3$ (note the different length scale).

$x$ and $z$ axes, respectively). We note that the corresponding $I$ value of 0.081 $e^2/a_0^3$ is much larger than even for the choice of a spherical atom.

The simplest "naive" choice would be to populate the $2p_y$ lone pair AO with two electrons and the $2p_x$ and $2p_z$ bonding AOs each with a single electron. Figure 3c,g shows that now the $p_y$ population is too large ($\Delta\rho < 0$ on the whole $y$ axis) and the $p_z$ population is too small (very similar to the situation in HF), while the $p_x$ population of 1 is reasonable (small $\Delta\rho$ on the $x$ axis). The $I$ value of 0.040 $e^2/a_0^3$ is still larger than for a spherical reference density.

These examples demonstrate again that the difference densities depend *extremely* sensitively upon the orbital populations and that it is therefore impossible to guess at good populations a priori. Each of the guessed sets, be it the "naive" one, the averaged one, or another one, yields a topologically different DD map, all of them differing qualitatively from the uniquely defined CDD map. Even the density maps for the various differently oriented ground configuration O atoms differ significantly, as shown in Figure 3i,k.

## 6. Hydrogen Peroxide

Difference densities were determined for two geometries. Figure 4a–c corresponds to the gas-phase geometry with a dihedral angle of about 120°, whereas Figure 4d–f corresponds to the geometry in the crystal with a dihedral angle of 90°. The results are remarkably similar as also shown in Table II.

The optimized chemical difference density yields an $I$ value of only 0.04 $e^2/a_0^3$ and is obtained for $p(OO)^{0.84}\ p(OH)^{1.39}\ p(n)^{1.77}$ (see Figure 4g,h). The following relevant features are exhibited in the CDD in Figure 4c,f:

(1) A *density increase in the O–O bond center* of 0.5 e/Å$^3$. This "bond density" is not apparent if spherically averaged atoms are subtracted (see below) as was already noticed in the experimental total DD.[14] Electron correlation reduces the value by 0.2 e/Å$^3$. The low but still positive $\Delta\rho$ value at the bond center is typical for the weak O–O $\sigma$ bond and comparable to the $\sigma$ bond in $F_2$.

(2) A *positive CDD on the O–H bond* with a typical maximum of +0.6 e/Å$^3$.

(3) A *dipolar density shift* from the O–O and O–H bond areas (minimum = −0.7 e/Å$^3$) towards the backside of the oxygen cores (maximum = +1.1 e/Å$^3$). It indicates the lone-pair formation in the backward direction bisecting the bond directions. Note again the trigonal character of the deformation density around the oxygen core.

(4) A *very small CDD increase at the proton* and an area of density decrease directly behind the proton. As mentioned before, these features indicate a hydrogen atom with a partial positive charge.

In contrast to the previously discussed molecules, the directions of the p AOs are not fixed by symmetry in $H_2O_2$. They result from our optimization process. Not unexpectedly the lone-pair $p(n)$ AOs are found to be approximately orthogonal to the O–O and O–H bonds (see footnote *b* of Table II). The other two pairs of p AOs lie nearly exactly in the O–O–H planes. The orientations of those of the upper oxygen atom are indicated by the orthogonal axes in Figure 4c,f. The orbital p(OO) with a population of 0.835 is only 10° off the O–O bond and thus qualifies as an O–O bonding AO. The orientation of the third p AO, designated as p(OH), represents a compromise between the diagonally backward polarized $2s^2$ lone-pair charge and the O–H bond charge. It forms an angle of 16° (22° in the solid) with the O–H bond and an angle of about 40° (about 34° in the solid) with the O–O–H in-plane lone-pair direction. Because of charge transfer, the Mulliken populations on oxygen are again bigger in absolute values than our populations, which correspond to neutral oxygens. Nonetheless there is again agreement within about 1% for the relative distribution of the total population over the three p orbitals.

Subtracting spherically averaged oxygen atoms yields difference densities that are, as usual, dominated by quadrupolar distributions around the oxygen cores and that show no charge in the O–O bond. The TDD maps (Figure 4a,d), which have been discussed extensively in the literature,[8,14] look similar to that of $F_2$ (Figure 1a); indeed, $F_2$ and $H_2O_2$ are isoelectronic. The quadrupolar TDD indicates that the p(OO) AOs contain much less than the average $^4/_3$ e, while the lone-pair $p(n)$ AOs perpendicular to the O–O–H

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[14] Savariault, J. H.; Lehmann, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 1298.

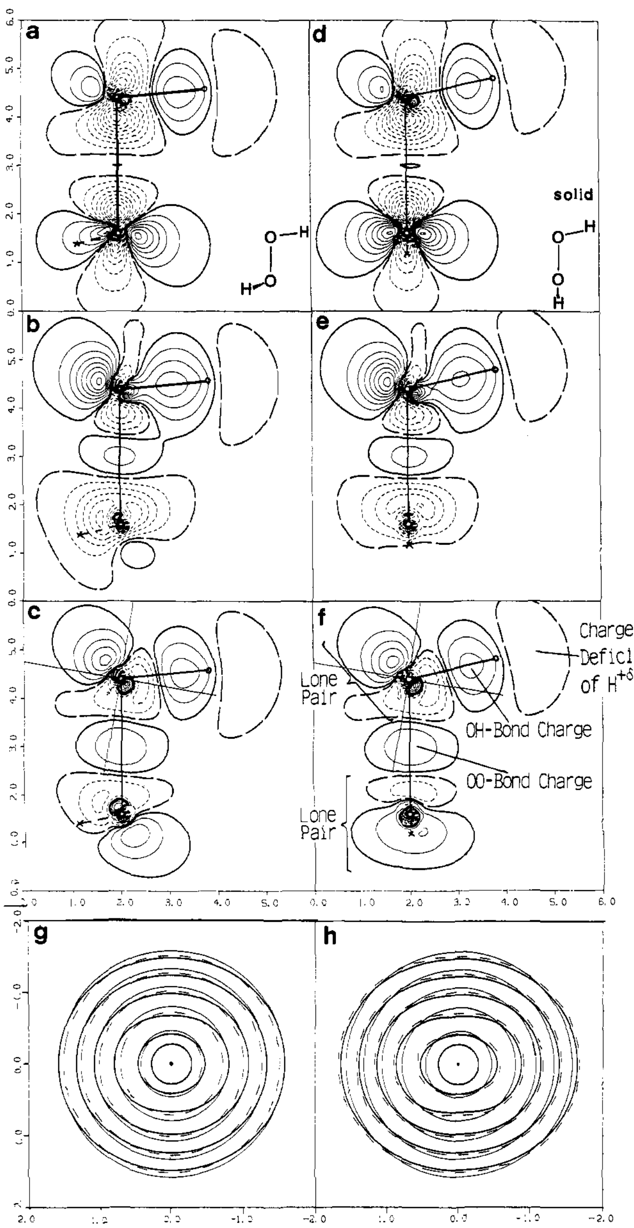

**Figure 4.** SCF difference density maps of molecular (left side) and solid (right side) $H_2O_2$ (see legend of Figure 1). (a, d) TDD, molecular density minus sphericalized atoms (O($1s^2\ 2s^2\ 2p_x^{4/3}\ 2p_y^{4/3}\ 2p_z^{4/3}$)). (b, e) Naive DD, molecular density minus 2H(1s), 2O($1s^2\ 2s^2\ 2p_{OO}^{1}2p_{OH}^{1}\ 2p_n^{2}$). (c, f) CDD, molecular density minus oriented atomic ground states (O($1s^2\ 2s^2\ 2p_{OO}^{0.8...}\ 2p_{OH}^{1.3...}\ 2p_n^{1.7...}$, for precise numbers see Table II). (g, h) Total ground-state density of the oxygen atom (solid $H_2O_2$; g: O–O–H plane, h: O–O– "lone-pair" plane); bold line, oriented O; dashed line, "naively oriented" O, thin line, spherically averaged O. Density values from outside to center: 0.075, 0.15, 0.3, 0.6, 1.2, 4.8 $e/a_0^3$ (note the different length scale).

planes contain more than that average. The $I$ value is large (0.11 $e^2/a_0^3$).

"Naively", one might populate the p AOs in the O–O–H bond plane (p(OO) and p(OH)) with a single electron each, and the orthogonal p($n$) lone-pair AO with two electrons. Figure 4b,e shows that now the p($n$) AO contains too much density (negative $\Delta\rho$ on the left and right sides of the lower oxygen) and the p(OH) AO contains too little density (positive $\Delta\rho$ on the right and left sides of the upper oxygen). This is similar to the situation in $H_2O$ (see Figure 3c,g). Correspondingly the $I$ value is still large, $I$ = 0.08 $e^2/a_0^3$.

While it was possible to guess the populations and orientations of the p AOs in $F_2$, this is clearly no longer so for the isoelectronic $H_2O_2$ molecule. The quadrupolar character of the oxygen $1s^2\ 2s^2\ 2p^4$ ground configuration is remarkable (Figure 4g,h).

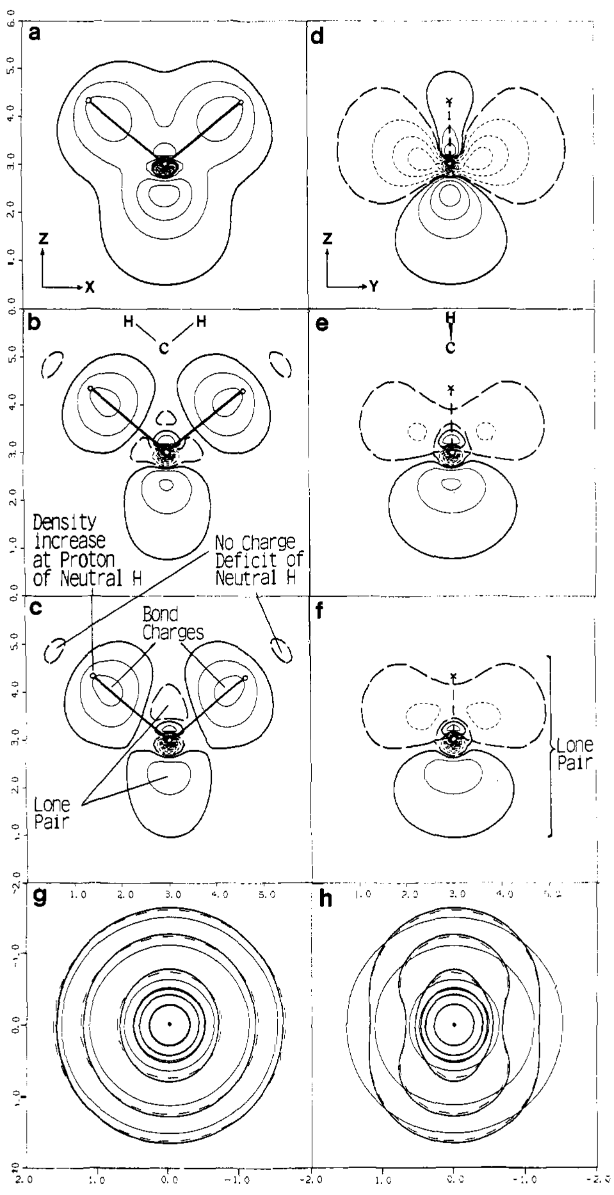

**Figure 5.** SCF difference density maps of $^1CH_2$ (see legend of Figure 1). (a, d) TDD, molecular density minus sphericalized atoms (C($1s^2\ 2s^2\ 2p_x^{2/3}\ 2p_y^{2/3}\ 2p_z^{2/3}$)). (b, e) Naive DD, molecular density minus 2H(1s), C($1s^2\ 2s^2\ 2p_x^{1}\ 2p_y^{0}\ 2p_z^{1}$). (c, f) CDD, molecular density minus oriented atomic ground states (C($1s^2\ 2s^2\ 2p_x^{0.888}\ 2p_y^{0}\ 2p_z^{1.112}$)). (g, h) Total ground-state density of the carbon atom; bold line, oriented C; dashed line, "naively oriented" C; thin line, spherically averaged C. Density values from outside to center: 0.075, 0.15, 0.3, 0.6, 1.2, 4.8 $e/a_0^3$ (note the different length scale).

## 7. Methylene

Difference density plots of triplet and singlet methylene are shown in Figures 5 and 6.

In the SCF wave function for *singlet methylene* (Figure 5), a strongly polarized C(2s) lone-pair orbital and two C(2p)–H(1s) bond orbitals in the *xz* plane are doubly occupied. Thus the molecule-adapted ground configuration of the carbon atom is far from being spherical (see Figure 5h). Its Mulliken populations are $2s^{1.47}\ 2p_x^{1.02}\ 2p_y^{0}\ 2p_z^{1.51}$. Due to partial s–p hybridization/promotion, which is much more important in C than in all other elements, the $2p_z(a_1)$ population has increased at the expense of the $2s(a_1)$ population.

It is axiomatic to our analysis that all those atomic density changes, which are associated with *atomic energy changes* tied to bond formation, are contained in the chemical difference density map. Therefore we do not allow for 2s–2p promotion in the atomic reference ensemble and the 2s population is kept fixed at 2.0. The optimized p populations are $2p_x^{0.89}\ 2p_y^{0}\ 2p_z^{1.11}$. The corresponding

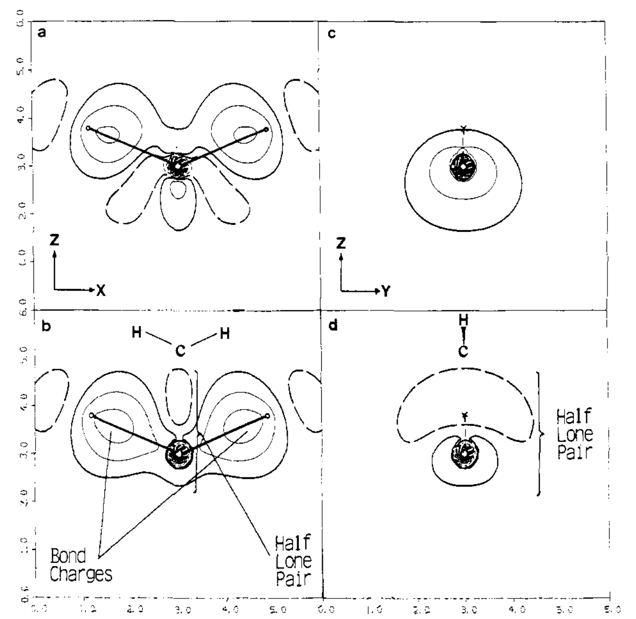

Figure 6. SCF difference density maps of $^3CH_2$ (see legend of Figure 1). (a, c) TDD, molecular density minus sphericalized atoms ($C(1s^2\ 2s^2\ 2p_x^{2/3}\ 2p_y^{2/3}\ 2p_z^{2/3})$). (b, d) CDD, molecular density minus oriented atomic ground states ($C(1s^2\ 2s^2\ 2p_x^{0.488}\ 2p_y^{1.016}\ 2p_z^{0.496})$).

CDD plots (Figure 5c,f) yield an ICDD value of 0.0206 $e^2/a_0^3$. These optimal populations reflect the fact that the $p_z(a_1)$ AO is more involved in molecule formation than the $p_x(b_2)$ AO, since $p_z$ contributes to both the lone-pair orbital and the symmetric linear combination of bond orbitals, while $p_x$ only contributes to the antisymmetric linear combination of bond orbitals. The optimized CDD of Figure 5c,f nicely exhibits (i) the dipolar lone-pair feature on carbon in the $z$ direction and (ii) the CH bond charges. Moreover, (iii), the "bond charge" lobes extend over the hydrogen nuclei and even to the back sides of the protons, leaving only a small region of density decrease farther away. As mentioned earlier, this is indicative for *neutrally* bonded hydrogens.

Even though our populations do not allow for promotional hybridization, the occupations of the reference density resulting from our criterion are related to the quoted Mulliken populations in the previously discussed manner. Table II shows that the relative percent deviations from the spherical average agree for the two methods. (One can also deduce "unpromoted" Mulliken populations by increasing the 2s population from 1.47 to 2 at the *equal* expense of all three p AOs, yielding $2s^2\ 2p_x^{0.84}\ 2p_y^{-0.18}\ 2p_z^{1.33}$. This result agrees reasonably well with p populations that are obtained by a minimization of IDD without restricting them to positive definite values: namely, $2p_x^{0.79}\ 2p_y^{-0.22}\ 2p_z^{1.41}$.)

It should be noted that the $^3P$ ground state of C is compatible only with p populations between 0 and 1. The optimized values in Table II (i.e., $p_z(a_1)^{1.11}$) correspond to some $^1D$ admixture in the atomic reference ensemble. This is also true for the optimized p populations of O in $H_2O_2$ ($p_{OO}^{0.85}$), where the $^3P$ ground state of oxygen restricts the p populations to lie between 1 and 2. However, the $^3P$–$^1D$ excitation energies (1.25 eV for C, 2 eV for O) are much smaller than the s–p promotion energies (9 eV for C, 17 eV for O), and it is therefore not inconsistent to include the $^1D$ state in the reference ensemble while excluding the s–p promoted configurations. Indeed, only small changes are found when the $^1D$ state is excluded as well (all p populations between 0 and 1), the optimized population values becoming $2p_x^{0.94}\ 2p_y^{0.06}\ 2p_z^{1.00}$, with $I = 0.021\ e^2/a_0^3$.

As already mentioned, the "naive" p populations $2p_x^1\ 2p_y^0\ 2p_z^1$ are not very different from the optimized ones (see above). They yield a quite low $I$ value (0.0213 $e^2/a_0^3$), and the corresponding DD maps (Figure 5b,e) are very similar to the CDD maps in Figure 5c,f. On the other hand the TDD maps in Figure 5a,d obtained from the spherically averaged carbon atom show the typical artifacts: the everywhere positive TDD in the $xz$ plane (Figure 5a) reflects the fact that there are more electrons in the $2p_x$ and $2p_z$ AOs than accounted for by a spherical average of $^2/_3$ e; the strongly quadrupolar distribution in the $yz$ plane (Figure 5d) is due to the $p_y(b_1)$ AO on C being empty whereas the $p_z(a_1)$ AO contains about twice the spherical average of $^2/_3$ e per AO. The $I$ value of the "spherical" TDD is comparatively large, namely, 0.055 $e^2/a_0^3$.

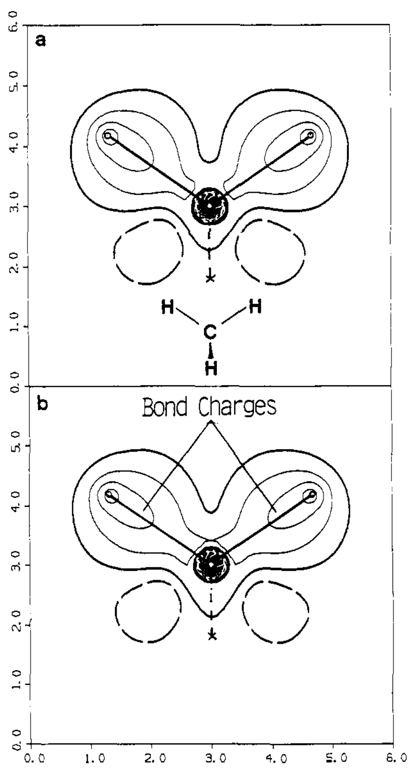

Figure 7. Difference density maps of $CH_4$, TDD = CDD (see legend of Figure 1): (a) SCF, (b) MCSCF (FORS).

In *triplet methylene* an electron is excited from the in-plane lone-pair $a_1$ MO with significant $2p_z$ population into the originally empty orthogonal $2p_y(b_1)$ orbital. Correspondingly the optimized population (see Table II) is 1 e in $2p_y(b_1)$ and $^1/_2$ e in each of the two p AOs in the molecular plane. The CDD (Figures 6b,d) clearly indicates unpolarized C–H bonds and "half" an in-plane lone pair (in addition to the out-of-plane $2p_y$ electron). A spherical reference atom, on the other hand, yields a less easily interpretable TDD (Figure 6a,c). The respective $I$ value (0.022 $e^2/a_0^3$) is only slightly larger than the optimal value (0.017 $e^2/a_0^3$). This is so because the carbon atom in triplet methylene is closer to being spherical than in singlet methylene, in this respect resembling the majority of C atoms in other compounds. The significant difference between our $p_y(b_1)$ population and the Mulliken population is not yet understood.

## 8. Methane and Lithium Hydride

For the sake of comparison, the difference density of *methane*, $CH_4$, is shown in Figure 7. Because of the high molecular symmetry, the *optimal* ground-state carbon density is spherical in this case so that there is no difference here between the TDD and the CDD. The typical charge accumulation in the bonds go along with a charge deficit on the back side of the carbon atom. This results in a dipolar but not in a quadrupolar charge distribution around the C. Electron correlation modifies the difference density only weakly.

In addition to the *neutrally* bonded hydrogen atoms in $CH_2$ and $CH_4$ (Figures 5–7) and the *positive* hydrogen atoms in HF, $H_2O$, and $H_2O_2$ (Figures 2–4), we also exhibit a *negatively* bonded H in *lithium hydride*, LiH (Figure 8). Because of the low electron density in this molecule, the contour value increments are chosen a factor of 4 smaller than in the other figures. A similar DD map was first shown and discussed by Bader et al.[13] Since both Li and

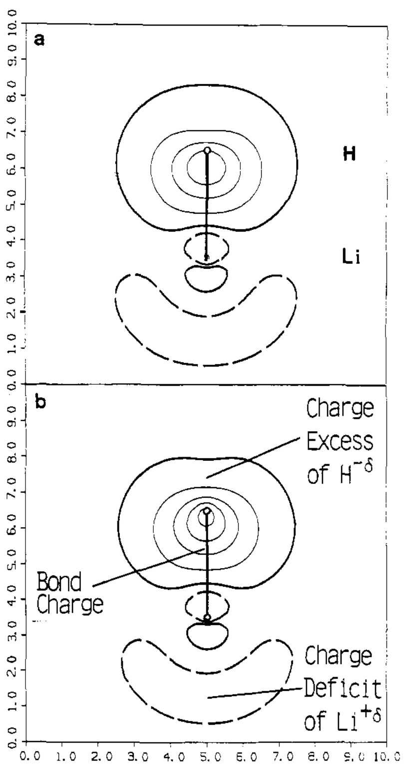

Figure 8. Difference density maps of LiH, TDD = CDD: thin line, $+0.01n$ e/$a_0^3$; dashed line, $-0.01n$ e/$a_0^3$; bold solid line and bold dashed line, $\pm 0.0025$ e/$a_0^3$. (a) SCF; (b) MCSCF (FORS).

H have spherical ground states, the TDD and CDD are identical here. Despite the negative excess charge on H, the density increase at the proton is only 0.3 e/Å$^3$ for the SCF function and 0.2 e/Å$^3$ for a full valence space (including p orbitals) MCSCF-FORS wave function. However, the CDD feature characteristic for partial *negative* charge is the *region of density increase* that extends *far to the back side* of the H atom. The bond density is low, viz., about $^1/_4$ e/Å$^3$. The density transferred to the regions of density increase is taken away from the outer molecular regions, especially from the back side of the Li atom.

## 9. Conclusions

**1. General Conclusions.** *Total difference densities* (TDDs), which are obtained by subtracting *spherically averaged* reference atoms from the molecular densities, are often dominated by quadrupolar density features that characterize *isoenergetic orientations* of free atoms. On the other hand, determination of the reference density through *adjustment of degenerate atomic ground-state ensembles* within the given molecule, as described in the preceding paper, yields *chemically interpretable deformation densities* (CDDs). The electrostatic interaction of oriented atomic ground-state densities contributes a large fraction to the total bond energy.[20] The chemical deformation density can then be associated with additional energy changes that accompany the bond formation.

The *atomic ensemble* that is suitable for the formation of this adjusted reference density is the degenerate ground-state manifold pertinent to *bond formation*. The resulting population and orientation parameters of the reference density contain chemically relevant numerical information that is *directly* extracted from the molecular density. The *populations* that are determined from such optimally adjusted densities are more useful than any that can be guessed at by some a priori intuition. The "optimized" AO populations correlate reasonably well with relative Mulliken populations, although a precise simple relation does not seem to exist between them. The information describing the atomic *orientations* is *quantitatively* expressed in terms of a few numbers rather than being *qualitatively* absorbed in the total difference density plot. The information regarding atomic orientations is thus treated on a par with that pertaining to atomic positions and vibrations in the usual X-ray structure determinations.

Even if the experimental accuracy does not suffice for the determination of reliable chemical difference densities, say if it is of the order of a few tenths of an e/Å$^3$ only, it may still be adequate for the determination of atomic orientations and populations. This is analogous to the common determination of atomic populations of predefined d AOs in transition-metal atoms with open d shells, as, for example, in ref 15.

**2. Atomic Ground-State Ensembles and Chemical Reference Densities.** In many cases the "oriented" atoms differ markedly from the spherical average as well as from any intuitive choice of open-shell AO populations. From previous experimental density determinations it is already known that *the AO populations in bonded* O and F *atoms are significantly nonuniform* as long as the spherical negative ions $F^-$ or $O^{2-}$ do not dominate the bonding pattern. Asymmetrically coordinated carbon atoms are also nonspherical, as, for instance, in singlet carbenes and also in strained ring systems.

In d valence shells,[15] several effects are found upon bond formation: (i) Different d AOs are differently populated in different compounds. In high-spin complexes the *optimal population* can be described by an appropriate orientation of the atomic ground state. In the case of low-spin compounds, a significant admixture of other LS states of the ground configuration is required. (ii) In octahedral surroundings the directions and shapes of the optimal d AOs are the standard ones ($d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{x^2-y^2}$, and $d_{z^2}$). For compounds of low site symmetry, it is necessary to optimize not only the populations but also the *directions* (which may differ from those of the crystal axes) as well as the *shapes* of the five orthogonal d AOs. The resulting d orbitals may then differ from the standard $d_{xy}$ and $d_{z^2}$ types. (iii) d AOs are especially prone to radical and angular *deformation*. This is known both from quantum chemical calculations and from experimental density determinations.

In applying the approach suggested here to d orbitals, one would determine not only the different d populations (effect i), as is rather usual, but also the optimal orientations and the optimal shapes of the "natural" d AOs (effect ii). The remaining deformation (effect iii) would then be visualized in the chemical DD map. Of course, not only transition-metal atoms with open d shells but also *main-group atoms with open p shells* should be treated in the same manner as was done here for atoms of the second period.

In the case of strongly ionic compounds (like HF, LiH, or salts and metal oxides) one may think of including ionic states in the atomic reference ensemble. It should be noted, however, that free negative atomic ions are very sensitive against perturbations and that many are in fact unstable in vacuum (e.g., $O^{2-}$). In addition, the SCF approximation is known to be especially unreliable for negative ions. Consequently the inclusion of *free SCF anions* in the reference ensemble does not seem promising, and this inference seems to have found some confirmation recently.[21] Still, it remains an interesting question whether the inclusion of *correlated* negative ions, *stabilized* in an appropriate Watson sphere, in the reference ensemble would yield a reasonable measure of the ionicity of the compound.

**3. Chemical Difference Densities.** The present approach yields *chemical difference density maps for different molecules that can be directly compared.* The CDD maps of O and F compounds are no longer peculiar exceptions as is the case for the corresponding TDD maps.[14,16-19] For all cases treated so far the integral

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(17) Dunitz, J. D.; Seiler, P. *J. Am. Chem. Soc.* **1983**, *105*, 7056. Dunitz, J. D.; Schweizer, W. B.; Seiler, P. *Helv. Chim. Acta* **1983**, *66*, 123; *Acta Crystallogr., Sect. B* **1984**, *40*, 319. Chakrabarati, P.; Seiler, P.; Dunitz, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 7378.

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(19) Stevens, E. D. *Mol. Phys.* **1979**, *37*, 27.

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(21) Seiler, P.; Dunitz, J. D. *Helv. Chim. Acta* **1986**, *69*, 1107.

over the squared CDD amounts to less than 0.02 $e^2/a_0^3$ per atom, while the integral over the squared TDD per atom varies drastically from molecule to molecule and may be as large as 0.1 $e^2/a_0^3$ for open p-shell atoms.

The following specific characteristics emerge from the molecules examined here:

(i) Nonpolar and polar *covalent bonds* between second-row atoms, including hydrogen, exhibit a density increase of common magnitude in the bond center. This bond charge, which is well-known from C, H, and N bonds, also exists in O and F bonds, being throughout of the order of $+^1/_2$ e/Å$^3$. This observation is subject to the following modifications: (1) Most results presented here are of SCF quality only. Correlation may quantitatively alter (usually diminish) the values somewhat, but probably not change them qualitatively. (2) In bonds that are lengthened and weakened by nonbonded repulsions between lone pairs, e.g., as the F–F bond in $F_2$ or the O–O bond in $H_2O_2$, the bond charges are less pronounced than in normal $\sigma$ bonds.

(ii) *Lone pairs* are characterized not only by a density *increase* in the "lone-pair region" but also by a density *decrease* on the opposite (bond) side of the atomic core. That is, the formation of lone pairs represents a migration in the valence shell that corresponds to a dipolar pattern in the chemical difference density.

(iii) *Bond pairs*, too, are characterized by a dipolar CDD pattern corresponding to a shift of electron density from the back side of the bonded atom toward the bond center. It has sometimes been stated in the literature[12] that bonded second and higher row atoms are characterized by a quadrupolar difference density. This quadrupolar distribution seems to be a mere artifact of an arbitrary nonoptimal choice of the promolecule, be it by spherical averaging of the atoms or by other definitions.

(iv) *Bonded hydrogens* always exhibit a density increase at the proton. It is most pronounced in "neutral" hydrogens and smaller in both positively as well as negatively charged H atoms. The partial charge on the hydrogen correlates with a density *increase* for $H^{\delta-}$ or *decrease* for $H^{\delta+}$ in the region *behind* the proton, i.e., away from the bond. The dipolar charge distribution around hydrogens carrying a partial positive charge are appropriate for the formation of linear hydrogen bonds.

We were able to attribute the characteristic patterns of the chemical deformation densities to interatomic quantum mechanical interference and to various types of atomic promotions accompanying the bond formation, namely, $nl \rightarrow n'l'$ promotion, A–B $\rightarrow$ $A^+$–$B^-$ charge transfer, and radial AO shrinking or swelling. Still, it is important to keep in mind that the chemical bond energy (at the level of the Born–Oppenheimer approximation) is the sum of four contributions, namely, the change in the electronic kinetic energy, the change in the interelectronic repulsion, the change in the internuclear repulsion, and the change in the electron–nuclear attraction. Only the last contribution is *directly* related to the diagonal one-electron density analyzed here, and a large part of it is already recovered by superimposing the undeformed atoms.[20] The first two mentioned contributions are determined by the off-diagonal part of $\rho(r,r')$ (i.e., by the density in momentum space $(p)$) and by the two-electron density $P(r_1,r_2)$, respectively. Changes in these two contributions are only very indirectly determined by changes in $\rho(r)$.

**Acknowledgment.** We are grateful to S. Y. Chu, J. D. Dunitz, D. Feil, R. Goddard, F. L. Hirshfeld, R. Jaquet, and E. N. Maslen for their constructive comments and to N. Roessler and D. H. Duong for their help in some calculations. W.H.E.S. expresses his cordial gratitude for the hospitality he has received at Iowa State University in Ames. We acknowledge financial support by NATO (Grant No. 298/83), by DFG (Grant No. 477/423), by Fonds der Chemischen Industrie (Grant No. 160273), and by the Office of Basic Energy Science, Division of Chemical Sciences, USDOE (Contract No. W-7405-ENG-82). The calculations were performed at the computer facilities of the Universities at Siegen, Köln, Braunschweig, and of the Ames Laboratory USDOE at Iowa State University, Ames. These services are gratefully acknowledged.

**Registry No.** $F_2$, 7782-41-4; HF, 7664-39-3; $H_2D$, 7732-18-5; $H_2O_2$, 7722-84-1; $CH_2$, 2465-56-7; $CH_4$, 74-82-8; LiH, 7580-67-8.